DYNAMICS OF POLYMERIC LIQUIDS

Volume 1 Fluid Mechanics

Volume 2 Kinetic Theory

DYNAMICS OF POLYMERIC LIQUIDS

VOLUME 2
KINETIC THEORY

SECOND EDITION

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PREFACE

Liquid motion has fascinated many generations of scientists and engineers. Although many years of research have been devoted to the study of fluids of low molecular weight, which are well described by the Navier–Stokes equations, many challenging problems in both theory and applications remain. But even more challenging are polymeric liquids, whose motions cannot be described at all by the Navier–Stokes equations. In Volume 1, *Fluid Mechanics*, we summarize the key experiments that show how polymeric fluids differ from structurally simple fluids, and we then present, in rough historical order, various methods for solving polymer fluid dynamics problems; in Volume 2, *Kinetic Theory*, we use molecular models and the methods of statistical mechanics to obtain relations between bulk flow behavior and polymer structure. Table 1 shows how we have chosen to organize the material of the two volumes.

Understanding polymer fluid dynamics is important in connection with plastics manufacture, performance of lubricants, application of paints, processing of foodstuffs, and movement of biological fluids. Rapid advances in all these areas, as well as in the associated fundamental sciences, have made it desirable to have an introductory textbook for students and research workers. Examples and problems have been included to assist the beginner and almost all the material in both volumes has been classroom tested. These volumes should also be useful as an introduction to the advanced monographs and research literature on continuum physics, rheometry, molecular theory, and polymer processing. Literature citations have been supplied throughout the text for the interested reader. Although these volumes have been prepared with fourth or fifth year chemical engineering and chemistry students in mind, they may also be of interest to students or research workers in polymer engineering and science, molecular biology, mechanical engineering, materials science, and applied mechanics.

Both experiment and theory in this field have undergone rapid development in recent years. Except for a few papers of historical interest, the literature citations are from the period after 1950, and many are from the 1970s and 1980s. These volumes summarize the efforts of our many colleagues around the world; they also contain a number of developments and ideas heretofore unpublished. Unfortunately the following subjects have had to be omitted from the text: optical and electrical phenomena, computer simulation techniques, boundary-layer theory, two-phase systems, thermodynamics, and liquid crystals. Research is going on in all these areas, but we have had to rule them outside the scope of these volumes.

In these two books there is enough material for two one-semester courses: a fluid dynamics course (Chapters 1 to 10), followed by a kinetic theory course (Chapters 11 to 20). Needless to say, many points can be better understood by working through the details of

TABLE 1

Contents of Volumes 1 and 2

VOLUME 1 FLUID MECHANICS

Part I. Newtonian versus Non-Newtonian Behavior
Chapter 1 Review of Newtonian Fluid Dynamics
Chapter 2 Flow Phenomena in Polymeric Liquids
Chapter 3 Material Functions for Polymeric Liquids

Part II. Elementary Constitutive Equations and Their Use in Solving Fluid Dynamics Problems
Chapter 4 The Generalized Newtonian Fluid
Chapter 5 The General Linear Viscoelastic Fluid

Part III. Nonlinear Viscoelastic Constitutive Equations and Their Use in Solving Fluid Dynamics Problems
Chapter 6 The Retarded Motion Expansion
Chapter 7 Differential Constitutive Equations
Chapter 8 Single-Integral Constitutive Equations

Part IV. Continuum Mechanics and Its Use in Solving Fluid Dynamics Problems
Chapter 9 Continuum Mechanics Concepts
Chapter 10 Fluid Dynamics of Rheometry

VOLUME 2 KINETIC THEORY

Part V. Polymer Models and Equilibrium Properties
Chapter 11 Mechanical Models for Polymer Molecules
Chapter 12 Equilibrium Configurations of Polymer Molecules

Part VI. Elementary Approach to Kinetic Theory
Chapter 13 Elastic Dumbbell Models
Chapter 14 The Rigid Dumbbell and Multibead-Rod Models
Chapter 15 Bead-Spring-Chain Models
Chapter 16 General Bead-Rod-Spring Models

Part VII. A General Phase-Space Kinetic Theory
Chapter 17 Phase-Space Kinetic Theory of Polymeric Liquids
Chapter 18 Phase-Space Theory for Dilute Solutions
Chapter 19 Phase-Space Theory for Concentrated Solutions and Melts

Part VIII. Elementary Kinetic Theory for Network Models
Chapter 20 Network Theories for Polymer Melts and Concentrated Solutions

specific problems, and to this end many illustrative examples have been included. Of particular importance are the problems at the end of the chapters, which are divided into four classes:

Class A Numerical calculations using equations from the chapter.
Class B Analyses similar to those in the text.
Class C More difficult or lengthy analyses.
Class D Mathematical developments.

Many of these problems are used to augment the material in the main text, and quite a few of them are referred to later in the book. No effort has been spared to provide generous crossreferencing within each volume and between the two volumes, and appendices are included to assist the reader in problem solving. Everywhere in the text and problems we have used SI units; viscosities are given in Pa·s (1 poise = 0.1 Pa·s = 0.1 N·s/m^2) and molecular dimensions are given in nm (1Å = 0.1 nm).

Volumes 1 and 2 cut across several fields and it is impossible to find notation that pleases everyone. Our aim has been to follow the recommendations of the Society of Rheology for the notation for rheological quantities: $\eta^* = \eta' - i\eta''$ for the complex viscosity, η for the shear-rate-dependent viscosity, η_0 for the zero-shear-rate viscosity, Ψ_1 and Ψ_2 for the normal-stress coefficients, and $\dot{\gamma}$ for the shear rate. Like many workers in kinetic theory and transport phenomena we write the total stress tensor as $\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau}$, where p is the pressure, $\boldsymbol{\delta}$ is the unit tensor, and $\boldsymbol{\tau}$ is that part of the stress tensor that vanishes at equilibrium; that is, both p and τ_{ii} are positive in compression, and furthermore $\boldsymbol{\tau}$ obeys the well-established sign convention that is used for heat and mass fluxes. Usually continuum mechanicists and mechanical engineers use a sign convention opposite to ours for $\boldsymbol{\pi}$ and $\boldsymbol{\tau}$. Bear in mind that misunderstandings can also arise because of differences in definitions of tensor operations; we use $(\nabla \boldsymbol{v})_{ij} = (\partial/\partial x_i)v_j$, and $[\nabla \cdot \boldsymbol{\tau}]_i = \sum_k (\partial/\partial x_k)\tau_{ki}$. In addition, we define the rate-of-strain tensor as $\dot{\boldsymbol{\gamma}} = \nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^\dagger$ and the vorticity tensor as $\boldsymbol{\omega} = \nabla \boldsymbol{v} - (\nabla \boldsymbol{v})^\dagger$, with no factors of $\frac{1}{2}$ included. Lists of notation are included at the beginning of each volume; Appendices A and E, dealing with vector and tensor operations, should also provide assistance in interpreting the notation.

In preparing these volumes we have drawn extensively on the research literature of the recent decades; we acknowledge with deep appreciation our many colleagues who have been working at the frontiers of the subject. Several of the staff members of the Rheology Research Center of the University of Wisconsin (Professors A. S. Lodge, M. W. Johnson, Jr., J. D. Ferry, J. L. Schrag, S. Kim, D. S. Malkus, and M. Renardy) have provided us with considerable assistance, as did several of our colleagues at the Massachusetts Institute of Technology (Professors R. A. Brown, J. F. Brady, and H. Brenner). Also, we wish to thank Professor M. Tirrell (University of Minnesota), Professor D. G. Baird (Virginia Polytechnic Institute), and their students, who used these volumes in manuscript form and supplied us with extensive lists of improvements. Especially helpful have been the detailed criticisms provided by those who have used the manuscript: H. C. Öttinger, John M. Wiest, Steven R. Burdette, Lewis E. Wedgewood, Tony W. Liu, Jay D. Schieber, Xi-Jun Fan, and Hassane H. Saab from the University of Wisconsin, Miguel A. Bibbo, Lidia M. Quinzani, Ali Nadim, Anthony N. Beris, John V. Lawler, Susan J. Muller, Robert C. King, Minas R. Apelian, and William P. Raiford from the Massachussetts Institute of Technology, and Sue Hirz, Neil A. Dotson, Mike Kent, Ted Frick, Gibson Batch, Robert Secor, and Kurt Hermann from the University of Minnesota.

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Comments on Volume 2

During the ten years since the first edition of Volume 2 was published, there has been so much activity in polymer kinetic theory that an extensive revision was called for. Every chapter from the original edition has been almost entirely rewritten and four new chapters have been added. Despite the revisions we have tried to adhere to our policy of proceeding from the simplest subject material to the more complex material in order to make polymer kinetic theory accessible to the largest number of readers.

In the first two chapters—which are new in the second edition—we treat two subjects that include important background information. Chapter 11 deals with the rationale behind the mechanical models used in polymer kinetic theory, and Chapter 12 gives the principal ideas of equilibrium statistical mechanics as applied to polymeric systems.

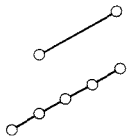
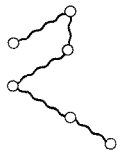
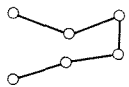
After this introductory material, we give in four chapters the main ideas of the kinetic theory and its application to molecular models of increasing complexity (see Table 1). The first of these, Chapter 13, is a rather lengthy discussion of various elastic dumbbell models. Even though these models are too simple to be of much interest to polymer chemists, they have been extremely helpful to rheologists and fluid dynamicists in elucidating the connection between molecular dynamics and nonlinear flow phenomena. Dumbbells with a rigid-rod connector, discussed in Chapter 14, illustrate the problems that arise in models with constraints. The full treatment of the problems of constraints is, however, postponed to Chapters 17 and 18. Once the dumbbell models have been discussed, it is natural to turn to more realistic models with many internal degrees of freedom.

The famous bead-spring chain model of Rouse and Zimm is treated in Chapter 15, and the equally famous, but less fully explored bead-rod chain models of Kramers and of Kirkwood and Riseman, are given in Chapter 16 (along with still more complex models). Here, in these two chapters, exactly the same physical ideas are used as those in the dumbbell chapters. Extensive summaries are also given in Chapter 16 of the main results for dilute solutions from Chapters 17 and 18 for the benefit of those readers who do not wish to work through these more advanced chapters; the adjoining table summarizes the kinds of models discussed in the various chapters.

Most of the kinetic theory papers in the research literature make use of developments in the configuration space of a single polymer molecule, and indeed that is the approach we have taken in Chapters 13–16. Even though these configuration-space theories are apparently simpler, they do not provide a complete enough understanding of the subject to handle model constraints, polymer–polymer interaction, and velocity-space averaging. Much more insight into these problems is obtained by starting out in the phase space of the entire polymeric liquid and systematically reducing the problem to the configuration space of a single macromolecule. Only by this procedure can one get a careful assessment of the assumptions that are inherent in the "classical" theories.

Readers will find in Chapter 17 a complete discussion of the basic procedure for developing a phase-space kinetic theory for arbitrary bead-spring-rod models in solutions,

TABLE 1

Chapter	Model	Constraints	Hydrodynamic Interaction	Structureless Beads	Friction Coefficient	m_v, ζ_v	Bead Arrangement	Type of Solution	Infinite Dilution
13		No	§13.6 (equilibrium averaged)	Yes	Scalar (except §13.7)	Same	Linear	1 solute; monodisperse	Yes (except §13.7)
14		Yes	§14.6 (complete)	Yes	Scalar	Same	Linear	1 solute; monodisperse	Yes
15		No	§15.4 (equilibrium averaged)	Yes	Scalar	Same	Linear	1 solute; monodisperse	Yes
16 and all bead-rod-spring models		No/Yes	Complete or equilibrium averaged	Yes	Scalar	May be different	Arbitrary	Many solutes or polydisperse	Yes
17, 18		No/Yes	Complete or equilibrium averaged	No	Tensor	May be different	Arbitrary	General	No

melts, and mixtures. Years ago, in 1944, the famous Dutch physicist, H. A. Kramers, published a seminal paper on the phase-space theory of bead-rod chains, branched chains, and even rings. Our development in Chapter 17 can be viewed as an extension of his approach. For dilute solutions we develop the phase-space theory further in Chapter 18, and with appropriate assumptions we are led to the starting points for the celebrated series of kinetic theory papers of J. G. Kirkwood and his coworkers, published in the decade following World War II.

Just in the past decade there has been considerable activity in the kinetic theory of concentrated solutions and melts. Of particular importance have been the articles of M. Doi and S. F. Edwards, in which the notion of "reptation," due to P-G. de Gennes, has been incorporated. Here the theory focuses attention on the dynamics of a single polymer chain moving in the mean field provided by its neighbors. Notwithstanding the complexity of this system, it is shown in Chapter 19 how these mean-field theories can be derived directly from the general phase-space theory of Chapters 17 and 18. Generation of the theory in this way makes it clear how the original reptation theories for melts can be extended and improved upon in the future. Knowledge of the phase-space theory seems to us essential for better understanding of the molecular theory of macromolecular systems.

In Chapter 20 we turn to an alternative type of kinetic theory for polymer melts that emphasizes the networklike structure in concentrated systems. Recent extensions of the network theories, pioneered by A. S. Lodge and M. Yamamoto, have led to useful constitutive equations for polymer rheologists and fluid dynamicists. Keep in mind that the network theories are much simpler than the reptation theories, and, in fact, Chapter 20 can be read immediately after Chapter 13.

We would like to conclude by pointing out that Volume 2 can be read without going through Volume 1. Only the Volume 1 material summarized in Appendix D is really needed for making the connection between the molecular ideas and the continuum mechanics formalism. Our aim, however, has been to provide as many cross references between the two volumes as possible in the belief that kinetic theorists and continuum mechanicians need to have a greater appreciation for each other's techniques and accomplishments. During the preparation of Volume 2, we collected various useful mathematical formulae and put them into Appendix E, so that the reader can concentrate on the physical ideas rather than on the mathematical manipulations.

R.B.B.
C.F.C.
R.C.A.
O.H.

CONTENTS
VOLUME 2

Notes on Notation for Volume 2 xix

PART V
POLYMER MODELS AND EQUILIBRIUM PROPERTIES

Chapter 11
Mechanical Models for Polymer Molecules 3

11.1 Macromolecular Structure 4
11.2 Chain Models with Fixed Bond Lengths and Bond Angles 9
11.3 The Freely Jointed Bead-Rod Chain Model 11
Example 11.3-1 Root-Mean-Square End-to-End Distance 12
Example 11.3-2 Equilibrium Distribution Function for the End-to-End Vector 13
Example 11.3-3 Average Tension in a Polymer Chain 15
11.4 The Freely Jointed Bead-Spring Models 16
Example 11.4-1 Mean-Square End-to-End Distance for a Rouse Chain 18
11.5 Dumbbell Models 19
11.6 The Geometry of Chainlike Molecules 22

Chapter 12
Equilibrium Configurations of Polymer Molecules 31

12.1 Generalized Coordinates and Momenta 31
Example 12.1-1 Base Vectors and Metric Matrix Components for the Freely Jointed Bead-Rod Chain with $N = 3$ 35
Example 12.1-2 Base Vectors and Metric Matrix Components for the Freely Jointed Bead-Spring Chain 36
12.2 Hamilton's Equations of Motion 37
12.3 Distribution Functions from Equilibrium Statistical Mechanics 38
12.4 Average Values 41
Example 12.4-1 Equilibrium Averaged Internal Kinetic Energy for Any Bead-Rod-Spring Model 43
12.5 Contracted Distribution Functions 44
Example 12.5-1 Distribution Function for the Vector Between Two Beads of a Rouse Chain 45
Example 12.5-2 Configurational Distribution Function for a Bead-Spring Chain with Infinitely Stiffened Springs 46

PART VI
ELEMENTARY APPROACH TO KINETIC THEORY

Chapter 13
Elastic Dumbbell Models 55

13.1 Modeling of Solutions of Flexible Polymers 56
13.2 The "Diffusion Equation" for the Configurational Distribution Function 59
Example 13.2-1 Time Rate of Change of Average Values 63
13.3 Expressions for the Stress Tensor 64
Example 13.3-1 Alternative Form for the Stress Tensor 70
13.4 Hookean Dumbbells 71
Example 13.4-1 Shear Flow Material Functions and Molecular Stretching 73
Example 13.4-2 Elongational Flow Material Functions and Molecular Stretching 74
13.5 Non-Hookean Dumbbells 76
Example 13.5-1 Steady Elongational Flow (FENE Dumbbells) 85
Example 13.5-2 An Approximate Constitutive Equation (FENE Dumbbells) 88
13.6 Hydrodynamic Interaction 92
Example 13.6-1 The Effect of Hydrodynamic Interaction on the Intrinsic Viscosity of a Suspension of Hookean Dumbbells 94
Example 13.6-2 Translational Diffusivity of Hookean Dumbbells 95
13.7 Anisotropic Effects 96

Chapter 14
The Rigid Dumbbell and Multibead-Rod Models 111

14.1 Modeling of Solutions of Rodlike Polymers 112
14.2 The "Diffusion Equation" for the Configurational Distribution Function 114
14.3 Expressions for the Stress Tensor 117
Example 14.3-1 Interrelation of Stress Tensor Formulas 118
14.4 Solution of the Kinetic Theory Equations for Special Flows 119
Example 14.4-1 Steady Shear Flow 120
Example 14.4-2 Steady Elongational Flow 125
14.5 Solution of the Kinetic Theory Equations for General Flows 127
14.6 Hydrodynamic Interaction 133
Example 14.6-1 The Viscometric Functions for Multibead Rods 136
Example 14.6-2 Steady Shear Flow Properties of Rigid Dumbbell Suspensions at Arbitrary Shear Rates (Numerical Calculation) 138
Example 14.6-3 Translational Diffusivity of Rigid Dumbbells in Dilute Solution 140

Chapter 15
The Bead-Spring Chain Models 151

15.1 The "Diffusion Equation" for the Configuration-Space Distribution Function 152
15.2 Expressions for the Stress Tensor 155
15.3 The Bead-Spring Chain with Hookean Springs (Rouse Model) 156
Example 15.3-1 Material Functions from the Rouse Model 161
Example 15.3-2 Chain Extension in Steady Shear Flow 163
15.4 The Bead-Spring Chain with Hookean Springs and Equilibrium-Averaged Hydrodynamic Interaction (Zimm Model) 164
Example 15.4-1 Stress Relaxation after Cessation of Steady Homogeneous Flows (Non-Hookean Springs) 173
Example 15.4-2 Translational Diffusion for Bead-Spring Chains 174

Chapter 16
General Bead-Rod-Spring Models **181**

16.1 Summary of Notation 182
Example 16.1-1 Calculations of Configurational Quantities for the Multibead-Rod Model 187
Example 16.1-2 Calculation of Configurational Quantities for the Three-Bead-Two-Rod Model 189
16.2 The "Diffusion Equation" for the Configurational Distribution Function 193
Example 16.2-1 The Diffusion Equation for the Orientational Distribution Function for the Multibead-Rod Model 195
16.3 Expressions for the Stress Tensor 198
Example 16.3-1 The Stress Tensor for the Multibead-Rod Model 202
16.4 Second-Order Fluid Constants for Arbitrary Bead-Rod-Spring Models with Equilibrium-Averaged Hydrodynamic Interaction 204
Example 16.4-1 Second-Order Fluid Constants for the Multibead-Rod Model with Equilibrium-Averaged Hydrodynamic Interaction 211
Example 16.4-2 Second-Order Fluid Constants for the Rigid Tridumbbell with Equilibrium-Averaged Hydrodynamic Interaction 213
Example 16.4-3 Second-Order Fluid Constants for the Elastic Rhombus 215
16.5 Steady Flows of Free-Draining Kramers Bead-Rod Chains 217
Example 16.5-1 Elongational Viscosity for the Kramers Bead-Rod Chain 219
16.6 Steady Flows for Free-Draining Kirkwood–Riseman Bead-Rod Chains 222
16.7 Unsteady Flows for Free-Draining Bead-Rod Models 229
Example 16.7-1 Calculation of the Relaxation Modulus for Arbitrary Rigid Axisymmetrical Bead-Rod Models 233

PART VII
A GENERAL PHASE-SPACE KINETIC THEORY

Chapter 17
Phase-Space Theory of Polymeric Liquids **245**

17.1 Classical Dynamics of a Complex System 246
Example 17.1-1 The Two-Needle Model 252
17.2 Ensemble Averages and Equations of Change 254
Example 17.2-1 The Effective Force for Models with No Constraints 260
17.3 Contracted Distribution Functions 261
17.4 The Stress Tensor in Terms of the Configuration Space Distribution Functions 264
17.5 Equations of Continuity for Configurational Distribution Functions 271
17.6 Simplified Expressions for the Stress Tensor and the Mass Flux 275

Chapter 18
Phase-Space Theory for Dilute Solutions **279**

18.1 The Short-Range Force Approximation 281
Example 18.1-1 The Stress Tensor for Models with Structureless Beads and No Constraints 284
18.2 Modified Stokes' Law Empiricisms for the Hydrodynamic Forces 285
18.3 Possible Approximations for the Brownian Forces 291
18.4 The Diffusion Equation, the Stress Tensor, and the Mass Flux 294
Example 18.4-1 The Diffusion Equation for the Multirod-Rod Model 300
Example 18.4-2 The Stress Tensor for the Multirod-Rod Model 302

Chapter 19
Phase-Space Theory for Concentrated Solutions and Melts **307**

19.1 The Hydrodynamic Forces 311
Example 19.1-1 The Link Tension Coefficient 313
19.2 The Brownian Forces 314
19.3 The Single-Link Distribution Function 317
19.4 The Stress Tensor and the Mass Flux 322
19.5 Solution of the Diffusion Equation for the Single-Link Distribution Function 328
19.6 The Constitutive Equation 332
Example 19.6-1 Effect of Polydispersity on Rheological Properties 337
19.7 Shear-Flow Rheological Properties 339
19.8 Elongational-Flow Rheological Properties 345

PART VIII
ELEMENTARY KINETIC THEORY FOR NETWORK MODELS

Chapter 20
Network Theories for Polymer Melts and Concentrated Solutions **353**

20.1 Descriptions of Network Models 354
20.2 Convection Equation for Network Segments 357
Example 20.2-1 Time Rate of Change of $\langle \boldsymbol{QQ} \rangle_{iN}$ 359
Example 20.2-2 The Distribution Function for a Network Solid 361
20.3 The Expression for the Stress Tensor 362
Example 20.3-1 Constitutive Equation for a Macromolecular Solid 364
20.4 The Lodge Network Model 368
Example 20.4-1 The Segment Distribution Function for the Lodge Network Model 371
20.5 Modified Network Models for Macromolecular Fluids 373
Example 20.5-1 Rheological Properties of a Non-Affine Lodge Network Model 376

APPENDICES

Appendix D
Summary of Continuum Mechanics Notation and Results **393**

D.1 Description of Flow Fields 393
D.2 Time Derivatives 395
D.3 Kinematic Tensors 396
D.4 Constitutive Equations for Incompressible Fluids 397
D.5 Definitions of Material Functions for Incompressible Fluids 398
D.6 The Equations of Change and the Fluxes 400

Appendix E
Useful Mathematical Formulas **403**

E.1 The Chain Rule for Partial Differentiation 403
E.2 Generalized Taylor Theorem 403
E.3 Integrals over All Three-Dimensional Space 404
E.4 The Dirac Delta Function 405
E.5 Unit Vectors in Spherical Coordinates 405
E.6 The Differential Operator $\partial/\partial \boldsymbol{u}$ 406

E.7 The Integral Operation $\int \cdots du$ 407
E.8 Spherical Harmonics and Legendre Polynomials 408
E.9 Fourth-Order Isotropic Tensors 409
E.10 Surface Spherical Harmonics 409
E.11 Euler Angles 410
E.12 The Functions $D^J(\alpha, \beta, \gamma)_{KM}$ 412

Author Index 417

Subject Index 421

NOTES ON NOTATION
FOR VOLUME 2

Notation (see Appendices A and E)

Scalars	Lightface	
Vectors	Boldface Italic	
Second-order Tensors	Boldface Greek	

Molecular Model Parameters

m_v; m_p	Mass of vth bead; mass of polymer	§12.1
ζ_v	Friction coefficient of vth bead	Eq. 13.2-5
N; $\bar{N}$	Number of beads; average number of beads per molecule	Eq. 17.5-11
H	Hookean spring constant	Table 11.5-1
a	Length of rigid link	Figs. 11.2-1, 11.3-1
$L = (N-1)a$	Contour length of chain or rod	Figs. 11.3-1, 14.1-2
Q_0	Maximum extension of spring	Table 11.5-1
b	Dimensionless parameter ($= HQ_0^2/kT$)	Table 11.5-1
n_α	Number density of species α	
ρ_α	Mass density of species α	

Time Constants

λ_H	For Hookean dumbbell	Eq. 13.4-4
λ	For rigid dumbbell	Eq. 14.2-6
λ_j	For jth mode in bead-spring chain	Eq. 15.3-16
λ_α	For species α in melt made up of bead-rod chains	Eq. 19.3-25
λ_j	For jth mode in network model	Eq. 20.4-10

Variables Describing Molecular Configurations (see §§12.1 and 16.1)

$\boldsymbol{r}_v$	Location of bead v with respect to arbitrary origin	Eq. 12.1-1
$\boldsymbol{r}_c$	Location of center of mass of molecule	Eq. 12.1-1
$\boldsymbol{r}_h$	Location of center of hydrodynamic resistance	Eq. 15.4-9
$\boldsymbol{r}_{\mu v}$	Interbead vector ($= \boldsymbol{r}_v - \boldsymbol{r}_\mu$)	Eq. 12.5-5
$\boldsymbol{R}_v$	Location of bead v with respect to the center of mass	Eq. 12.1-2
$\boldsymbol{Q}_k$	Connector vector ($= \boldsymbol{r}_{k+1} - \boldsymbol{r}_k$)	Fig. 11.4-1
Q_s	Generalized coordinate	§12.1
$\boldsymbol{Q}$	Segment vector	Fig. 20.1-1

$\boldsymbol{s}_k$, $\boldsymbol{t}_k$, $\boldsymbol{u}_k$	Triad of unit vectors associated with link k	Fig. 11.3-1, Eq. 11.6-16 Tables E.5-1 and 2
$\boldsymbol{c}_{1k}$, $\boldsymbol{c}_{2k}$, $\boldsymbol{d}_{1k}$, $\boldsymbol{d}_{2k}$	Base vectors associated with link k	Table E.5-1
θ_k, ϕ_k	Polar angles giving orientation of link k	Eq. 11.3-1
α, β, γ	Euler angles	Eq. 16.1-2, Fig. E.11-1

Configurational Matrices, Vectors, and Tensors (see Table 16.1-1)

(B_{vk}), $(\bar{B}_{kv})$	Non-square matrices interrelating position vectors and connector vectors	Tables 15.1-1 and 4
(A_{jk})	Rouse matrix, with eigenvalues a_j	Eq. 11.6-8
(C_{jk})	Kramers matrix, with eigenvalues c_j	Eq. 11.6-7
(Ω_{jk})	Matrix that diagonalizes Rouse matrix	Eq. 15.3-1
(g_{st}), (G_{st})	Metric matrix and inverse	Eqs. 12.1-7 and 8
g	Determinant of metric matrix ($g = \det(g_{st})$)	Eq. 12.1-7
$\boldsymbol{b}_{vs}$	Base vectors	Eq. 12.1-6
$\mathbf{K}$	Structure tensor	Eq. 16.2-8
$\mathbf{K}_{ij}$	Kramers tensors	Eq. 16.5-9

Quantities Associated with Hydrodynamic Interaction (see Table 16.1-2)

$\boldsymbol{\Omega}$	Hydrodynamic interaction tensor	Eq. 13.6-3
h	Hydrodynamic interaction parameter	Eq. 14.6-3
h^*	Modified hydrodynamic interaction parameter	Eq. 15.4-24

Molecular Dynamics Quantities

$\boldsymbol{p}_v$	Momentum of bead v	§12.1
$\boldsymbol{p}_c$	Momentum of center of mass	Eq. 12.1-9
P_s	Generalized momentum	Eq. 12.1-10
$\mathscr{L}$	Liouville operator	Eq. 17.2-4
$\mathscr{H}$	Hamiltonian	Eq. 12.2-1
$\mathscr{K}$	Kinetic energy	Eq. 12.1-4
ϕ, Φ	Potential energy	Eqs. 12.2-1, 17.1-19

Distribution Functions

f	Phase-space distribution function	Chapters 12 and 17
f	Orientational distribution function	Chapter 14
f	Single-link orientational distribution function	Chapter 19
Ψ, Ψ_α	Configuration-space distribution function	Eqs. 12.3-2 and 17.3-7
ψ	Configuration-space distribution function	Eq. 12.3-2
$\Psi_{\alpha\beta}$, $\tilde{\Psi}_{\alpha\beta}$	Pair distribution functions	Eq. 17.3-9
$(\cdots)_{\text{eq}}$	Equilibrium	

Rheological Properties (see Appendix D)

η_s	Solvent viscosity
$\eta(\dot{\gamma})$	(Non-Newtonian) viscosity
$\Psi_1(\dot{\gamma})$	First normal stress coefficient
$\Psi_2(\dot{\gamma})$	Second normal stress coefficient
η_0, $\Psi_{1,0}$, $\Psi_{2,0}$	Zero-shear-rate viscometric functions
$[\eta]$	Intrinsic viscosity
$\eta'(\omega)$, $\eta''(\omega)$	Components of complex viscosity η^*
$\bar{\eta}(\dot{\varepsilon})$	Elongational viscosity

b_1, b_2, b_{11}, etc.	Retarded-motion coefficients	
$G(t-t')$	Relaxation modulus	
J_e^0	Steady-state compliance	

Average Values (§§12.4 and 17.2)

$\langle\ \rangle$	Phase-space average	Eqs. 12.4-1 and 17.2-5
$[\![\ ]\!]$	Momentum-space average	Eqs. 12.4-2 and 17.3-13
$\langle\ \rangle_{iN}$	Average in network theory	Eq. 20.2-8

Forces (see Tables 16.1-3, 17.4-1, 17.5-1, 17.6-1, 18.1-1)

$\boldsymbol{F}_\nu^{(h)}$	Hydrodynamic force on bead ν	Eq. 13.2-1
$\boldsymbol{F}_\nu^{(e)}$	External force on bead ν	Eq. 13.2-1
$\boldsymbol{F}_\nu^{(b)}$	Brownian force on bead ν	Eq. 13.2-1
$\boldsymbol{F}_\nu^{(\phi)}$	Spring force on bead ν	Eq. 13.2-1
$\boldsymbol{F}_k^{(c)}$	Tension in link k	Eq. 13.2-7

Fluid Dynamic Quantities (see Appendix D)

$\boldsymbol{v}$	Fluid velocity	
$\boldsymbol{v}'$	Velocity perturbation due to hydrodynamic interaction	
$\boldsymbol{\kappa}$	Same as $(\nabla\boldsymbol{v})^\dagger$ (that is, $\kappa_{ij} = \partial v_i/\partial x_j$)	
$\dot{\boldsymbol{\gamma}}$	Rate-of-deformation tensor $(= \nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^\dagger)$	
$\boldsymbol{\omega}$	Vorticity tensor $(= \nabla\boldsymbol{v} - (\nabla\boldsymbol{v})^\dagger)$	
$\boldsymbol{\pi}$	Total stress tensor $(= p\boldsymbol{\delta} + \boldsymbol{\tau})$	
$\boldsymbol{\tau}$	Stress tensor	
$\boldsymbol{j}_\alpha$	Mass-flux vector for species α	
$\boldsymbol{\gamma}_{[0]}, \boldsymbol{\gamma}^{[0]}$	Relative finite strain tensors	
$\dot{\gamma}$	Shear rate	
$\dot{\varepsilon}$	Elongation rate	
ω	Frequency	

Mathematical Symbols (see Appendix E)

$\boldsymbol{\delta}$	Unit tensor	Eq. 13.3-1
$\boldsymbol{\delta}_n$	Unit vector	Eqs. 12.1-20 and 16.1-1
δ_{ij}	Kronecker delta	Eq. 11.3-7
$\delta(x)$	Dirac delta function	§E.4
$\check{\boldsymbol{\delta}}_n$	Embedded unit vectors	Eq. 16.1-1
(Ω_{mn})	Rotation matrix	Eq. 16.1-2
$\boldsymbol{n}$	Outwardly directed unit normal vector	Fig. 13.3-1
∇	Del operator in 3-space	Appendix A
$\mathscr{R}e\{z\}$	Real part of the complex number z	
P_n^m	Associated Legendre polynomials	§E.8
s, S, c, C	Sin ϕ, sin θ, cos ϕ, cos θ in spherical coordinates	Eq. 12.1-16
$s, S, \$; c, C, ¢$	Sin α, sin β, sin γ; cos α, cos β, cos γ (where α, β, γ are Euler angles)	Eq. 16.1-2
$\overline{(\cdots)}$	Complex conjugate	

Miscellaneous

k	Boltzmann constant	
T	Absolute temperature	
$\tilde{N}$	Avogadro number	
$D_{\text{rot}}, D_{\text{tr}}$	Rotatory, translational diffusivity	

PART V

POLYMER MODELS AND EQUILIBRIUM PROPERTIES

The principal aim of this volume is a molecular study of the rheological properties of polymeric liquids. We make use of various mechanical models for macromolecules and then use the principles of nonequilibrium statistical mechanics to obtain information about the way in which the macromolecules are distributed over all possible configurations: that is, we obtain a configurational distribution function. From the latter we can then obtain relations between the mechanical-model parameters and the macroscopic properties of the fluids; in particular we are interested in the stress tensor and the rheological properties. Knowledge of the stress tensor is of central importance in understanding polymer fluid dynamics, as has been seen in Volume 1.

An actual polymer molecule is an extremely complex mechanical system with an enormous number of degrees of freedom. To study the detailed motions of this complicated system and their relations to the nonequilibrium properties would be prohibitively difficult. As a result it has been customary for polymer scientists to resort to mechanical models to simulate the mechanical behavior of the macromolecule. In Chapter 11 we present some of the most widely used mechanical models and give some idea as to how these models originated and to what extent they describe molecular behavior.

Then in Chapter 12 we use some of these models to calculate the configurational distribution function for solutions of polymers at equilibrium. Here we can use classical equilibrium statistical mechanics, which provides a general formula for obtaining the configurational distribution function. From the latter we can then get various equilibrium properties, such as the average of the square of the end-to-end distance and the radius of gyration of a polymer chain.

Although our principal concern in this volume is the understanding of nonequilibrium behavior, it is important to understand equilibrium phenomena first. Much of the information in Chapter 12 on distribution functions, contracted distribution functions, average values, and the mathematics of complex multi-particle models is used in the subsequent chapters.

CHAPTER 11
MECHANICAL MODELS FOR POLYMER MOLECULES

"The time has come," the penguin said,
"To speak of many things:
Of flowing macromolecules,
And little beads and springs
That join together into 'chains'
Or even 'stars' or 'rings'."

—With apologies to Lewis Carroll

Even in the kinetic theory of gases it is necessary to use simplified models to represent molecules in order to minimize the mathematical complications. In the earliest theories the rigid sphere model was used, and this accounted roughly for the strong repulsive forces between molecules, but completely neglected the weak attractive forces. Later kinetic theorists used point masses that interact according to a Lennard–Jones potential; this two-constant empirical model accounts semi-quantitatively for both attractive and repulsive forces. As the kinetic theories became more and more refined and as more powerful computers were developed, more elaborate molecular models were developed to take into account the molecular shape and the charge distribution within the molecules. Since the statistical mechanical calculation of equilibrium properties (thermodynamic properties and virial coefficients) is far easier than that of nonequilibrium properties (viscosity, thermal conductivity, and diffusivity) it is not surprising that the molecular modeling in equilibrium statistical mechanics has reached a higher level of realism and complexity than in the nonequilibrium part of the field.

In polymer kinetic theory we find a similar development: in the 1930s, when the subject was just beginning, the crude "dumbbell" models were introduced; in the ensuing years bead-rod and bead-spring chains were used for representing chainlike macromolecules; still more complex models accounting for steric hindrance, excluded volume, chain branching, and other effects were developed much later. If one is interested only in the equilibrium configurations and properties derived therefrom, one can afford to use rather realistic and complex modeling. However, if the object is to describe macromolecular configurations in nonequilibrium systems and the associated rheological properties—a far more difficult problem—then it becomes necessary to use considerably simpler models in order to do the mathematics and the numerical work. Inasmuch as this volume is primarily dedicated to the latter problem, the emphasis here will be on the simpler models, which have contributed greatly to our understanding of polymer rheology and fluid dynamics.

This chapter is devoted to a brief discussion of some of the mechanical models that are used in this book and in the research literature. We give some of the physical arguments that have led to these models and present the nomenclature that is used in the description of their configurations. In each of these models a few parameters are introduced. Ultimately numerical values must be given for these parameters, either by relating them to fundamental constants describing the true molecule or by choosing them in such a way that certain rheological data (viscosity, normal stresses, complex viscosity, etc.) are described. The use of empirical mechanical contrivances in lieu of the true molecule inevitably introduces parameters that have some degree of fuzziness; this is simply the price that one pays for the mathematical and numerical simplification achieved by the use of a mechanical model.

§11.1 MACROMOLECULAR STRUCTURE

Polymer molecules differ from the small molecules treated in the usual kinetic theory of gases and liquids in several important ways:

a. *Great diversity in structure.* Organic chemists have succeeded in synthesizing straight chain polymers, branched polymers, block copolymers, closed-ring polymers, ionomers, and rigid polymers. Ultimately it will be desirable to have kinetic theory calculations for models representing each of these (and still other) classes of polymers. To date most of the research has been done in linear flexible polymers, and this book reflects that emphasis.

b. *Molecular weight distributions.* When polymers are synthesized, the molecules in the sample do not all have the same length (i.e., they are not "monodisperse") but instead they are of varying length (i.e., they are "polydisperse"). Polydispersity has an enormous effect on the macroscopic properties; small amounts of very high molecular-weight components can alter the rheological properties significantly. Consequently, kinetic theories must be able to account for molecular weight distributions.

c. *Large number of internal degrees of freedom.* Since many polymeric materials contain molecules with molecular weights in the millions, each molecule in the material is capable of existing in a huge number of configurations. A kinetic theory of polymeric materials must therefore be able to account for the stretching, rotation, and deformation of the constituent molecules. The force transmitted along the chain backbones of the molecules in these various configurations is a key factor in obtaining an expression for the stress tensor, the central object of study in rheology.

Because of these three features of polymeric liquids, the molecular modeling and the kinetic theory development will be considerably different from the analogous topics in the kinetic theory of gases and simple liquids. For those interested in the development of molecular models and the history of kinetic theory, the two volumes of collected reprints assembled by Hermans will be valuable.[1]

To get some idea about the nature of the true systems that are the object of our study in this volume, let us look at the photographs of Fisher-Hirschfelder-Taylor models in Fig. 11.1-1. In (*a*) and (*b*) we show portions of polyethyleneoxide and polyethylene chains in several different configurations; this is a reminder of the complexity of polymer motions. In (*c*) we show portions of polystyrene and polyisobutylene chains; these photographs emphasize the importance of side-group substituents on the dynamics of chains. Finally, in

[1] J. J. Hermans, Ed., *Polymer Solution Properties: Part I, Statistics and Thermodynamics; Part II, Hydrodynamics and Light Scattering*, Dowden, Hutchinson, and Ross, Inc., Stroudsburg, PA (1978).

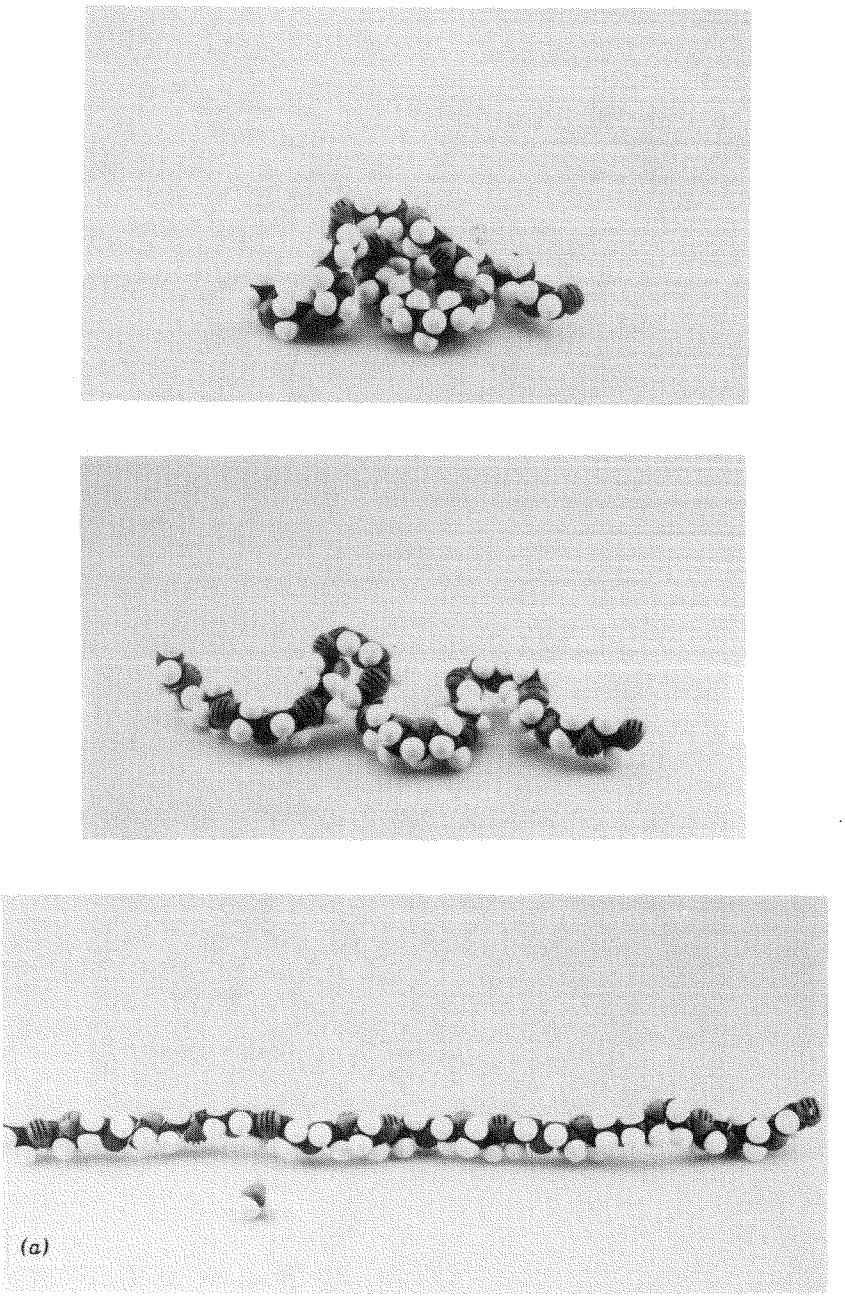


FIGURE 11.1-1. Photographs of molecular models: (*a*) 20 monomer units of a polyethyleneoxide chain, in three different conformations; under the fully stretched-out conformation is shown a water molecule for comparison. In (*a*), (*b*), and (*c*) only short portions of the chain are shown; in most polymeric fluids of interest, chains with 10^3–10^6 monomer units are typically encountered. Photographs prepared by J. D. Schieber and T. W. Liu, Chemical Engineering Department, University of Wisconsin-Madison (1984).

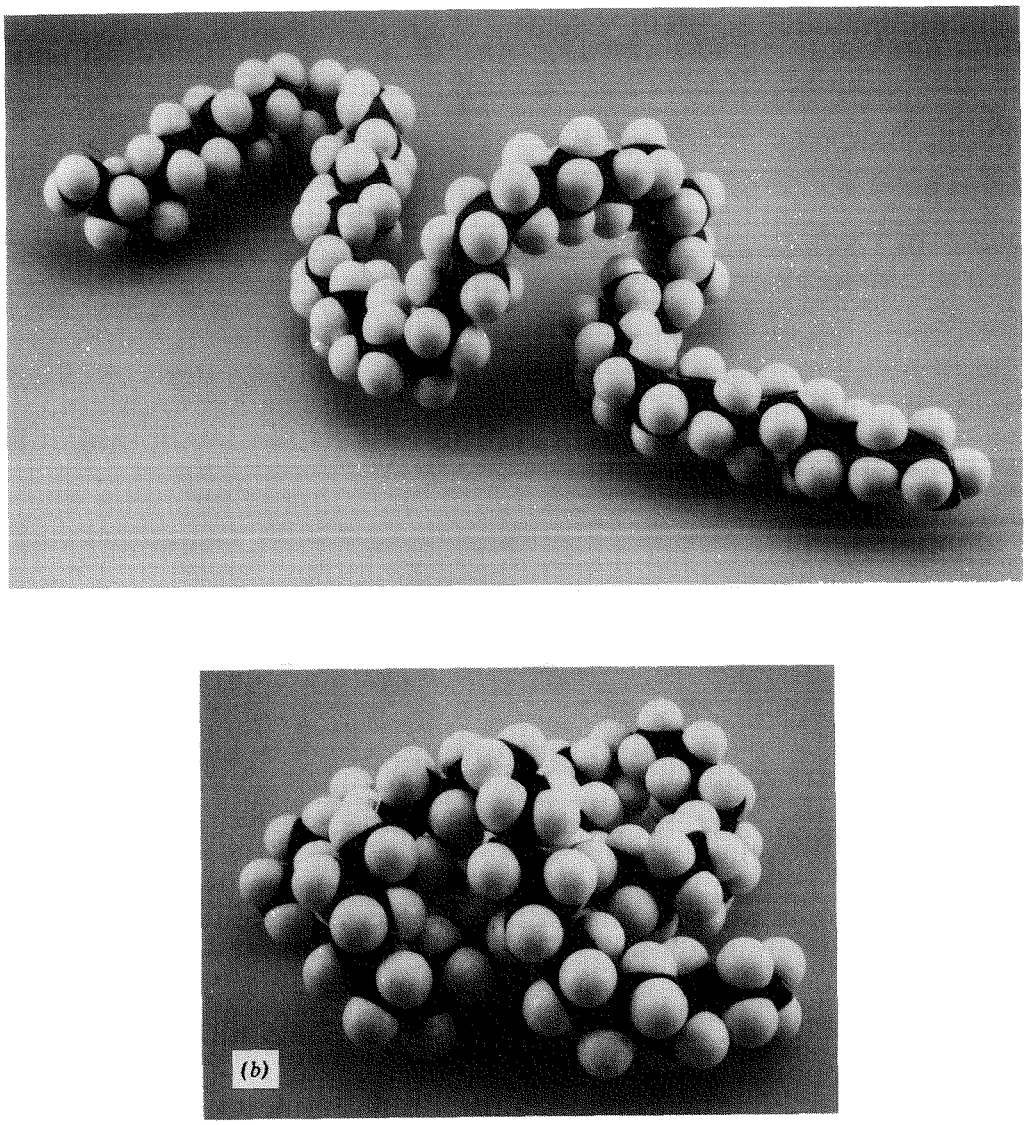
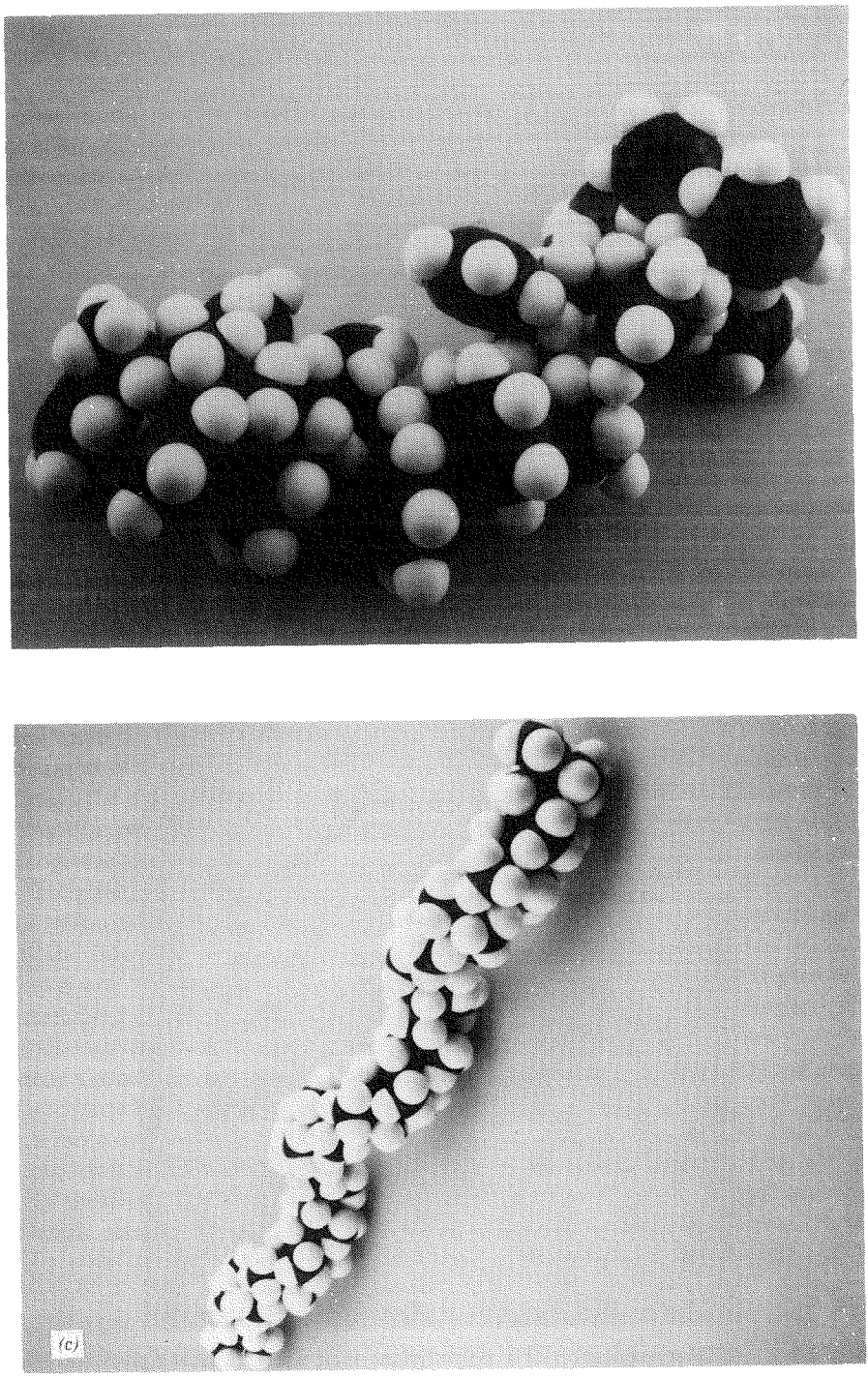
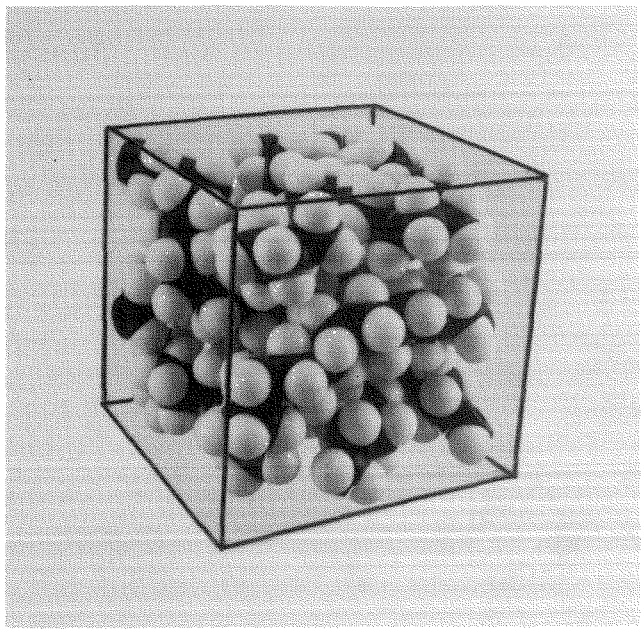


FIGURE 11.1-1. (*b*) 34 monomer units of a polyethylene chain, in two different conformations.



JRE 11.1-1. (*c*) 14 monomer units of a polystyrene chain showing the large side groups; and 22 ɔmer units of a polyisobutylene chain, which cannot move easily into other configurations ɪse of the steric hindrance of the side groups.



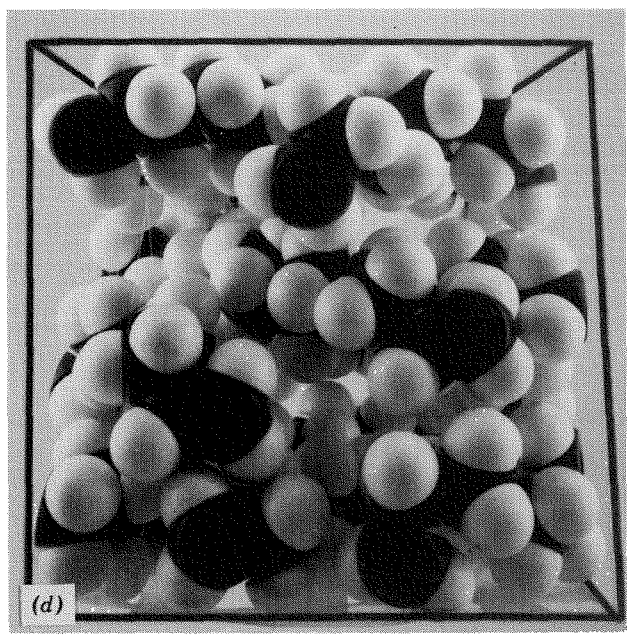


FIGURE 11.1-1. (*d*) Representation of a polyethylene melt showing how tightly the chains are packed; the cube, 15 Å on a side, contains 118 carbon atoms, or 58 monomer units.

(*d*) we show a region of an undiluted sample of polyethylene; this gives some idea as to the amount of empty space that a molecule has to move about in as well as the sort of environment that a portion of a macromolecule "sees" in an undiluted system. These photographs should be kept in mind as we discuss mechanical models in this chapter and as we develop kinetic theories in the ensuing chapters.

Of course, the photographs in Fig. 11.1-1 show only what the molecules look like at one instant of time. In the true system all of the molecules will be in a continual state of motion. The thermal energy of the system gives rise to the frenetic motion of the solvent molecules, which in turn bang into the polymer molecule and cause it to writhe around in a very complicated way. There will be large-scale motions of the polymer chain as a whole, and superimposed on this there will be more rapid wiggly motions of portions of the chain. This latter kind of motion is generally referred to as Brownian motion. Of course there will also be vibration of the bonds and torsional vibrations of the pendant groups as they oscillate back and forth within the constraints of steric hindrance. Since quantum mechanical phenomena are not important in systems such as this, the motion of the entire assembly of molecules can be described satisfactorily by classical mechanics.

In most of the theories developed to date, two major simplifications are made: (a) the Brownian motion is described by the gradient of a distribution function, which serves as a driving force; and (b) the intermolecular forces are accounted for by the use of some kind of Stokes' law expression that accounts approximately for the forces exerted on portions of the macromolecule. Later, in Chapter 17, we adopt a more fundamental viewpoint and obtain much more general expressions for both of these effects in terms of appropriate averages involving the intermolecular forces.

It should be evident that the system we are studying is extraordinarily complicated. From the point of view of the rheologist and the fluid dynamicist, the question is: Just how detailed does the modeling need to be in order to obtain useful results? The word "useful" has a different meaning to the fluid dynamicist who wants to describe flow behavior than to the rheologist interested in accurate description of material functions, or to the polymer chemist fascinated by differences in structure and molecular architecture. Even within one group of researchers the needs may be different. For example, for the rheologist it is primarily the slow bending and expanding motions of the chain that have to be described accurately if one is interested in the steady state shear flow properties; it is primarily the overall stretching of the chains that is important for the elongational flow properties; and it is the small-scale motions that are of interest in connection with the complex viscosity and other linear viscoelastic properties. Consequently an elastic dumbbell model for a polymer may be adequate for a polymer fluid dynamicist primarily interested in steady-state flows, whereas a more detailed model accounting for rapid vibrational and torsional motions may be required for a polymer chemist studying polymer structure by means of high frequency oscillatory shear and birefringence experiments. The question of "usefulness" must be kept in mind while reading about the various mechanical models in the next few sections.

§11.2 CHAIN MODELS WITH FIXED BOND LENGTHS AND BOND ANGLES

It has been pointed out by Flory[1] that the bond lengths and the angles between adjacent bonds are restricted to quite narrow ranges. At ordinary temperatures the amplitudes of the oscillations in bond lengths and bond angles are about 3% of their

[1] P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York (1969), p. 13.

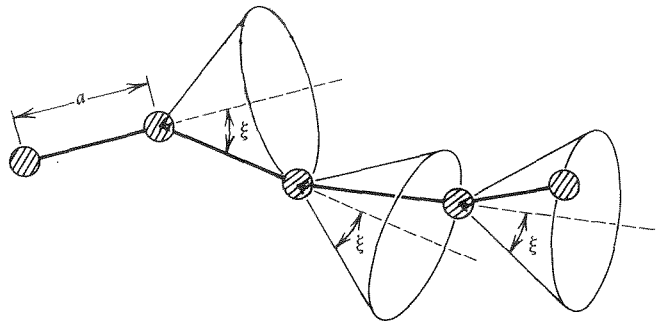


FIGURE 11.2-1. Chain of carbon atoms in the backbone of a polyethylene molecule. ◍, Carbon atom in a polyethylene chain. $\xi = \arccos(\frac{1}{3}) = 70.5°$.

average values. Therefore in constructing a mechanical model of a polymer molecule it seems reasonable to fix the bond lengths and angles at their mean values.

If we consider for a moment a polyethylene chain, $CH_3(CH_2)_nCH_3$, and if we ignore the pendant hydrogen atoms, then the chain can be represented as a set of mass points (often called "beads" in polymer kinetic theory) joined by massless "rods." The angle between successive C–C bonds is restricted to be $\xi = \arccos \frac{1}{3} = 70.5°$ (see Fig. 11.2-1). However, because of the presence of the hydrogen atoms, there are rotational energy barriers that prevent the successive links from rotating freely. Some approximate analytical expressions have been developed for the potential energy of the rotational barriers for polyethylene and other chains, and with these, various quantities, such as mean square end-to-end distance, have been calculated.[2]

A somewhat less detailed model is the *rotational isomeric state model.* In this model one presumes that the details of the rotational energy barrier are not needed, but that each succeeding link in the chain can exist in one of several (usually three) distinct rotational positions. This type of modeling has been used extensively by Flory and his collaborators in their studies of the configurations of specific polymer chains at equilibrium.[3] To date no nonequilibrium calculations have been made for these chain models that account for hindered rotation, with either continuous or discrete rotational states.

This leads us to discuss a still less detailed model in which one ignores altogether the restrictions on the rotations about the chemical bonds although the bond angles are kept fixed. This *freely rotating chain* model was the subject of extensive formal nonequilibruim kinetic theory studies by Kirkwood and his school.[4] Kirkwood assumed that the beads obey a Maxwellian velocity distribution and also that each bead in the chain experiences a Stokes' law drag force as it moves through the surrounding solvent molecules; in this way a bead "friction coefficient" ζ is introduced that accounts in some kind of average way for the resistance encountered by the bead when the chain moves through a succession of configurations. Having made these two assumptions, Kirkwood then formulated the partial differential equation from which the configurational distribution function could in principle be obtained. This partial differential equation has been solved only for potential flows, and very limited calculations of rheological properties have been made (see §16.6). In addition,

[2] A very readable account of this type of modeling can be found in L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed., Oxford University Press, London (1975), Chapter III.

[3] P. J. Flory, op. cit., Chapters III–VII.

[4] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967); this is a collection of twenty papers dealing with polymer kinetic theory.

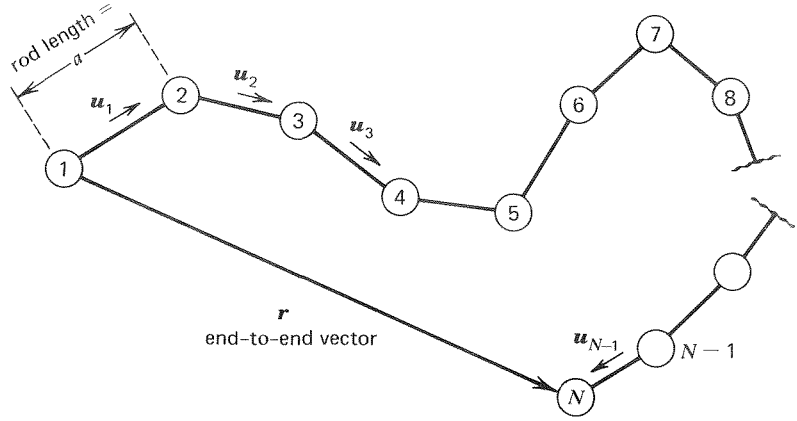


FIGURE 11.3-1. The Kramers freely jointed bead-rod chain model formed from N "beads" and $N - 1$ rigid "rods". The rod orientations are given by the unit vectors $\boldsymbol{u}_k$ ($k = 1, 2, \ldots, N - 1$).

some calculations of equilibrium properties have been given, based not on rigorous statistical mechanics but on a modified random walk calculation in which the constancy of the bond angles is accounted for.[5]

Another chain model, closely related to the Kirkwood-Riseman freely rotating chain, is the Porod-Kratky *wormlike chain*.[6] This is essentially a continuous version of the freely rotating chain, in that the beads have been smoothed out into a continuous wormlike structure of constant curvature with the plane of the curvature varying randomly.

§11.3 THE FREELY JOINTED BEAD-ROD CHAIN MODEL

We turn next to a model which is considerably less detailed, namely the *freely jointed chain* of N beads of mass m and friction coefficient ζ connected by $N - 1$ rigid, massless rods of length a. In this model the beads do not represent the atoms of the polymer chain backbone, but merely some portion of the polymer chain, say 10 or 20 monomer units. The quantities N and a are thus imprecisely defined quantities, but $(N - 1)a$ is the contour length of the true molecule being represented by the model. We have thus sacrificed some rigor in this model for the sake of simplicity. Since this model was the object of study by Kramers[1] in a key paper in polymer kinetic theory, we often refer to it as the *Kramers chain* model; it has also been referred to as the *pearl necklace* model. It is pictured in Fig. 11.3-1.

Although the freely jointed bead-rod chain does not pretend to portray the chemical structure of a linear macromolecule, it does possess a number of features that are characteristic of these molecules: it has a large number of internal degrees of freedom; it can be oriented, stretched, and deformed; it has a constant contour length. These are all properties that are significant in formulating a kinetic theory for the rheological behavior of a polymeric liquid. Keep in mind that the model contains two adjustable constants: the drag coefficient ζ and the rod length a (the bead mass m turns out to be unimportant since

[5] L. R. G. Treloar, loc. cit.; H. Eyring, *Phys. Rev.*, **39**, 746-748 (1932); F. T. Wall, *J. Chem. Phys.*, **11**, 67-71, 485-488, 527-530 (1943).

[6] P. J. Flory, op. cit., Appendix G; G. Porod, *Monatsh. Chem.*, **80**, 251-255 (1949); O. Kratky and G. Porod, *Rec. Trav. Chim.*, **68**, 1106-1122 (1949). H. Yamakawa, *Ann. Revs. Phys. Chem.*, **35**, 23-47 (1984).

[1] H. A. Kramers, *Physica*, **11**, 1-19 (1944).

inertial effects are generally neglected, and the number of beads N is determined from the contour length L by $L = (N - 1)a$).

Because of the importance of the freely jointed chain model in the polymer chemistry literature, we interrupt our discussion of model-building to obtain a few standard results that we need later. In order to obtain these results, it is necessary to have an expression for the configurational distribution function for the chain. In Chapter 12 we derive an expression for the equilibrium distribution function for a single bead-rod chain in a dilute solution starting from the principles of equilibrium statistical mechanics. We find that to a good approximation the distribution function is the "random walk" distribution; that is, the polar angles θ_i and ϕ_i for the ith link in the chain are completely random. The probability that the ith link is found to be within the range $d\theta_i\, d\phi_i$ about θ_i, ϕ_i is then

$$\psi_{i,\mathrm{eq}}(\theta_i, \phi_i)d\theta_i\, d\phi_i = \frac{1}{4\pi} \sin\theta_i\, d\theta_i\, d\phi_i \tag{11.3-1}$$

Since each link is assumed to be oriented independently of all other links, the configurational distribution function for the entire chain at equilibrium is the product of the single link distribution functions:[2]

$$\psi_{\mathrm{eq}}(\theta^{N-1}, \phi^{N-1}) = \prod_{i=1}^{N-1} \psi_{i,\mathrm{eq}} = \left(\frac{1}{4\pi}\right)^{N-1} \prod_{i=1}^{N-1} \sin\theta_i \tag{11.3-2}$$

The average value of any property $B(\theta^{N-1}, \phi^{N-1})$ that depends on the configuration is then given by

$$\langle B\rangle_{\mathrm{eq}} = \iint B\psi_{\mathrm{eq}}\, d\theta^{N-1}\, d\phi^{N-1} \tag{11.3-3}$$

This is the average value over the entire ensemble of systems, where in this case a system is a single polymer molecule. This average value is that which would be measured in some kind of an experiment that is made over a macroscopic time interval. That is, we assume that time averages are the same as ensemble averages. Average values are discussed more fully in Chapter 12.

In the illustrative examples that follow we use this random-walk distribution to obtain expressions for some important statistical quantities: the mean square end-to-end distance, the probability distribution for the end-to-end vector, and the mean tension in the chain.

EXAMPLE 11.3-1 Root-Mean-Square End-to-End Distance

In a dilute solution a polymer molecule is being continually bombarded by the solvent molecules. As a result its configuration is continually changing, as are various derived quantities, such as the end-to-end distance of the molecule. The end-to-end vector is

$$\boldsymbol{r} = \sum_{i=1}^{N-1} a\boldsymbol{u}_i \tag{11.3-4}$$

[2] Here and elsewhere in this volume we use the abbreviated notation θ^{N-1}, ϕ^{N-1} instead of $\theta_1, \phi_1, \theta_2, \phi_2, \ldots, \theta_{N-1}, \phi_{N-1}$ and $\iint d\theta^{N-1}\, d\phi^{N-1}$ for $\int\cdots\int d\theta_1\, d\phi_1\, d\theta_2\, d\phi_2 \cdots d\theta_{N-1}\, d\phi_{N-1}$. Also, note that in Eq. 11.3-1 we choose to include the factor $\sin\theta_i$ in the distribution function rather than in the differential element of area; we do this in order to be consistent with the use of generalized coordinates in the next chapter.

where the $\boldsymbol{u}_i$ are the unit vectors in the directions of the links of the chain. The square of the end-to-end distance is then given by

$$r^2 = (\boldsymbol{r} \cdot \boldsymbol{r}) = a^2 \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} (\boldsymbol{u}_i \cdot \boldsymbol{u}_j) \tag{11.3-5}$$

We are normally interested only in average quantities, that is, quantities averaged over an entire ensemble of systems. In this case the system is a single polymer molecule, and the distribution function in Eq. 11.3-2 describes the distribution of configurations for a large collection of chains. Find the average value of r^2 in a solution at rest (that is, at rest when viewed macroscopically) by using the configurational distribution function in Eq. 11.3-2.

SOLUTION According to Eq. 11.3-3 the average value of r^2 is

$$\langle r^2 \rangle_{\text{eq}} = a^2 \sum_i \sum_j \iint (\boldsymbol{u}_i \cdot \boldsymbol{u}_j) \psi_{\text{eq}} \, d\theta^{N-1} \, d\phi^{N-1} \tag{11.3-6}$$

The dot products of the unit vectors can be calculated by noting that the x-, y-, and z-components of $\boldsymbol{u}_i$ are $\sin\theta_i \cos\phi_i$, $\sin\theta_i \sin\phi_i$, and $\cos\theta_i$, respectively; when the integrations are performed we find that

$$\begin{aligned} \langle r^2 \rangle_{\text{eq}} &= a^2 \sum_i \sum_j \delta_{ij} \\ &= a^2(N-1) \end{aligned} \tag{11.3-7}$$

in which δ_{ij} is the Kronecker delta ($\delta_{ij} = 1$ if $i = j$, $\delta_{ij} = 0$ if $i \neq j$). Therefore the root-mean-square end-to-end distance is

$$\sqrt{\langle r^2 \rangle_{\text{eq}}} = \sqrt{N-1}\, a \tag{11.3-8}$$

Since the length of the fully extended chain is $(N-1)a$, a polymer molecule can in the extreme be stretched by a factor of $\sqrt{N-1}$ from its equilibrium value. Since N can be of the order of magnitude of 100 for reasonable models of macromolecules, it can be expected that this enormous change in molecular shape will profoundly effect the optical and rheological properties of polymeric materials in a state of flow.

If instead of the freely jointed chain we use the freely rotating chain with $\xi = \arccos \frac{1}{3}$ we find Eyring's result[3] that $\langle r^2 \rangle_{\text{eq}} = 2(N-1)a^2$. This is just 2 times the value for the freely jointed chain.

In obtaining Eq. 11.3-8 and also the Eyring result just quoted, the finite size of the cross-section of the chain is not accounted for. If this "excluded volume effect" is accounted for, the root-mean-square end-to-end distance will be increased still further.[3,4]

EXAMPLE 11.3-2 Equilibrium Distribution Function for the End-to-End Vector

In Eq. 11.3-2 we have given the equilibrium distribution function for the configuration of a freely jointed bead-rod chain model of a polymer molecule. For some purposes we need less complete distribution functions. By way of example, suppose we want only the probability that the first link in

[3] See L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed., Oxford University Press, London (1975), Chapter VI.

the chain will have an orientation θ, ϕ. This can be obtained in one of two ways. The simplest is to integrate the full chain distribution function over the orientation variables for all links except the first:

$$\psi_{1,\mathrm{eq}}(\theta, \phi) = \underbrace{\int \cdots \int}_{2(N-2)\text{-fold}} \psi_{\mathrm{eq}}(\theta^{N-1}, \phi^{N-1}) d\theta_2 \, d\phi_2 \cdots d\theta_{N-1} \, d\phi_{N-1} \Big|_{\theta_1 = \theta, \phi_1 = \phi} \tag{11.3-9}$$

Alternatively one can evaluate the average of the product of the Dirac delta functions:

$$\psi_{1,\mathrm{eq}}(\theta, \phi) = \underbrace{\int \cdots \int}_{2(N-1)\text{-fold}} \psi_{\mathrm{eq}}(\theta^{N-1}, \phi^{N-1}) \delta(\theta_1 - \theta) \delta(\phi_1 - \phi) d\theta^{N-1} \, d\phi^{N-1} \tag{11.3-10}$$

The delta function has the property that $\int \delta(x - a) f(x) dx = f(a)$. When this property is used it can be seen that Eq. 11.3-10 reduces to Eq. 11.3-9. Often this second way of getting reduced distribution functions is more straightforward to apply. For more on the Dirac delta function, see Appendix E.

Let us now apply this second procedure to get the probability that a polymer molecule has an end-to-end vector in the range dr about r. That is, we write

$$P_{\mathrm{eq}}(\boldsymbol{r}) = \int\int \delta\left(\boldsymbol{r} - a \sum_i \boldsymbol{u}_i\right) \psi_{\mathrm{eq}} \, d\theta^{N-1} \, d\phi^{N-1} \tag{11.3-11}$$

To obtain $P_{\mathrm{eq}}(\boldsymbol{r})$ in the random-walk approximation, we have to introduce the distribution function from Eq. 11.3-2 and perform the integration. The mathematical details of the evaluation of the multiple integrals in Eq. 11.3-11 are not given here. If N is very large and the end-to-end distance is smaller than about $0.5\, Na$, it may be shown[4] that $P_{\mathrm{eq}}(\boldsymbol{r})$ is to a very good approximation

$$P_{\mathrm{eq}}(\boldsymbol{r}) \doteq \left(\frac{3}{2\pi(N-1)a^2}\right)^{3/2} e^{-3r^2/2(N-1)a^2} \tag{11.3-12}$$

This result is known as the Gaussian distribution for the end-to-end vector of the freely jointed chain with $N - 1$ links of length a. It can be seen that $P_{\mathrm{eq}}(\boldsymbol{r})$ has a maximum at $\boldsymbol{r} = \boldsymbol{0}$. That is, if one end of the molecule is located at the origin, the most probable location of the other end is also at the origin. This does not mean, however, that the most likely value of the end-to-end distance $r = |\boldsymbol{r}|$ is zero. Indeed we already know that the average value of the square of the end-to-end distance is $(N - 1)a^2$. Show that although the Gaussian distribution for the end-to-end vector is only approximately valid, it still gives the correct value of the mean square end-to-end distance in the random-walk approximation.

SOLUTION Using Eq. 11.3-12 gives

$$\begin{aligned}
\langle r^2 \rangle_{\mathrm{eq}} &= \int r^2 P_{\mathrm{eq}}(\boldsymbol{r}) d\boldsymbol{r} \\
&= \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} r^2 \left(\frac{3}{2\pi(N-1)a^2}\right)^{3/2} e^{-3r^2/2(N-1)a^2} r^2 \sin\theta \, dr \, d\theta \, d\phi \\
&= (N-1)a^2
\end{aligned} \tag{11.3-13}$$

in agreement with Eq. 11.3-7. In the next example we see a further use of Eq. 11.3-12.

[4] H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 15; P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley, New York (1969), Chapter VIII. See also Problem 12D.1.

EXAMPLE 11.3-3 Average Tension in a Polymer Chain

The Helmholtz free energy $A = U - TS$ (where U is the internal energy and S is the entropy) of any system at equilibrium at temperature T is given by statistical mechanics as

$$A = -kT \ln Z \tag{11.3-14}$$

where Z is the *partition function*. Aside from a multiplicative constant the partition function is given by the integral of $e^{-\mathscr{H}/kT}$ over the phase space of the system. The Hamiltonian $\mathscr{H}$ is given as the sum of the kinetic and potential energies:

$$\mathscr{H} = \mathscr{K} + \phi \tag{11.3-15}$$

expressed in terms of generalized coordinates and momenta (see Chapter 12).

Here we consider a polymer chain with a fixed end-to-end vector $\boldsymbol{r}$ suspended in a sea of solvent molecules at a temperature T. For an ensemble of such systems it can be shown (see Eq. 12.3-5 with $\sqrt{g} = \prod_i \sin \theta_i$) that in the random-walk approximation the partition function is given, except for a multiplicative factor independent of $\boldsymbol{r}$, by $P_{eq}(\boldsymbol{r})$ as defined in Eq. 11.3-11. Hence the Helmholtz free energy of the polymer chain with end-to-end vector $\boldsymbol{r}$ is

$$A(\boldsymbol{r}) = A^{(0)} - kT \ln P_{eq}(\boldsymbol{r}) \tag{11.3-16}$$

where $A^{(0)}$ does not contain $\boldsymbol{r}$. Use this result to find the average tension in a polymer chain for large values of N and for $|\boldsymbol{r}| < \frac{1}{2}Na$.

SOLUTION When the length of the chain is changed by a small amount at constant T, the change of the Helmholtz free energy is given from Eq. 11.3-16 and Eq. 11.3-12 by

$$\begin{aligned} dA &= -kT\, d \ln P_{eq}(\boldsymbol{r}) \\ &\doteq -kT\, d\left[\frac{-3(\boldsymbol{r}\cdot\boldsymbol{r})}{2(N-1)a^2}\right] \\ &= \frac{3kT}{(N-1)a^2}(\boldsymbol{r}\cdot d\boldsymbol{r}) \end{aligned} \tag{11.3-17}$$

However, we also know that for an isothermal process the change in the Helmholtz free energy of the chain is related to the tension $\boldsymbol{F}^{(c)}$ in the chain by

$$dA = (\boldsymbol{F}^{(c)}\cdot d\boldsymbol{r}) \tag{11.3-18}$$

When these last two expressions are equated we get

$$\left(\left[\boldsymbol{F}^{(c)} - \frac{3kT}{(N-1)a^2}\boldsymbol{r}\right]\cdot d\boldsymbol{r}\right) = 0 \tag{11.3-19}$$

This scalar product must be equal to zero for all infinitesimal increments $d\boldsymbol{r}$, but that can be true only if the vector within the bracket is zero. Consequently

$$\boldsymbol{F}^{(c)}(\boldsymbol{r}) = -\frac{3kT}{(N-1)a^2}\boldsymbol{r} \qquad (N \text{ large}, |\boldsymbol{r}| < \tfrac{1}{2}Na) \tag{11.3-20}$$

Thus the freely jointed bead-rod chain acts like a Hookean spring with a force constant given by $H = 3kT/(N-1)a^2$ and length zero in the absence of an external force; that is, its rest length is zero. Since this calculation is based on the Gaussian distribution, Eq. 11.3-20 is often called a *Gaussian spring*; because of the connection with the entropy of the chain the term "entropic spring" is also used.

Now that an expression has been derived for the Hookean spring constant, we can rewrite the expressions for the distribution function for the end-to-end vector and the root-mean-square end-to-end distance as

$$P_{eq}(\boldsymbol{r}) \doteq \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)(\boldsymbol{r}\cdot\boldsymbol{r})} \tag{11.3-21}$$

$$\langle r^2\rangle_{eq} = \frac{3kT}{H} \tag{11.3-22}$$

These expressions are now in forms similar to those appearing in later chapters.

As mentioned previously the Gaussian approximation is good only for large N and extensions r smaller than about $0.5Na$. As a result Eq. 11.3-20 cannot be generally valid, and indeed it allows the chain to be stretched to any length provided that enough force is applied. In actuality the spring must stiffen up as the chain becomes fully extended. To take account of this fact various modified force laws have been proposed; we cite two of these:

i. *Inverse Langevin Force Law* (derivable from molecular arguments):[3]

$$F^{(c)}(r) = \frac{kT}{a}\mathscr{L}^{-1}\left[\frac{r}{(N-1)a}\right] \tag{11.3-23}$$

where $\mathscr{L}^{-1}$ is the function inverse to the Langevin function given by $\mathscr{L}(x) = (\coth x) - x^{-1}$.

ii. *Warner Force Law* (a useful empiricism):[5]

$$F^{(c)}(r) = \frac{3kTr/(N-1)a^2}{[1-(r/(N-1)a)^2]} \tag{11.3-24}$$

Springs obeying this force law are often called *FENE* (finitely extensible nonlinear elastic) springs.

In these last two equations $F^{(c)} = |\boldsymbol{F}^{(c)}|$ denotes the tension in the spring.

These various spring force-law functions are shown in Fig. 11.3-2. Note that the Warner force law has all of the desired physical characteristics: linear behavior at small extensions, and a finite length $(N-1)a$ in the limit of an infinite force; it has the advantage that it is much simpler than the inverse Langevin function.

§11.4 THE FREELY JOINTED BEAD-SPRING MODELS

In the foregoing section we saw that a freely jointed bead-rod chain suspended in a solvent and thereby subjected to random Brownian motion behaves something like a

[5] H. R. Warner, Jr., *Ind. Eng. Chem. Fundamentals*, **11**, 379-387 (1972).

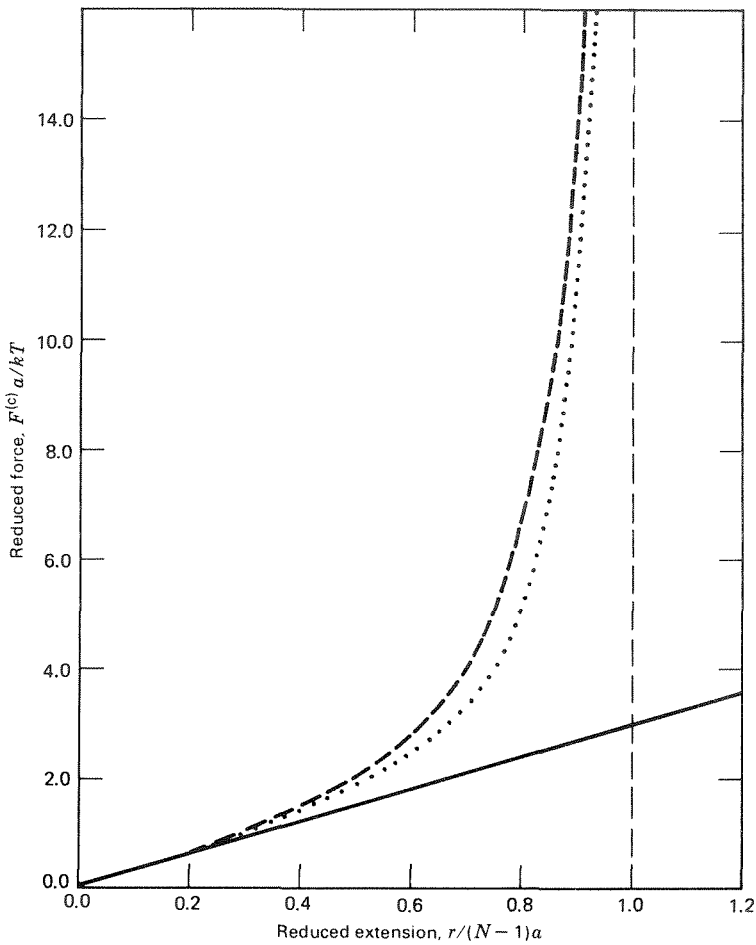


FIGURE 11.3-2. Plots of three approximate expressions for the ensemble average tension $F^{(c)}$ in a freely jointed chain of $(N-1)$ links of length a with end-to-end distance r. ——, Hookean, Eq. 11.3-20; ·····, inverse Langevin, Eq. 11.3-23; - - - -, Warner, Eq. 11.3-24.

spring. A similar result would have been obtained for a freely rotating chain. This suggests that a suitable way to model a linear polymer chain is to replace a portion of the chain containing several hundred backbone atoms by a "spring" and concentrate the masses of the atoms in "beads." This leads to the freely jointed bead-spring chain (see Fig. 11.4-1). Each bead is presumed to experience a drag force as it moves through the solvent, and this force is customarily described by Stokes' law. This model is considerably simpler to handle than the corresponding bead-rod chain because it contains no internal constraints; this point is elaborated on in the next chapter.

If the springs are taken to be Hookean springs, then the bead-spring chain is often referred to as a *Rouse chain*, or a *Rouse-Zimm chain*, the names being associated with the authors of two landmark papers in polymer kinetic theory.[1] This model has been widely

[1] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272-1280 (1953); B. H. Zimm, *J. Chem. Phys.*, **24**, 269 278 (1956). For the corrections of some errors in the latter paper see M. C. Williams, *J. Chem. Phys.*, **42**, 2988 -2989 (1965), **43**, 4542 (1965). See also M. C. Williams, *AIChE J.*, **21**, 1-25 (1975) for an extensive literature review on macromolecular modeling.

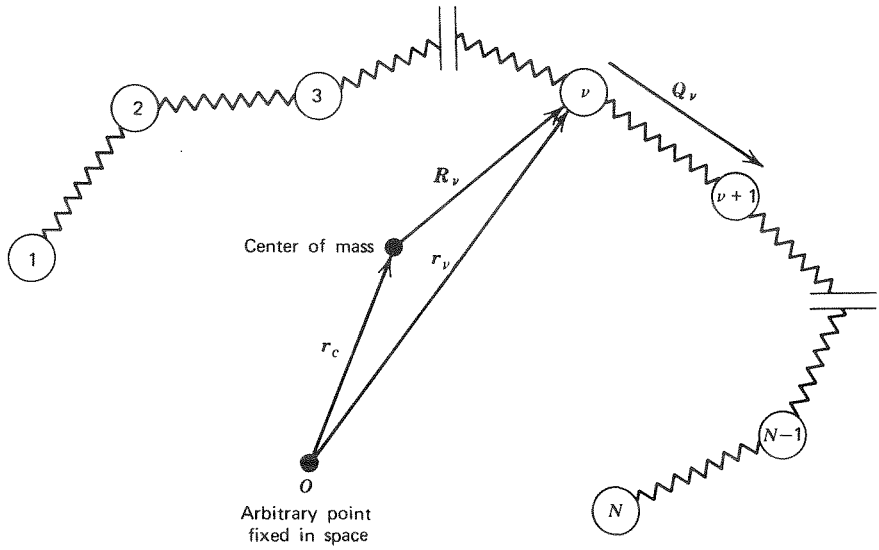


FIGURE 11.4-1. The freely jointed bead-spring chain model formed from N "beads" and $N-1$ "springs". The spring configurations are given by the connector vectors $\boldsymbol{Q}_\nu$ ($\nu = 1, 2, 3, \ldots, N-1$).

used in kinetic theory because it has a large number of internal degrees of freedom and exhibits orientability and stretchability; however it has the distinct disadvantage that it does not have a constant contour length and in fact can be stretched out to any length whatsoever. The model has been particularly popular—and, in fact, probably overused—because the linear spring force law has enabled polymer scientists to obtain a wide spectrum of analytical solutions to equilibrium and nonequilibrium problems alike. The Rouse-Zimm chain contains three model parameters: the number of beads N, the Hooke-law force constant H for the springs, and the Stokes' law friction coefficient ζ.

If one wishes to include finitely extensible springs (the Warner, or "FENE," springs, for example) then the contour length of the chain model cannot exceed a certain limit, and there are four model parameters: N and ζ mentioned above, and then two constants in the spring force law (a spring constant H, and the maximum extensibility of an individual spring Q_0). These finitely extensible chains have had only limited use, inasmuch as it is apparently not possible to get analytical solutions to nonequilibrium kinetic theory problems.

EXAMPLE 11.4-1 Mean-Square End-to-End Distance for a Rouse Chain

It is shown in Chapter 12 that the equilibrium configurational distribution function for the Rouse chain is

$$\psi_{\text{eq}} = \left(\frac{H}{2\pi kT}\right)^{3(N-1)/2} e^{-(H/2kT)\sum_i(\boldsymbol{Q}_i\cdot\boldsymbol{Q}_i)}$$

$$= \prod_{j=1}^{N-1}\left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_j^2} \tag{11.4-1}$$

It is not too surprising that this equation appears to be a generalization of Eq. 11.3-21 for the end-to-end vector distribution function for a bead-rod chain in the Gaussian limit. Find the mean-square end-to-end distance.

SOLUTION The mean square end-to-end distance can be found for the Rouse chain by using a derivation similar to that in Example 11.3-1:

$$\langle r^2 \rangle_{eq} = \int \sum_i \sum_j (\boldsymbol{Q}_i \cdot \boldsymbol{Q}_j) \psi_{eq}(\boldsymbol{Q}_1 \cdots \boldsymbol{Q}_{N-1}) d\boldsymbol{Q}^{N-1}$$

$$= \sum_i \int Q_i^2 \prod_{j=1}^{N-1} \left(\frac{H}{2\pi kT} \right)^{3/2} e^{-(H/2kT)Q_j^2} \, d\boldsymbol{Q}^{N-1}$$

$$= \sum_i \left(\frac{H}{2\pi kT} \right)^{3/2} 4\pi \int_0^\infty Q_i^2 e^{-(H/2kT)Q_i^2} Q_i^2 \, dQ_i$$

$$= \frac{3(N-1)kT}{H} \tag{11.4-2}$$

Finally by means of the method outlined in Example 12.5-2 it can be shown that the probability for the end-to-end vector $\boldsymbol{r}$ for the Rouse chain is:

$$P_{eq}(\boldsymbol{r}) = \left[\frac{H}{2(N-1)\pi kT} \right]^{3/2} e^{-[H/2(N-1)kT](\boldsymbol{r} \cdot \boldsymbol{r})} \tag{11.4-3}$$

Equations 11.4-2 and 11.4-3 should be compared with Eqs. 11.3-22 and 11.3-21 respectively. Further discussions of Rouse chains are given in Chapter 12.

§11.5 DUMBBELL MODELS

In the foregoing two sections we discussed chains of N beads connected together linearly with rigid rods or springs. In this section we consider the very simplified models that result when N is set equal to 2—the *dumbbell models.* The *rigid dumbbell*[1] and the *elastic dumbbell*[2] are shown in Fig. 11.5-1. Of course, there are many kinds of elastic dumbbell models depending on the choice of the spring force law. Table 11.5-1 contains a summary of information about various commonly encountered dumbbell models.

The dumbbell models are only very crude representations of polymer molecules. The rigid dumbbell can be regarded as an ultrasimplified model of a rigid linear polymer, such as tobacco mosaic virus (see electron micrograph in Fig. 11.5-2). The model of a rod connecting two point masses does not account for the finite volume of the molecule nor does it even involve the same kinds of hydrodynamics as it rotates and translates through the solvent. Nonetheless it does have the property of being oriented by a solvent flow field, and many of the rheological properties are described qualitatively by this elementary rigid dumbbell model.

[1] W. Kuhn, *Zeits. f. phys. Chem.*, **161**, 1–32 (1932); *Kolloid-Zeitschrift*, **62**, 269–285 (1933); W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **28**, 97–127 (1945).

[2] J. J. Hermans, *Physica*, **10**, 777 789 (1943); G. K. Fraenkel, *J. Chem. Phys.*, **20**, 642–647 (1952).

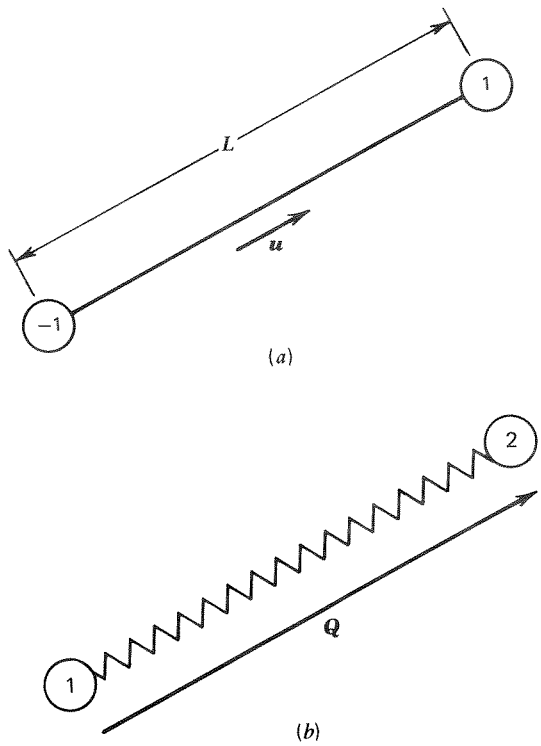


FIGURE 11.5-1. (*a*) Rigid dumbbell model of length L with orientation given by unit vector $\boldsymbol{u}$. (*b*) Elastic dumbbell with configuration given by vector $\boldsymbol{Q}$, whose components are X, Y, Z.

The elastic dumbbell model is also too crude to be of much interest to a polymer chemist, since it in no way accounts for the details of the molecular architecture. It certainly does not have enough internal degrees of freedom to describe the very rapid motions that contribute, for example, to the complex viscosity at high frequencies. On the other hand, the elastic dumbbell model is orientable and stretchable, and these two properties are essential for the qualitative description of steady-state rheological properties and those involving slow changes with time. In fact, the elastic dumbbell models have proven to be very helpful in developing an elementary but broad understanding of the relation between macromolecular motions and rheological phenomena.

Above all, by using the crude dumbbell models it is possible to perform kinetic theory derivations and calculations for nonlinear rheological properties, to continue even further to get constitutive equations, and then finally to solve some nontrivial flow problems. All of this can be done with a limited amount of mathematical effort and analytical results in closed form can be obtained. In other words one can go through the entire program of endeavor—from molecular model to fluid dynamics—for illustrative purposes, in order to point the way towards the task that has ultimately to be performed for more realistic models. The analytical results for the dumbbell models can be used also to check computer simulation procedures in molecular dynamics and Brownian dynamics.

Dumbbell models must, to some extent then, be regarded as mechanical playthings, somewhat disconnected from the real world of polymers. When used intelligently, however, they can be useful pedagogically and very helpful in developing a qualitative understanding of rheological phenomena.

TABLE 11.5-1

Expressions for Spring Forces and Equilibrium Configurational Distribution Functions for Elastic Dumbbells

Name	Connector Force Law and Connector Potential $\boldsymbol{F}^{(c)} = +(\hat{c}/\partial \boldsymbol{Q})\phi^{(c)}$		Comments	Non-Normalized Distribution Function[a] $= \exp(-\phi^{(c)}/kT)$	
Hooke[b] ("Linear")	$\boldsymbol{F}^{(c)} = H\boldsymbol{Q}$	(A)	This spring is infinitely stretchable, and when there is no force in the connector, Q is zero (that is, the beads coalesce).	$e^{-HQ^2/2kT}$	(I)
	$\phi^{(c)} = \frac{1}{2}HQ^2$	(B)			
Fraenkel[c]	$\boldsymbol{F}^{(c)} = H\left(1 - \frac{Q_0}{Q}\right)\boldsymbol{Q}$	(C)	In the absence of tension, the distance between the bead centers is Q_0. When $Q_0 \to 0$ we obtain Hookean springs, and when $H \to \infty$, we get a rigid rod of length Q_0.	$e^{-H(Q-Q_0)^2/2kT}$	(J)
	$\phi^{(c)} = \frac{1}{2}H(Q - Q_0)^2$	(D)			
Tanner[d] ("Linear-Locked")	$\boldsymbol{F}^{(c)} = H\boldsymbol{Q}, \quad Q < Q_0$	(E)	These "linear-locked" springs can stretch only as far as $Q = Q_0$, but for $Q \le Q_0$ they are described by Hooke's law.	$\begin{cases} e^{-HQ^2/2kT} & \text{for } Q < Q_0 \\ 0 & \text{for } Q \ge Q_0 \end{cases}$	(K)
	$\phi^{(c)} = \frac{1}{2}HQ^2, \quad Q < Q_0$	(F)			
Warner[e] ("FENE")	$\boldsymbol{F}^{(c)} = \dfrac{H\boldsymbol{Q}}{1 - (Q/Q_0)^2}, \quad Q < Q_0$	(G)	These "finitely extendable nonlinear elastic" (or "FENE") connectors have an upper limiting length of $Q = Q_0$ The parameter b is given by $b = HQ_0^2/kT$.	$\begin{cases} \left[1 - \left(\dfrac{Q}{Q_0}\right)^2\right]^{HQ_0^2/2kT} & \text{for } Q < Q_0 \\ 0 & \text{for } Q \ge Q_0 \end{cases}$	(L)
	$\phi^{(c)} = -\frac{1}{2}HQ_0^2 \ln[1 - (Q/Q_0)^2] \quad Q < Q_0$	(H)			

[a] The normalization constant for the equilibrium distribution function is $J_{eq} = \iiint \exp(-\phi^{(c)}/kT)dX\,dY\,dZ$, in which X, Y, and Z are the Cartesian components of $\boldsymbol{Q}$. For Hookean dumbbells, $J_{eq} = (H/2\pi kT)^{3/2}$, and for FENE dumbbells, $J_{eq} = 2\pi Q_0^3 B(\frac{3}{2}, (b+2)/2)$ in which $B(x, y)$ is the beta function of x and y.

[b] See Example 11.3-3 and Eq. 11.3-20.

[c] G. K. Fraenkel, *J. Chem. Phys.*, **20**, 642–647 (1952); G. Wilemski and G. Tanaka, *Macromolecules*, **14**, 1531–1538 (1981).

[d] R. I. Tanner and J. Stehrenberger, *J. Chem. Phys.*, **55**, 1958–1964 (1971); erratum, *ibid.*, **61**, 2486 (1974); see also R. I. Tanner, *Trans. Soc. Rheol.*, **19**, 37–65 (1975).

[e] H. R. Warner, Jr., *Ind. Eng. Chem. Fundamentals*, **11**, 379–387 (1972); see Fig. 11.3-2 for a graph of Eq. G. See also, R. C. Armstrong, *J. Chem. Phys.*, **60**, 724–728, 729–733 (1974), and X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 251–265 (1985).

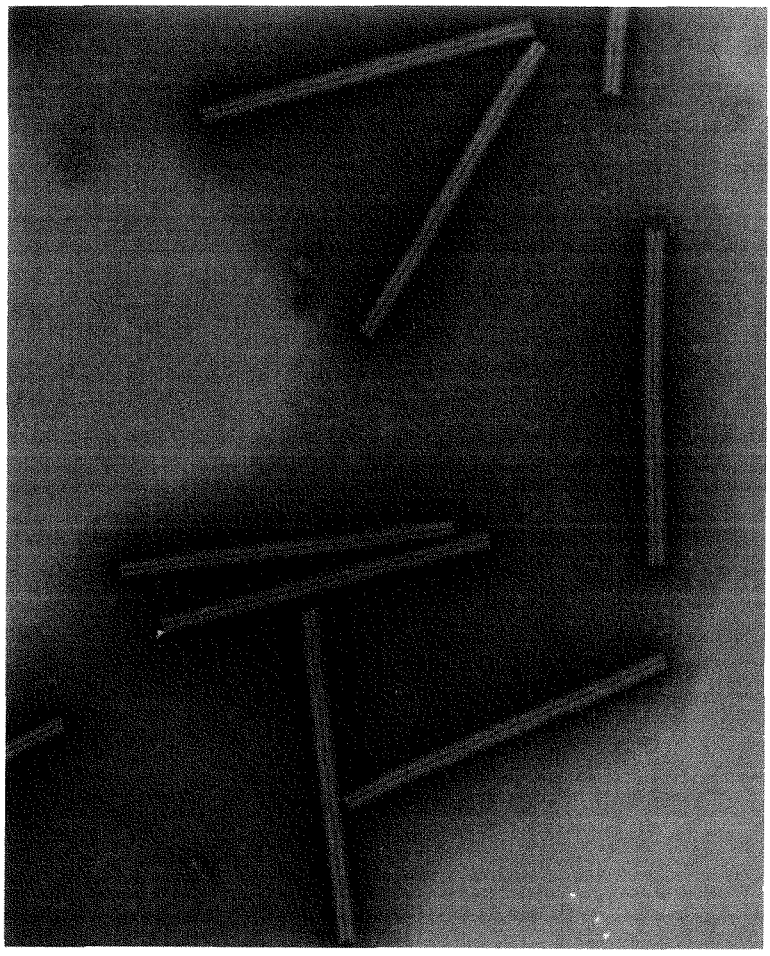


FIGURE 11.5-2. Electron micrograph of tobacco mosaic virus embedded in negative stain. The magnification is $\times 150{,}000$. Courtesy of the Virus Laboratory, University of California, Berkeley.

§11.6 THE GEOMETRY OF CHAINLIKE MOLECULES

Many parts of this book involve the kinetic theory of chainlike macromolecules, modeled as bead-rod or bead-spring chains. In discussions of these models it is helpful to have some standardized notation for the quantities needed to describe the chain configuration. In this section we give the various systems of notation used for describing the configuration of a chain of N identical "beads" joined together linearly by $N-1$ "connectors"; we also give the interrelations among the various systems of notation. The choice of system of notation depends predominantly on the kinds of constraints that are built into the chain, that is, fixed connector lengths, fixed bond angles, and so on. A more complete discussion of constraints and generalized coordinates is given in Chapter 12, but the discussion here should be a useful introduction to the subject.

a. Bead Vectors

The simplest way to give the configuration of a chain model is to specify the locations of all the beads by means of position vectors $\boldsymbol{r}_\nu$ with respect to some fixed

coordinate system (see Fig. 11.4-1). In some discussions we like to use position vectors $\boldsymbol{R}_v = \boldsymbol{r}_v - \boldsymbol{r}_c$ with respect to the center of mass of the chain.

b. Connector Vectors

An alternative way to specify the configuration of a chain is to give the position vector of the center of mass, $\boldsymbol{r}_c$, and the $N-1$ "connector vectors" $\boldsymbol{Q}_k$, which connect pairs of adjacent beads. (See Fig. 11.4-1). That is, we use

$$\boldsymbol{r}_c = \frac{1}{N}\sum_v \boldsymbol{r}_v \tag{11.6-1}$$

$$\boldsymbol{Q}_k = \boldsymbol{r}_{k+1} - \boldsymbol{r}_k \qquad k = 1, 2, \ldots, N-1 \tag{11.6-2}$$

Next we give the relations needed to go back and forth between these two sets of vectors. Here and throughout the book we use the following index conventions:

$v, \mu, \eta \ldots$	Numbering of beads	$1, 2, 3, \ldots, N$
$i, j, k \ldots$	Numbering of connectors	$1, 2, 3, \ldots, N-1$

Then it will usually not be necessary to state explicitly the upper limits on summations, the range of free indices, and the orders of matrices.

We express the relations between the two systems by writing

$$\boldsymbol{Q}_k = \sum_v \bar{B}_{kv}\boldsymbol{r}_v \tag{11.6-3}$$

$$\boldsymbol{r}_v - \boldsymbol{r}_c = \sum_k B_{vk}\boldsymbol{Q}_k \tag{11.6-4}$$

Here the matrix elements $\bar{B}_{kv}$ and B_{vk} are defined by

$$\bar{B}_{kv} = \delta_{k+1,v} - \delta_{kv} \tag{11.6-5}$$

$$B_{vk} = \begin{cases} \dfrac{k}{N} & (k < v) \\ -\left[1 - \left(\dfrac{k}{N}\right)\right] & (k \geq v) \end{cases} \tag{11.6-6}$$

Of course the combination of Eqs. 11.6-3 and 11.6-5 is exactly equivalent to Eq. 11.6-2. In terms of the $\bar{B}_{kv}$ and B_{vk} matrix elements we can define two $(N-1) \times (N-1)$ symmetric, nonsingular matrices (C_{ij}) and (A_{ij}) as follows:

$$\sum_v B_{vi}B_{vj} = C_{ij} = \begin{cases} i(N-j)/N, & \text{if } i \leq j \\ j(N-i)/N, & \text{if } j \leq i \end{cases} \tag{11.6-7}$$

$$\sum_v \bar{B}_{iv}\bar{B}_{jv} = A_{ij} = \begin{cases} 2 & \text{if } i = j \\ -1 & \text{if } i = j \pm 1 \\ 0 & \text{otherwise} \end{cases} \tag{11.6-8}$$

The (A_{ij})-matrix is generally referred to as the *Rouse matrix*[1] and the (C_{ij})-matrix can be called the *Kramers matrix*.[2] These matrices, which are inverse to one another, have eigenvalues a_j and c_j, respectively, given by[3];

$$a_j = \frac{1}{c_j} = 4 \sin^2\left(\frac{j\pi}{2N}\right) \tag{11.6-9}$$

Furthermore, we note for later use that[4]

$$\sum_j c_j = \sum_j C_{jj} = \frac{N^2 - 1}{6} \tag{11.6-10}$$

$$\sum_j \sum_k C_{jk} = \frac{N(N^2 - 1)}{12} \tag{11.6-11}$$

$$\sum_j c_j^2 = \sum_j \sum_k C_{jk}^2 = \frac{(N^2 - 1)(2N^2 + 7)}{180} \tag{11.6-12}$$

$$\sum_i \sum_j \sum_k C_{ik} C_{kj} = \frac{N(N^4 - 1)}{120} \tag{11.6-13}$$

$$\sum_j c_j^3 = \frac{(N^2 - 1)(8N^4 + 29N^2 + 71)}{7560} \tag{11.6-14}$$

$$\prod_j c_j = \det(C_{ij}) = \frac{1}{N} \tag{11.6-15}$$

c. Polar Angles

Another way to specify the chain configuration is to give the location of the center of mass $\boldsymbol{r}_c$, the lengths of the connectors Q_k, and the polar angles θ_k and ϕ_k for the connectors (or alternatively the unit vectors $\boldsymbol{u}_k$ in lieu of the polar angles). This specification is particularly useful for the freely jointed bead-rod chain, inasmuch as the connector lengths are all equal: $Q_k = a$.

In some developments it is convenient to associate with each connector in the chain a triad of unit vectors, $\boldsymbol{s}_k$, $\boldsymbol{t}_k$, $\boldsymbol{u}_k$; the third of these is the unit vector in the direction from bead k to bead $k + 1$. The first and second are unit vectors in the positive θ and ϕ directions. The components and spatial derivatives of these unit vectors are summarized in Appendix E, §E.5.

[1] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272-1280 (1953).

[2] H. A. Kramers, *Physica*, **11**, 1-19 (1944), used matrix elements $g_{\mu\nu}$ that differ by a factor of N from the matrix elements C_{ij} used here.

[3] F. B. Hildebrand, *Methods of Applied Mathematics*, Prentice-Hall, Englewood Cliffs, NJ (1952), p. 366, Problem 54; the (A_{ij})-matrix is a symmetric Jacobi matrix.

[4] H. A. Kramers, loc. cit.; O. Hassager, *J. Chem. Phys.*, **60**, 2111-2124 (1974).

d. Included Angles

Another method for giving the chain orientation is to give the center of mass vector $\boldsymbol{r}_c$, the connector lengths Q_k, the polar angles $\theta_1(\equiv\xi_1)$ and $\phi_1(\equiv\xi_{01})$ for the first connector, a set of angles $\xi_2, \xi_3, \ldots, \xi_{N-1}$, and another set of angles $\xi_{12}, \xi_{23}, \ldots, \xi_{N-2,N-1}$. The angle ξ_k is the angle (at bead k) between vectors $\boldsymbol{Q}_{k-1}$ and $\boldsymbol{Q}_k$, and has the range $0 \leq \xi_k < \pi$. The angle $\xi_{k,k+1}$ is the angle (at the connector between beads k and $k+1$) measured clockwise from the plane containing $\boldsymbol{Q}_{k-1}$ and $\boldsymbol{Q}_k$, to the plane containing $\boldsymbol{Q}_k$ and $\boldsymbol{Q}_{k+1}$, when sighting along the direction of the vector $\boldsymbol{Q}_k$; the range of this angle is $0 \leq \xi_{k,k+1} < 2\pi$ and $\xi_{k,k+1}$ is defined to be zero when beads $k-1$ through $k+2$ are coplanar, and when the triangle formed from beads $k-1$, k, $k+1$ overlaps the triangle formed from beads k, $k+1$, $k+2$. (To define the angle ξ_{12} one needs to introduce a fictitious $\boldsymbol{Q}_0$ which is pointing in the direction of the positive z-axis.) The angles ξ_1, ξ_{01}, and ξ_{12} specify the orientation of the entire chain in space, and the Q_k, $\xi_k(k \geq 2)$, and $\xi_{k-1,k}(k \geq 3)$ give the relative internal configuration (see Fig. 11.6-1).

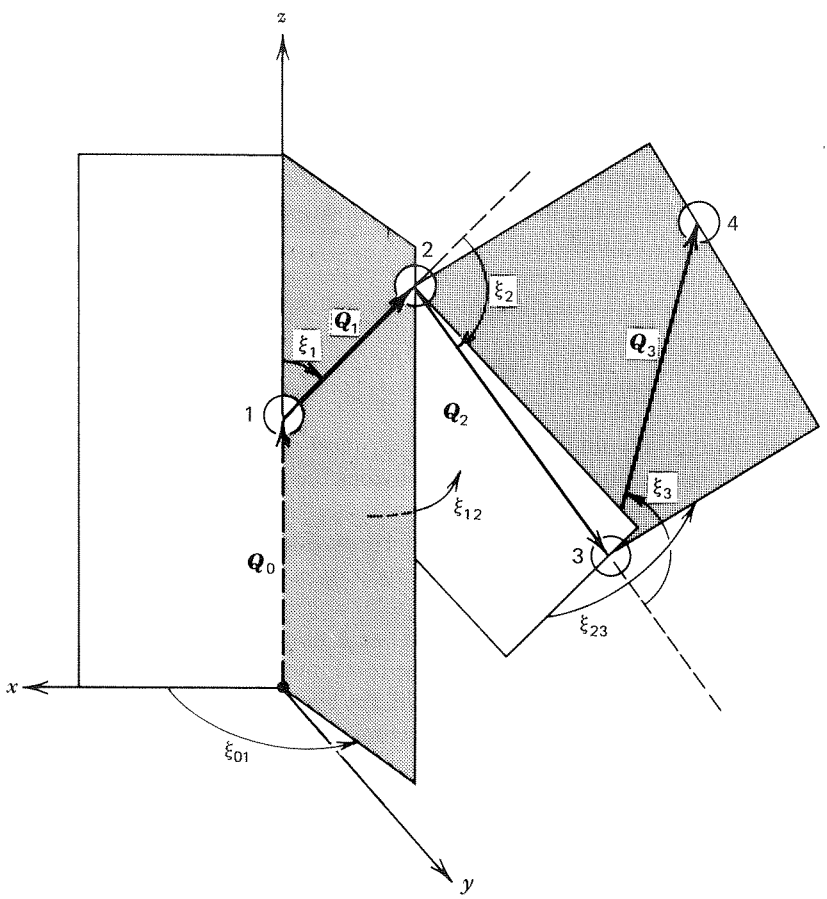


FIGURE 11.6-1. Use of included angles to specify chain configurations.

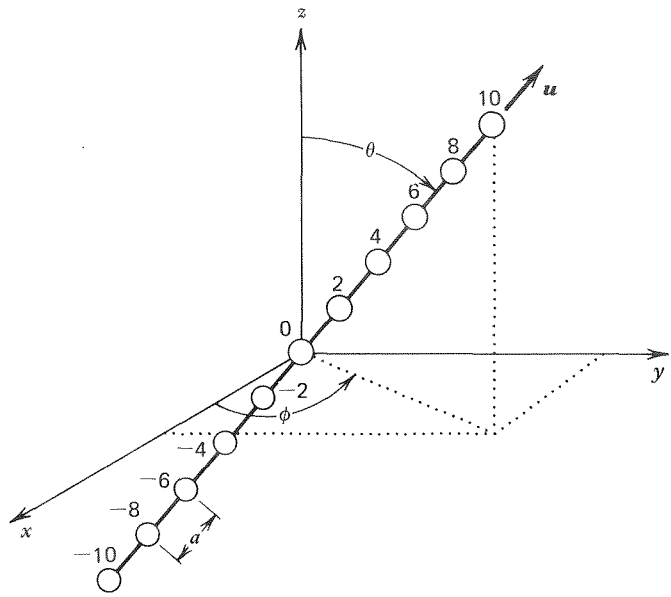


FIGURE 11.6-2. Multibead rod with orientation given by θ and ϕ. A rod with N beads separated by distance a has a total length of $L = (N - 1)a$.

The description of a configuration by means of the included angles is useful for the freely jointed chain (for which the Q_k are constant)[5], and is particularly useful for the freely rotating chain (for which the Q_k and the $\xi_k (k \geq 2)$ are all constants).[6]

A triad of unit vectors can be installed in each connector as described in §11.6c. The unit vectors associated with link k are related to those associated with link $k - 1$ by means of a transformation matrix as follows:

$$\begin{pmatrix} \boldsymbol{s}_k \\ \boldsymbol{t}_k \\ \boldsymbol{u}_k \end{pmatrix} = \begin{pmatrix} C_k c_k & C_k s_k & -S_k \\ -s_k & c_k & 0 \\ S_k c_k & S_k s_k & C_k \end{pmatrix} \begin{pmatrix} \boldsymbol{s}_{k-1} \\ \boldsymbol{t}_{k-1} \\ \boldsymbol{u}_{k-1} \end{pmatrix} \tag{11.6-16}$$

in which $C_k = \cos \xi_k$, $S_k = \sin \xi_k$, $c_k = \cos \xi_{k-1,k}$, and $s_k = \sin \xi_{k-1,k}$. Note that $\boldsymbol{s}_0$, $\boldsymbol{t}_0$, $\boldsymbol{u}_0$ are taken to be $\boldsymbol{\delta}_x$, $\boldsymbol{\delta}_y$, $\boldsymbol{\delta}_z$. Equation 11.6-16 provides the relations between the polar angles θ_i, ϕ_i and the included angles ξ_k, $\xi_{k-1,k}$.

We conclude this section by giving the notation to be used for the linear, rigid multibead-rod model (see Fig. 11.6-2). The configuration of this model is given by specifying the location of the center of mass and the two polar angles θ and ϕ giving its orientation. As may be seen in Fig. 11.6-2 it is convenient to use a numbering system for the beads that makes use of the symmetry of the model; if the total number of beads N is even, the beads are given odd numbers only, whereas if N is odd, the beads are designated by even numbers.

In this section we have discussed the geometrical relations and notation for linear models. Of course there are similar models for star-shaped polymers, comb polymers, and various shapes of rigid biopolymers. Such models are discussed only infrequently in this book, and hence it is not worthwhile to summarize notation for them here.

[5] C. F. Curtiss and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **2**, 392–396 (1977).

[6] P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York (1969).

PROBLEMS

11A.1 Configurational Matrices for Chainlike Models

a. Display the $\bar{B}_{kv}$, B_{vk}, A_{ij}, and C_{ij} in matrix form for $N = 5$.
b. Verify Eqs. 11.6-10 to 11.6-13 using the numbers from the matrices in (a).

11A.2 Eigenvalues of the Rouse Matrix

For a 4-bead Rouse chain, find the eigenvalues of the Rouse matrix by getting the roots of the characteristic equation. Compare the eigenvalues thus obtained with the formula in Eq. 11.6-9.

11A.3 The Angle Between Successive C–C Bonds

Show that the angle between successive C–C bonds in a polyethylene chain is $\xi = \arccos(\frac{1}{3}) = 70.5°$.

11B.1 The Radius of Gyration

The radius of gyration s of a chain is defined by

$$s^2 = \frac{1}{N}\sum_{v=1}^{N} (\boldsymbol{R}_v \cdot \boldsymbol{R}_v) \tag{11B.1-1}$$

where $\boldsymbol{R}_v$ is the bead position vector with respect to the center of mass of the chain. The mean-square radius of gyration for a chain at equilibrium is then

$$\langle s^2 \rangle_{eq} = \frac{1}{N}\sum_{v=1}^{N} \int (\boldsymbol{R}_v \cdot \boldsymbol{R}_v)\psi_{eq}\, d\boldsymbol{Q}^{N-1} \tag{11B.1-2}$$

a. Show that for the Rouse freely jointed bead-spring chain

$$\langle s^2 \rangle_{eq} = \frac{(N^2-1)kT}{2NH} = \frac{1}{6}\frac{N+1}{N}\langle r^2 \rangle_{eq} \tag{11B.1-3}$$

b. Show that for the Kramers freely jointed bead-rod chain

$$\langle s^2 \rangle_{eq} = \frac{(N^2-1)a^2}{6N} = \frac{1}{6}\frac{N+1}{N}\langle r^2 \rangle_{eq} \tag{11B.1-4}$$

if the random-walk distribution function is used.

c. Kramers[1] has shown that for the freely rotating bead-rod chain with $\xi = \arccos(\frac{1}{3}) = 70.5°$ as the included angle (see Fig. 11.2-1)

$$\langle s^2 \rangle_{eq} = \tfrac{1}{6}Na^2 \cot^2 \tfrac{1}{2}\xi \tag{11B.1-5}$$

in the limit of very large N, where N is the number of beads. Calculate $\sqrt{\langle s^2 \rangle_{eq}}$ for a polyethylene chain of molecular weight 10^6 g/mol. Each "bead" represents one carbon atom, and the C–C bond length is 0.15 nm. What is the analogous result for the freely jointed chain?

[1] H. A. Kramers, *Physica*, **11**, 1–19 (1944).

11B.2 Equilibrium Averages for the Random-Walk Chain

a. Verify the step from Eq. 11.3-6 to Eq. 11.3-7.
b. Show further that $\langle u_i u_j \rangle_{eq} = (\frac{1}{3})\delta_{ij}\,\boldsymbol{\delta}$.
c. What is $\langle r \rangle_{eq}$?

11B.3 Probability for the End-to-End Vector

a. What assumptions are implied in Eq. 11.3-12?
b. Verify that $\int P_{eq}(\boldsymbol{r})d\boldsymbol{r} = 1$.
c. What is the probability density that a chain has a length r?

11B.4 Normalization Constants and Mean-Square End-to-End Distance for Elastic Dumbbells

a. In Table 11.5-1, verify that the normalization constant J_{eq} is

$$J_{eq} = \left(\frac{H}{2\pi kT}\right)^{-3/2} \tag{11B.4-1}$$

for Hookean dumbbells.
b. Show that for the Warner (FENE) dumbbells

$$J_{eq} = 2\pi Q_0^3 \mathrm{B}\left(\frac{3}{2}, \frac{b+2}{2}\right) \tag{11B.4-2}$$

where the "beta function" $\mathrm{B}(x, y) = \int_0^1 t^{x-1}(1-t)^{y-1}\,dt = \Gamma(x)\Gamma(y)/\Gamma(x+y)$, in which $\Gamma(x)$ is the gamma function.
c. Show that $\langle Q^2 \rangle_{eq} = 3kT/H$ for Hookean dumbbells.
d. Find $\langle Q^2 \rangle_{eq}$ for FENE dumbbells.

Hint: $$\int_0^{Q_0}\left[1-\left(\frac{Q}{Q_0}\right)^2\right]^{b/2} Q^n\,dQ = \left(\frac{Q_0^{n+1}}{2}\right)\mathrm{B}\left[\frac{1}{2}(n+1), \frac{1}{2}(b+2)\right]$$

11B.5 Configuration Matrices for the Simplest "Star" Polymer Model

In Fig. 11B.5 is a model with a center (bead "0") and three side chains leading to beads "1", "2", and "3". All beads have the same mass. Let the bead locations be $\boldsymbol{r}_0, \boldsymbol{r}_1, \boldsymbol{r}_2$, and $\boldsymbol{r}_3$. Let the center of mass location be given by the position vector $\boldsymbol{r}_c$, and the vectors $\boldsymbol{Q}_k$ be defined by $\boldsymbol{Q}_k = \boldsymbol{r}_k - \boldsymbol{r}_0$. Let these various vectors be related by:

$$\boldsymbol{Q}_k = \sum_v \bar{B}_{kv}\boldsymbol{r}_v \tag{11B.5-1}$$

$$\boldsymbol{r}_v = \boldsymbol{r}_c + \sum_k B_{vk}\boldsymbol{Q}_k \tag{11B.5-2}$$

a. Show that $\bar{B}_{kv} = \delta_{kv} - \delta_{v0}$ and that $B_{vk} = \delta_{vk} - \frac{1}{4}$.
b. Then verify that $A_{ij} = \delta_{ij} + 1$ and $C_{ij} = \delta_{ij} - \frac{1}{4}$, and show that the matrices (A_{ij}) and (C_{ij}) are inverse to one another.
c. Show that the eigenvalues of the (A_{ij})-matrix are $a_1 = a_2 = 1$, and $a_3 = 4$.
d. Which will have the greater value of $\langle s^2 \rangle_{eq}$, a Rouse chain with four beads, or the four-bead model considered here?

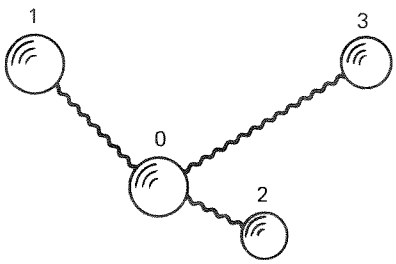


FIGURE 11B.5. Very simple mechanical model of a star polymer.

11D.1 Relation of FENE-Dumbbell Distribution Function to Hookean-Dumbbell Distribution Function

Verify that the normalized equilibrium distribution function ψ_{eq} for FENE dumbbells given in Table 11.5-1 simplifies to the corresponding quantity for Hookean dumbbells in the limit as $Q_0 \rightarrow \infty$. To do this use Stirling's approximation for large x:

$$\Gamma(x+1) \sim \left(\frac{x}{e}\right)^x \sqrt{2\pi x} \qquad (x \rightarrow \infty) \tag{11D.1-1}$$

and the fact that:

$$(x+\tfrac{1}{2})^x \sim x^x \sqrt{e} \qquad (x \rightarrow \infty) \tag{11D.1-2}$$

CHAPTER 12

EQUILIBRIUM CONFIGURATIONS OF POLYMER MOLECULES

In the foregoing chapter we discussed the various bead-rod-spring models that have been used in polymer kinetic theory. The aim of this chapter is to show how to obtain the equilibrium configurational distribution functions for these models and then to estimate some equilibrium properties of polymer systems.

Even though the main object of this volume is the study of nonequilibrium phenomena, there are several good reasons for including a brief survey of equilibrium properties at this point. Equilibrium statistical mechanics enables us to write down immediately the phase-space distribution function, from which the configurational distribution may be obtained; it is the deviation from this distribution function that is of primary interest in later chapters, and, indeed, the equilibrium distribution function may be taken as the starting point for a perturbation-theory development. In addition the study of polymer systems at equilibrium provides a convenient vehicle for introducing the nomenclature associated with molecular geometry and distribution functions to be used later. Finally the equilibrium properties are in themselves of interest in polymer chemistry and engineering.

Here and in later chapters we use classical mechanics and classical statistical mechanics throughout, inasmuch as quantum mechanical effects are of little importance in the study of the rheological properties of very large molecules. It is well known that the quantum effects are appreciable in the transport properties of gases and liquids only at extremely low temperatures and then only for helium and hydrogen.

We start by defining generalized coordinates and momenta for bead-rod-spring models, and then we give the equations of motion in terms of the Hamiltonian for the system. After that we give the general expression for the phase-space distribution function for the bead-rod-spring models at equilibrium; from this distribution function we can obtain a variety of equilibrium properties as average values. In the final section we discuss lower-order distribution functions and changes of variables in distribution functions. A careful study of this chapter provides much of the mathematics and physics needed for the remainder of the book.

§12.1 GENERALIZED COORDINATES AND MOMENTA

We begin by considering a general macromolecular model consisting of N beads of mass m_ν ($\nu = 1, 2, \ldots, N$) connected in an arbitrary way by springs and/or rigid rods. The total mass of the polymer molecule is then $m_p = \sum_\nu m_\nu$.

The location of bead ν is given by the position vector $\boldsymbol{r}_\nu$ ($\nu = 1, 2, \ldots, N$) with respect to an arbitrary origin of coordinates; the velocity of the bead is $\dot{\boldsymbol{r}}_\nu = d\boldsymbol{r}_\nu/dt$ with respect to the same origin. The center of mass $\boldsymbol{r}_c$ of the macromolecule and its velocity $\dot{\boldsymbol{r}}_c$ are defined by

$$\boldsymbol{r}_c = \frac{1}{m_p}\sum_{\nu=1}^{N} m_\nu \boldsymbol{r}_\nu; \qquad \dot{\boldsymbol{r}}_c = \frac{1}{m_p}\sum_{\nu=1}^{N} m_\nu \dot{\boldsymbol{r}}_\nu \tag{12.1-1a,b}$$

It is convenient to introduce another set of bead position vectors and bead velocity vectors by

$$\boldsymbol{R}_\nu = \boldsymbol{r}_\nu - \boldsymbol{r}_c; \qquad \dot{\boldsymbol{R}}_\nu = \dot{\boldsymbol{r}}_\nu - \dot{\boldsymbol{r}}_c \tag{12.1-2a,b}$$

The vector $\boldsymbol{R}_\nu$ locates the νth bead with respect to the center of mass, and $\dot{\boldsymbol{R}}_\nu$ is the velocity relative to the center of mass. The $\boldsymbol{R}_\nu$ and $\dot{\boldsymbol{R}}_\nu$ are not all independent since

$$\sum_{\nu=1}^{N} m_\nu \boldsymbol{R}_\nu = \boldsymbol{0}; \qquad \sum_{\nu=1}^{N} m_\nu \dot{\boldsymbol{R}}_\nu = \boldsymbol{0} \tag{12.1-3a,b}$$

In classical mechanics and classical statistical mechanics it is necessary to use the minimum number of coordinates needed to locate all the particles. For N particles with no constraints (e.g., for beads connected by springs and no fixed angles between adjacent springs), $3N - 3$ "internal coordinates" are needed to specify the locations of the beads in a center-of-mass coordinate system: for N particles with constraints (e.g., for beads joined by rigid rods or with fixed angles between adjacent connector rods) the number of degrees of freedom d in the system is less than $3N - 3$; in general the coordinates required to specify the internal coordinates are then called $Q_1, Q_2, \ldots, Q_d (d \leq 3N - 3)$. Examples from Chapter 11 are the following N-bead chains:

Model	Number of Internal Coordinates	Generalized Coordinates
Freely jointed bead-spring chain	$3N - 3$	$\boldsymbol{Q}_1, \boldsymbol{Q}_2, \ldots, \boldsymbol{Q}_{N-1}$
Freely jointed bead-rod chain	$2N - 2$	$\boldsymbol{u}_1, \boldsymbol{u}_2, \ldots, \boldsymbol{u}_{N-1}$
Freely rotating bead-rod chain (i.e., with fixed bond angles)	N	$\xi_1, \xi_{01}, \xi_{12}, \xi_{23}, \ldots, \xi_{N-2,N-1}$

The choice of generalized coordinates is not unique. For example the internal configuration of the freely jointed bead-rod chain with $N = 3$ may be specified by giving the polar angles for each link $\theta_1, \phi_1, \theta_2, \phi_2$; or one may use the included angles $\xi_1, \xi_{01}, \xi_{12}$, (to specify the orientation of the chain in space) and ξ_2 (to specify the angle between the two rods). The time rate of change of the sth generalized coordinate is designated by $\dot{Q}_s = dQ_s/dt$; these are called "generalized velocities."

We usually use the following conventions for indices:

$\nu, \mu, \eta, \ldots$	to designate beads	$1, 2, \ldots, N$
$s, t, u, v, \ldots$	to designate generalized coordinates	$1, 2, \ldots, d \leq 3N - 3$
$i, j, k, \ldots$	to designate links in chain models	$1, 2, \ldots, N - 1$
$m, n, p, q, \ldots$	to designate Cartesian components	1, 2, 3

The kinetic energy associated with the macromolecular model is then:[1]

$$\begin{aligned}\mathscr{K} &= \frac{1}{2}\sum_{\nu} m_\nu \dot{\boldsymbol{r}}_\nu^2 \\ &= \frac{1}{2} m_p \dot{\boldsymbol{r}}_c^2 + \frac{1}{2}\sum_{\nu} m_\nu \dot{\boldsymbol{R}}_\nu^2 \end{aligned} \tag{12.1-4}$$

Equation 12.1-3b is used to get the second expression, which just states that the total kinetic energy is the sum of the kinetic energy of the center of mass and the kinetic energies of the beads with respect to the center of mass. Equation 12.1-4 may now be rewritten in terms of generalized coordinates by eliminating the $\boldsymbol{R}_\nu$ in favor of the Q_s by use of the chain rule of partial differentiation:

$$\begin{aligned}\mathscr{K} &= \frac{1}{2} m_p \dot{\boldsymbol{r}}_c^2 + \frac{1}{2}\sum_{s}\sum_{t}\sum_{\nu}\left(\sqrt{m_\nu}\frac{\partial}{\partial Q_s}\boldsymbol{R}_\nu\right)\cdot\left(\sqrt{m_\nu}\frac{\partial}{\partial Q_t}\boldsymbol{R}_\nu\right)\dot{Q}_s\dot{Q}_t \\ &= \frac{1}{2} m_p \dot{\boldsymbol{r}}_c^2 + \frac{1}{2}\sum_{s}\sum_{t}\sum_{\nu}(\boldsymbol{b}_{\nu s}\cdot\boldsymbol{b}_{\nu t})\dot{Q}_s\dot{Q}_t \\ &= \frac{1}{2} m_p \dot{\boldsymbol{r}}_c^2 + \frac{1}{2}\sum_{s}\sum_{t} g_{st}\dot{Q}_s\dot{Q}_t \end{aligned} \tag{12.1-5}$$

Here we have introduced the *base vectors*[2] $\boldsymbol{b}_{\nu s}$:

$$\boldsymbol{b}_{\nu s} = \sqrt{m_\nu}\frac{\partial}{\partial Q_s}\boldsymbol{R}_\nu \tag{12.1-6}$$

and the components of the *metric matrix* g_{st}:

$$g_{st} = \sum_{\nu}(\boldsymbol{b}_{\nu s}\cdot\boldsymbol{b}_{\nu t}) \tag{12.1-7}$$

As can be seen in Eq. 12.1-5 the definition of these quantities arises quite naturally in writing the kinetic energy in terms of the generalized coordinates; these quantities may also be interpreted in terms of a hyperspace, although it is really not necessary to make use of this

[1] We use the abbreviation $\boldsymbol{r}_\nu^2$ in lieu of the lengthier $(\boldsymbol{r}_\nu\cdot\boldsymbol{r}_\nu)$

[2] These base vectors satisfy the relation

$$\sum_{\nu}\sqrt{m_\nu}\boldsymbol{b}_{\nu t} = \boldsymbol{0} \tag{12.1-6a}$$

because of Eq. 12.1-3a.

idea.[3] It is important to note that the base vectors $\boldsymbol{b}_{vs}$ and the metric matrix components g_{st} in general depend on the generalized coordinates Q_s. The determinant of the g_{st} matrix often appears in the following development; we designate this quantity by $g = \det(g_{st})$. We also find it useful to have notation for the components G_{st} of the matrix inverse to the (g_{st})-matrix; that is, we define the G_{st} by

$$\sum_t G_{st} g_{tu} = \delta_{su} \tag{12.1-8}$$

Once the generalized coordinates have been selected for a specific macromolecular model, the g_{st} may be obtained; inverting the matrix to get the G_{st} is in general extremely difficult.

Thus far we have been concerned only with the coordinates needed for specifying the configuration of a bead-spring-rod model for a macromolecule. We now turn to the notation for momenta. The momentum of bead v is $\boldsymbol{p}_v = m_v \dot{\boldsymbol{r}}_v$, and the momentum of the center of mass $\boldsymbol{p}_c$ is $m_p \dot{\boldsymbol{r}}_c$; we note incidentally that the latter can also be obtained by differentiating the kinetic energy with respect to the velocity of the center of mass, thus

$$\boldsymbol{p}_c = \frac{\partial}{\partial \dot{\boldsymbol{r}}_c} \mathscr{K} = m_p \dot{\boldsymbol{r}}_c \tag{12.1-9}$$

The generalized momenta for the internal degrees of freedom are then defined by an analogous differentiation:

$$P_s = \frac{\partial}{\partial \dot{Q}_s} \mathscr{K} = \sum_t g_{st} \dot{Q}_t \tag{12.1-10}$$

[3] Let $\boldsymbol{R}$ be a vector in a $3N$-dimensional space with components $\sqrt{m_1} X_{11}$, $\sqrt{m_1} X_{12}$, $\sqrt{m_1} X_{13}, \ldots, \sqrt{m_N} X_{N1}$, $\sqrt{m_N} X_{N2}$, $\sqrt{m_N} X_{N3}$ (X_{N3} is the z-component of $\boldsymbol{R}_N$). The unit vectors in this space are $\boldsymbol{\delta}_{vn}$ (v = bead number, n = Cartesian component). Then we define the base vectors in the d-dimensional subspace as (cf. §A.8)

$$\boldsymbol{g}_t = \frac{\partial}{\partial Q_t} \boldsymbol{R} = \sum_v \sum_n \frac{\partial}{\partial Q_t} (\boldsymbol{\delta}_{vn} \sqrt{m_v} X_{vn}) \tag{12.1-6b}$$

and the metric matrix components as

$$\begin{aligned} g_{st} &= (\boldsymbol{g}_s \cdot \boldsymbol{g}_t) \\ &= \sum_v \sum_n \left(\sqrt{m_v} \frac{\partial}{\partial Q_s} X_{vn} \right) \left(\sqrt{m_v} \frac{\partial}{\partial Q_t} X_{vn} \right) \end{aligned} \tag{12.1-7a}$$

This may be reorganized by introducing the unit vectors $\boldsymbol{\delta}_n$ in three-space and the three-space position vectors $\boldsymbol{R}_v$:

$$\begin{aligned} g_{st} &= \sum_v \sum_n \sum_m \left(\sqrt{m_v} \frac{\partial}{\partial Q_s} X_{vn} \boldsymbol{\delta}_n \right) \cdot \left(\sqrt{m_v} \frac{\partial}{\partial Q_t} X_{vm} \boldsymbol{\delta}_m \right) \\ &= \sum_v \left(\sqrt{m_v} \frac{\partial}{\partial Q_s} \boldsymbol{R}_v \right) \cdot \left(\sqrt{m_v} \frac{\partial}{\partial Q_t} \boldsymbol{R}_v \right) \\ &= \sum_v (\boldsymbol{b}_{vs} \cdot \boldsymbol{b}_{vt}) \end{aligned} \tag{12.1-7b}$$

In which the 3-space base vectors $\boldsymbol{b}_{vs}$ finally appear.

Note that the generalized momenta may or may not have the dimensions of momentum depending on the dimensions of the generalized coordinates that have been selected. Equation 12.1-10 can be inverted to give

$$\dot{Q}_s = \sum_t G_{st} P_t \tag{12.1-11}$$

When this is substituted into Eq. 12.1-5 we get

$$\mathscr{K} = \frac{1}{2m_p} \boldsymbol{p}_c^2 + \frac{1}{2} \sum_s \sum_t G_{st} P_s P_t \tag{12.1-12}$$

which gives the kinetic energy of the macromolecular model in terms of the momentum of the center of mass and the generalized momenta of the beads.

In the two illustrative examples that follow we show how the notation of this section is used in the description of two important polymer chain models: the bead-rod chain and the bead-spring chain. The results obtained in these two examples will be useful in later sections and chapters.

EXAMPLE 12.1-1 Base Vectors and Metric Matrix Components for the Freely Jointed Bead-Rod Chain with $N = 3$

Consider the Kramers chain with all links of length a and all masses identical (i.e., $m_v = m$ for all v). Obtain the formal expressions for the base vectors, and then display the matrix of the $\boldsymbol{b}_{vs}$ for $N = 3$. Then proceed to get the g_{st} and the determinant of the (g_{st})-matrix for $N = 3$.

SOLUTION We take the generalized coordinates to be the polar angles of the rods: θ_k and ϕ_k. In some formulas we actually use the unit vectors associated with the links, $\boldsymbol{s}_k$, $\boldsymbol{t}_k$, $\boldsymbol{u}_k$, keeping in mind that these are expressible in terms of the polar angles; using the unit vectors just saves having to write out lengthy expressions involving trigonometric functions.

After the generalized coordinates have been selected, the next task is to express the position vectors $\boldsymbol{R}_v$ in terms of the generalized coordinates; to do this we use Eq. 11.6-4:

$$\boldsymbol{R}_v = a \sum_k B_{vk} \boldsymbol{u}_k \tag{12.1-13}$$

Then, making use of the formulas for differentiating the unit vectors (given in §E.5) we find

$$\begin{aligned} \boldsymbol{b}_{v,\theta_k} &= a\sqrt{m} B_{vk} \boldsymbol{s}_k \\ \boldsymbol{b}_{v,\phi_k} &= a\sqrt{m} B_{vk} \boldsymbol{t}_k \sin\theta_k \end{aligned} \tag{12.1-14}$$

When we specialize to $N = 3$, the $\boldsymbol{b}_{vs}$ may be displayed in the following way:

$$\left(\frac{\boldsymbol{b}_{vs}}{a\sqrt{m}}\right) = \begin{pmatrix} -\frac{2}{3}\boldsymbol{s}_1 & -\frac{2}{3}\boldsymbol{t}_1 \sin\theta_1 & -\frac{1}{3}\boldsymbol{s}_2 & -\frac{1}{3}\boldsymbol{t}_2 \sin\theta_2 \\ \frac{1}{3}\boldsymbol{s}_1 & \frac{1}{3}\boldsymbol{t}_1 \sin\theta_1 & -\frac{1}{3}\boldsymbol{s}_2 & -\frac{1}{3}\boldsymbol{t}_2 \sin\theta_2 \\ \frac{1}{3}\boldsymbol{s}_1 & \frac{1}{3}\boldsymbol{t}_1 \sin\theta_1 & \frac{2}{3}\boldsymbol{s}_2 & \frac{2}{3}\boldsymbol{t}_2 \sin\theta_2 \end{pmatrix} \tag{12.1-15}$$

Here the rows correspond to the beads ($v = 1, 2, 3$) and the columns to the four generalized coordinates in the order θ_1, ϕ_1, θ_2, ϕ_2. Then the g_{st} are obtained from Eq. 12.1-7:

$$\left(\frac{g_{st}}{ma^2}\right) = \begin{pmatrix} \frac{2}{3} & 0 & \frac{1}{3}(C_1C_2c + S_1S_2) & \frac{1}{3}C_1S_2s \\ 0 & \frac{2}{3}S_1^2 & -\frac{1}{3}S_1C_2s & \frac{1}{3}S_1S_2c \\ \frac{1}{3}(C_1C_2c + S_1S_2) & -\frac{1}{3}S_1C_2s & \frac{2}{3} & 0 \\ \frac{1}{3}C_1S_2s & \frac{1}{3}S_1S_2c & 0 & \frac{2}{3}S_2^2 \end{pmatrix} \tag{12.1-16}$$

in which $S_1 = \sin\theta_1$, $C_1 = \cos\theta_1$, $s = \sin(\phi_1 - \phi_2)$, $c = \cos(\phi_1 - \phi_2)$. From this matrix we then get

$$g = \det(g_{st}) = \tfrac{4}{27}m^4a^8S_1^2S_2^2\left[1 - \tfrac{1}{4}(C_1C_2 + S_1S_2c)^2\right] \tag{12.1-17}$$

The quantity $(C_1C_2 + S_1S_2c)$ turns out to be just $\cos\xi_2 = (\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)$. To find the G_{st} for this very short two-link chain requires inverting the 4×4 matrix in Eq. 12.1-16.

Performing the analogous operations for a long chain would clearly be exceedingly tedious. If all one needs is the determinant of the (g_{st})-matrix, then some help can be had by using a recursion formula derived by Fixman[4] that allows one to get g_N (g for a chain of N beads) from g_{N-1} and g_{N-2}, aside from a constant multiplicative factor. One first defines h_N by

$$g_N \propto (ma^2)^{2(N-1)}h_N\prod_{k=1}^{N-1}\sin^2\theta_k \tag{12.1-18}$$

and then h_N is given by the recursion relation,

$$h_N = 2h_{N-1} - h_{N-2}\cos^2\xi_{N-1} \tag{12.1-19}$$

in which $h_1 = 1$ and $h_2 = 2$.

EXAMPLE 12.1-2 Base Vectors and Metric Matrix Components for the Freely Jointed Bead-Spring Chain

Obtain the $\boldsymbol{b}_{vs}$ and the g_{st} for a chain of N beads, all of mass m, connected linearly by $N - 1$ springs.

SOLUTION For this model there are $3N - 3$ degrees of freedom. It is sensible to choose as the generalized coordinates the Cartesian components Q_{kp} of the connector vectors $\boldsymbol{Q}_k$ defined by

$$\boldsymbol{Q}_k = \sum_p \boldsymbol{\delta}_p Q_{kp} \tag{12.1-20}$$

where $\boldsymbol{\delta}_p$ is the unit vector in the pth coordinate direction. This complicates the notation somewhat, since where we previously had generalized coordinates with one index (i.e., the "s" in Q_s), we now have two indices (the "kp" in Q_{kp}). From Eq. 11.6-4 we find for the bead locations with respect to the center of mass:

$$\boldsymbol{R}_v = \sum_p\sum_k \boldsymbol{\delta}_p B_{vk} Q_{kp} \tag{12.1-21}$$

[4] M. Fixman, *Proc. Nat. Acad. Sci., U.S.A.*, **71**, 3050–3053 (1974).

The base vectors are then

$$\boldsymbol{b}_{v,kp} = \sqrt{m}\frac{\partial}{\partial Q_{kp}}\boldsymbol{R}_v = \sqrt{m}B_{vk}\boldsymbol{\delta}_p \tag{12.1-22}$$

and the metric matrix components are

$$g_{ip,jq} = \sum_v (\boldsymbol{b}_{v,ip}\cdot\boldsymbol{b}_{v,jq}) = mC_{ij}\delta_{pq} \tag{12.1-23}$$

where Eq. 11.6-7 has been used to introduce the elements C_{ij} of the Kramers matrix. The inverse matrix has components given by

$$G_{ip,jq} = m^{-1}A_{ij}\delta_{pq} \tag{12.1-24}$$

In order to get $g = \det(g_{ip,jq})$ it is convenient to arrange the rows in the sequence $ip = 11, 21, 31, \ldots; 12, 22, 32, \ldots; 13, 23, 33, \ldots$ and the columns, labeled by jq, in the same sequence so that

$$g = \det(g_{ip,jq}) = \begin{vmatrix} D & 0 & 0 \\ 0 & D & 0 \\ 0 & 0 & D \end{vmatrix} \tag{12.1-25}$$

in which D is the $(N-1)\times(N-1)$ matrix with elements mC_{ij}. Then

$$g = [\det(mC_{ij})]^3 = \left(\frac{m^{N-1}}{N}\right)^3 \tag{12.1-26}$$

where Eq. 11.6-15 has been used. We see thus that for the freely jointed bead-spring chain the quantity g can be evaluated for a chain of any length, and that the result is just a constant.

§12.2 HAMILTON'S EQUATIONS OF MOTION

The classical Hamiltonian may be written as the sum of the kinetic energy and the potential energy, expressed in terms of the coordinates and momenta (not velocities!). For a system of N particles *with no constraints* we may use the Cartesian components of the position and momentum vectors of each of the particles as independent coordinates in phase space; then the Hamiltonian is

$$\mathscr{H} = \sum_v \frac{1}{2m_v}\boldsymbol{p}_v^2 + \phi(\boldsymbol{r}^N) \tag{12.2-1}$$

Here ϕ is the potential energy of the system, which depends on the coordinates of all the particles.

The dynamics of the system of particles is described by giving the equations of motion. These are "Hamilton's canonical equations," a set of $6N$ scalar first-order partial differential equations

$$\frac{\partial\mathscr{H}}{\partial\boldsymbol{r}_v} = -\dot{\boldsymbol{p}}_v; \qquad \frac{\partial\mathscr{H}}{\partial\boldsymbol{p}_v} = \dot{\boldsymbol{r}}_v \tag{12.2-2a,b}$$

These equations are equivalent to the more familiar Newton's second law of motion, as may be seen as follows: First substitute $\mathscr{H}$ from Eq. 12.2-1 into Hamilton's equations of motion to get

$$\frac{\partial \phi}{\partial \boldsymbol{r}_v} = -\dot{\boldsymbol{p}}_v; \qquad \frac{1}{m_v}\boldsymbol{p}_v = \dot{\boldsymbol{r}}_v \tag{12.2-3a,b}$$

Then combine these two equations and introduce the force on particle v, defined by $\boldsymbol{F}_v = -(\partial/\partial \boldsymbol{r}_v)\phi$ to obtain

$$\boldsymbol{F}_v = m_v \ddot{\boldsymbol{r}}_v \tag{12.2-4}$$

This is Newton's second law of motion for particle v.

For systems *with constraints* the Cartesian coordinates discussed above cannot be used, and the classical Hamiltonian has to be written in terms of generalized coordinates and momenta. Even for systems without constraints it is usually convenient to use the position and momentum of the center of mass as phase-space coordinates along with the appropriate generalized coordinates and momenta; then the Hamiltonian becomes

$$\mathscr{H} = \frac{1}{2m_p}\boldsymbol{p}_c^2 + \frac{1}{2}\sum_s \sum_t G_{st} P_s P_t + \phi(\boldsymbol{r}_c, Q_1, Q_2, \ldots Q_d) \tag{12.2-5}$$

and Hamilton's canonical equations of motion are

$$\text{Center of mass} \qquad \frac{\partial \mathscr{H}}{\partial \boldsymbol{r}_c} = -\dot{\boldsymbol{p}}_c; \qquad \frac{\partial \mathscr{H}}{\partial \boldsymbol{p}_c} = \dot{\boldsymbol{r}}_c \tag{12.2-6a,b}$$

$$\text{Internal coordinates} \qquad \frac{\partial \mathscr{H}}{\partial Q_s} = -\dot{P}_s; \qquad \frac{\partial \mathscr{H}}{\partial P_s} = \dot{Q}_s \tag{12.2-7a,b}$$

These equations play a key role in the development of the general phase-space kinetic theory in Chapter 17.

§12.3 DISTRIBUTION FUNCTIONS FROM EQUILIBRIUM STATISTICAL MECHANICS

In this section we take as the object of our study a dilute solution of polymer molecules, these molecules being represented by bead-rod-spring models. The solution is at a temperature T and is contained in a volume V; there are n polymer molecules per unit volume. The solvent acts as a "temperature bath"; a typical polymer molecule is being jostled by the solvent molecules, and hence it goes through many configurations, and its various parts (i.e., the beads) can have many different velocities or momenta. We now want to know how the molecules in the solution are distributed over all the possible configuration and momentum coordinates.

In order to simplify the notation we let Q be the abbreviation for the collection of coordinates $Q_1, Q_2, \ldots, Q_d$, and we use the abbreviation dQ for $dQ_1 dQ_2 \ldots dQ_d$; we use similar abbreviated notation for the generalized momenta. We now introduce the *single-molecule-phase-space distribution function* $f_{eq}(\boldsymbol{r}_c, Q, \boldsymbol{p}_c, P)$ for the system at equilibrium. This quantity has the following significance: $f_{eq}(\boldsymbol{r}_c, Q, \boldsymbol{p}_c, P)d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP$ is the number of

polymer molecules in the solution having a configuration in the range $d\boldsymbol{r}_c\, dQ$ about $\boldsymbol{r}_c$, Q, and having momenta in the range $d\boldsymbol{p}_c\, dP$ around $\boldsymbol{p}_c$, P.

The distribution function f_{eq} is then given by the product of the number of polymer molecules in the system and the probability density; the probability density in turn is given by equilibrium statistical mechanics as proportional to $\exp(-\mathscr{H}/kT)$, where $\mathscr{H}$ is the Hamiltonian of the single polymer molecule in the temperature bath at temperature T; in order to be properly normalized the exponential has to be divided by the integral of the exponential over all the phase-space variables. Therefore, according to the standard formula from equilibrium statistical mechanics,[1,2]

$$f_{eq}(\boldsymbol{r}_c, Q, \boldsymbol{p}_c, P) = \frac{nVe^{-\mathscr{H}/kT}}{\iiiint e^{-\mathscr{H}/kT}\, d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP} = \frac{ne^{-\mathscr{H}/kT}}{\iiint e^{-\mathscr{H}/kT}\, dQ\, d\boldsymbol{p}_c\, dP} \tag{12.3-1}$$

The second form given here is possible as long as the potential energy ϕ does not depend on the coordinates of the center of mass; then the integration over $\boldsymbol{r}_c$ in the denominator can be performed to give a factor of V, as indicated above.

In many instances we are interested only in the *configurational distribution function* $\Psi_{eq}(\boldsymbol{r}_c, Q)$. The quantity $\Psi_{eq} d\boldsymbol{r}_c dQ$ gives the number of polymer molecules in the configuration range $d\boldsymbol{r}_c\, dQ$ about $\boldsymbol{r}_c$, Q. It is obtained by integrating f_{eq} over all momenta:

$$\begin{aligned}\Psi_{eq}(\boldsymbol{r}_c, Q) &= \iint f_{eq}\, d\boldsymbol{p}_c\, dP \\ &= \frac{n \iint e^{-\mathscr{H}/kT}\, d\boldsymbol{p}_c\, dP}{\iiint e^{-\mathscr{H}/kT}\, d\boldsymbol{p}_c\, dP\, dQ} \\ &= n\psi_{eq}(Q)\end{aligned} \tag{12.3-2}$$

We have noted that if, as is usually the case, the potential energy does not depend on the center of mass, the distribution function Ψ_{eq} does not depend on the center of mass and can be replaced by $n\psi_{eq}$. When $\mathscr{H}$ from Eq. 12.2-5 is inserted into the integrals in Eq. 12.3-2, the integral over $\boldsymbol{p}_c$ factors out in both the numerator and the denominator, and hence cancels out. As a result

$$\psi_{eq}(Q) = \frac{\int \exp(-\sum_s \sum_t G_{st} P_s P_t / 2kT) dP\, e^{-\phi(Q)/kT}}{\iint \exp(-\sum_s \sum_t G_{st} P_s P_t / 2kT) e^{-\phi(Q)/kT}\, dP\, dQ} \tag{12.3-3}$$

The integration over the P's can be performed (see Appendix E, §E.3) to give $(2\pi kT)^{d/2}/\sqrt{\det(G_{st})}$. Hence we get, finally, after setting $g(Q) = \det(g_{st}) = 1/\det(G_{st})$:

$$\boxed{\psi_{eq}(Q) = \frac{\sqrt{g(Q)}e^{-\phi(Q)/kT}}{\int \sqrt{g(Q)}e^{-\phi(Q)/kT}\, dQ}} \tag{12.3-4}$$

[1] R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, London (1938), §33.
[2] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, New York (1940), Chapter 10.

Note that ψ_{eq} is normalized so that $\int \psi_{eq}(Q)dQ = 1$; therefore $\psi_{eq}\, dQ$ is just the probability that the internal configuration is in the range dQ about Q. Equation 12.3-4 is the key equation to be used throughout the remainder of the chapter. In order to get the configurational distribution function, ψ_{eq}, all one needs to know is the potential energy $\phi(Q)$, describing the "springs" in the system, and the geometrical quantity g, which may be obtained from the generalized coordinates describing the mechanical model being used.[3]

Because of the importance of chainlike models, we conclude this section by showing what Eq. 12.3-4 yields for such models when all the bead masses are taken to be the same ($m_v = m$):

a. The Freely Jointed Bead-Rod Chain (Kramers Chain)

For this model there are no springs between the beads and no bending potentials at the link junctions, so that $\phi = 0$. Hence Eq. 12.3-4 becomes for a chain of N beads

$$\psi_{eq} = \frac{\sqrt{g}}{\iint \sqrt{g}\, d\theta^{N-1}\, d\phi^{N-1}} \tag{12.3-5}$$

For the chain with three beads ($N = 3$), we can use the expression for g given in Eq. 12.1-17 to get:

$$\psi_{eq}(\theta_1, \phi_1, \theta_2, \phi_2) = \frac{S_1S_2[1 - \frac{1}{4}(C_1C_2 + S_1S_2c)^2]^{1/2}}{\iiiint S_1S_2[1 - \frac{1}{4}(C_1C_2 + S_1S_2c)^2]^{1/2}\, d\theta_1\, d\phi_1\, d\theta_2\, d\phi_2}$$
$$= \frac{\sin\theta_1 \sin\theta_2}{(4\pi)^2}\left[\frac{(1 - \frac{1}{4}\cos^2\xi_2)^{1/2}}{\frac{1}{4}\sqrt{3} + \frac{1}{6}\pi}\right] \tag{12.3-6}$$

This result should be compared with the random-walk distribution in Eq. 11.3-2. Note that equilibrium statistical mechanics when applied to a chain with rigid links, gives a result that deviates from the random walk. The factor given in brackets in Eq. 12.3-6, for $N = 3$, says that the probability of having the links perpendicular to each other, for a given solid angle, is about 15.5% larger than the probability of their being parallel or antiparallel, for the same amount of solid angle. This result, which has been known for a long time,[4] has also

[3] The choice of the generalized coordinates Q_s is arbitrary, and each choice leads to a different g and a different ψ_{eq}. Suppose that we had chosen a set of coordinates Q'_s, so that

$$\psi_{eq}(Q') = \frac{\sqrt{g(Q')}e^{-\phi(Q')/kT}}{\int \sqrt{g(Q')}e^{-\phi(Q')/kT}\, dQ'} \tag{12.3-4a}$$

It must be emphasized that $\psi_{eq}(Q')$ and $\psi_{eq}(Q)$ are *different* functions of their arguments; the same applies to g and ϕ. Since the probability of finding a molecule in any finite region of the configuration space is independent of the choice of generalized coordinates,

$$\psi_{eq}(Q') = \psi_{eq}(Q)\left|\frac{\partial(Q_1, Q_2, \ldots, Q_d)}{\partial(Q'_1, Q'_2, \ldots, Q'_d)}\right| \tag{12.3-4b}$$

Thus we see that the Jacobian of the transformation is $\sqrt{g(Q')/g(Q)}$. A specific example of this is given in Problem 12B.1.

[4] H. A. Kramers, *Physica*, **11**, 1-19 (1944).

been confirmed by Gottlieb[5] by a molecular dynamics calculation. He put a 3-bead-2-rod model into a sea of 47 solvent molecules, assigning them initial random positions and momenta. The interactions between solvent molecules, as well as those between solvent molecules and the beads of the polymer model, were taken to be of the Lennard-Jones type. The equations of motion of classical mechanics for the entire system were then integrated numerically. This computer simulation gave results in general agreement with Eq. 12.3-6, and definitely not with the random walk result (Eq. 12.3-6 without the factor in brackets).

b. The Freely Jointed Bead-Spring Chain (e.g., the Rouse-Zimm Chain)

In these models, if we use the generalized coordinates in Eq. 12.1-20, the quantity g in Eq. 12.3-4 is a constant (see Eq. 12.1-26). Consequently the equilibrium configurational distribution function is

$$\psi_{eq}(\boldsymbol{Q}^{N-1}) = \frac{e^{-\phi/kT}}{\int e^{-\phi/kT}\, d\boldsymbol{Q}^{N-1}} \tag{12.3-7}$$

If, now, we specialize to the chain model used by Rouse and Zimm, in which the beads are linked together by Hookean springs, with a spring constant H, the internal potential energy is then

$$\phi(\boldsymbol{Q}^{N-1}) = \tfrac{1}{2}H \sum_k \boldsymbol{Q}_k^2 \tag{12.3-8}$$

When this is substituted into Eq. 12.3-7 and the integration performed in the denominator we get

$$\begin{aligned}\psi_{eq}(\boldsymbol{Q}^{N-1}) &= \left(\frac{H}{2\pi kT}\right)^{3(N-1)/2} e^{-(H/2kT)\sum_j \boldsymbol{Q}_j^2} \\ &= \prod_j \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_j^2}\end{aligned} \tag{12.3-9}$$

Gottlieb has performed computer simulations for the three-bead-two-spring chain model (using Fraenkel springs) and found good agreement with Eq. 12.3-7. The confirmation of distribution functions by computer simulations is relatively new; these calculations are particularly interesting, since distribution functions are not experimentally accessible. Also, computer simulations can be carried out for mechanical models that lead to mathematical complexities when approached purely analytically. This is particularly true when nonequilibrium calculations are involved.[6]

§12.4 AVERAGE VALUES

Experimentally accessible quantities are inevitably the result of measurements on a sample containing an enormous number of molecules. Consequently the sensing device in the experiment detects the response of molecules in a very wide variety of configurations. To

[5] M. Gottlieb and R. B. Bird, *J. Chem. Phys.*, **65**, 2467 2468 (1976); M. Gottlieb, *Computers in Chemistry*, **1**, 155-160 (1977).

[6] P. J. Dotson, *J. Chem. Phys.*, **79**, 5730-5731 (1983).

make a comparison between experiment and theory, we therefore have to be able to compute averages of physical quantities over all configurations and all momenta.

The average value of a function $B(\boldsymbol{r}_c, Q, \boldsymbol{p}_c, P)$ in the phase space of a single polymer molecule is

$$\langle B\rangle_{\text{eq}} = \frac{\iiiint B f_{\text{eq}}\, d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP}{\iiiint f_{\text{eq}}\, d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP} = \frac{1}{nV}\iiiint B f_{\text{eq}}\, d\boldsymbol{r}_c\, dQ\, d\boldsymbol{p}_c\, dP \tag{12.4-1}$$

It is this average that is of concern in connecting molecular dynamics with physical, macroscopic observables. Another average that is particularly useful in later chapters is the average of the quantity B over all the momenta:

$$[\![B]\!]_{\text{eq}} = \frac{\iint B f_{\text{eq}}\, d\boldsymbol{p}_c\, dP}{\iint f_{\text{eq}}\, d\boldsymbol{p}_c\, dP} = \frac{1}{\Psi_{\text{eq}}}\iint B f_{\text{eq}}\, d\boldsymbol{p}_c\, dP \tag{12.4-2}$$

Throughout the entire book we shall always use the angular brackets to indicate an average over a phase space and the double brackets to designate a momentum-space average. Note that the momentum-space average can be used to rewrite the phase-space average formally in this way:

$$\langle B\rangle_{\text{eq}} = \frac{1}{nV}\iint [\![B]\!]_{\text{eq}}\Psi_{\text{eq}}\, d\boldsymbol{r}_c\, dQ \tag{12.4-3}$$

The factor nV appears in Eqs. 12.4-1 and 12.4-3 because of the way that f_{eq} was defined in Eq. 12.3-1.

If the quantity B depends only on the configuration coordinates $\boldsymbol{r}_c$ and Q, then Eq. 12.4-3 becomes

$$\langle B\rangle_{\text{eq}} = \frac{1}{nV}\iint B\Psi_{\text{eq}}\, d\boldsymbol{r}_c\, dQ \tag{12.4-4}$$

If the quantity B depends only on the internal configuration coordinates Q, and if the potential energy ϕ also depends only on the internal coordinates Q, the integration over $\boldsymbol{r}_c$ can be performed and the average value of B becomes just an integral over the internal configuration space:

$$\langle B\rangle_{\text{eq}} = \int B\psi_{\text{eq}}\, dQ \tag{12.4-5}$$

If now the expression for ψ_{eq} from Eq. 12.3-4 is inserted into this integral we obtain

$$\boxed{\langle B\rangle_{\text{eq}} = \frac{\int B\sqrt{g}e^{-\phi/kT}\, dQ}{\int \sqrt{g}e^{-\phi/kT}\, dQ}} \tag{12.4-6}$$

This much-used result does carry with it the restriction that both B and ϕ be functions of the internal coordinates Q only. In order to use this result it is necessary to have the quantity g, the determinant of the metric matrix for the macromolecule configuration space. As we have seen in Example 12.1-1, obtaining an expression for g is a difficult problem even for some relatively simple models, when constraints are present. When there are no constraints—that is, when the model contains springs rather than rods—and when Cartesian components are used, g is a constant and it is not necessary to calculate $\sqrt{g}$. In the illustrative example that follows, it is shown how to use Eq. 12.4-3.

EXAMPLE 12.4-1 Equilibrium Averaged Internal Kinetic Energy for Any Bead-Rod-Spring Model

According to Eq. 12.1-12 the kinetic energy is the sum of two parts: that associated with the center of mass $\mathscr{K}_c = (1/2m_p)\boldsymbol{p}_c^2$ and that associated with the internal degrees of freedom, $\mathscr{K}_{\text{int}} = (1/2)\sum_s \sum_t G_{st} P_s P_t$. Find the average value of $\mathscr{K}_{\text{int}}$ at equilibrium. Keep in mind that the G_{st} in general depend on the Q's. Assume that the potential energy is independent of $\boldsymbol{r}_c$.

SOLUTION Inasmuch as the quantity to be averaged, $\mathscr{K}_{\text{int}}$, contains no $\boldsymbol{r}_c$ and since the potential energy is independent of $\boldsymbol{r}_c$, we can write Eq. 12.4-3 as

$$\langle \mathscr{K}_{\text{int}} \rangle_{\text{eq}} = \int [\![\mathscr{K}_{\text{int}}]\!]_{\text{eq}} \psi_{\text{eq}} \, dQ$$

$$= \frac{1}{2} \sum_s \sum_t \int G_{st} [\![P_s P_t]\!]_{\text{eq}} \psi_{\text{eq}} \, dQ \tag{12.4-7}$$

The momentum-space average of $P_s P_t$ is then

$$[\![P_s P_t]\!]_{\text{eq}} = \frac{\iint P_s P_t e^{-\mathscr{H}/kT} \, d\boldsymbol{p}_c \, dP}{\iint e^{-\mathscr{H}/kT} \, d\boldsymbol{p}_c \, dP} \tag{12.4-8}$$

Because $\mathscr{H} = \mathscr{K}_c + \mathscr{K}_{\text{int}} + \phi$, the integration over $\boldsymbol{p}_c$ and the factor $\exp(-\phi/kT)$ in the numerator and denominator cancel one another, and we end up with

$$[\![P_s P_t]\!]_{\text{eq}} = \frac{\int P_s P_t \exp[-(1/2kT) \sum_u \sum_v G_{uv} P_u P_v] dP}{\int \exp[-(1/2kT) \sum_u \sum_v G_{uv} P_u P_v] dP} \tag{12.4-9}$$

The integrations can be performed by using standard matrix methods (see §E.3) with the result that

$$[\![P_s P_t]\!]_{\text{eq}} = \frac{(2\pi kT)^{d/2} \sqrt{g} \, kT g_{st}}{(2\pi kT)^{d/2} \sqrt{g}} = kT g_{st} \tag{12.4-10}$$

When this is substituted into Eq. 12.4-7 we obtain finally

$$\langle \mathscr{K}_{\text{int}} \rangle_{\text{eq}} = \frac{1}{2} kT \sum_s \sum_t \int G_{st} g_{st} \psi_{\text{eq}} \, dQ$$

$$= \frac{1}{2} kT \sum_s \int \delta_{ss} \psi_{\text{eq}} \, dQ$$

$$= \frac{1}{2} dkT \tag{12.4-11}$$

in which d is the number of internal degrees of freedom of the macromolecular model. This result just shows that at equilibrium there is a contribution of $(1/2)kT$ for each degree of freedom.

§12.5 CONTRACTED DISTRIBUTION FUNCTIONS

In Section 12.3 we started with the distribution function f_{eq} in the phase space of a single polymer molecule. By integrating over the momenta we obtained the distribution function Ψ_{eq} in the configuration space of a polymer molecule. When the potential energy is independent of the center of mass, a further integration leads to the definition of a distribution function ψ_{eq} in the internal configuration space of a single macromolecule.

This process of "contraction" to a smaller and smaller variable-space can, of course, be continued. For example, let us consider the Rouse chain for which we know the equilibrium distribution function in Eq. 12.3-9. Suppose we wish to know what the distribution function is for the first link in the chain only; that is, we want to know the probability $\psi_{1,eq}(\boldsymbol{Q})d\boldsymbol{Q}$ that the connector vector $\boldsymbol{Q}_1$ of the first spring will be in the range $d\boldsymbol{Q}$ about $\boldsymbol{Q}$. This distribution function may be obtained by integrating Eq. 12.3-9 over the variables $\boldsymbol{Q}_2, \boldsymbol{Q}_3, \ldots, \boldsymbol{Q}_{N-1}$ and then replacing $\boldsymbol{Q}_1$ by $\boldsymbol{Q}$:

$$\begin{aligned}
\psi_{1,eq}(\boldsymbol{Q}) &= \int \cdots \int \psi_{eq}(\boldsymbol{Q}^{N-1}) d\boldsymbol{Q}_2\, d\boldsymbol{Q}_3 \ldots d\boldsymbol{Q}_{N-1}\big|_{\boldsymbol{Q}_1 = \boldsymbol{Q}} \\
&= \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_1^2} \prod_{k=2}^{N-1} \int \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_k^2}\, d\boldsymbol{Q}_k\big|_{\boldsymbol{Q}_1 = \boldsymbol{Q}} \\
&= \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}^2}
\end{aligned} \tag{12.5-1}$$

Another method for getting the same result is to integrate over the entire configuration space, including a Dirac delta-function to select just the information needed in the final distribution function:

$$\begin{aligned}
\psi_{1,eq}(\boldsymbol{Q}) &= \langle \delta(\boldsymbol{Q}_1 - \boldsymbol{Q}) \rangle_{eq} \\
&= \int \delta(\boldsymbol{Q}_1 - \boldsymbol{Q}) \psi_{eq}(\boldsymbol{Q}^{N-1}) d\boldsymbol{Q}^{N-1} \\
&= \int \delta(\boldsymbol{Q}_1 - \boldsymbol{Q}) \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_1^2}\, d\boldsymbol{Q}_1 \\
&\quad \cdot \int \cdots \int \left[\prod_{k=2}^{N-1} \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}_k^2}\right] d\boldsymbol{Q}_2\, d\boldsymbol{Q}_3 \ldots d\boldsymbol{Q}_{N-1} \\
&= \left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)\boldsymbol{Q}^2}
\end{aligned} \tag{12.5-2}$$

In formal developments we usually prefer to use the Dirac delta-function procedure; also in getting some contracted distribution functions we find that the delta-function method is easier to exploit. Example 12.5-1 is an illustration of this point.

In Eq. 12.5-2 $\psi_{1,eq}(\boldsymbol{Q})dQ_x\, dQ_y\, dQ_z$ is the probability that the first link has a connector vector with Cartesian components in the range $dQ_x\, dQ_y\, dQ_z$ about Q_x, Q_y, Q_z. If we want the probability $\psi_{1,eq}(Q, \theta, \phi)dQ\, d\theta\, d\phi$—the probability that the first link has a

length within the range dQ about Q, and an orientation within the range $d\theta\, d\phi$ about θ, ϕ—then this can be obtained from Eq. 12.5-2 by multiplying by the appropriate Jacobian

$$\psi_{1,\mathrm{eq}}(Q,\theta,\phi) = \psi_{1,\mathrm{eq}}(Q_x, Q_y, Q_z)\cdot\frac{\partial(Q_x, Q_y, Q_z)}{\partial(Q,\theta,\phi)}$$
$$= \psi_{1,\mathrm{eq}}(Q_x, Q_y, Q_z)Q^2\sin\theta \tag{12.5-3}$$

Finally if we want just the distribution of the connector length for the first link, we can integrate over the polar angles θ, ϕ:

$$\psi_{1Q,\mathrm{eq}}(Q) = \iint \psi_{1,\mathrm{eq}}(Q,\theta,\phi)d\theta\, d\phi$$
$$= 4\pi Q^2\left(\frac{H}{2\pi kT}\right)^{3/2} e^{-(H/2kT)Q^2} \tag{12.5-4}$$

We have illustrated here how one goes from a single molecule phase-space distribution function all the way down to the distribution of lengths in one link of the chain; this has been done for a Rouse chain, but similar developments can be made for other models as well.

EXAMPLE 12.5-1 Distribution Function for the Vector Between Two Beads of a Rouse Chain

(a) Let $\boldsymbol{r}_{\mu\nu}$ be the vector from bead μ to bead ν. Obtain the probability density $P_{\mathrm{eq}}(\boldsymbol{r}_{\mu\nu})$ that the vector $\boldsymbol{r}_{\mu\nu}$ be in the range $d\boldsymbol{r}_{\mu\nu}$ about $\boldsymbol{r}_{\mu\nu}$.

(b) Use the result in **(a)** to evaluate $\langle 1/r_{\mu\nu}\rangle_{\mathrm{eq}}$.

SOLUTION **(a)** The distribution function for the bead-to-bead vector is obtained from the complete chain distribution function by using the Dirac delta-function method; here, in order to be specific, we take $\nu > \mu$:

$$P_{\mathrm{eq}}(\boldsymbol{r}_{\mu\nu}) = \int \delta\left(\boldsymbol{r}_{\mu\nu} - \sum_{j=\mu}^{\nu-1}\boldsymbol{Q}_j\right)\psi_{\mathrm{eq}}(\boldsymbol{Q}^{N-1})d\boldsymbol{Q}^{N-1} \tag{12.5-5}$$

Into this we substitute Eq. 12.3-9 for the Rouse chain distribution function and Eq. E.4-5 for a representation of the Dirac delta function:

$$P_{\mathrm{eq}}(\boldsymbol{r}_{\mu\nu}) = \int\left\{\frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty}\exp\left[i\left(\boldsymbol{r}_{\mu\nu} - \sum_{j=\mu}^{\nu-1}\boldsymbol{Q}_j\right)\cdot\boldsymbol{s}\right]d\boldsymbol{s}\right\}$$
$$\cdot\left\{\prod_{h=1}^{N-1}\left(\frac{H}{2\pi kT}\right)^{3/2}\exp\left[-\frac{H}{2kT}\boldsymbol{Q}_h^2\right]\right\}d\boldsymbol{Q}^{N-1} \tag{12.5-6}$$

The integrals over $\boldsymbol{Q}_k$ outside the range $h = \mu$ to $h = \nu - 1$ can be performed, and the order of integration can be changed to give

$$P_{\mathrm{eq}}(\boldsymbol{r}_{\mu\nu}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty}\exp(i\boldsymbol{r}_{\mu\nu}\cdot\boldsymbol{s})\prod_{h=\mu}^{\nu-1}\left(\frac{H}{2\pi kT}\right)^{3/2}$$
$$\cdot\left\{\int\exp\left[-\frac{H}{2kT}(\boldsymbol{Q}_h\cdot\boldsymbol{Q}_h) - i(\boldsymbol{Q}_h\cdot\boldsymbol{s})\right]d\boldsymbol{Q}_h\right\}d\boldsymbol{s} \tag{12.5-7}$$

The integral within braces is known (see Eq. E.3-6) and when it is evaluated we get

$$P_{eq}(\boldsymbol{r}_{\mu\nu}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty} \exp(i\boldsymbol{r}_{\mu\nu}\cdot\boldsymbol{s}) \prod_{h=\mu}^{\nu} \left(\frac{H}{2\pi kT}\right)^{3/2} \cdot\left\{\left(\frac{2\pi kT}{H}\right)^{3/2} \exp\left[-\frac{kT}{2H}(\boldsymbol{s}\cdot\boldsymbol{s})\right]\right\} d\boldsymbol{s}$$

$$= \frac{1}{(2\pi)^3}\int_{-\infty}^{+\infty} \exp\left[-(\nu-\mu)\frac{kT}{2H}(\boldsymbol{s}\cdot\boldsymbol{s}) + i(\boldsymbol{s}\cdot\boldsymbol{r}_{\mu\nu})\right] d\boldsymbol{s} \tag{12.5-8}$$

If $\nu < \mu$ we have the same result except for the fact that $(\nu - \mu)$ is replaced by $(\mu - \nu)$; therefore, the result in Eq. 12.5-8 can be made to apply to all values of $\nu \neq \mu$ by replacing $(\nu - \mu)$ by $|\nu - \mu|$. Once again we have an integral of the form of Eq. E.3-6 which is then evaluated to give the final result:

$$P_{eq}(\boldsymbol{r}_{\mu\nu}) = \left(\frac{H}{2|\nu-\mu|\pi kT}\right)^{3/2} \exp\left(-\frac{H}{2|\nu-\mu|kT}\boldsymbol{r}_{\mu\nu}^2\right) \tag{12.5-9}$$

For the special case that $\nu = 2$ and $\mu = 1$, this result simplifies to that in Eq. 12.5-2. When $\nu = N$ and $\mu = 1$, Eq. 12.5-9 simplifies to Eq. 11.4-3 for the probability density for the end-to-end vector $\boldsymbol{r}$.

(b) To get the equilibrium average value of $1/r_{\mu\nu}$ we now have to do one more integration:

$$\left\langle \frac{1}{r_{\mu\nu}} \right\rangle_{eq} = \left(\frac{H}{2|\nu-\mu|\pi kT}\right)^{3/2} \int \frac{1}{r_{\mu\nu}} \exp\left(-\frac{H}{2|\nu-\mu|kT}\boldsymbol{r}_{\mu\nu}^2\right) d\boldsymbol{r}_{\mu\nu} \tag{12.5-10}$$

This integral is easily performed in spherical coordinates, with the result that

$$\left\langle \frac{1}{r_{\mu\nu}} \right\rangle_{eq} = \sqrt{\frac{2H}{|\nu-\mu|\pi kT}} \tag{12.5-11}$$

This result is used in Chapter 15.

EXAMPLE 12.5-2 Configurational Distribution Function for a Bead-Spring Chain with Infinitely Stiffened Springs

Write the distribution function for a chain with N beads connected linearly with Fraenkel springs, for which $\phi = (H/2)\sum_k (Q_k - a)^2$ (see Table 11.5-1). Then let the Fraenkel spring constant H go to infinity so that the springs approach rigid rods of length a. Do you get the result of Eq. 12.3-6?

SOLUTION For the Fraenkel-spring chain the analog of Eq. 12.3-9 is

$$\psi_{eq}(\boldsymbol{Q}^{N-1}) = \frac{\prod_k F_k}{\prod_k \int F_k\, d\boldsymbol{Q}_k} \tag{12.5-12}$$

where $F_k = \exp[-(H/2kT)(Q_k - a)^2]$. If we now switch to polar coordinates, we have

$$\psi_{eq}(Q^{N-1}, \theta^{N-1}, \phi^{N-1}) = \frac{\prod_k F_k Q_k^2 \sin\theta_k}{\prod_k \iiint F_k Q_k^2 \sin\theta_k\, dQ_k\, d\theta_k\, d\phi_k} \tag{12.5-13}$$

We now integrate over the length coordinates Q_k to get

$$\psi_{eq}(\theta^{N-1}, \phi^{N-1}) = \frac{\prod_k \sin\theta_k}{(4\pi)^{N-1}} \tag{12.5-14}$$

Thus after the integration, the factors involving the Q_k in numerator and denominator cancel, and in this cancellation the parameters H and a of the Fraenkel spring have disappeared. Hence, if we "freeze" the connectors by letting H go to infinity we still get the result in Eq. 12.5-14, which is just the random-walk distribution (see Eq. 11.3-2).

Several points need to be made with regard to Example 12.5-2. Chain models with "stiffened springs" are *not* the same as chain models with "rigid rods." Furthermore there is no unique way to take the limit of stiffened springs, whereas the rigid-rod models are unique. It should be noted that the phenomenon encountered here also arises in Example 12.4-1 where the internal kinetic energy of a bead-spring chain with stiffened Fraenkel springs is $(3/2)(N-1)kT$, whereas that of a Kramers bead-rod chain is $(N-1)kT$. For a very interesting discussion of this problem of freezing out degrees of freedom, which is not normally addressed in books on statistical mechanics, see the article by van Kampen.[1]

Finally we need to address the question of whether it is better to use a stiffened-spring chain model or one with rigid rods. Although only limited calculations are available that would enable us to compare the two types of models in nonequilibrium situations, it is very likely that quantitative differences between them would be small for chains with a large number of links. Furthermore the discrepancy between the two types of models is probably small compared to the discrepancy between either model and the true system. Generally the choice of mechanical model will be made by selecting the one which is mathematically most convenient. For more on bead-rod chains see §§16.5 and 16.6.

PROBLEMS

12A.1 Deviation from Random-Walk Distribution

a. How much does Eq. 12.3-6 deviate from the corresponding random-walk distribution?
b. Plot the functions in Eqs. 12C.1-1 and 12D.1-6, and interpret the results.

12B.1 Equilibrium Properties of a Dilute Polymer Solution Modeled as a Suspension of Elastic Dumbbells

The choice of generalized coordinates is arbitrary. Here we work through some of the subjects covered in this chapter for elastic dumbbells, using two different sets of generalized coordinates:

I. X, Y, Z (the Cartesian components of the connector vector $\boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1$)
II. Q, θ, ϕ (the polar coordinates for the connector vector $\boldsymbol{Q}$; in this discussion we use $S \equiv \sin\theta$, $C \equiv \cos\theta$, $s \equiv \sin\phi$, $c \equiv \cos\phi$)

a. Express $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$ in terms of the generalized coordinates; take the mass of each bead to be m.

b. Find the (g_{st})- and (G_{st})-matrices:

$$\textbf{I.}\quad (g_{st}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \frac{m}{2}; \qquad (G_{st}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \frac{2}{m} \tag{12B.1-1a,b}$$

$$\textbf{II.}\quad (g_{st}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & Q^2 & 0 \\ 0 & 0 & Q^2S^2 \end{pmatrix} \frac{m}{2}; \qquad (G_{st}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & Q^{-2} & 0 \\ 0 & 0 & Q^{-2}S^{-2} \end{pmatrix} \frac{2}{m} \tag{12B.1-2a,b}$$

c. Next obtain the Hamiltonian:

$$\text{I.} \qquad \mathscr{H} = \frac{1}{4m}\boldsymbol{p}_c^2 + \frac{1}{m}(P_X^2 + P_Y^2 + P_Z^2) + \phi^{(c)} \tag{12B.1-3}$$

$$\text{II.} \qquad \mathscr{H} = \frac{1}{4m}\boldsymbol{p}_c^2 + \frac{1}{m}(P_Q^2 + Q^{-2}P_\theta^2 + Q^{-2}S^{-2}P_\phi^2) + \phi^{(c)} \tag{12B.1-4}$$

How are the P's related to the generalized velocities? In these equations $\phi^{(c)} = \frac{1}{2}HQ^2 = \frac{1}{2}H(X^2 + Y^2 + Z^2)$ for Hookean dumbbells.

d. Next show that

$$\text{I.} \qquad \psi_{eq}(X, Y, Z) = \frac{[e^{-\phi^{(c)}/kT}]}{\iiint [e^{-\phi^{(c)}/kT}]dX\, dY\, dZ} \tag{12B.1-5}$$

$$\text{II.} \qquad \psi_{eq}(Q, \theta, \phi) = \frac{[e^{-\phi^{(c)}/kT}]Q^2 \sin\theta}{\iiint [e^{-\phi^{(c)}/kT}]Q^2 \sin\theta\, dQ\, d\theta\, d\phi} \tag{12B.1-6}$$

Note that

$$\psi_{eq}(Q, \theta, \phi) = \psi_{eq}(X, Y, Z) \cdot \left|\frac{\partial(X, Y, Z)}{\partial(Q, \theta, \phi)}\right| \tag{12B.1-7}$$

e. Next evaluate the integrals in the denominators of the above expressions for ψ_{eq} for Hookean dumbbells.

f. Obtain the mean square end-to-end distance $\langle Q^2\rangle_{eq}$ for Hookean dumbbells.

g. Finally prove that for any kind of elastic dumbbell

$$\langle \boldsymbol{QF}^{(c)}\rangle_{eq} = kT\boldsymbol{\delta} \tag{12B.1-8}$$

Here $\boldsymbol{F}^{(c)}$ is the force in the connector, defined by

$$\boldsymbol{F}^{(c)} = \boldsymbol{F}_1^{(\phi)} = -\frac{\partial}{\partial \boldsymbol{r}_1}\phi^{(c)} = +\frac{\partial}{\partial \boldsymbol{Q}}\phi^{(c)} = \frac{\boldsymbol{Q}}{Q}\phi^{(c)\prime} = \boldsymbol{u}\phi^{(c)\prime} \tag{12B.1-9}$$

where $\phi^{(c)\prime} \equiv d\phi^{(c)}/dQ$ and $\boldsymbol{u}$ is the unit vector in the direction from bead "1" to bead "2." First show that

$$\begin{aligned}\langle \boldsymbol{QF}^{(c)}\rangle_{eq} &= \frac{\int \boldsymbol{uu}\phi^{(c)\prime}(e^{-\phi^{(c)}/kT})Q\, d\boldsymbol{Q}}{\int (e^{-\phi^{(c)}/kT})d\boldsymbol{Q}} \\ &= \frac{\int_0^\infty \phi^{(c)\prime}(e^{-\phi^{(c)}/kT})Q^3\, dQ \int \boldsymbol{uu}\, d\boldsymbol{u}}{\int_0^\infty (e^{-\phi^{(c)}/kT})Q^2\, dQ \int d\boldsymbol{u}}\end{aligned} \tag{12B.1-10}$$

in which $d\boldsymbol{u} \equiv \sin\theta\, d\theta\, d\phi$. Use Appendix E to evaluate the integrals over $\boldsymbol{u}$. Then integrate the Q-integral by parts to obtain Eq. 12B.1-8.

12B.2 Equilibrium Distribution Function for a Bead-Spring Chain with Finitely Extensible Springs

Obtain an expression analogous to Eq. 12.3-9 for $\psi_{eq}(\boldsymbol{Q}^{N-1})$ for a chain model that has FENE springs (see Problem 11B.4b).

12B.3 Two-Link Distribution Function for a Rouse Chain

In §12.5 we obtained the one-link distribution function for a Rouse chain, $\psi_{1,eq}(\boldsymbol{Q})$ which is the probability density that spring "1" have a configuration $\boldsymbol{Q}$. Find the analogous quantity for two links, $\psi_{12,eq}(\boldsymbol{Q}, \boldsymbol{Q}')$, which gives the probability density that spring "1" has a connector vector $\boldsymbol{Q}$ and that spring "2" has a connector vector $\boldsymbol{Q}'$.

12C.1 Probability of End-to-End Vector for a Three-Bead Kramers Chain[1]

a. The probability density $P(\boldsymbol{r})$ for the end-to-end vector for a three-bead Kramers chain is given in Eq. 12D.1-6 in the random-walk approximation. Show that in the absence of this approximation ($0 < r < 2a$)

$$P_{eq}(\boldsymbol{r}) = \frac{1}{8\pi a^2 r}\left[\frac{\sqrt{1 - \frac{1}{4}[1 - \frac{1}{2}(r/a)^2]^2}}{\frac{1}{4}\sqrt{3} + \frac{1}{6}\pi}\right] \tag{12C.1-1}$$

b. Use the result of (a) to obtain $\langle r^2 \rangle_{eq}$.

12C.2 Change of Variables in Distribution Functions

In Eq. 12.3-6 we give ψ_{eq} for the 3-bead-2-rod chain, with the polar angles θ_1, ϕ_1, θ_2, ϕ_2 as the independent variables. Show that, in terms of the included angles:

$$\psi_{eq}(\xi_1, \xi_{01}, \xi_2, \xi_{12}) = \frac{\sin \xi_1 \sin \xi_2 \sqrt{1 - \frac{1}{4}\cos^2 \xi_2}}{4\pi^2(\sqrt{3} + \frac{2}{3}\pi)} \tag{12C.2-1}$$

12D.1 Probability of End-to-End Vector for a Bead-Rod Chain (Random-Walk Approximation)[2,3]

a. Use the Dirac delta-function method for getting the probability density $P_{eq}(\boldsymbol{r})$ for the freely jointed bead-rod chain in the random-walk approximation. Show that this leads to

$$P_{eq}(\boldsymbol{r}) = \frac{1}{(2\pi)^3(4\pi)^{N-1}} \int_{-\infty}^{+\infty} e^{i(\boldsymbol{r}\cdot\boldsymbol{s})}\left[\int e^{-ia\boldsymbol{u}\cdot\boldsymbol{s}}\, d\boldsymbol{u}\right]^{N-1} d\boldsymbol{s} \tag{12D.1-1}$$

in which $\boldsymbol{u}$ is a unit vector with polar angles θ, ϕ, and $d\boldsymbol{u} = \sin\theta\, d\theta\, d\phi$. In the inner integral imagine that the coordinates are rotated so that $\boldsymbol{s}$ is in the direction of the z-axis; then the inner integral can be evaluated in spherical coordinates since $\int_0^\pi (\exp(\alpha \cos\theta)) \sin\theta\, d\theta = (2/\alpha)\sinh\alpha$. Show that this leads to

$$P_{eq}(\boldsymbol{r}) = \frac{1}{(2\pi)^3} \int_{-\infty}^{+\infty} e^{i(\boldsymbol{r}\cdot\boldsymbol{s})}\left(\frac{\sin as}{as}\right)^{N-1} d\boldsymbol{s} \tag{12D.1-2}$$

[1] M. Gottlieb and R. B. Bird, *J. Chem. Phys.*, **65**, 2467-2468 (1976); M. Gottlieb, *Computers in Chemistry*, **1**, 155-160 (1977).

[2] H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), Sec. 5.

[3] P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York (1969).

Once again rotate coordinates and perform the integration in spherical coordinates to get Rayleigh's equation:[4]

$$P_{eq}(r) = \frac{1}{2\pi^2 r}\int_0^x (\sin rs)\left(\frac{\sin as}{as}\right)^{N-1} s\,ds \tag{12D.1-3}$$

b. It can be shown[2] that part of the integrand in Eq. 12D.1-3 can be expanded thus:

$$\left(\frac{\sin as}{as}\right)^{N-1} = e^{-(N-1)a^2s^2/6}\left[1 - \frac{1}{180}(N-1)(as)^4 + \cdots\right] \tag{12D.1-4}$$

Show that when this expansion is used, Eq. 12D.1-3 yields

$$P_{eq}(r) = \left(\frac{3}{2\pi(N-1)a^2}\right)^{3/2} e^{-3r^2/2(N-1)a^2} \cdot\left\{1 - \frac{3}{20(N-1)}\left[5 - \frac{10r^2}{(N-1)a^2} + \frac{3r^4}{(N-1)^2a^4}\right] + \cdots\right\} \tag{12D.1-5}$$

When N is very large and $r^2 \ll (N-1)a^2$, this simplifies to Eq. 11.3-12.

c. Show that for $N = 3$ the integral in Eq. 12D.1-3 can be evaluated analytically to give

$$P_{eq}(r) = \frac{1}{8\pi a^2 r}, \qquad 0 < r < 2a \tag{12D.1-6}$$

12D.2 Effect of Ring-Closure on Radius of Gyration[5]

Consider a flexible closed-ring model formed by inserting a spring between beads "1" and "N" in the Rouse bead-spring chain model. All springs have a spring constant H.

a. Do Eqs. 11.6-1 through 9 need to be modified for this model? Explain.

b. How does Eq. 12.3-9 have to be modified?

c. Show that for this model

$$\langle s^2\rangle = \frac{\sum_k\sum_l C_{kl}\int (\boldsymbol{Q}_k\cdot\boldsymbol{Q}_l)\exp[-(H/2kT)\sum_i\sum_j D_{ij}(\boldsymbol{Q}_i\cdot\boldsymbol{Q}_j)]d\boldsymbol{Q}^{N-1}}{N\int \exp[-(H/2kT)\sum_i\sum_j D_{ij}(\boldsymbol{Q}_i\cdot\boldsymbol{Q}_j)]d\boldsymbol{Q}^{N-1}} \tag{12D.2-1}$$

in which $D_{ij} = (\delta_{ij} + 1)$; for later use verify that $D_{ij}^{-1} = \delta_{ij} - (1/N)$. Let d_i be the eigenvalues of the (D_{ij})-matrix; these are N and 1, the latter being $(N-2)$-fold.

d. Next introduce a new set of internal coordinates by letting

$$\boldsymbol{Q}_k = \sum_i \Omega_{ki}\boldsymbol{Q}'_i \tag{12D.2-2}$$

where the Ω_{ki} are the elements of an $(N-1)\times(N-1)$ orthogonal matrix which diagonalizes the (D_{ij})-matrix. Show that the introduction of these new coordinates leads to

$$\langle s^2\rangle = \frac{1}{N}\sum_k\sum_l\sum_j C_{ki}\,\Omega_{kj}\Omega_{ij}\frac{\int_0^\infty Q_j'^4\exp[-(H/2kT)d_jQ_j'^2]dQ_j'}{\int_0^\infty Q_j'^2\exp[-(H/2kT)d_jQ_j'^2]dQ_j'} \tag{12D.2-3}$$

[4] Lord Rayleigh, *Phil. Mag.*, **37**, 321-347 (1919).

[5] B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301-1314 (1949).

e. Perform the integrations in this equation and obtain finally

$$\langle s^2 \rangle = \frac{3kT}{NH} \sum_j \sum_k C_{jk} D_{kj}^{-1} = \frac{(N^2 - 1)kT}{4NH} \tag{12D.2-4}$$

Compare this result with that in Problem 11B.1 and note that the ring closure cuts the value of $\langle s^2 \rangle$ in half.

12D.3 Arbitrary Bead-Spring Models with No Constraints

Consider a molecular model consisting of beads, not necessarily all of the same mass, connected in an arbitrary manner by springs, with *no constraints*. In such a model, the beads may be numbered in any manner, and "connector vectors" $\boldsymbol{Q}_k$ can be introduced as in Eq. 11.6-2. There will, however, not always be a one-to-one correspondence between springs and connector vectors.

a. Show that if the Cartesian components of these connector vectors are used as the coordinates Q_s, then the base vectors, $\boldsymbol{b}_{vs}$, and the components of the metric matrices, g_{st} and G_{st}, are independent of the Q_s.

b. For these models the full set of $\boldsymbol{r}_v$ may be used as the independent variables in lieu of $\boldsymbol{r}_c$ and the Q_s. Show that for any function $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N) = F(\boldsymbol{r}_c, Q_1, Q_2, \ldots Q_d)$

$$\frac{\partial f}{\partial \boldsymbol{r}_v} = \frac{m_v}{m_p} \frac{\partial F}{\partial \boldsymbol{r}_c} + \sum_s \left(\frac{\partial Q_s}{\partial \boldsymbol{r}_v} \right) \frac{\partial F}{\partial Q_s} \tag{12D.3-1}$$

$$\frac{\partial F}{\partial \boldsymbol{r}_c} = \sum_v \frac{\partial f}{\partial \boldsymbol{r}_v}; \qquad \frac{\partial F}{\partial Q_s} = \sum_v \frac{1}{\sqrt{m_v}} \left(\boldsymbol{b}_{vs} \cdot \frac{\partial f}{\partial \boldsymbol{r}_v} \right) \tag{12D.3-2,3}$$

c. Apply Eq. 12D.3-1 with $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots \boldsymbol{r}_N) = \boldsymbol{r}_\mu$ to get

$$\sum_s \frac{1}{\sqrt{m_\mu}} \boldsymbol{b}_{\mu s} \left(\frac{\partial Q_s}{\partial \boldsymbol{r}_v} \right) = \left(\delta_{v\mu} - \frac{m_v}{m_p} \right) \boldsymbol{\delta} \tag{12D.3-4}$$

Use this relation to prove that

$$\sum_s \sum_t G_{st} \boldsymbol{b}_{vs} \boldsymbol{b}_{\mu t} = \left(\delta_{v\mu} - \frac{\sqrt{m_v m_\mu}}{m_p} \right) \boldsymbol{\delta} \tag{12D.3-5}$$

To obtain this, begin by multiplying Eq. 12D.3-4 by $\sqrt{m_\mu} \boldsymbol{b}_{\mu t}$ and summing on μ. Then multiply the resulting equation by G_{tu} and sum on t. Next multiply by $(1/\sqrt{m_\mu}) \boldsymbol{b}_{\mu u}$ and sum on u, after which Eq. 12D.3-4 can be used again to get the desired result. Equation 12D.3-5 is used in Chapters 16 and 18.

PART VI

ELEMENTARY APPROACH TO KINETIC THEORY

The simplest mechanical models for polymer molecules are the "dumbbell models": the elastic dumbbell model, for describing a linear flexible molecule; and the rigid dumbbell model, for describing rigid rodlike macromolecules. These very crude models are the subject of study in the first two chapters of this part of the book. We know full well that these elementary models are, from a physical point of view, quite inadequate. Real polymer molecules do not look like dumbbells. So why should we devote two chapters to them?

There are really two reasons for presenting this material. The first is that the use of simple models enables us to explain the ideas and procedures of the kinetic theory rather quickly and with a minimum of mathematics. Once the reader has worked through these chapters with their relatively simple analytical results, he or she is then in a position to go on to the study of much more realistic molecular models, where the mathematics becomes more involved and where numerical methods have to be used. In fact most of the remainder of the book can be read "just for the story" if the reader does not wish to be burdened with the intricate mathematical detail presented there.

A second reason for starting out with the dumbell models is that these very crude mechanical models are actually very helpful in understanding rheological properties. The models are not generally capable of giving quantitative results, but the qualitative understanding that they provide has proven to be quite valuable. It is enlightening to know even roughly how macroscopic fluid behavior is related to molecular orientation and stretching. Also by experimenting with different kinds of modifications of the basic dumbbell models one can begin to develop some kind of intuition about the essential elements of effective model building.

In Chapter 13 we introduce the kinetic theory of polymers by means of the elastic dumbbell models. These models have no internal constraints and as a result the mathematics is particularly simple; in fact, if the dumbbell consists of two point masses joined by a Hookean spring (that is, a linear relation between the tension and the separation between the two point masses), then a number of particularly simple analytical results can be obtained. Also we can obtain a constitutive equation of a form encountered in Chapter 7. Most of the main physical notions incorporated into molecular models are presented in Chapter 13.

In Chapter 14 a discussion of the rigid dumbbell model is given. This is the simplest model that has an internal constraint; that is, the separation of the two mass points is required to be a constant. The incorporation of constraints requires the use of generalized coordinates and generalized momenta; as a result the forms of many of the key equations in Chapters 13 and 14 are found to be different. Although the derivations in Chapter 14 are carried out for the rigid dumbbell model, it is pointed out without proof that all of the results can be generalized to include the multi-bead rod model—a weightless rod with mass points distributed along it.

In later chapters frequent reference will be made to Chapters 13 and 14. Often it will be shown how rather general formulas can be simplified to the analogous formulas for the elementary dumbbell models. In particular, in Chapters 17 to 19, where a higher level of abstraction is used, it is particularly helpful to have the dumbbell results readily available as a "crutch" when a specific example is needed.

The next two chapters in this part of the book deal with more realistic models for describing linear flexible macromolecules. In particular the bead-spring chain associated with the names of Rouse and Zimm, and the bead-rod chain associated with the names of Kuhn and Kramers are emphasized.

Chapter 15 is devoted to the bead-spring chain models. For many years these models played a key role in the molecular interpretation of rheological phenomena. If Hookean springs are used in the model, a number of interesting and important results can be obtained analytically; actually one can show that for this chain model many results can be regarded as a superposition of Hookean dumbbell results, each dumbbell having a characteristic time constant. That is, by using a mechanical model with a large number of degrees of freedom we end up being able to describe a spectrum of relaxation times.

Chapter 16 deals with a variety of more complex models. Here it is necessary to make use of some of the results of Chapters 17 and 18 inasmuch as we explore some models—such as the Kramers bead-rod chain model—that contain constraints. This material is accessible to readers who prefer not to involve themselves with the phase-space kinetic theories in the later chapters. In addition, Chapter 16 is set up in such a way that the opening sections give the reader a summary of the formulas needed for the inclusion of hydrodynamic interaction (complete or equilibrium averaged) and unequal masses of the beads of the model. This information is important to those who wish to pursue more complex and more complete molecular modeling in kinetic theory calculations.

Strictly speaking the material in Chapters 13 through 16 is applicable only to dilute polymer solutions. However, some of these results have been applied empirically to concentrated solutions, although this requires some reinterpretation of the parameters. A more complete understanding of concentrated solutions and melts is postponed until Chapters 19 and 20.

Although the principal focus of attention in Chapters 13 through 16 is on the stress tensor and constitutive equations, some material is also included on the calculation of the diffusivity of polymers. The study of the mass flux vector and the diffusivity is presented in a more complete form in Chapters 17 through 19.

CHAPTER 13

ELASTIC DUMBBELL MODELS

This chapter is intended to provide an overview of the kinetic theory of polymers by using an ultrasimplified model for a polymer molecule, namely an elastic dumbbell. In equilibrium systems one can write down a formal expression for the configurational distribution function directly by means of equilibrium statistical mechanics. For nonequilibrium systems, on the other hand, the situation is much more complicated; the best we can do, in general, is to derive a second-order partial differential equation (called the "diffusion equation") for the configurational distribution function. Only for particularly simple macromolecular models has this equation been solved analytically.

Once the configurational distribution function has been obtained (usually by means of perturbation theory or by numerical methods), one then needs an expression for the stress tensor in order to make the connection with rheological behavior and fluid dynamics. This stress tensor expression accounts for the various mechanisms by which forces are transmitted through the fluid.

In §13.1 we describe in some detail the way in which a flowing polymer solution is to be modeled and the assumptions that are made in setting up the kinetic theory. Then in §13.2 and §13.3 we give the two main parts of the kinetic theory: (1) the establishment of the "diffusion equation" for the configurational distribution function, and (2) the development of an expression for the stress tensor. All of this is done for any kind of elastic dumbbell, that is, the force law for the spring is not specified. The kinetic theories discussed in later chapters also consist of the same two main parts.

In §13.4 we take the spring to be "Hookean," the tension in the spring being proportional to the bead separation; we then show that the equations for this particularly simple model can be solved exactly. In fact, we are able to get a complete constitutive equation and then all of the rheological properties for the model system. By contrast, in §13.5 we take the spring to be nonlinear; for this slightly more complicated model we obtain only a perturbation solution for steady, homogeneous flows and a numerical solution for steady shear flow.

In §13.6 we take up the subject of "hydrodynamic interaction," which accounts for the fact that the beads of the dumbbell perturb the flow field in the neighborhood of the dumbbell. Inclusion of hydrodynamic interaction makes the theory somewhat more involved, but several approximate procedures are available to take this effect into account. Finally in §13.7 we examine some of the consequences of allowing the hydrodynamic drag and Brownian motion to be anisotropic; such effects would be expected to be important in the modeling of concentrated systems and melts.

Much of what we do in this chapter is used directly in Chapter 15, where we deal with bead-spring chains. In that chapter it is found that chains with Hookean springs have a rheological response equivalent to a set of Hookean dumbbells with a spectrum of time

constants. In addition the notation, physical ideas, and general procedures will carry over directly into this later development.

§13.1 MODELING OF SOLUTIONS OF FLEXIBLE POLYMERS

We are concerned here with a dilute solution of a polymer, with n polymer molecules per unit volume. The solvent is taken to be a Newtonian fluid[1] with viscosity η_s. Throughout most of the chapter it is assumed that the solution is sufficiently dilute that the polymer molecules do not interact with one another.

In this chapter we idealize the polymer molecule as an elastic dumbbell—two beads, each of mass m, joined by a nonbendable spring. The beads are labeled "1" and "2" and their instantaneous locations in space are called $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The "connector vector," $\boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1$, describes the overall orientation and the internal configuration of the polymer molecule. We may thus describe the configuration either by specifying $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ or by giving $\boldsymbol{r}_c$ and $\boldsymbol{Q}$. Further comments on this model are given in §11.5.

The flow field of the polymer solution is taken to be homogeneous, in the sense that the rate-of-strain tensor is the same at all points in the flow field. Therefore we can always write the mass-average velocity of the solution as $\boldsymbol{v} = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}]$ where $\boldsymbol{v}_0$ is a vector independent of position, $\boldsymbol{r}$ is the position vector, and $\boldsymbol{\kappa}$ is a traceless tensor that is independent of position but that may depend on the time t; the requirement that $\text{tr}\,\boldsymbol{\kappa} = 0$ is needed because the fluid is assumed to be incompressible. Table 13.1-1 gives several examples of homogeneous velocity fields that are used in the kinetic theory discussions in this volume. The assumption of a homogeneous velocity field is normally not a serious one; it is only when the velocity gradient changes appreciably over a distance comparable to the size of the polymer molecule that this assumption has to be avoided.

It has been customary in most kinetic theories to assume that the phase-space distribution function can be written as the product of a configuration-space distribution function and a velocity-space distribution function; it is then assumed further that the velocity-space distribution function is Maxwellian about the solution velocity at the center of mass of the dumbbell, and that the configuration-space distribution function is independent of the location of the center of mass of the polymer molecule. Although we will use these conventional assumptions throughout most of this chapter, we start by being somewhat more general.

We begin by replacing the distribution function $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{p}_1, \boldsymbol{p}_2, t)$ in the phase space by $F(\boldsymbol{r}_1, \boldsymbol{r}_2, \dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2, t)$, the corresponding distribution function in position-velocity space. We then define the configuration-space distribution function $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)$ by

$$F(\boldsymbol{r}_1, \boldsymbol{r}_2, \dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2, t) = \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t)\Xi(\dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2, \boldsymbol{r}_1, \boldsymbol{r}_2, t) \tag{13.1-1}$$

where the velocity-space distribution function Ξ satisfies the normalization condition $\iint \Xi\, d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2 = 1$. Then we assume that the configuration-space distribution functon Ψ can be factored

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = n\psi(\boldsymbol{Q}, t) \tag{13.1-2}$$

to indicate that the distribution of configurations is independent of the location of the dumbbells in space; the distribution function $\psi(\boldsymbol{Q}, t)$ satisfies the normalization condition $\int \psi(\boldsymbol{Q}, t) d\boldsymbol{Q} = 1$. If we wish to make the assumption that the velocity distribution is

[1] The use of a viscoelastic solvent has been considered by S. Hayashi, *J. Phys. Soc. Japan*, **19**, 2306–2312 (1964).

TABLE 13.1-1

Homogeneous Velocity Fields with $v_0 = 0$

Examples of the flow:

$$v_x = \kappa_{xx}x + \kappa_{xy}y + \kappa_{xz}z$$

$$v_y = \kappa_{yx}x + \kappa_{yy}y + \kappa_{yz}z$$

$$v_z = \kappa_{zx}x + \kappa_{zy}y + \kappa_{zz}z$$

where the κ_{ij} are possibly functions of time; it is required that $\sum_i \kappa_{ii} = 0$ because the fluid is incompressible.

Type of Flow	Velocity Components		Standard Abbreviations[a]	Reference to Chapter 3
Simple shear flows	$v_x = \kappa_{xy}y$ $v_y = 0$ $v_z = 0$	(A)	$\kappa_{xy} = \dot{\gamma}$	§3.1
Shearfree flows $(0 \le b \le 1)$	$v_x = -\frac{1}{2}\kappa_{zz}(1 + b)x$ $v_y = -\frac{1}{2}\kappa_{zz}(1 - b)y$ $v_z = \kappa_{zz}z$	(B)	$\kappa_{zz} = \dot{\varepsilon}$	§3.1
Eccentric disk (or orthogonal rheometer) flow	$v_x = -W\left(y - \frac{a}{b}z\right)$ $v_y = Wx$ $v_z = 0$	(C)	—	Problem 3B.1
Homogeneous, potential flows	$\boldsymbol{v} = -\nabla\Phi$, with $\Phi = -\frac{1}{2}(\boldsymbol{\kappa} : \boldsymbol{rr})$ and $\boldsymbol{\kappa} = \boldsymbol{\kappa}^\dagger$.	(D)		

[a] The quantity $\dot{\gamma}$, called the "shear rate," is defined as $\dot{\gamma} = \sqrt{\frac{1}{2}(\bar{\dot{\gamma}}:\dot{\gamma})}$ and is always positive. Hence for steady shear flows we can write $v_x = \dot{\gamma}y$, whereas for unsteady shear flows we use the more general notation $v_x(t) = \dot{\gamma}_{yx}(t)y$. The quantity $\dot{\varepsilon}$, on the other hand, may be positive or negative.

Maxwellian[2] about the mass-average velocity of the solution $\boldsymbol{v}$ at the center of mass of the dumbbell,[3] then we write

$$\Xi_{eq}(\dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2) = \frac{\exp\{-[\frac{1}{2}m(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})^2 + \frac{1}{2}m(\dot{\boldsymbol{r}}_2 - \boldsymbol{v})^2]/kT\}}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \exp\{-[\frac{1}{2}m(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})^2 + \frac{1}{2}m(\dot{\boldsymbol{r}}_2 - \boldsymbol{v})^2]/kT\} d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2} \tag{13.1-3}$$

This assumption is tantamount to saying that the velocity distribution in a flow system is the same as that in a solution at equilibrium; it is sometimes called the assumption of "equilibration in momentum space" (see §18.3(a)). It is essential that this assumption be

[2] This is consistent with Eq. 12.3-1 from which we get in general

$$\Xi_{eq} = \frac{e^{-\mathscr{H}/kT}}{\iint e^{-\mathscr{H}/kT}\, d\boldsymbol{p}_c\, dP} \tag{13.1-3a}$$

[3] One could assume a velocity distribution Maxwellian about $\boldsymbol{v}_v$, the solution velocity at bead v; it has been shown that, for chains with Hookean springs, the rheological properties are negligibly different from those calculated with Eq. 13.1-3 [R. B. Bird, X. J. Fan, and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **15**, 85 92 (1984)].

used only when absolutely necessary, and that turns out to be only in the Brownian motion term in the equation of motion and in the bead-momentum flux contribution to the stress tensor.

In this chapter we use the same notation for average values that we introduced in Chapter 12. A velocity-space average of a time-independent function $B(\mathbf{r}_1, \mathbf{r}_2, \dot{\mathbf{r}}_1, \dot{\mathbf{r}}_2)$ is given by:

$$[\![B]\!] = \iint B\Xi \, d\dot{\mathbf{r}}_1 \, d\dot{\mathbf{r}}_2 \tag{13.1-4}$$

and this average is in general a function of $\mathbf{r}_1$, $\mathbf{r}_2$, and t. The phase-space average of $B(\mathbf{r}_1, \mathbf{r}_2, \dot{\mathbf{r}}_1, \dot{\mathbf{r}}_2)$ is then

$$\langle B \rangle = \frac{1}{nV} \iint [\![B]\!] \Psi \, d\mathbf{r}_1 \, d\mathbf{r}_2 \tag{13.1-5}$$

and this average is in general a function of the time t. These equations should be compared with Eqs. 12.4-2 and 12.4-3, respectively. Note that if B depends only on $\boldsymbol{Q}$, then $\langle B \rangle = \int B\psi \, d\boldsymbol{Q}$.

In the next section we write an equation of motion for each of the beads of the dumbbell. In so doing, it is assumed that the inertial term (that is, "mass × acceleration") can be neglected, because of the small mass and the sluggish motion of the beads as they move through the viscous medium. This neglect of inertia terms in the equation of motion is a standard assumption in the kinetic theories of polymers. Each bead is presumed to experience four kinds of forces:

a. *A hydrodynamic drag force* $\boldsymbol{F}_\nu^{(h)}$. This is the force of resistance experienced by a bead as it moves through the solution. A simple expression that we can use for this force is one that is reminiscent of Stokes' law; specifically, we take the drag force to be proportional to the difference between the (appropriately averaged) bead velocity and the mass-average velocity of the solution. More complicated expressions can be used that take into account hydrodynamic interaction (see §13.6) or that allow for anisotropy of the hydrodynamic drag (see §13.7). All these expressions are empiricisms that purport to account approximately for the very complex intermolecular forces between the polymer and solvent molecules.

b. *A Brownian force* $\boldsymbol{F}_\nu^{(b)}$. Because of thermal fluctuations in the liquid, the beads are jostled about in an irregular manner. The average of this rapidly fluctuating force can, however, be described by an expression that involves the configurational distribution function. The origin of this expression is far from obvious; in Chapter 18 it is derived from first principles, but in this chapter we accept it as a suitable way to describe the "time smoothed" Brownian force.

c. *An intramolecular force* $\boldsymbol{F}_\nu^{(\phi)}$. This is the force on one bead resulting from the "spring" in the dumbbell. This is given as the negative of the gradient of the spring potential energy ϕ. The various kinds of springs used in molecular models are summarized in Table 11.5-1.

d. *An external force* $\boldsymbol{F}_\nu^{(e)}$. Examples of external forces are gravitational and electrical forces. Artificial gravitational forces, such as those produced in an ultracentrifuge, are of particular interest in polymeric systems.

Explicit formulas for these forces are given in subsequent sections. Suffice it to say at this point that, roughly speaking, the hydrodynamic forces (and in some instances the external forces) tend to orient and distort the polymer molecule, the intramolecular forces tend to restore the molecule to its original shape, and Brownian forces tend to randomize the orientations of the molecules.

In this section we have described, mostly in words, the kind of modeling that is done in the kinetic theory that follows. It is evident that several assumptions are inherent in the theoretical development. At the very outset there is the choice of the molecular model used to represent the polymer molecule. Then there are the assumptions for the velocity distribution function and the expression for the hydrodynamic drag. All of these elements of the theory can be and are being challenged. Attempts to improve the modeling add considerably to the complexity of the theory and calculations, but the basic framework of the theory remains unchanged.

§13.2 THE "DIFFUSION EQUATION" FOR THE CONFIGURATIONAL DISTRIBUTION FUNCTION

As mentioned in the introduction to this chapter, the kinetic theory consists of two main parts, one of which is the development of an equation for the configurational distribution function. This second-order partial differential equation is called the "diffusion equation," since it describes how the system points "diffuse" in the multidimensional configuration space appropriate for the molecular model. It has nothing to do with the spatial movement of the centers of mass of the polymer molecules in three-dimensional space. This diffusion equation is obtained by combining the equations of motion of the beads with an equation of continuity that describes the conservation of system points in the configuration space.

a. The Equations of Motion for the Beads of the Dumbbell

We can write an equation of motion for each bead of the dumbbell indicating that the mass of the bead times its acceleration is equal to the sum of all forces acting on the bead. When we neglect the inertial terms containing the bead masses, we get a "force balance" among the four forces described qualitatively in the foregoing section:

$$\boldsymbol{F}_v^{(h)} + \boldsymbol{F}_v^{(b)} + \boldsymbol{F}_v^{(\phi)} + \boldsymbol{F}_v^{(e)} = \boldsymbol{0} \qquad (v = 1, 2) \tag{13.2-1}$$

in which

$$\boldsymbol{F}_v^{(h)} = -\boldsymbol{\zeta}\cdot[[\dot{\boldsymbol{r}}_v]] - (\boldsymbol{v}_v + \boldsymbol{v}'_v)] \tag{13.2-2}$$

$$\boldsymbol{F}_v^{(b)} = -\frac{1}{\Psi}\frac{\partial}{\partial \boldsymbol{r}_v}\cdot[[[m(\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v})]]\Psi] \tag{13.2-3}$$

$$\boldsymbol{F}_v^{(\phi)} = -\frac{\partial}{\partial \boldsymbol{r}_v}\phi \tag{13.2-4}$$

We now discuss each of the contributions to the force balance.

Equation 13.2-2 describes the hydrodynamic force acting on bead v. According to this expression the force is proportional to the difference between the bead velocity $\dot{\boldsymbol{r}}_v$ (appropriately averaged with respect to the velocity distribution) and the velocity $(\boldsymbol{v}_v + \boldsymbol{v}'_v)$ of the solution at bead v. The velocity $\boldsymbol{v}_v = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_v]$ is the imposed homogeneous flow field at bead v, and $\boldsymbol{v}'_v$ is the perturbation of the flow field at bead v resulting from the motion of the other bead; this perturbation is referred to as "hydrodynamic interaction." Throughout most of this chapter we neglect hydrodynamic interaction and $\boldsymbol{v}'_v$. We note further that,

according to Eq. 13.2-2, the hydrodynamic drag force is not necessarily collinear with the velocity difference, since the coefficient of proportionality is a symmetric second-order tensor $\boldsymbol{\zeta}$, called the "friction tensor." In most of this chapter we take this tensor to be isotropic, so that $\boldsymbol{\zeta} = \delta\zeta$, where the scalar ζ is called the "friction coefficient." The beads actually execute very tortuous paths as they move about in the solvent, but by using the velocity average of $\dot{\boldsymbol{r}}_\nu$ we obtain a kind of "smoothed out" drag force. It must be emphasized that we do not evaluate this velocity-averaged quantity $[\![\dot{\boldsymbol{r}}_\nu]\!]$ by using the Maxwell velocity distribution, since this would give the fluid velocity $\boldsymbol{v}$; it turns out that it is not necessary to evaluate this average explicitly inasmuch as this quantity is substituted later into the equation of continuity.

Equation 13.2-3 represents the force associated with Brownian motion (see §18.3b). The true Brownian motion force would be a rapidly and irregularly fluctuating function. Instead of the latter we use a statistically averaged force, the origin of which can be understood from the complete phase-space kinetic theory given in Chapter 18. It should be noted that the expression for the Brownian force has the form of the divergence of a momentum flux with respect to the solution velocity $\boldsymbol{v}$ at the center of mass of the dumbbell. In almost all kinetic theories published so far, equilibration in momentum space has been tacitly assumed; that is, Eq. 13.1-3 is used to evaluate the velocity space average in Eq. 13.2-3. When this is done the Brownian force contribution assumes the much simpler form $\boldsymbol{F}_\nu^{(b)} = -kT(\partial \ln \Psi/\partial \boldsymbol{r}_\nu)$. It is this standard expression that we use in this chapter, except in the last section.

Equation 13.2-4 gives the force $\boldsymbol{F}_\nu^{(\phi)}$ on the νth bead resulting from the intramolecular potential energy. For the simple model under consideration this is just the force acting through the spring in the dumbbell. Expressions for the intramolecular potentials of dumbbells are given in Table 11.5-1. For the dumbbell models the forces on the two beads are equal and opposite, so that it is useful to define a "connector force" $\boldsymbol{F}^{(c)}$ *by* $\boldsymbol{F}^{(c)} = \boldsymbol{F}_1^{(\phi)} = -\boldsymbol{F}_2^{(\phi)}$.

If we now assume that the friction tensor is a multiple of the unit tensor, and if the Maxwellian velocity distribution is used in the Brownian motion term, then the equation of motion becomes

$$-\zeta([\![\dot{\boldsymbol{r}}_\nu]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu]) - kT\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln\Psi + \boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)} = \boldsymbol{0} \qquad (\nu = 1, 2) \quad (13.2\text{-}5)$$

When these two equations are added together[1] and then divided by 2, we get the equation of motion for the center of mass $\boldsymbol{r}_c = \frac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2)$; when they are subtracted,[1] we get the equation of motion for the dumbbell connector vector $\boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1$:

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_c] + \frac{1}{2\zeta}\sum_\nu \boldsymbol{F}_\nu^{(e)} \qquad (13.2\text{-}6)$$

$$[\![\dot{\boldsymbol{Q}}]\!] = [\boldsymbol{\kappa}\cdot\boldsymbol{Q}] - \frac{2kT}{\zeta}\frac{\partial}{\partial \boldsymbol{Q}}\ln\psi - \frac{2}{\zeta}\boldsymbol{F}^{(c)} + \frac{1}{\zeta}[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}] \qquad (13.2\text{-}7)$$

[1] In doing these operations we need to use Eq. 13.1-2 and the chain rule of partial differentiation (see §E.1):

$$\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln\Psi = \left(\frac{\partial}{\partial \boldsymbol{r}_\nu}\boldsymbol{r}_c\right)\cdot\frac{\partial}{\partial \boldsymbol{r}_c}\ln n\psi + \left(\frac{\partial}{\partial \boldsymbol{r}_\nu}\boldsymbol{Q}\right)\cdot\frac{\partial}{\partial \boldsymbol{Q}}\ln n\psi \qquad (13.2\text{-}5a)$$

Then $(\partial/\partial \boldsymbol{r}_c)\ln n\psi = \boldsymbol{0}$ since n is assumed to be constant (i.e., no concentration gradients) and $\psi = \psi(\boldsymbol{Q}, t)$; furthermore $(\partial/\partial \boldsymbol{r}_1)\boldsymbol{Q} = -\boldsymbol{\delta}$ and $(\partial/\partial \boldsymbol{r}_2)\boldsymbol{Q} = +\boldsymbol{\delta}$.

The first of these equations shows that, in the absence of external forces, the center of mass of the dumbbell moves on the average with the solution velocity at the location of the center of mass. The second equation is used presently to obtain the diffusion equation for $\psi(\boldsymbol{Q}, t)$. For the remainder of this discussion it is assumed that the external forces $\boldsymbol{F}_\nu^{(e)}$ are independent of $\boldsymbol{r}_c$.

b. The Equation of Continuity for $\psi(\boldsymbol{Q}, t)$

The location and orientation of a single dumbbell is given by specifying x_1, y_1, z_1 and x_2, y_2, z_2 for the locations of the beads. This set of six coordinates can be represented as a single "system point" in a six-dimensional configuration space. For a solution containing a large number of dumbbells, the time rate of change of system points within a six-dimensional hypercube of volume $\Delta x_1\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2$ is

$$\frac{\partial}{\partial t} \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) \Delta x_1\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2 \tag{13.2-8}$$

The rate at which system points enter the hypercube is

$$\begin{aligned}(\llbracket \dot{x}_1 \rrbracket \Psi)|_{x_1}\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2 - (\llbracket \dot{x}_1 \rrbracket \Psi)|_{x_1 + \Delta x_1}\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2 \\ + \text{10 additional terms describing motion in the other five coordinate directions}\end{aligned} \tag{13.2-9}$$

These two expressions can now be equated and then divided by $\Delta x_1\, \Delta y_1\, \Delta z_1\, \Delta x_2\, \Delta y_2\, \Delta z_2$; when Δx_1, Δy_1, and so on, are allowed to approach zero, we then get

$$\frac{\partial \Psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{r}_1} \cdot \llbracket \dot{\boldsymbol{r}}_1 \rrbracket \Psi\right) - \left(\frac{\partial}{\partial \boldsymbol{r}_2} \cdot \llbracket \dot{\boldsymbol{r}}_2 \rrbracket \Psi\right) \tag{13.2-10}$$

which is called the *equation of continuity* for Ψ, because of its similarity with the equation of continuity in hydrodynamics. This equation can be rewritten in terms of $\boldsymbol{r}_c$ and $\boldsymbol{Q}$:

$$\frac{\partial \Psi}{\partial t} = -\underline{\left(\frac{\partial}{\partial \boldsymbol{r}_c} \cdot \llbracket \dot{\boldsymbol{r}}_c \rrbracket \Psi\right)} - \left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \llbracket \dot{\boldsymbol{Q}} \rrbracket \Psi\right) \tag{13.2-11}$$

When Eqs. 13.2-6 and 13.1-2 are used, it is found that the dashed-underlined term is zero, so that we finally obtain

$$\frac{\partial \psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \llbracket \dot{\boldsymbol{Q}} \rrbracket \psi\right) \tag{13.2-12}$$

It is this form of the equation of continuity that we need presently.

c. The "Diffusion Equation" for $\psi(\boldsymbol{Q}, t)$

Substitution of $[\![\dot{\boldsymbol{Q}}]\!]$ from Eq. 13.2.7 into Eq. 13.2-12 gives the *diffusion equation*:[2]

$$\boxed{\frac{\partial \psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \left\{[\boldsymbol{\kappa} \cdot \boldsymbol{Q}]\psi - \frac{2kT}{\zeta}\frac{\partial}{\partial \boldsymbol{Q}}\psi - \frac{2}{\zeta}\boldsymbol{F}^{(c)}\psi + \frac{1}{\zeta}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\psi\right\}\right)} \tag{13.2-13}$$

This is the second-order partial differential equation that describes the way in which the distribution of configurations changes with time when the time-dependent homogeneous velocity field is specified by $\boldsymbol{\kappa}(t)$.

Before leaving the diffusion equation for ψ, which was the principal goal of this section, we point out that two important results may be obtained from Eq. 13.2-13 without specifying the nature of the spring force. First, for the steady-state, homogeneous, potential flow of a dilute solution of dumbbells with any physically reasonable spring force law and with no external forces, the diffusion equation has the solution[3,4]

$$\begin{aligned}\psi(\boldsymbol{Q}) &= \left[\frac{1}{J_{eq}} e^{-\phi^{(c)}/kT}\right]\left[\frac{J_{eq}}{J} e^{(\zeta/4kT)(\boldsymbol{\kappa}:\boldsymbol{Q}\boldsymbol{Q})}\right] \\ &\equiv \psi_{eq}\phi_{fl}\end{aligned} \tag{13.2-14}$$

Here J_{eq} is the normalization constant for the equilibrium distribution function ψ_{eq}, and J is that for the nonequilibrium distribution function; J depends on the parameters appearing in the spring connector force $\boldsymbol{F}^{(c)} = +\partial\phi^{(c)}/\partial\boldsymbol{Q}$ as well as on the constants describing the flow field through the tensor $\boldsymbol{\kappa}$. The potential-flow distribution is the product of the equilibrium distribution function ψ_{eq} and a dimensionless factor ϕ_{fl} that contains information about the flow pattern.

Second, we can multiply Eq. 13.2-13 by any function of the connector vector, $B(\boldsymbol{Q})$, and then integrate over all the configuration space. This gives the *equation of change* for $\langle B \rangle$:

$$\begin{aligned}\frac{d}{dt}\langle B\rangle = &\left(\boldsymbol{\kappa}:\left\langle \boldsymbol{Q}\frac{\partial}{\partial \boldsymbol{Q}}B\right\rangle\right) + \frac{2kT}{\zeta}\left\langle\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\frac{\partial}{\partial \boldsymbol{Q}}B\right)\right\rangle - \frac{2}{\zeta}\left\langle\left(\boldsymbol{F}^{(c)}\cdot\frac{\partial}{\partial \boldsymbol{Q}}B\right)\right\rangle \\ &+ \frac{1}{\zeta}\left\langle\left([\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}]\cdot\frac{\partial}{\partial \boldsymbol{Q}}B\right)\right\rangle\end{aligned} \tag{13.2-15}$$

[2] Note that Eq. 13.2-13 (with no external forces) can be rearranged as

$$\frac{\partial \psi}{\partial t} + \left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\frac{\partial}{\partial \boldsymbol{Q}}\psi\right) = \frac{2kT}{\zeta}\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\frac{\partial}{\partial \boldsymbol{Q}}\psi\right) + \frac{2}{\zeta}\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\boldsymbol{F}^{(c)}\psi\right) \tag{13.2-13a}$$

This is similar in form to a diffusion equation with the "convective" terms on the left, and the "diffusive" and "source" terms on the right; in the diffusive term the *rotatory diffusivity* is given by

$$D_{rot} = \frac{2kT}{\zeta} \tag{13.2-13b}$$

with dimensions (length)^2/time. It is thus clear why Eq. 13.2-13 is called the *diffusion equation for* ψ. The D_{rot} in Eq. 13.2-13b is *not* the (translational) diffusivity for the diffusion of dumbbells through the solvent, which is $D_{tr} = kT/2\zeta$. For a discussion of translational diffusivity see Example 13.6-2 and §18.4; see also H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), pp. 271–272, 279–280.

[3] R. B. Bird, M. W. Johnson, Jr., and C. F. Curtiss, *J. Chem. Phys.*, **51**, 3023–3026 (1969).

[4] J. F. Stevenson and R. B. Bird, *Trans. Soc. Rheol.*, **15**, 135–145 (1971).

The details of the integration are given in Example 13.2-1. In obtaining this equation, use is made of the fact that ψ approaches zero rapidly enough as $\boldsymbol{Q}$ goes to infinity that surface integrals can be discarded. A similar relation holds for a tensor function $\mathbf{B}(\boldsymbol{Q})$ of any order. We shall be particularly interested in the case where $\mathbf{B}$ is the second-order tensor $\boldsymbol{QQ}$:

$$\frac{d}{dt}\langle \boldsymbol{QQ}\rangle - \{\boldsymbol{\kappa}\cdot\langle \boldsymbol{QQ}\rangle\} - \{\langle \boldsymbol{QQ}\rangle\cdot\boldsymbol{\kappa}^{\dagger}\} = \frac{4kT}{\zeta}\,\boldsymbol{\delta} - \frac{4}{\zeta}\langle \boldsymbol{QF}^{(c)}\rangle + \frac{1}{\zeta}\langle [\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}]\boldsymbol{Q} + \boldsymbol{Q}[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}]\rangle \quad (13.2\text{-}16)$$

or

$$\langle \boldsymbol{QQ}\rangle_{(1)} = \frac{4kT}{\zeta}\,\boldsymbol{\delta} - \frac{4}{\zeta}\langle \boldsymbol{QF}^{(c)}\rangle + \frac{1}{\zeta}\langle (\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\boldsymbol{Q} + \boldsymbol{Q}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\rangle \quad (13.2\text{-}17)$$

That is, we designate the left side of Eq. 13.2-16 by the abbreviation $\langle \boldsymbol{QQ}\rangle_{(1)}$ given in Appendix D, Eq. D.2-4a; this is consistent with the notation for "convected time derivatives" introduced in Chapter 9, although no use of the theory of such derivatives will be needed here. To understand the connection with the notation of Chapter 9, note that the term $\{\boldsymbol{v}\cdot\boldsymbol{\nabla}\langle \boldsymbol{QQ}\rangle\}$ is identically zero for homogeneous flows, and that $\boldsymbol{\nabla v} = \boldsymbol{\kappa}^{\dagger}$ and $(\boldsymbol{\nabla v})^{\dagger} = \boldsymbol{\kappa}$. Finally we note that, in a system at equilibrium (that is, $\boldsymbol{\kappa} = \mathbf{0}$ and $\boldsymbol{F}_v^{(e)} = \mathbf{0}$), Eq. 13.2-17 gives

$$\langle \boldsymbol{QF}^{(c)}\rangle_{\text{eq}} = kT\,\boldsymbol{\delta} \quad (13.2\text{-}18)$$

a result we need in the next section.

EXAMPLE 13.2-1 Time Rate of Change of Average Values

Derive Eq. 13.2-15 for the "equation of change for $\langle B\rangle$" in the absence of external forces.

SOLUTION First, we multiply Eq. 13.2-12 by B and integrate over the entire configuration space:

$$\int B\frac{\partial\psi}{\partial t}\,d\boldsymbol{Q} = -\int\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot[\![\dot{\boldsymbol{Q}}]\!]\psi\right)B\,d\boldsymbol{Q} \quad (13.2\text{-}19)$$

Because B is independent of t, the time derivative can be taken outside the integral on the left side. The integral on the right side can be rearranged:

$$\frac{d}{dt}\int B\psi\,d\boldsymbol{Q} = -\int\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot[\![\dot{\boldsymbol{Q}}]\!]\psi B\right)d\boldsymbol{Q} + \int\left([\![\dot{\boldsymbol{Q}}]\!]\psi\cdot\frac{\partial}{\partial \boldsymbol{Q}}B\right)d\boldsymbol{Q} \quad (13.2\text{-}20)$$

The first integral on the right side can be transformed into a surface integral by the use of the Gauss divergence theorem (see Appendix A), and the distribution function is zero on this infinitely large surface. Hence Eq. 13.2-20 becomes

$$\frac{d}{dt}\langle B\rangle = \left\langle\left([\![\dot{\boldsymbol{Q}}]\!]\cdot\frac{\partial}{\partial \boldsymbol{Q}}B\right)\right\rangle \quad (13.2\text{-}21)$$

Next we insert $[\![\dot{Q}]\!]$ from Eq. 13.2-7:

$$\frac{d}{dt}\langle B\rangle = \left\langle\left([\boldsymbol{\kappa}\cdot Q]\cdot\frac{\partial}{\partial Q}B\right)\right\rangle - \frac{2kT}{\zeta}\left\langle\left(\frac{\partial}{\partial Q}\ln\psi\cdot\frac{\partial}{\partial Q}B\right)\right\rangle - \frac{2}{\zeta}\left\langle\left(F^{(c)}\cdot\frac{\partial}{\partial Q}B\right)\right\rangle \tag{13.2-22}$$

The average value in the second term on the right side can be rewritten as

$$\begin{aligned}\int\left(\frac{\partial}{\partial Q}\ln\psi\cdot\frac{\partial}{\partial Q}B\right)\psi\,dQ &= \int\left(\frac{\partial}{\partial Q}\psi\cdot\frac{\partial}{\partial Q}B\right)dQ \\ &= \int\left(\frac{\partial}{\partial Q}\cdot\psi\frac{\partial B}{\partial Q}\right)dQ - \int\psi\left(\frac{\partial}{\partial Q}\cdot\frac{\partial B}{\partial Q}\right)dQ \\ &= \int_{\substack{\text{surface}\\ \text{at } Q=\infty}}\left(\boldsymbol{n}\cdot\psi\frac{\partial B}{\partial Q}\right)dS - \left\langle\left(\frac{\partial}{\partial Q}\cdot\frac{\partial}{\partial Q}B\right)\right\rangle\end{aligned} \tag{13.2-23}$$

Here again the Gauss divergence theorem has been used, and the surface integral is zero. When this result is inserted into Eq. 13.2-22 and the term containing $\boldsymbol{\kappa}$ rearranged slightly, Eq. 13.2-15 (with no external force terms) is finally obtained.

§13.3 EXPRESSIONS FOR THE STRESS TENSOR

The total stress tensor $\boldsymbol{\pi}$ (as defined in Chapter 1) in a polymer solution is presumed to be the sum of a contribution from the solvent, $\boldsymbol{\pi}_s$, and another, $\boldsymbol{\pi}_p$, resulting from the presence of the polymer molecules (here idealized as elastic dumbbells):

$$\begin{aligned}\boldsymbol{\pi} &= \boldsymbol{\pi}_s + \boldsymbol{\pi}_p \\ &= (p_s\boldsymbol{\delta} + \boldsymbol{\tau}_s) + (p_p\boldsymbol{\delta} + \boldsymbol{\tau}_p) \\ &= p\boldsymbol{\delta} + \boldsymbol{\tau}\end{aligned} \tag{13.3-1}$$

where $p = p_s + p_p$ and $\boldsymbol{\tau} = \boldsymbol{\tau}_s + \boldsymbol{\tau}_p = -\eta_s\dot{\boldsymbol{\gamma}} + \boldsymbol{\tau}_p$; here η_s is the solvent viscosity, $\dot{\boldsymbol{\gamma}} = \nabla\boldsymbol{v} + (\nabla\boldsymbol{v})^\dagger$ is the rate-of-strain tensor and $\boldsymbol{\delta}$ is the unit tensor. The stress tensor $\boldsymbol{\tau}$ is zero at equilibrium. For additional comments see §D.6.

In order to obtain a kinetic theory expression for $\boldsymbol{\pi}_p$, we follow the elementary physical derivation provided by Kramers,[1] which we know from more elaborate and complete kinetic theory developments[2,3] accounts for the most important effects. The dumbbells will contribute to the stress in the suspension for three principal reasons: (1) an arbitrary plane in the suspension may at any moment be straddled by the two beads of the dumbbell, and there will in general be a force of tension or compression transmitted through the connector; (2) a similar contribution arises from the effects of different external forces acting on the two beads of the dumbbell straddling the plane; and (3) the beads themselves may cross the arbitrary plane and bring with them a certain amount of momentum. The resulting connector, external force, and bead contributions to the stress

[1] H. A. Kramers, *Physica*, **11**, 1–19 (1944); *J. Chem. Phys.*, **14**, 415–424 (1946); see also R. B. Bird, H. R. Warner, Jr. and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1–90 (1971).

[2] See Chapters 17 and 18, which are an updated version of C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (1976).

[3] C. F. Curtiss and R. B. Bird, *Physica*, **118A**, 191–204 (1983); R. B. Bird and J. R. DeAguiar, *J. Non-Newtonian Fluid Mech.*, **13**, 149–160 (1983).

tensor will be labeled $\pi_p^{(c)}$, $\pi_p^{(e)}$, and $\pi_p^{(b)}$. There may be still other mechanisms by which the polymer molecule contributes to the stress tensor, but these can be discovered only by taking a more fundamental approach to the subject.[2]

a. Contribution from the Intramolecular Potential, $\pi_p^{(c)}$

Consider an arbitrary plane of area S in the solution moving with the local solution velocity $\boldsymbol{v}$; the orientation of the plane is given by a unit vector $\boldsymbol{n}$. See Fig. 13.3-1*a* for the specification of the nomenclature and sign convention. First we ask the question: how many dumbbells with connector vector $\boldsymbol{Q}$ will be straddling the plane, with bead "1" on the negative side and bead "2" on the positive side? This quantity is given by the product of

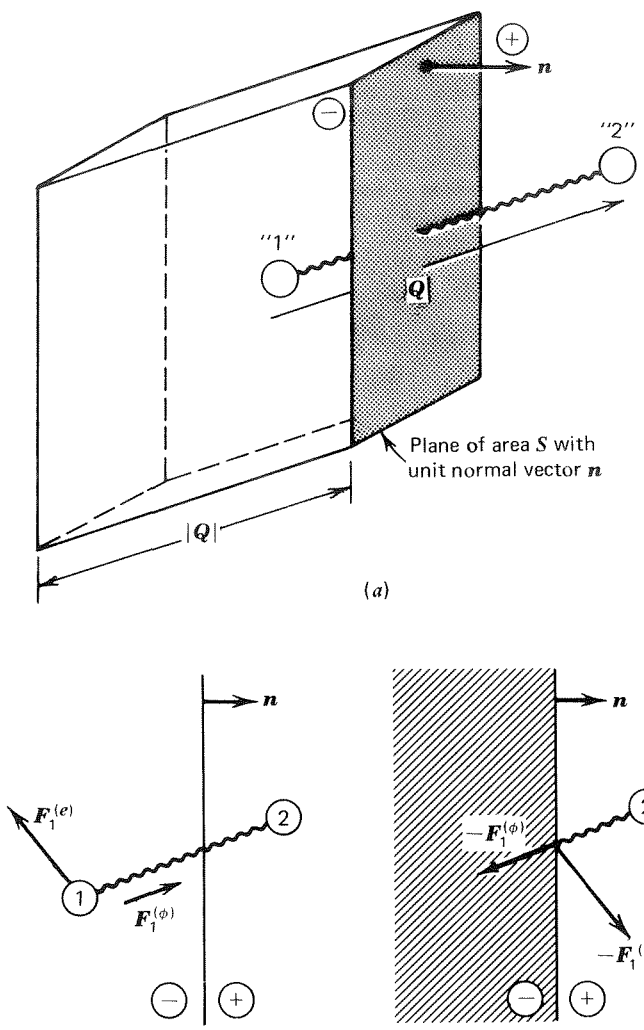


FIGURE 13.3-1. In (*a*) is shown the volume that may be occupied by bead "1" when the connector vector is $\boldsymbol{Q}$ and the dumbbell intersects the shaded plane. In (*b*) it is shown how the "negative material" can be replaced by the forces $-\boldsymbol{F}_1^{(\phi)}$ and $-\boldsymbol{F}_1^{(e)}$.

three factors: the number of dumbbells per unit volume, n; the volume in which bead "1" must be, namely $(\boldsymbol{n}\cdot\boldsymbol{Q})S$; and the probability $\psi(\boldsymbol{Q},t)d\boldsymbol{Q}$ that the dumbbell is in the configuration range $d\boldsymbol{Q}$ about $\boldsymbol{Q}$. Because of these dumbbells there will be a contribution to the force of the "negative material" on the "positive material" in the amount of $-\boldsymbol{F}_1^{(\phi)}$. This can be seen in the following way: There is a force $\boldsymbol{F}_1^{(\phi)}$ exerted on bead "1" through the connector. When all the negative material is replaced by an equivalent continuum, this force must be replaced by a force $\boldsymbol{F}_1^{(\phi)}$ exerted by the positive material on the negative continuum. Thus the force of the negative continuum on the positive material is $-\boldsymbol{F}_1^{(\phi)}$ (see Fig. 13.3-1*b*.) The contribution of dumbbells of all orientations, with bead "1" in the negative region and bead "2" in the positive region, to the stress (force per unit area) is then

$$\int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is positive}}} n(\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_1^{(\phi)})d\boldsymbol{Q} \tag{13.3-2}$$

Similarly the stress contribution of the dumbbells of all orientations with bead "2" in the negative region and bead "1" in the positive region is

$$\int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is negative}}} n(-\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_2^{(\phi)})d\boldsymbol{Q} \tag{13.3-3}$$

We next introduce the "connector tension" $\boldsymbol{F}^{(c)}$, defined to be equal to $\boldsymbol{F}_1^{(\phi)}$ and $-\boldsymbol{F}_2^{(\phi)}$. Then the two integrals can be combined to give

$$-\int_{\substack{\text{Integral}\\ \text{over all } \boldsymbol{Q}}} n(\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)\boldsymbol{F}^{(c)}\,d\boldsymbol{Q} = -\left[\boldsymbol{n}\cdot n\int \boldsymbol{Q}\boldsymbol{F}^{(c)}\psi(\boldsymbol{Q},t)d\boldsymbol{Q}\right] \tag{13.3-4}$$

But this average is to be identified with $[\boldsymbol{n}\cdot\boldsymbol{\pi}_p^{(c)}]$; hence the contribution of the dumbbell spring connectors to the stress in the solution is

$$\boldsymbol{\pi}_p^{(c)} = -n\int \boldsymbol{Q}\boldsymbol{F}^{(c)}\,\psi(\boldsymbol{Q},t)d\boldsymbol{Q} = -n\langle\boldsymbol{Q}\boldsymbol{F}^{(c)}\rangle \tag{13.3-5}$$

Since $\boldsymbol{F}^{(c)}$ is directed along the line connecting the two beads, the force $\boldsymbol{F}^{(c)}$ can be replaced by $F^{(c)}\boldsymbol{Q}/Q$, where $F^{(c)}$ is the magnitude of the force. It is thus clear that we may write either $\langle\boldsymbol{Q}\boldsymbol{F}^{(c)}\rangle$ or $\langle\boldsymbol{F}^{(c)}\boldsymbol{Q}\rangle$ in Eq. 13.3-5, and that $\boldsymbol{\pi}_p^{(c)}$ is a symmetric tensor.

b. Contribution from the External Forces, $\boldsymbol{\pi}_p^{(e)}$

Suppose that beads of type "1" may be subjected to an external force $\boldsymbol{F}_1^{(e)}$ and that beads of type "2" may be acted on by a force $\boldsymbol{F}_2^{(e)}$. These may be, for example, electrical forces resulting from an electric field acting on the charges on the beads. For the moment we let these forces be arbitrary, and we inquire as to the contribution to the stress tensor from dumbbells that straddle an arbitrary fluid plane (as depicted in Fig. 13.3-1*a*).

By arguments similar to those in §13.3 (a) we find that the contributions to the stress tensor corresponding to those in Eqs. 13.3-2 and 3 are

$$\int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is positive}}} n(\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_1^{(e)})d\boldsymbol{Q} + \int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is negative}}} n(-\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_2^{(e)})d\boldsymbol{Q} \quad (13.3\text{-}6)$$

To get this result we use the picture provided in Fig. 13.3-1*b*. We could, however, just as well have calculated the force exerted by the "positive material" on the "negative material." This would lead to the expression:

$$\int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is positive}}} n(\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_2^{(e)})d\boldsymbol{Q} + \int_{\substack{\text{Integral over}\\ \text{all } \boldsymbol{Q} \text{ for which}\\ (\boldsymbol{n}\cdot\boldsymbol{Q}) \text{ is negative}}} n(-\boldsymbol{n}\cdot\boldsymbol{Q})\psi(\boldsymbol{Q},t)(-\boldsymbol{F}_1^{(e)})d\boldsymbol{Q} \quad (13.3\text{-}7)$$

But this quantity has to be the negative of that in Eq. 13.3-6. Therefore one-half of the difference of these last two expressions can be identified as $[\boldsymbol{n}\cdot\boldsymbol{\pi}_p^{(e)}]$, so that

$$\boldsymbol{\pi}_p^{(e)} = \tfrac{1}{2}n\langle\boldsymbol{Q}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\rangle \quad (13.3\text{-}8)$$

This contribution to the stress tensor is not necessarily symmetric: if the same force acts on each bead, the external force contribution to the stress tensor is zero, although such forces lead to the external force term in the equation of motion (see Eq. 17.4-25).

c. Contribution from Bead Motion, $\boldsymbol{\pi}_p^{(b)}$

We know that the motion of the beads across an arbitrary plane will contribute to the stress tensor because of the momentum transported by the beads. In order to get the contribution associated with this mechanism, we must first ask: how many "1" beads with velocity $\dot{\boldsymbol{r}}_1$ will cross an arbitrary surface in time Δt? This will be given by the volume of the parallelepiped in Fig. 13.3-2, multiplied by the number of dumbbells per unit volume:

$$n((\dot{\boldsymbol{r}}_1 - \boldsymbol{v})\cdot\boldsymbol{S}\boldsymbol{n})\Delta t \quad (13.3\text{-}9)$$

The amount of momentum transported across the plane is then

$$n((\dot{\boldsymbol{r}}_1 - \boldsymbol{v})\cdot\boldsymbol{S}\boldsymbol{n})m(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})\Delta t \quad (13.3\text{-}10)$$

Hence the average value of the momentum flux (momentum per unit time per unit area) resulting from beads "1" of all possible velocities and dumbbells of all possible configurations will be

$$n\boldsymbol{n}\cdot\int[\![m(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})(\dot{\boldsymbol{r}}_1 - \boldsymbol{v})]\!]\psi(\boldsymbol{Q},t)d\boldsymbol{Q} \quad (13.3\text{-}11)$$

Then the average value of the momentum flux resulting from both beads is obtained by adding to the above a similar contribution for beads of type "2." This average value must

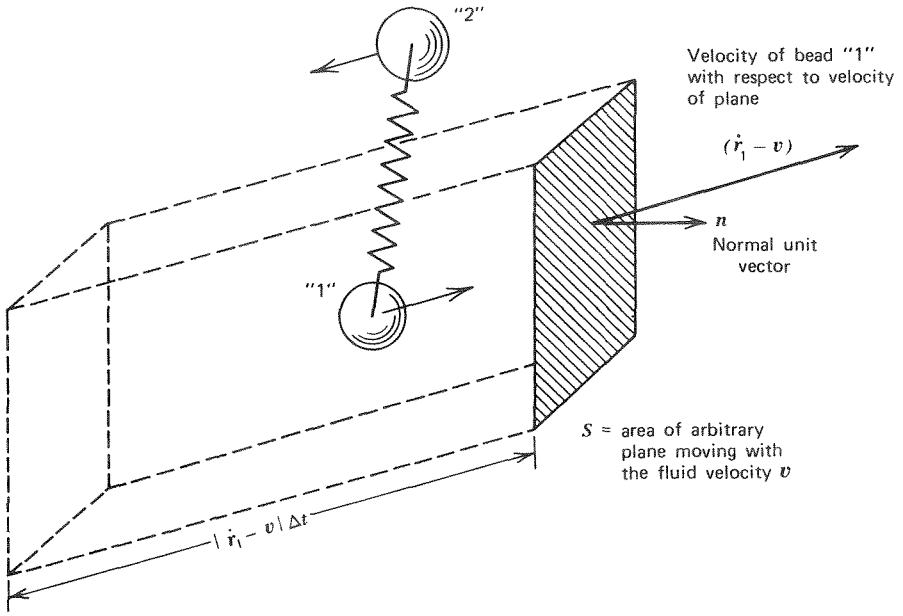


FIGURE 13.3-2. A bead of a dumbbell crossing an arbitrary surface and contributing to the stress tensor π.

then be identified with $[\boldsymbol{n} \cdot \boldsymbol{\pi}_p^{(b)}]$ and, hence, the contribution of the bead motion to the stress will be

$$\boldsymbol{\pi}_p^{(b)} = n \int \left[\!\!\left[\sum_{v=1}^{2} m(\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v}) \right]\!\!\right] \psi(\boldsymbol{Q}, t) d\boldsymbol{Q} \tag{13.3-12}$$

This is then the contribution due to the bead motion; we sometimes refer to this as the "Brownian motion contribution" (note the appearance here of the momentum flux $m(\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v})$ which also appears in Eq. 13.2-3). When the integrations implied by $[\![\ ]\!]$ are performed using the Maxwellian distribution in Eq. 13.1-3 we get finally

$$\boldsymbol{\pi}_p^{(b)} = 2nkT\boldsymbol{\delta} \quad \text{(Maxwellian)} \tag{13.3-13}$$

Since the expression in Eq. 13.3-13 is isotropic, this contribution will not normally be of rheological interest. The fact that each bead gives a contribution of $nkT\boldsymbol{\delta}$ is a direct consequence of the "equilibration in momentum space."

When the contributions from the solvent and polymer are finally combined, we obtain for the stress tensor of a dilute solution of dumbbells without the Maxwellian velocity distribution function assumption:

$$\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\langle \boldsymbol{Q}\boldsymbol{F}^{(c)} \rangle + \tfrac{1}{2}n\langle \boldsymbol{Q}[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}] \rangle + nm \sum_{v=1}^{2} \langle (\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v}) \rangle \tag{13.3-14}$$

Solvent contribution	Contribution of intramolecular forces	Contribution of external forces	Contribution of the bead motion

This expression can be slightly modified by writing the intramolecular force contribution in terms of the forces on the individual beads ($\boldsymbol{F}_\nu^{(\phi)} = -\partial\phi/\partial\boldsymbol{r}_\nu$) and the location of the beads relative to the dumbbell center of mass ($\boldsymbol{R}_\nu = \boldsymbol{r}_\nu - \boldsymbol{r}_c$):

$$\boldsymbol{\pi} = \boldsymbol{\pi}_s + n\sum_{\nu=1}^{2}\langle \boldsymbol{R}_\nu(\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)})\rangle + nm\sum_{\nu=1}^{2}\langle(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})\rangle \tag{13.3-15}$$

Next one can use Eq. 13.2-1 to replace $\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)}$ by $-\boldsymbol{F}_\nu^{(h)} - \boldsymbol{F}_\nu^{(b)}$. When the Brownian force given by Eq. 13.2-3 is inserted into $\sum_\nu\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(b)}\rangle$ an integration by parts and other manipulations can be performed to get[3]

$$\boxed{\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\sum_\nu\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)}\rangle + 2nm\langle(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})\rangle} \tag{13.3-16}$$

In going from Eq. 13.3-15 to Eq. 13.3-16 the only assumption is that Ξ is an even function of $\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}$ (see Example 13.3-1). Equations 13.3-14 to 13.3-16 are valid whether or not hydrodynamic interaction is included and whether or not the friction tensor is isotropic.

In most kinetic theory publications, it is assumed that the velocity distribution is Maxwellian; in this chapter we adopt the same assumption except in the final section. Then the last term in Eqs. 13.3-14 and 13.3-15 becomes $2nkT\boldsymbol{\delta}$, and the last term of Eq. 13.3-16 becomes $nkT\boldsymbol{\delta}$.

Finally we may express the stress tensor in terms of $\boldsymbol{\tau}$ (see Eq. 13.3-1) by subtracting from Eq. 13.3-14 the corresponding expression at equilibrium, [i.e., with $\boldsymbol{\kappa} = \boldsymbol{0}$ and $\boldsymbol{F}_\nu^{(e)} = \boldsymbol{0}$], namely, $p\boldsymbol{\delta} = p_s\boldsymbol{\delta} - n\langle\boldsymbol{QF}^{(c)}\rangle_{eq} + 2nkT\boldsymbol{\delta} = p_s\boldsymbol{\delta} + nkT\boldsymbol{\delta}$ (where Eq. 13.2-18 has been used). When, in addition, we insert the explicit expression for the Newtonian solvent contribution to the stress tensor, we get finally Eq. A of Table 13.3-1, which we henceforth refer to as the *Kramers form for the stress tensor.*[1] Equations B and C correspond to Eqs. 13.3-15 and 13.3-16. The latter we call the *Kramers–Kirkwood form of the stress tensor*, since this also appears in Kramers' landmark publication,[1] but was exploited by Kirkwood in his

TABLE 13.3-1

Expressions for the Stress Tensor for Elastic Dumbbells[a] (Maxwellian Velocity Distribution Assumed)

Kramers:[b]	$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\langle\boldsymbol{QF}^{(c)}\rangle + \frac{1}{2}n\langle\boldsymbol{Q}[\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}]\rangle + nkT\boldsymbol{\delta}$	(A)
Modified-Kramers:	$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + n\sum_\nu\langle \boldsymbol{R}_\nu[\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)}]\rangle + nkT\boldsymbol{\delta}$	(B)
Kramers–Kirkwood:[c]	$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\sum_\nu\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)}\rangle$	(C)
Giesekus:[d]	$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + \frac{1}{4}n\zeta\langle\boldsymbol{QQ}\rangle_{(1)} + \frac{1}{4}n\langle\boldsymbol{Q}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)}) - (\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\boldsymbol{Q}\rangle$	(D)

[a] R. B. Bird and C. F. Curtiss, *J. Polym. Sci.: Polym. Symp.*, **73**, 187–199 (1985).
[b] H. A. Kramers, *Physica*, **11**, 1–19 (1944).
[c] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).
[d] H. Giesekus, *Rheol. Acta*, **2**, 50–62 (1962); this expression is less general than Eqs. A–C, in that the friction tensor must be isotropic and hydrodynamic interaction is neglected. For a discussion of hydrodynamic interaction, see §13.6 and Problem 13B.8.

impressive series of papers on kinetic theory.[4] Equation D, the *Giesekus form of the stress tensor*,[5] in Table 13.3-1 is obtained by eliminating $\langle \boldsymbol{Q}\boldsymbol{F}^{(c)} \rangle$ from Eq. A by using Eq. 13.2-17. Each of the entries in this table has been used in the kinetic theory literature. The table should be helpful in keeping track of which forces are being used [$\boldsymbol{F}^{(c)}$, $\boldsymbol{F}_\nu^{(\phi)}$, $\boldsymbol{F}_\nu^{(e)}$, or $\boldsymbol{F}_\nu^{(h)}$], which sign precedes the force term, and whether or not $nkT\boldsymbol{\delta}$ appears in the expression.

In most of the rest of this chapter the external forces are left out of consideration. They are included in the discussion of the equations of motion for the beads in §13.6, where hydrodynamic interaction is incorporated into the theory. The external force terms are needed there for the discussion of translational diffusivity in Example 13.6-2. Furthermore, external forces are included in the phase-space kinetic theory in Chapters 17 and 18.

EXAMPLE 13.3-1 Alternative Form for the Stress Tensor

Show how to go from Eq. 13.3-15 to Eq. 13.3-16.

SOLUTION When $\boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)}$ is replaced by $-\boldsymbol{F}_\nu^{(h)} - \boldsymbol{F}_\nu^{(b)}$ in Eq. 13.3-15 we are confronted with:

$$-n\sum_\nu \langle \boldsymbol{R}_\nu \boldsymbol{F}_\nu^{(b)} \rangle = nm \sum_\nu \int \boldsymbol{R}_\nu \frac{\partial}{\partial \boldsymbol{r}_\nu} \cdot (\llbracket (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rrbracket \psi) d\boldsymbol{Q} \tag{13.3-17}$$

Then use of the chain rule enables us to replace $\partial/\partial \boldsymbol{r}_\nu$ by derivatives with respect to $\boldsymbol{r}_c$ and $\boldsymbol{Q}$. Since $\llbracket (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rrbracket \psi$ does not depend on $\boldsymbol{r}_c$, the right side of Eq. 13.3-17 becomes:

$$nm \sum_\nu \int \boldsymbol{R}_\nu (-1)^\nu \frac{\partial}{\partial \boldsymbol{Q}} \cdot (\llbracket (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rrbracket \psi) d\boldsymbol{Q} = -\tfrac{1}{2} nm \int \sum_\nu \llbracket (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rrbracket \psi \, d\boldsymbol{Q} \tag{13.3-18}$$

where integration by parts has been performed. We now consider the expression

$$\begin{aligned} \sum_\nu \llbracket (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rrbracket &= \sum_\nu \llbracket (\dot{\boldsymbol{R}}_\nu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v}))(\dot{\boldsymbol{R}}_\nu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v})) \rrbracket \\ &= \sum_\nu \llbracket \dot{\boldsymbol{R}}_\nu \dot{\boldsymbol{R}}_\nu \rrbracket + 2 \llbracket (\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v}) \rrbracket \end{aligned} \tag{13.3-19}$$

But if it is assumed that the velocity distribution is even in $\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}$, we may equally well write the expression in Eq. 13.3-19 as

$$\begin{aligned} \sum_\nu \sum_\mu \llbracket (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\mu - \boldsymbol{v}) \rrbracket &= \sum_\nu \sum_\mu \llbracket (\dot{\boldsymbol{R}}_\nu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v}))(\dot{\boldsymbol{R}}_\mu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v})) \rrbracket \\ &= \left\llbracket \left(\sum_\nu (\dot{\boldsymbol{R}}_\nu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v})) \right) \left(\sum_\mu (\dot{\boldsymbol{R}}_\mu + (\dot{\boldsymbol{r}}_c - \boldsymbol{v})) \right) \right\rrbracket \\ &= 4 \llbracket (\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v}) \rrbracket \end{aligned} \tag{13.3-20}$$

Twice Eq. 13.3-19 minus Eq. 13.3-20 then yields

$$\sum_\nu \llbracket (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rrbracket = 2 \sum_\nu \llbracket \dot{\boldsymbol{R}}_\nu \dot{\boldsymbol{R}}_\nu \rrbracket \tag{13.3-21}$$

[4] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).

[5] H. Giesekus, *Rheol. Acta*, **5**, 29–35 (1966); see also A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539–553 (1971).

so that

$$-n\sum_{\nu}\langle \boldsymbol{R}_{\nu}\boldsymbol{F}_{\nu}^{(b)}\rangle = -nm\sum_{\nu}\langle \dot{\boldsymbol{R}}_{\nu}\dot{\boldsymbol{R}}_{\nu}\rangle \tag{13.3-22}$$

When this is used in Eq. 13.3-15, after some additional rearrangement, Eq. 13.3-16 results.

§13.4 HOOKEAN DUMBBELLS

Up to this point the theory has been developed for dumbbells with any kind of elastic connector, linear or nonlinear. In this section we specialize to the Hookean spring connector for which

$$\boldsymbol{F}^{(c)} = H\boldsymbol{Q} \tag{13.4-1}$$

where H is the spring constant. For this model the polymer contribution to the stress tensor $\boldsymbol{\tau}_p$ is then given by Eqs. A and D of Table 13.3-1 as

$$\text{Kramers:} \qquad \boldsymbol{\tau}_p = -nH\langle \boldsymbol{QQ}\rangle + nkT\boldsymbol{\delta} \tag{13.4-2}$$

$$\text{Giesekus:} \qquad \boldsymbol{\tau}_p = +\frac{n\zeta}{4}\langle \boldsymbol{QQ}\rangle_{(1)} \tag{13.4-3}$$

In order to use either of these expressions, one would have to know the distribution function $\psi(\boldsymbol{Q}, t)$ for evaluating the average values. However, for the Hookean dumbbells one can simply eliminate $\langle \boldsymbol{QQ}\rangle$ between these two equations and obtain a rheological equation of state directly.[1,2] This is done by subtracting $nkT\boldsymbol{\delta}$ from both sides of Eq. 13.4-2, then multiplying by $\lambda_H = \zeta/4H$ (which is the time constant for the Hookean dumbbells), and then performing the operation of convected differentiation given in Eq. D.2-4a (indicated by the subscript $_{(1)}$); in doing this we note that $\boldsymbol{\delta}_{(1)} = -\boldsymbol{\gamma}_{(1)}$. Then the resulting equation is added to Eq. 13.4-3 to obtain:

$$\boldsymbol{\tau}_p + \lambda_H\boldsymbol{\tau}_{p(1)} = -nkT\lambda_H\boldsymbol{\gamma}_{(1)} \tag{13.4-4}$$

When written in terms of $\boldsymbol{\tau}$ this equation becomes

$$\boxed{\boldsymbol{\tau} + \lambda_1\boldsymbol{\tau}_{(1)} = -\eta_0(\boldsymbol{\gamma}_{(1)} + \lambda_2\boldsymbol{\gamma}_{(2)})} \tag{13.4-5}$$

in which $\boldsymbol{\gamma}_{(1)}$ and $\boldsymbol{\gamma}_{(2)}$ are kinematic tensors defined in §D.3 and

$$\eta_0 = \eta_s + nkT\lambda_H \tag{13.4-6}$$

$$\lambda_1 = \lambda_H \tag{13.4-7}$$

$$\lambda_2 = \left(\frac{\eta_s}{\eta_s + nkT\lambda_H}\right)\lambda_H \tag{13.4-8}$$

[1] H. Giesekus, *Rheol. Acta*, **1**, 2-20 (1958); **5**, 29-35 (1966).
[2] A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539-553 (1971); P. H. van Wiechen and H. C. Booij, *J. Eng. Math.*, **5**, 89-98 (1971).

Equation 13.4-5 is then the *constitutive equation* for a dilute solution of polymer molecules modeled as Hookean dumbbells; it is exactly of the form of a "convected Jeffreys model" (called the "Oldroyd-B model") discussed in §7.2. Therefore many results from continuum mechanics can be taken over directly. For example, it was shown in Example 9.4-1 how differential constitutive equations can be transformed into integral constitutive equations. The Hookean-dumbbell-solution constitutive equation may be put into the form[2]

$$\boxed{\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + \int_{-\infty}^{t} \left\{ \frac{nkT}{\lambda_H} e^{-(t-t')/\lambda_H} \right\} \boldsymbol{\gamma}_{[0]}(t, t')dt'} \tag{13.4-9}$$

in which $\boldsymbol{\gamma}_{[0]}$ is the finite strain tensor defined in Eq. D.3-4; the quantity in braces plus $2\eta_s\ (\partial/\partial t')\ \delta\ (t\text{-}t')$ is called the "memory function" (see Eq. D.4-2).

Since the complete constitutive equation is known for this molecular model, the derivation of expressions for the material functions is straightforward (see Examples 13.4-1 and 2). In addition the average value of the square of the end-to-end distance is easily obtained by taking the trace of Eq. 13.4-2

$$\langle Q^2 \rangle = \frac{3kT}{H} - \frac{\text{tr}\ \boldsymbol{\tau}_p}{nH} \tag{13.4-10}$$

Then, using Eq. 13.4-9 we can get the ratio of $\langle Q^2 \rangle$ to its value at equilibrium:

$$\begin{aligned} \frac{\langle Q^2 \rangle}{\langle Q^2 \rangle_{\text{eq}}} &= 1 - \frac{\text{tr}\ \boldsymbol{\tau}_p}{3nkT} \\ &= 1 - \frac{1}{3\lambda_H} \int_{-\infty}^{t} e^{-(t-t')/\lambda_H}\ \text{tr}\ \boldsymbol{\gamma}_{[0]}(t, t')dt' \end{aligned} \tag{13.4-11}$$

This result gives us a measure of the molecular stretching in any flow situation, either in terms of the stresses or in terms of the finite strain tensor $\boldsymbol{\gamma}_{[0]}(t, t')$. The ratio $\langle Q^2 \rangle / \langle Q^2 \rangle_{\text{eq}}$ can be measured by means of light scattering.[3]

All the results thus far were obtained without solving the diffusion equation to get the configurational distribution function $\psi(\boldsymbol{Q}, t)$. If one wishes to have the distribution of dumbbell orientations, the distribution of the end-to-end distance, or other more detailed information, then it is necessary to have the configurational distribution function. For Hookean dumbbell solutions this has been found to be:[2]

$$\boxed{\psi(\boldsymbol{Q}, t) = \frac{(H/2\pi kT)^{3/2}}{\sqrt{\det \boldsymbol{\alpha}}} e^{-(H/2kT)(\boldsymbol{\alpha}^{-1} : \boldsymbol{QQ})}} \tag{13.4-12}$$

$$\boxed{\boldsymbol{\alpha}(t) = \boldsymbol{\delta} - \frac{1}{\lambda_H} \int_{-\infty}^{t} e^{-(t-t')/\lambda_H} \boldsymbol{\gamma}_{[0]}(t, t')dt'} \tag{13.4-13}$$

[3] F. R. Cottrell, E. W. Merrill, and K. A. Smith, *J. Polymer Sci.*, Part A-2, 7, 1415–1434 (1969). See also *Light Scattering from Polymer Solutions*, M. B. Huglin ed., Academic Press, New York (1972). Equation 13.4-11 has been used for classification of flow fields as "strong" or "weak" [R. I. Tanner, *Engineering Rheology*, Oxford University Press, London (1985), pp. 185–193].

The combination $\mathbf{B} = \boldsymbol{\delta} - \boldsymbol{\gamma}_{[0]}$, a weighted average of which is $\boldsymbol{\alpha}$, is shown in Chapter 9 to be positive definite. For any given flow field (described by $\kappa(t)$ in Eq. 13.2-13), one can obtain the finite strain tensor $\boldsymbol{\gamma}_{[0]}(t, t')$ and hence the distribution function $\psi(\boldsymbol{Q}, t)$. For a system at rest, the finite strain tensor is zero and the equilibrium distribution function in Table 11.5-1 is obtained. The Hookean dumbbell is the only dumbbell model for which $\psi(\boldsymbol{Q}, t)$ has been found for arbitrary time-dependent flow patterns.

EXAMPLE 13.4-1 Shear Flow Material Functions and Molecular Stretching

Use the results of this section to find **(a)** the material functions and **(b)** the stretching of the dumbbells as a function of the shear rate in steady shear flow; also find **(c)** the components of the complex viscosity.

SOLUTION **(a)** For the steady-state shear flow $v_x = \dot{\gamma}y$, $v_y = 0$, $v_z = 0$, Eq. 13.4-4 can be shown to give (see Appendix C):

$$\begin{pmatrix} \tau_{p,xx} & \tau_{p,xy} & \tau_{p,xz} \\ \tau_{p,xy} & \tau_{p,yy} & \tau_{p,yz} \\ \tau_{p,xz} & \tau_{p,yz} & \tau_{p,zz} \end{pmatrix} + \lambda_H \begin{pmatrix} -2\tau_{p,xy} & -\tau_{p,yy} & -\tau_{p,yz} \\ -\tau_{p,yy} & 0 & 0 \\ -\tau_{p,yz} & 0 & 0 \end{pmatrix} \dot{\gamma} = -nkT\lambda_H \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \dot{\gamma} \tag{13.4-14}$$

This matrix equation is equivalent to a set of six linear algebraic equations. The solution to these equations is

$$\tau_{p,xx} = -2nkT\lambda_H^2\dot{\gamma}^2 \tag{13.4-15}$$

$$\tau_{p,xy} = \tau_{p,yx} = -nkT\lambda_H\dot{\gamma} \tag{13.4-16}$$

all the other $\tau_{p,ij}$ being zero.[4] Then using $\tau = -\eta_s\dot{\gamma} + \tau_p$ and the definitions of the material functions given in Eqs. D.5-1 to 3, we find

$$\eta = \eta_s + nkT\lambda_H \tag{13.4-17}$$

$$\Psi_1 = 2nkT\lambda_H^2 \tag{13.4-18}$$

$$\Psi_2 = 0 \tag{13.4-19}$$

It is found thus that all the material functions are constant. But we know (see Fig. 3.3-4) that even for extremely dilute polymer solutions, the viscosity decreases with increasing shear rate. Therefore we have to conclude that the model is inadequate for describing the behavior of dilute polymer solutions as the shear rate is increased.

(b) From the stress-tensor components in part **(a)** we find that $\text{tr}\,\boldsymbol{\tau}_p = \tau_{p,xx} + \tau_{p,yy} + \tau_{p,zz} = -2nkT\lambda_H^2\dot{\gamma}^2$. Substitution into the first line of Eq. 13.4-11 then gives:

$$\frac{\langle Q^2 \rangle}{\langle Q^2 \rangle_{\text{eq}}} = 1 + \tfrac{2}{3}(\lambda_H\dot{\gamma})^2 \tag{13.4-20}$$

This shows that the Hookean dumbbells continue to stretch as the shear rate is increased. The failure of the model to give a non-Newtonian (shear-rate dependent) viscosity may be linked to this infinite extensibility.

[4] The stresses $\tau_{p,xz}$, $\tau_{p,yz}$, $\tau_{p,zx}$, and $\tau_{p,zy}$ turn out to be zero according to the kinetic theory; this is consistent with the continuum mechanics arguments given in §3.2.

(c) For small-amplitude oscillatory motion, Eq. 13.4-4 simplifies to the Maxwell model for linear viscoelasticity, Eq. 5.2-2, so that

$$\eta' = \eta_s + \frac{nkT\lambda_H}{1 + (\lambda_H\omega)^2} \tag{13.4-21}$$

$$\eta'' = \frac{nkT\lambda_H^2\omega}{1 + (\lambda_H\omega)^2} \tag{13.4-22}$$

It is clear that the suspension of Hookean dumbbells does not predict the observed similarities in the shapes of $\eta(\dot{\gamma})$ and $\eta'(\omega)$ (cf. §3.6) and in the shapes of $\Psi_1/2$ and η''/ω. The curves predicted from Eqs. 13.4-21 and 22 are, however, qualitatively reasonable.

EXAMPLE 13.4-2 Elongational Flow Material Functions and Molecular Stretching

For an arbitrary simple elongational flow, specified by $v_z = \dot{\varepsilon}(t)z$, $v_x = -\frac{1}{2}\dot{\varepsilon}(t)x$, and $v_y = -\frac{1}{2}\dot{\varepsilon}(t)y$, find the expressions for the components of the polymer contribution to the stress tensor. Then find the expression for $\langle Q^2\rangle/\langle Q^2\rangle_{eq}$ for **(a)** a sudden elongational displacement, **(b)** the sudden inception of steady elongational flow, and **(c)** steady-state elongational flow.

SOLUTION For time-dependent simple elongational flow the rate-of-strain tensor is

$$\dot{\gamma} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}\dot{\varepsilon}(t) \tag{13.4-23}$$

Substitution of this into Eq. 13.4-4 gives for the polymer contribution to the stress tensor

$$\left(1 + \lambda_H\frac{\partial}{\partial t}\right)\begin{pmatrix} \tau_{p,xx} & \tau_{p,xy} & \tau_{p,xz} \\ \tau_{p,xy} & \tau_{p,yy} & \tau_{p,yz} \\ \tau_{p,xz} & \tau_{p,yz} & \tau_{p,zz} \end{pmatrix} - \lambda_H\dot{\varepsilon}\begin{pmatrix} -\tau_{p,xx} & -\tau_{p,xy} & \frac{1}{2}\tau_{p,xz} \\ -\tau_{p,xy} & -\tau_{p,yy} & \frac{1}{2}\tau_{p,yz} \\ \frac{1}{2}\tau_{p,xz} & \frac{1}{2}\tau_{p,yz} & 2\tau_{p,zz} \end{pmatrix} = -nkT\lambda_H\dot{\varepsilon}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{13.4-24}$$

From this matrix equation, three differential equations for $\tau_{p,xx}$, $\tau_{p,yy}$, and $\tau_{p,zz}$ are obtained.[5] The solutions of these equations are

$$\tau_{p,xx} = \tau_{p,yy} = nkT\int_{-\infty}^{t}\dot{\varepsilon}(t')\exp\left\{-\frac{1}{\lambda_H}\int_{t'}^{t}[1 + \lambda_H\dot{\varepsilon}(t'')]dt''\right\}dt' \tag{13.4-25}$$

$$\tau_{p,zz} = -2nkT\int_{-\infty}^{t}\dot{\varepsilon}(t')\exp\left\{-\frac{1}{\lambda_H}\int_{t'}^{t}[1 - 2\lambda_H\dot{\varepsilon}(t'')]dt''\right\}dt' \tag{13.4-26}$$

We now use these results to get information about the stretching of the dumbbells in various flows.

(a) Sudden Elongational Displacement

Let the fluid sample be subjected to a sudden elongational displacement at $t = 0$; that is, we take

$$\dot{\varepsilon}(t) = \varepsilon_0\delta(t) \tag{13.4-27}$$

[5] We obtain all $\tau_{p,ij}$ equal to zero for $i \neq j$; this is consistent with the continuum mechanics arguments given in §3.2.

where $\delta(t)$ is the Dirac delta function (see §E.4). Then for $t > 0$

$$\tau_{p,xx} = \tau_{p,yy} = nkT\varepsilon_0 \exp\left[-\frac{t}{\lambda_H} - \varepsilon_0\right] \tag{13.4-28}$$

$$\tau_{p,zz} = -2nkT\varepsilon_0 \exp\left[-\frac{t}{\lambda_H} + 2\varepsilon_0\right] \tag{13.4-29}$$

Hence

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{\text{eq}}} = 1 + \tfrac{2}{3}\varepsilon_0(e^{2\varepsilon_0} - e^{-\varepsilon_0})e^{-t/\lambda_H} \tag{13.4-30}$$

Thus, the molecules reach maximum extension at the instant of sudden strain and then gradually go back to their equilibrium lengths. There is no limit to the extent to which the dumbbells can be stretched.

(b) Sudden Inception of Steady Elongational Flow

Next consider the inception of a steady simple elongational flow at $t = 0$.

$$\dot{\varepsilon}(t) = \dot{\varepsilon}_0 H(t) \tag{13.4-31}$$

where $H(t)$ is the Heaviside unit step function.[6] This gives for $-1/\lambda_H < \dot{\varepsilon}_0 < 1/2\lambda_H$

$$\tau_{p,xx} = \tau_{p,yy} = \frac{nkT\lambda_H\dot{\varepsilon}_0}{1 + \lambda_H\dot{\varepsilon}_0}[1 - e^{-(1+\lambda_H\dot{\varepsilon}_0)t/\lambda_H}] \tag{13.4-32}$$

$$\tau_{p,zz} = -\frac{2nkT\lambda_H\dot{\varepsilon}_0}{1 - 2\lambda_H\dot{\varepsilon}_0}[1 - e^{-(1-2\lambda_H\dot{\varepsilon}_0)t/\lambda_H}] \tag{13.4-33}$$

The elastic Hookean dumbbell models then stretch by an amount

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{\text{eq}}} = 1 + \frac{2}{3}\left\{\frac{\lambda_H\dot{\varepsilon}_0}{1 - 2\lambda_H\dot{\varepsilon}_0}[1 - e^{-(1-2\lambda_H\dot{\varepsilon}_0)t/\lambda_H}] - \frac{\lambda_H\dot{\varepsilon}_0}{1 + \lambda_H\dot{\varepsilon}_0}[1 - e^{-(1+\lambda_H\dot{\varepsilon}_0)t/\lambda_H}]\right\} \tag{13.4-34}$$

Note that if $\dot{\varepsilon}_0 > 1/2\lambda_H$ or $\dot{\varepsilon}_0 < -1/\lambda_H$ steady state will not be attained and the molecules will continue stretching without limit.

(c) Steady Simple Elongational Flow

From Eq. 13.4-34 the stretch ratio for steady state is easily found to be

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{\text{eq}}} = \frac{1 - \lambda_H\dot{\varepsilon}_0}{(1 + \lambda_H\dot{\varepsilon}_0)(1 - 2\lambda_H\dot{\varepsilon}_0)} \tag{13.4-35}$$

In addition from Eqs. 13.4-32 and 33 and the definition of the elongational viscosity in Eq. D.5-14 we find

$$\bar{\eta} = 3\eta_s + \frac{3nkT\lambda_H}{(1 + \lambda_H\dot{\varepsilon}_0)(1 - 2\lambda_H\dot{\varepsilon}_0)} \tag{13.4-36}$$

Equation 13.4-36 predicts that the elongational viscosity goes to infinity for a steady-state elongational rate of $1/2\lambda_H$ or $-1/\lambda_H$. However, we see from Eq. 13.4-35 that the molecules are also being stretched to infinite length at the same elongational rate. Inasmuch as real macromolecules have finite extensibility, neither one of these results can be taken seriously for high elongational rates. Once again we are confronted with the serious defect of the Hookean dumbbell model: it puts no limit on the

[6] $H(t) = 0$ for $t < 0$, and $H(t) = 1$ for $t > 0$.

extent to which the molecules can be elongated. In the next section, therefore, we turn our attention to the finitely extensible nonlinear elastic dumbbells (FENE dumbbells) in order to get some improvement in the prediction of material functions.

§13.5 NON-HOOKEAN DUMBBELLS[1,2,3,4]

In the previous section we saw that the Hookean dumbbell suspension gives steady-state shear flow material functions that are independent of the shear rate, and also a steady-state elongational viscosity that goes to infinity at a finite elongation rate; evidence was presented that this unlikely behavior results because the Hookean dumbbell model permits infinite extension. However we know from the elementary statistical mechanical considerations in Chapter 11 that for small extensions the Hookean spring seems appropriate. It therefore seems reasonable, as a second attempt to model a flexible macromolecule, to try a force law of the following form:

$$F^{(c)} = \frac{HQ}{1 - (Q/Q_0)^2} \qquad Q \leq Q_0 \tag{13.5-1}$$

A spring with this force law will be linear (Hookean) for small extensions, but will get stiffer as the spring is extended; furthermore the spring cannot be extended beyond a separation Q_0. This *f*initely *e*xtensible *n*onlinear *e*lastic (FENE) connector force law was first used for kinetic theory calculations by Warner,[2] and later by Armstrong.[3] Equation 13.5-1 is simpler than the inverse Langevin function (Eq. 11.3-23) that had been used earlier by Stevenson[4] and by Peterlin.[1]

For the FENE dumbbells we can define two time constants, one (λ_H) that is the same as that which we used in §13.4 for Hookean dumbbells, and another (λ_Q) that is constructed like the time constant used for rigid dumbbells (in Chapter 14):

$$\lambda_H = \frac{\zeta}{4H} \tag{13.5-2}$$

$$\lambda_Q = \frac{\zeta Q_0^2}{12kT} \tag{13.5-3}$$

where ζ is the friction coefficient defined in §13.2. In addition it will be useful to have a symbol for the dimensionless ratio:

$$b = \frac{3\lambda_Q}{\lambda_H} = \frac{HQ_0^2}{kT} \tag{13.5-4}$$[5]

[1] A. Peterlin, *Makr. Chem.*, **44–46**, 338–346 (1961); *Kolloid-Zeitschrift*, **182**, 110–115 (1962).

[2] H. R. Warner, Jr., Ph.D. Thesis, University of Wisconsin, Madison (1971); *Ind. Eng. Chem. Fundamentals*, **11**, 379–387 (1972). In the latter the factors of $(b + 7)$ in the denominators in the second and third lines of Eq. 40 on p. 385 should be removed; also, in Figure 7, the curves should approach zero at high ω. We thank Dr. Warner for communicating these errors to us.

[3] R. C. Armstrong, *J. Chem. Phys.*, **60**, 724–728, 729–733 (1974).

[4] J. F. Stevenson, *Trans. Soc. Rheol.*, **15**, 135–145 (1971).

[5] From Eq. 11.3-20 it may be seen that for a chain of $N - 1$ freely jointed rods of length a, $H = 3kT/(N - 1)a^2$. If we take $Q_0 \doteq (N - 1)a$, then $b \doteq 3(N - 1)$. Since one link is approximately 10 to 20 monomer units, we can expect that b will be roughly in the range 50 to 1000. Comparison of the material functions with experimental data gives b values that are roughly in this range [R. L. Christiansen and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **3**, 161–177 (1977/1978)].

Here all the kinetic theory results will be expressed in terms of one time constant (we usually use λ_H) and the dimensionless constant b. We also note that if b is allowed to approach infinity, then the formulas for the Hookean dumbbell are recovered.

For a nonlinear force law, such as that in Eq. 13.5-1, we cannot go directly to a constitutive equation as we did for the Hookean dumbbell in §13.4. Instead we must first solve the partial differential equation for the distribution function. We do this here only for steady-state flows so that the left side of Eq. 13.2-13 is zero. We already know that at equilibrium, the normalized distribution function, ψ_{eq}, is given by Eq. L of Table 11.5-1. In order to get the distribution function for slow flow conditions we then expand about the known equilibrium function thus:

$$\psi = \psi_{eq}\phi_{f1} = \psi_{eq}(1 + \phi_1 + \phi_2 + \cdots) \tag{13.5-5}$$

Here ϕ_k is of kth order in the velocity gradients.

The configurational distribution function for steady-state, homogeneous, potential flow, given in Eq. 13.2-14, can be put in the form of Eq. 13.5-5 by expanding in powers of the velocity gradients, thus:

$$\psi = \psi_{eq}\left\{1 + \left(\frac{\zeta}{8kT}\right)(\dot{\gamma} : \boldsymbol{QQ}) + \left(\frac{\zeta}{8kT}\right)^2\left[\frac{1}{2}(\dot{\gamma} : \boldsymbol{QQ})^2 - \frac{1}{15}\langle Q^4\rangle_{eq}(\dot{\gamma} : \dot{\gamma})\right] + \cdots\right\} \tag{13.5-6}$$

in which $\langle Q^4\rangle_{eq} = \int Q^4\psi_{eq}\, d\boldsymbol{Q}$ and, for potential flow, $\dot{\gamma}$ equals 2κ. (See Problem 13B.4 for further details.) Therefore in solving Eq. 13.2-13 in the form of Eq. 13.5-5, the ϕ_k must include the corresponding terms in Eq. 13.5-6 as well as some additional terms containing $\boldsymbol{\omega}$.

When the assumed form of ψ in Eq. 13.5-5 is substituted into Eq. 13.2-13, we then get a series of differential equations for the ϕ_k (see Problem 13B.5):

$$\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\frac{\partial}{\partial \boldsymbol{Q}}\phi_1\right) - \left(\frac{\boldsymbol{F}^{(c)}}{kT}\cdot\frac{\partial}{\partial \boldsymbol{Q}}\phi_1\right) = -\frac{\zeta}{2kT}\left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\frac{\boldsymbol{F}^{(c)}}{kT}\right) \tag{13.5-7}$$

$$\left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\frac{\partial}{\partial \boldsymbol{Q}}\phi_2\right) - \left(\frac{\boldsymbol{F}^{(c)}}{kT}\cdot\frac{\partial}{\partial \boldsymbol{Q}}\phi_2\right) = -\frac{\zeta}{2kT}\left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\left[\frac{\boldsymbol{F}^{(c)}\phi_1}{kT} - \frac{\partial}{\partial \boldsymbol{Q}}\phi_1\right]\right) \tag{13.5-8}$$

$$\vdots$$

These equations must be solved for $\phi_1, \phi_2, \ldots$ subject to the condition that ψ be normalized to unity. Since ψ_{eq} in Eq. L of Table 11.5-1 has been normalized to unity, we then must require that

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty}\psi_{eq}\phi_k Q^2\, dQ \sin\theta\, d\theta\, d\phi = 0 \qquad k = 1, 2, \ldots \tag{13.5-9}$$

In addition the ϕ_k must be such that $\psi_{eq}\phi_k$ remains bounded at all points in the configuration space. Let us now work through the details for ϕ_1 and ϕ_2.

There are several ways of attacking this problem. One is to write out Eqs. 13.5-7, 13.5-8, and so on, in spherical coordinates and then solve the equations for specific flows.[2] Another is to guess the general form of the solution and then get the coefficients by substituting the postulated solution into the differential equation.[3] We shall take the latter

approach here since it is somewhat speedier, although it does require more maturity and insight. We know that ϕ_k must:

i. Be of kth order in the velocity gradients (i.e., $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa}^\dagger$ or, alternatively, $\dot{\boldsymbol{\gamma}}$ and $\boldsymbol{\omega}$, as defined in Eqs. D.1-2 and D.1-3).

ii. Be a scalar.

iii. Be formed from $\dot{\boldsymbol{\gamma}}$, $\boldsymbol{\omega}$, and $\boldsymbol{Q}$.

iv. Vanish for any flow that is a rigid rotation. (This excludes any tensor products containing $\boldsymbol{\omega}$ but no $\dot{\boldsymbol{\gamma}}$.)

v. Simplify to the kth order term in Eq. 13.5-6 for steady-state, homogeneous, potential flows.

Note that these requirements are satisfied by the expansion in Eq. 13.5-6.

In order to guess the form of ϕ_1, we have to construct scalars, of first order in the velocity gradients, from $\dot{\boldsymbol{\gamma}}$, $\boldsymbol{\omega}$, and $\boldsymbol{Q}$. The only possible combination satisfying requirements i to v above is $(\dot{\boldsymbol{\gamma}} : \boldsymbol{QQ})$. By comparing Eqs. 13.5-5 and 13.5-6 we are led to the conclusion that for any spring force law, we must have

$$\phi_1 = \frac{\zeta}{8kT}(\dot{\boldsymbol{\gamma}} : \boldsymbol{QQ}) \tag{13.5-10}$$

It is not too difficult to verify that this satisfies Eq. 13.5-7 (see Problem 13B.6).

Guessing the form of ϕ_2 is somewhat more difficult. From $\dot{\boldsymbol{\gamma}}$, $\boldsymbol{\omega}$, and $\boldsymbol{Q}$ three scalars can be constructed, satisfying restrictions i to iv, which contain products of velocity gradients: $(\dot{\boldsymbol{\gamma}} : \mathbf{QQ})^2$, $(\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})$, and $(\{\dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\omega}\} : \boldsymbol{QQ})$. By looking at Eq. 13.5-6 we then know that ϕ_2 must have the form

$$\phi_2 = \left(\frac{\zeta}{8kT}\right)^2 \left(\frac{1}{2}(\dot{\boldsymbol{\gamma}} : \boldsymbol{QQ})^2 - \frac{1}{15}\langle Q^4 \rangle_{\text{eq}} (\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}}) + A(Q)(\{\dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\omega}\} : \boldsymbol{QQ})\right) \tag{13.5-11}$$

in which $A(Q)$ is a function of Q, which has to be be determined by requiring that ϕ_2 satisfy the differential equation in Eq. 13.5-8. If into the latter we substitute ϕ_2 from Eq. 13.5-11 we obtain

$$\frac{d^2A}{dQ^2} + \left(\frac{6}{Q} - \frac{F^{(c)}}{kT}\right)\frac{dA}{dQ} - \frac{2}{Q}\frac{F^{(c)}A}{kT} = -4 \tag{13.5-12}$$

Equations 13.5-11 and 12 and the boundary conditions constitute a formal solution for ϕ_2 for *any* kind of elastic dumbbell.

If we now specialize to the FENE dumbbell with force law given by Eq. 13.5-1, then Eq. 13.5-12 can be solved for $A(Q)$ to get

$$A(Q) = \frac{4Q_0^2}{2b+7}\left[1 - \frac{1}{2}\left(\frac{Q}{Q_0}\right)^2\right] \tag{13.5-13}$$

Since Eq. 13.5-12 is a second-order differential equation the general solution consists of the particular integral (given in Eq. 13.5-13) plus a complementary function containing two constants. It may be shown, however, that this complementary function does not satisfy the

boundary conditions. In addition $\langle Q^4 \rangle_{eq}$ is given explicitly as

$$\langle Q^4 \rangle_{eq} = \frac{15}{(b+5)(b+7)} Q_0^4 \tag{13.5-14}$$

Therefore we obtain finally for the configurational distribution function for the suspension of FENE dumbbells:

$$\psi = \frac{1}{J_{eq}} \left[1 - \left(\frac{Q}{Q_0} \right)^2 \right]^{b/2} \left(1 + \left(\frac{H\lambda_H}{2kT} \right) (\dot{\gamma} : \boldsymbol{QQ}) + \left(\frac{H\lambda_H}{2kT} \right)^2 \left[- \frac{Q_0^4}{(b+5)(b+7)} (\dot{\gamma} : \dot{\gamma}) \right. \right.$$
$$\left. \left. + \frac{4Q_0^2}{(2b+7)} \left(1 - \frac{1}{2} \left(\frac{Q}{Q_0} \right)^2 \right) (\{\dot{\gamma} \cdot \boldsymbol{\omega}\} : \boldsymbol{QQ}) + \frac{1}{2} (\dot{\gamma} : \boldsymbol{QQ})^2 \right] + \cdots \right) \tag{13.5-15}$$

where J_{eq} is the normalization constant given in fn. *a* of Table 11.5-1.

Next we turn to the development of an expression for the stress tensor, taking as our starting point the Giesekus expression, Eq. D in Table 13.3-1. If into the latter we insert Eqs. 13.5-5, 13.5-10, and 13.5-11, we get for *any* kind of elastic dumbbell to second order

$$\tau_p = - \frac{n\zeta}{12} \langle Q^2 \rangle_{eq} \dot{\gamma}$$
$$+ \frac{n\zeta^2}{480kT} \langle Q^4 \rangle_{eq} (\{\boldsymbol{\omega} \cdot \dot{\gamma} - \dot{\gamma} \cdot \boldsymbol{\omega}\} - 2\{\dot{\gamma} \cdot \dot{\gamma}\}) + \cdots \tag{13.5-16}$[6]$$

When we specialize to the FENE dumbbells and include in addition the results from Eq. 13.5-15, we get

$$\tau_p = - \frac{bnkT\lambda_H}{b+5} \dot{\gamma} + \frac{1}{2} \frac{b^2 nkT\lambda_H^2}{(b+5)(b+7)} (\{\boldsymbol{\omega} \cdot \dot{\gamma} - \dot{\gamma} \cdot \boldsymbol{\omega}\} - 2\dot{\gamma}^2)$$
$$- \frac{1}{4} \frac{b^3(2b+11)nkT\lambda_H^3}{(2b+7)(b+5)(b+7)(b+9)} \{\boldsymbol{\omega} \cdot \{\boldsymbol{\omega} \cdot \dot{\gamma} - \dot{\gamma} \cdot \boldsymbol{\omega}\} - \{\boldsymbol{\omega} \cdot \dot{\gamma} - \dot{\gamma} \cdot \boldsymbol{\omega}\} \cdot \boldsymbol{\omega}\}$$
$$+ \frac{1}{4} \frac{b^3(6b+25)nkT\lambda_H^3}{(2b+7)(b+5)(b+7)(b+9)} \{\boldsymbol{\omega} \cdot \dot{\gamma}^2 - \dot{\gamma}^2 \cdot \boldsymbol{\omega}\}$$
$$- \frac{1}{2} \frac{b^3(b+3)nkT\lambda_H^3}{(b+5)^2(b+7)(b+9)} (\dot{\gamma} : \dot{\gamma}) \dot{\gamma} + \cdots \tag{13.5-17}$[7]$$

where λ_H and b are defined by Eqs. 13.5-2 and 13.5-4. Equation 13.5-17 is the principal result of this section; in sharp contrast with the Hookean dumbbells for which we obtained a complete constitutive equation, we have succeeded here in getting an analytical expression only for steady state, and then only up to the terms cubic in the velocity gradients.

[6] See Eqs. E.7-4, E.7-5, and E.7-6 for the evaluation of the integrals of polyads of the unit normal over the surface of a sphere.

[7] To get this result we need the following formula for FENE dumbbells

$$\frac{\langle Q^n \rangle_{eq}}{\langle Q^{n-2} \rangle_{eq}} = \frac{(n+1)Q_0^2}{n+b+3} \tag{13.5-17a}$$

The result in Eq. 13.5-17 can be used to relate the constants in a constitutive equation from continuum mechanics to the structural parameters in the model. For example, if we simplify Eq. D.4-3 for steady, homogeneous flow, we can then make a term-by-term comparison with Eq. 13.5-17 and obtain the following expressions for the b's in Eq. D.4-3 (the retarded-motion expansion):

$$b_1 = \eta_s + \frac{bnkT\lambda_H}{b+5} \tag{13.5-18}$$

$$b_2 = -\frac{b^2 nkT\lambda_H^2}{(b+5)(b+7)} \tag{13.5-19}$$

$$b_{11} = 0 \tag{13.5-20}$$

$$b_3 = \frac{b^3(2b+11)nkT\lambda_H^3}{(2b+7)(b+5)(b+7)(b+9)} \tag{13.5-21}$$

$$b_{12} = \frac{4b^3 nkT\lambda_H^3}{(2b+7)(b+5)(b+7)(b+9)} \tag{13.5-22}$$

$$b_{1:11} = \frac{6b^3 nkT\lambda_H^3}{2(2b+7)(b+5)^2(b+7)(b+9)} \tag{13.5-23}$$

Thus the b's are given explicitly in terms of the spring constant H, the maximum extension Q_0, the number density n, the solvent viscosity η_s, and the temperature. It should be noted that whereas Eq. 13.5-17 applies only to steady-state flow, Eq. D.4-3 with the above expressions for the b's is valid for slowly varying flows. By making use of continuum mechanics results we have thus succeeded in generalizing slightly the molecular theory results.

From the retarded-motion expansion we can get the viscometric functions for small shear rates and the components of the complex viscosity for small frequencies; to get the $\dot{\gamma}^2$-term in Ψ_1 and the ω^2 term in η''/ω, it is necessary to solve Eq. 13.2-13 for the specific flows of interest. The results are

$$\frac{\eta - \eta_s}{nkT\lambda_H} = \frac{b}{b+5}\left[1 - \frac{2b^2(4b+17)}{(b+5)(b+7)(b+9)(2b+7)}(\lambda_H\dot{\gamma})^2 + \cdots\right] \tag{13.5-24}$$

$$\frac{\Psi_1}{nkT\lambda_H^2} = \frac{2b^2}{(b+5)(b+7)}\left[1 - \frac{2b^2(20b^3+315b^2+1578b+2569)}{(b+5)(b+7)(b+9)(b+11)(2b+7)^2}(\lambda_H\dot{\gamma})^2 + \cdots\right] \tag{13.5-25}$$

and

$$\frac{\eta' - \eta_s}{nkT\lambda_H} = \frac{b}{b+5}\left[1 - \frac{b^2(2b+11)}{(b+7)(b+9)(2b+7)}(\lambda_H\omega)^2 + \cdots\right] \tag{13.5-26}$$

$$\frac{\eta''/\omega}{nkT\lambda_H^2} = \frac{b^2}{(b+5)(b+7)}\left[1 - \frac{b^2(4b^2+52b+151)}{(b+9)(b+11)(2b+7)^2}(\lambda_H\omega)^2 + \cdots\right] \tag{13.5-27}$$

From Eq. 13.2-13 one can also get an expansion in powers of $1/\omega$ for the small-amplitude oscillatory properties:

$$\frac{\eta' - \eta_s}{nkT\lambda_H} = \frac{(b+3)(b^2-6b+14)}{(b-2)(b-4)(b-6)} \frac{1}{(\lambda_H\omega)^2} + \cdots \tag{13.5-28}$$

$$\frac{\eta''/\omega}{nkT\lambda_H^2} = \frac{b}{b-2} \frac{1}{(\lambda_H\omega)^2} + \cdots \tag{13.5-29}$$

The functions $\eta'(\omega)$ and $\eta''(\omega)$ are shown in Fig. 13.5-1.

The perturbation series of Eq. 13.5-5 probably converges only for $\lambda_H\dot{\gamma}$ somewhat less than unity (see comments following Eq. 14.4-20). To describe nonlinear behavior for larger $\lambda_H\dot{\gamma}$, it is necessary to solve the diffusion equation numerically.[8]

Figure 13.5-2 shows some intrinsic viscosity data for a series of monodisperse poly-α-methylstyrene samples in toluene plotted along with some curves calculated for FENE dumbbells, Hookean dumbbells, and rigid dumbbells. In plotting the FENE dumbbell curves, the time constant has been determined from the zero-shear-rate intrinsic viscosity by using only the zero-shear-rate term in Eq. 13.5-24, so that

$$\lambda_H = \left(\frac{b+5}{b}\right) \frac{[\eta]_0\eta_s M}{\tilde{N}kT} \tag{13.5-30}$$

It can be seen that the calculated curves for the FENE dumbbells have approximately the correct shape and that they allow for a series of curves; this is a considerable improvement over the Hookean dumbbells. Values of b between 10 and 100 seem to be appropriate for describing the data in Fig. 13.5-2.

In Fig. 13.5-3 we see a comparison of the FENE dumbbell results with experimental data for the material functions for small-amplitude oscillatory motion. It can be seen that no value of b can be chosen to match the η' and η'' data, and that the FENE dumbbell model offers virtually no improvement over the Hookean dumbbell. This is to be expected, since the small-amplitude experiment does not probe the nonlinear aspect of the spring representing the polymer. To describe this experiment we need to incorporate more beads and springs into the model to simulate the large number of degrees of freedom and the spectrum of time constants (see Chapter 15). The apparent ability of the model to describe $\eta(\dot{\gamma})$ but not $\eta'(\omega)$ is investigated further in Problem 13A.1.

We would like to conclude from the above that taking into account the nonlinear stretching of the polymer molecules is the most important correction that should be made to the Hookean model in order to describe real systems. However, there are many other effects—such as hydrodynamic interaction,[9] excluded volume,[10] internal viscosity,[11] perturbation of the velocity gradient,[12] wall effects,[13] friction coefficient varying with dumbbell

[8] X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 125-144 (1985).

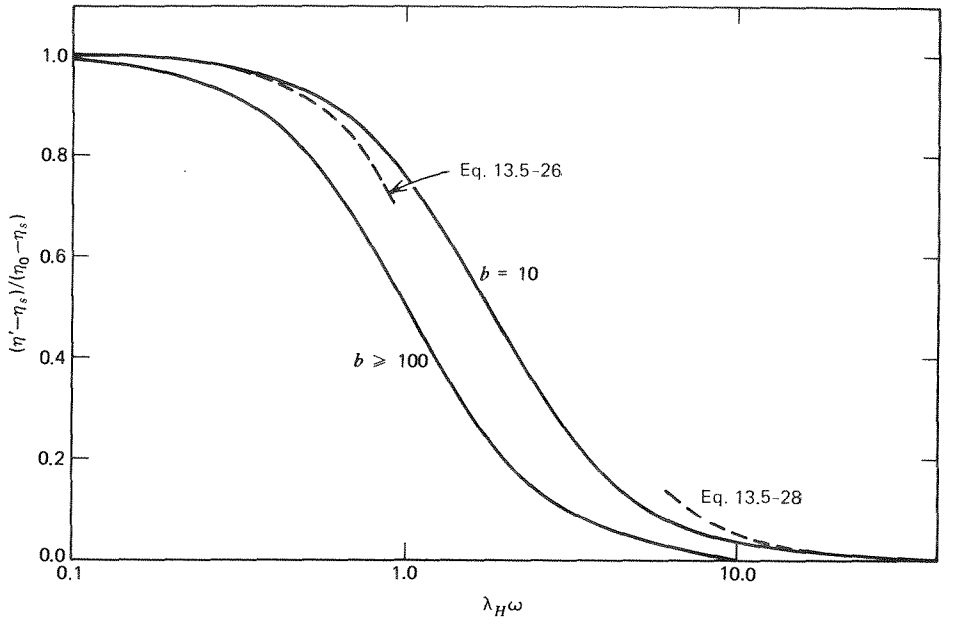
[9] See §13.6 and Problem 13B.2.

[10] In connection with the many effects that can be included in bead-spring theories see the survey articles of A. Peterlin, *Adv. in Macr. Chem.*, **1**, 225-281 (1968) and M. Fixman and W. H. Stockmayer, *Ann. Rev. Phys. Chem.*, **21**, 407-428, (1970).

[11] See Problem 13C.2.

[12] K. Higashitani, Ph.D. Thesis, University of Wisconsin, Madison (1973), Appendix G, pp. 238 253. P. Schümmer and B. Otten, *Proc. IXth Internat. Congress on Rheology*, Mexico (1984), pp. 399-403.

[13] P. Brunn, *Rheol. Acta*, **15**, 23 29 (1976).



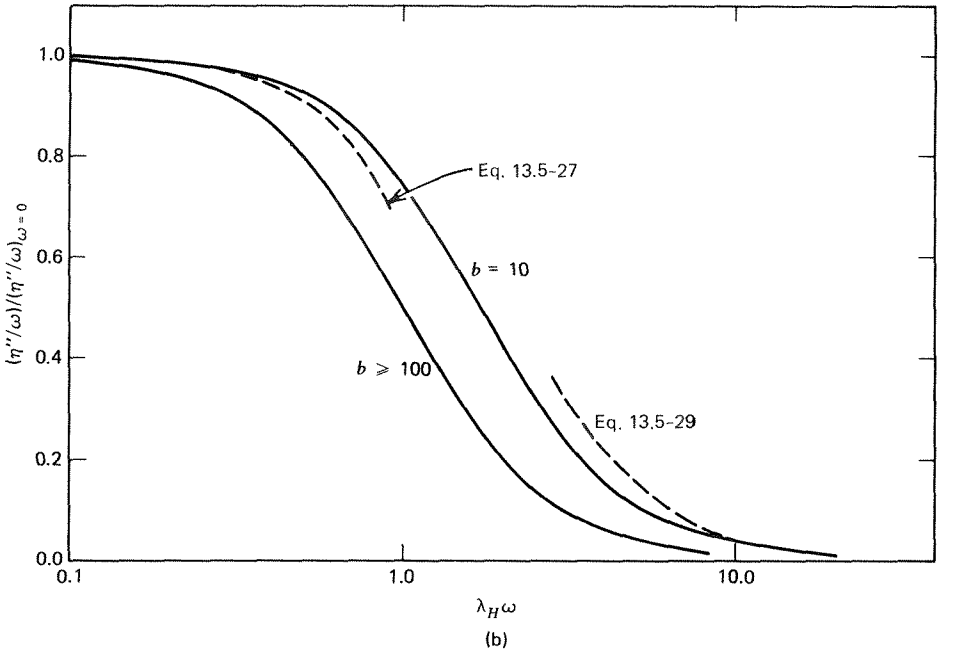


FIGURE 13.5-1. The small-amplitude oscillatory material functions for FENE dumbbells. The solid curves for $b = 10$ and $b \geq 100$ were calculated by Warner.[2] The dashed lines are obtained from the first few terms of asymptotic expansions given in Eqs. 13.5-26 to 13.5-29. The time constant is defined as $\lambda_H = \zeta/4H$, and the dimensionless parameter b is HQ_0^2/kT. Reprinted from R. L. Christiansen and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **3**, 161–177 (1977/1978).

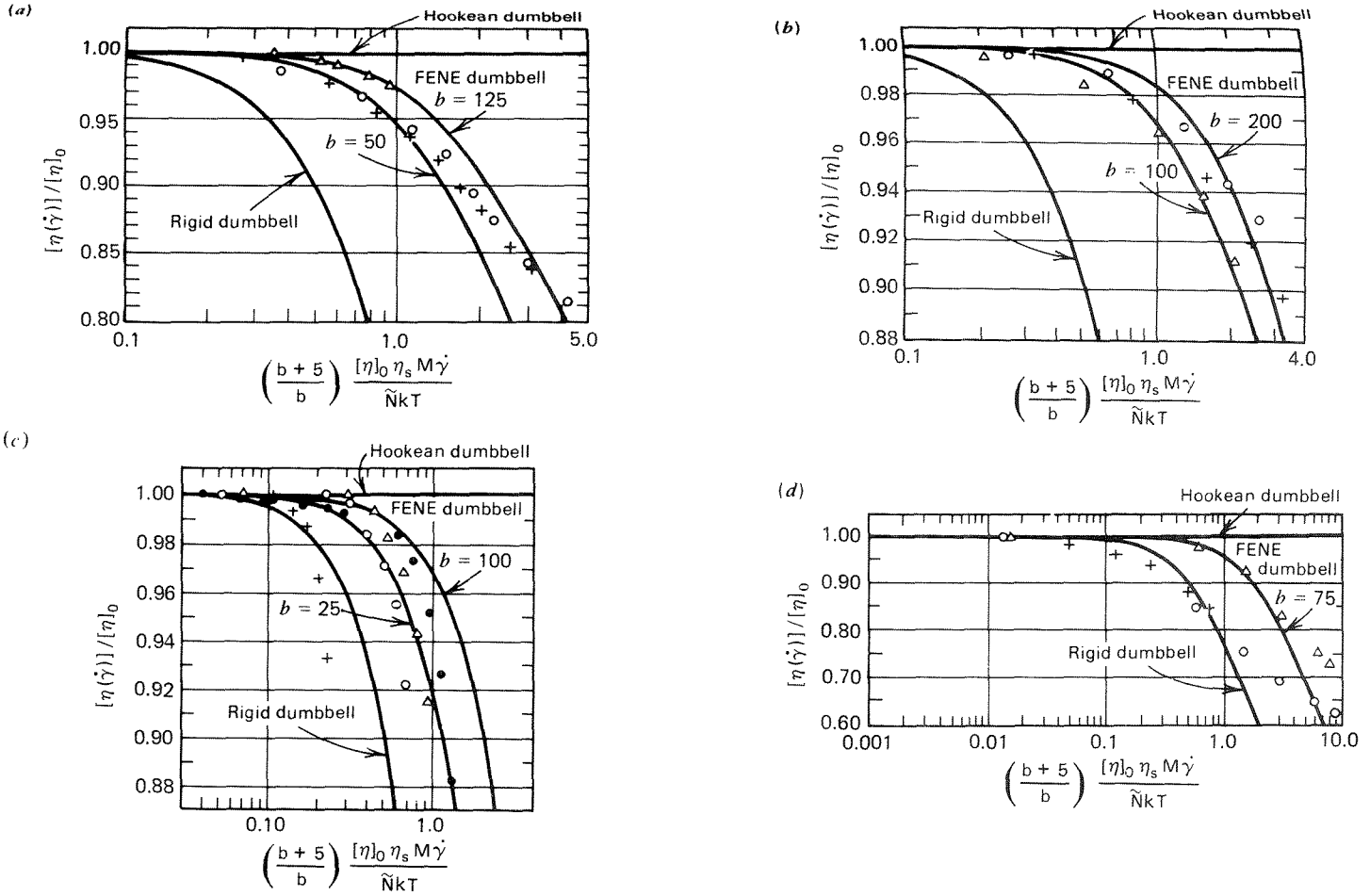


FIGURE 13.5-2. Comparison of experimental intrinsic viscosities and calculated curves from the FENE dumbbell model. (*a*) Polystyrene in benzene at 30°C for several molecular weights: 6×10^6 (+), 7.14×10^6 (○), 3.16×10^6 (△). Data of H. Suzuki, T. Kotaka, and H. Inagaki, *J. Chem. Phys.*, **51**, 1279-1285 (1969). (*b*) Polystyrene (molecular weight 10^7) in toluene for several temperatures: 20 C (+), 40 C (○), 60 C (△). Data of H. van Oene and L. H. Cragg, *J. Polym. Sci.*, **57**, 209-225 (1962). (*c*) Poly-α-methylstyrene in toluene at 25 C for several molecular weights: 0.696×10^6 (+), 1.24×10^6 (○), 1.46×10^6 (△), 1.82×10^6 (●). Data of I. Noda, Y. Yamada, and M. Nagasawa, *J. Phys. Chem.*, **72**, 2890-2898 (1968). (*d*) Cellulose in cadoxene at 25°C for several molecular weights: 0.330×10^6 (△), 0.109×10^6 (+), 0.429×10^6 (○). Data of E. Riande and J. M. Pereña, *Makromol. Chemie*, **175**, 2923-2938 (1974). Reprinted with permission from X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 125-144 (1985).

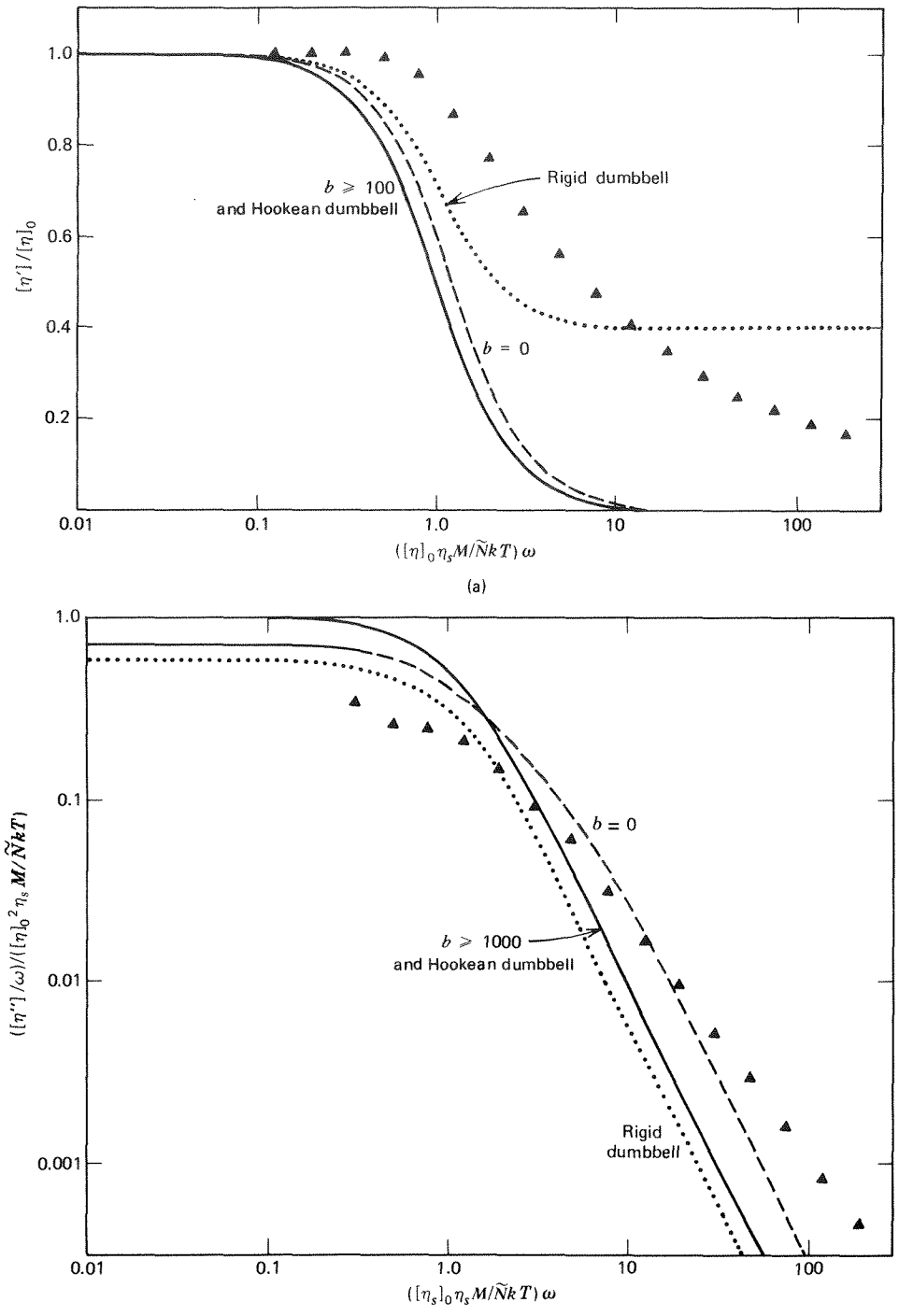


FIGURE 13.5-3. Comparison of theoretical calculations of FENE dumbbell solutions with experimental data. The solid triangles are the data points of D. J. Massa, Ph.D. Thesis, University of Wisconsin, Madison (1970); the experimental fluid is polystyrene ($\bar{M}_w = 860{,}000$; $\bar{M}_w/\bar{M}_n = 1.15$) in Aroclor 1248. The FENE dumbbell curves for $b \geq 1000$ are indistinguishable from that for Hookean dumbbells; the $b = 0$ curves (dashed) are only approximate, included in order to give some estimate as to the limited spread of the curves for various b values. The rigid dumbbell curves (dotted lines) are shown for comparison. Based on R. L. Christiansen and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **3**, 161-177 (1977/1978).

extension,[14] and nonisotropic frictional drag[15]—that can also be invoked, and that might be able to describe the shear-rate dependence of the viscosity. Keep in mind also that the dumbbell models allow only for interaction with the solvent at two points in the molecule (that is, at the two beads), whereas in any real molecule there will be many points along the molecule where the "hydrodynamic drag" will be felt. Nonetheless this section has shown how we can compare model results with experimental data to evolve better macromolecular models.

EXAMPLE 13.5-1 Steady Elongational Flow (FENE Dumbbells)

Obtain a formal expression for the elongational viscosity of a dilute solution of FENE dumbbells. Then obtain an approximate expression asymptotically valid for large rates of elongation. Finally obtain the perturbation expansion for small rates of elongation. Combine these two asymptotic calculations to sketch the elongational viscosity over the entire elongation-rate range.

SOLUTION **(a)** Formal Solution for $\bar{\eta}$.

This is a steady, homogeneous, potential flow for which $\psi(\boldsymbol{Q})$ is given by Eq. 13.2-14; when this expression is used in the Giesekus form for the stress tensor we get

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - \frac{n\zeta}{4}\int\{\boldsymbol{\kappa}\cdot\boldsymbol{QQ} + \boldsymbol{QQ}\cdot\boldsymbol{\kappa}\}\psi_{eq}\phi_{fl}\,d\boldsymbol{Q} \tag{13.5-31}$$

For this flow $\boldsymbol{\kappa}$ is given in Eq. (B) of Table 13.1-1 with $b = 0$ and $\dot{\varepsilon}$ = a constant, and

$$\{\boldsymbol{\kappa}\cdot\boldsymbol{QQ} + \boldsymbol{QQ}\cdot\boldsymbol{\kappa}\} = \begin{pmatrix} -S^2c^2 & -S^2sc & \frac{1}{2}SCc \\ -S^2sc & -S^2s^2 & \frac{1}{2}SCs \\ \frac{1}{2}SCc & \frac{1}{2}SCs & 2C^2 \end{pmatrix} Q^2\dot{\varepsilon} \tag{13.5-32}$$

$$(\boldsymbol{\kappa}:\boldsymbol{QQ}) = -\tfrac{1}{2}Q^2(1 - 3C^2)\dot{\varepsilon} \tag{13.5-33}$$

in which Q, θ, and ϕ give the length and polar angles of the $\boldsymbol{Q}$ vector and $S = \sin\theta$, $C = \cos\theta$, $s = \sin\phi$, and $c = \cos\phi$. Then from the definition of $\bar{\eta}$ given in Eq. D.5-14 (or Eq. 3.5-3) we get from Eq. 13.5-31

$$\begin{aligned}\bar{\eta} &= \frac{\tau_{yy} - \tau_{zz}}{\dot{\varepsilon}} \\ &= 3\eta_s + \frac{n\zeta}{4}\frac{\int_0^{2\pi}\int_0^{\pi}\int_0^{Q_0} Q^2(S^2s^2 + 2C^2)\psi'_{eq}\phi'_{fl}Q^2\,dQ\,S\,d\theta\,d\phi}{\int_0^{2\pi}\int_0^{\pi}\int_0^{Q_0}\psi'_{eq}\phi'_{fl}Q^2\,dQ\,S\,d\theta\,d\phi} \\ &= 3\eta_s + \frac{n\zeta}{4}\frac{\int_0^{\pi/2}\int_0^{Q_0} Q^2(\frac{1}{2}S^2 + 2C^2)\psi'_{eq}\phi'_{fl}Q^2\,dQ\,S\,d\theta}{\int_0^{\pi/2}\int_0^{Q_0}\psi'_{eq}\phi'_{fl}Q^2\,dQ\,S\,d\theta}\end{aligned} \tag{13.5-34}$$

[14] P. G. deGennes, *J. Chem. Phys.*, **60**, 5030–5042 (1974); R. I. Tanner, *Trans. Soc. Rheol.*, **19**, 557–582 (1975); E. J. Hinch, *Phys. Fluids*, **20**, S22–S30 (1977); G. G. Fuller and L. G. Leal, *J. Non-Newtonian Fluid Mech.*, **8**, 271–310 (1981); N. Phan-Thien, O. Manero, and L. G. Leal, *Rheol. Acta*, **23**, 151–162 (1984); X. J. Fan, R. B. Bird, and M. Renardy, *J. Non-Newtonian Fluid Mech.*, **18**, 255–272 (1985).

[15] H. Giesekus, *J. Non-Newtonian Fluid Mech.*, **11**, 69–109 (1982); R. B. Bird and J. M. Wiest, *J. Rheol.*, **29**, 519–532 (1985); see also §13.7.

in which

$$\psi'_{eq} = \left[1 - \left(\frac{Q}{Q_0}\right)^2\right]^{b/2} \tag{13.5-35}$$

$$\phi'_{fl} = \exp\left[-\frac{b}{2}\left(\frac{Q}{Q_0}\right)^2 (1 - 3C^2)\lambda_H \dot{\varepsilon}\right] \tag{13.5-36}$$

Here we have replaced $\psi = \psi_{eq}\phi_{fl}$ of Eq. 13.2-14 by $(1/J)\psi'_{eq}\phi'_{fl}$; note that the triple integral in the denominator of the second line of Eq. 13.5-34 is just J.

(b) Asymptotic Expansion for High Elongation Rates

Now consider the integrands in the limit as $\lambda_H\dot{\varepsilon}$ approaches infinity. We see that both integrands in the last line of Eq. 13.5-34 have a maximum close to the point $(Q, \theta) = (Q_0, 0)$. Moreover, because of the exponential function we expect this maximum to become very sharp in the limit as $\lambda_H\dot{\varepsilon}$ tends to infinity. Let us therefore consider the integrands close to the point $(Q, \theta) = (Q_0, 0)$. First we introduce a change of variable such that

$$x = 1 - \frac{Q}{Q_0} \tag{13.5-37}$$

With this change the peak is now close to $(x, \theta) = (0, 0)$. We now expand the various functions in the integrands as follows:

$$\phi'_{fl} = e^{(b/2)\lambda_H\dot{\varepsilon}(2 - 4x - 3\theta^2 + \cdots)} \tag{13.5-38a}$$

$$Q^2\psi'_{eq} = Q_0^2(2x)^{b/2}\left(1 - \frac{b+8}{4}x + \cdots\right) \tag{13.5-38b}$$

$$Q^4\psi'_{eq} = Q_0^4(2x)^{b/2}\left(1 - \frac{b+16}{4}x + \cdots\right) \tag{13.5-38c}$$

$$S = \theta\left(1 - \frac{\theta^2}{6} + \cdots\right) \tag{13.5-38d}$$

$$(\tfrac{1}{2}S^2 + 2C^2)S = 2\theta(1 - \tfrac{11}{12}\theta^2 + \cdots) \tag{13.5-38e}$$

Roughly speaking we have expanded the "smooth" part of the functions around $(x, \theta) = (0, 0)$. Notice that ψ'_{eq} does not have a Taylor expansion around (0, 0) but that it has been written as a fractional power multiplied by a polynomial expansion. Now both integrands in Eq. 13.5-34 may be factored into parts containing the x-dependence and the θ-dependence separately. These factors have the general forms

$$f(\theta) = \theta(1 - \alpha\theta^2 + \cdots)e^{-(3b/2)\theta^2\lambda_H\dot{\varepsilon}} \tag{13.5-39}$$

$$g(x) = x^{b/2}(1 - \beta x + \cdots)e^{-2bx\lambda_H\dot{\varepsilon}} \tag{13.5-40}$$

By taking derivatives of these functions we see that in the limit $\lambda_H\dot{\varepsilon} \to \infty$ the maximum in the integrands in Eq. 13.5-34 is to a first approximation located at $(x, \theta)_{max} = ((4\lambda_H\dot{\varepsilon})^{-1}, (3b\lambda_H\dot{\varepsilon})^{-1/2})$. Indeed since b is positive, the peak approaches (0, 0) in the limit $\lambda_H\dot{\varepsilon} \to \infty$. Loosely we may say that the peak is located inside the radius of convergence of the polynomial expansions in Eq. 13.5-39 and 13.5-40, and that we have obtained good approximations to the integrands in the neighborhood of the peak. With this information we may now approximate Eqs. 13.5-34 to 13.5-36 by

$$\bar{\eta} \doteq 3\eta_s + \frac{n\zeta Q_0^2 I_{Nx} I_{N\theta}}{4 I_{Dx} I_{D\theta}} \tag{13.5-41}$$

where the I-integrals are dimensionless quantities given by

$$I_{Nx} = \int_0^\infty x^{b/2}\left(1 - \frac{b+16}{4}x\right)e^{-2b\lambda_H\dot{\varepsilon}x}\,dx$$
$$= \frac{\Gamma[(b+2)/2]}{(2b\lambda_H\dot{\varepsilon})^{(b+2)/2}}\left[1 - \frac{(b+16)(b+2)}{16b}\frac{1}{\lambda_H\dot{\varepsilon}}\right] \tag{13.5-42}$$

$$I_{N\theta} = 2\int_0^\infty \theta\left(1 - \frac{11}{12}\theta^2\right)e^{-(3b/2)\lambda_H\dot{\varepsilon}\theta^2}\,d\theta$$
$$= \frac{2}{3b\lambda_H\dot{\varepsilon}}\left[1 - \frac{11}{12}\left(\frac{2}{3b}\right)\frac{1}{\lambda_H\dot{\varepsilon}}\right] \tag{13.5-43}$$

I_{Dx} is the same as I_{Nx} with the factor $(b+16)$ replaced by $(b+8)$, and $I_{D\theta}$ is one-half $I_{N\theta}$ with the factor $\frac{11}{12}$ replaced by $\frac{1}{6}$. In obtaining these integrals we have made use of an important property of the approximations written symbolically in Eqs. 13.5-39 and 13.5-40; the approximating functions approach zero exponentially away from the peak. Hence in the limit $\lambda_H\dot{\varepsilon} \to \infty$ the ranges of integration may be extended to infinity with negligible error. When the expressions for I_{Nx}, $I_{N\theta}$, I_{Dx}, and $I_{D\theta}$ are introduced in Eq. 13.5-41, we obtain finally in the limit of large elongation rates:

$$\bar{\eta} = 3\eta_s + 2bnkT\lambda_H\left[1 - \frac{b+3}{2b}\frac{1}{\lambda_H\dot{\varepsilon}} + \cdots\right] \tag{13.5-44}$$

We see that for finite b the elongational viscosity approaches a limiting value as $\lambda_H\dot{\varepsilon} \to \infty$. This is in contrast with the behavior of Hookean dumbbells.

(c) Expansion for Low Elongation Rates

An expansion for $\bar{\eta}$ for small elongation rates may be obtained directly from the general slow flow expansion in Eq. 13.5-17. With the velocity field represented by Eq. (B) of Table 13.1-1, with $b = 0$, we find

$$\bar{\eta} = 3\eta_s + \frac{3bnkT\lambda_H}{b+5}\left[1 + \frac{b}{b+7}(\lambda_H\dot{\varepsilon}) + \frac{3b^2(b+3)}{(b+5)(b+7)(b+9)}(\lambda_H\dot{\varepsilon})^2 + \cdots\right] \tag{13.5-45}$$

Equations 13.5-44 and 13.5-45 may be combined to give a good approximation to $\bar{\eta}$ over the entire range of elongation rates, as illustrated in Fig. 13.5-4. For small elongation rates the elongational viscosity is assumed to follow the perturbation expansion in Eq. 13.5-45. In a small intermediate region the perturbation expansion and the asymptotic expansion overlap. For larger elongation rates the elongational viscosity is assumed to follow the asymptotic expansion. The validity of this simple graphical splicing procedure in the region around $\lambda_H\dot{\varepsilon} = \frac{1}{2}$ is supported by numerical calculations.[2] Unfortunately no experimental $\bar{\eta}(\dot{\varepsilon})$ data are available to compare with the theory.[16]

[16] The main results of this illustrative example have been used with some success in studies on turbulent drag reduction and on flows in porous media [F. Durst and R. Haas, *Rheol. Acta*, **20**, 179–192 (1981); R. Haas and F. Durst, *ibid.*, **21**, 150–166 (1982); F. Durst, R. Haas, and W. Interthal, *Rheol. Acta*, **21**, 572–577 (1982); F. Durst, R. Haas, W. Interthal, and T. Keck, *Chemie-Ingenieur Technik*, **54**, 213–221 (1982). The analogous results for the Kramers bead-rod chain (see §16.5) have been used by S. T. J. Peng and R. F. Landel [in G. Astarita, G. Marrucci, and L. Nicolais, eds., *Rheology*, Plenum, New York (1980), pp. 385–391] in their study of the tubeless siphon experiment.

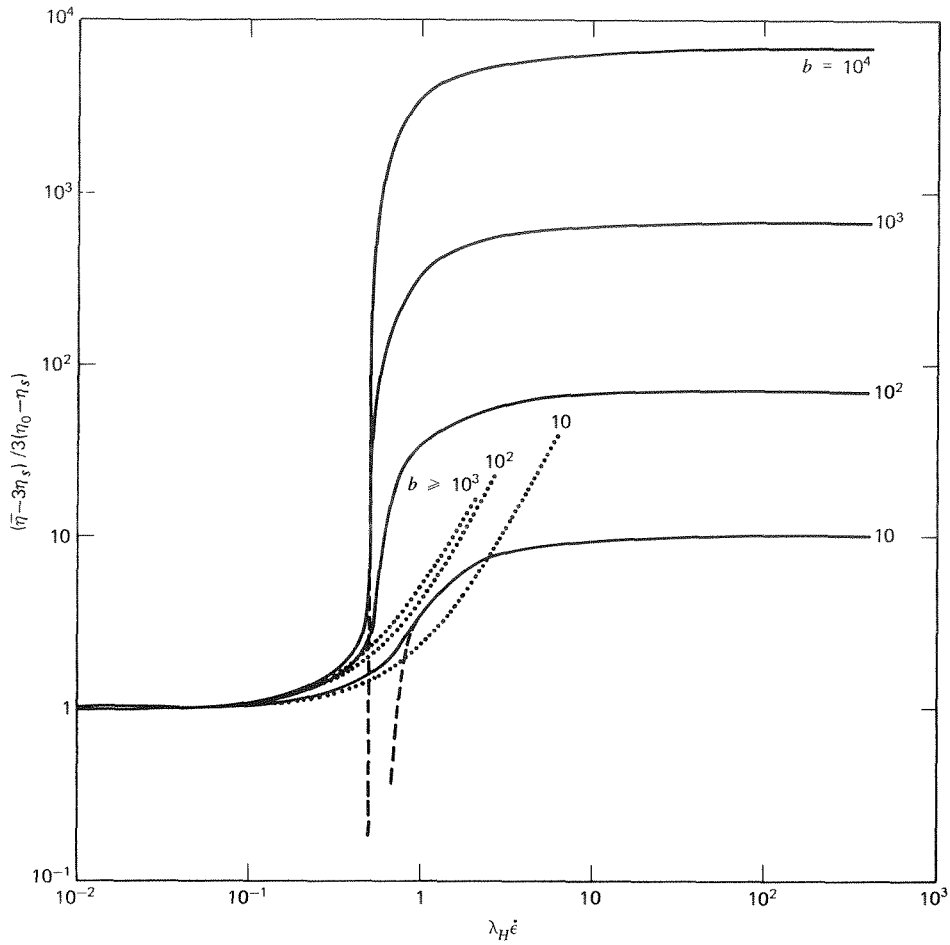


FIGURE 13.5-4. Elongational viscosity curves for FENE dumbbells. An approximation for arbitrary rates of elongation is obtained by graphical splicing of a perturbation expansion valid for small elongation rates and an asymptotic expansion valid for large elongation rates. ....., Perturbation expansion Eq. 13.5-45; ------, Asymptotic expansion Eq. 13.5-44; _____, Graphically matched approximation.

EXAMPLE 13.5-2 An Approximate Constitutive Equation (FENE Dumbbells)

For the FENE dumbbell model the Kramers and Giesekus forms of the polymer contribution to the stress tensor are

$$\text{Kramers:} \quad \tau_p = -nH\left\langle \frac{\boldsymbol{QQ}}{1-(Q^2/Q_0^2)} \right\rangle + nkT\boldsymbol{\delta} \tag{13.5-46}$$

$$\text{Giesekus:} \quad \tau_p = \frac{n\zeta}{4}\langle \boldsymbol{QQ} \rangle_{(1)} \tag{13.5-47}$$

It is not possible to apply the procedure used in Eqs. 13.4-2 to 13.4-5 to get a constitutive equation by eliminating the average values. Show that this procedure can, however, be applied if in Eq. 13.5-46 we

approximate the average value in the following way:

$$\left\langle \frac{\boldsymbol{QQ}}{1-(Q^2/Q_0^2)} \right\rangle \doteq \frac{\langle \boldsymbol{QQ} \rangle}{1-\langle Q^2/Q_0^2 \rangle} + \varepsilon Q_0^2 \boldsymbol{\delta} \tag{13.5-48}$$

where ε is a constant. That is, replace the average of the ratio by the ratio of averages, and then add an extra isotropic term containing a constant in order to improve the approximation.[8,17] Determine the constant ε by requiring that the trace of the above relation be true at equilibrium.

SOLUTION **(a)** Let $x = Q/Q_0$, and then require that

$$\left\langle \frac{x^2}{1-x^2} \right\rangle_{\text{eq}} = \frac{\langle x^2 \rangle_{\text{eq}}}{1-\langle x^2 \rangle_{\text{eq}}} + 3\varepsilon \tag{13.5-49}$$

Since $\psi_{\text{eq}} \propto (1-x^2)^{b/2}$ (according to Eq. L of Table 11.5-1) these integrals can be evaluated and we find that

$$\frac{3}{b} = \frac{3/(b+5)}{1-[3/(b+5)]} + 3\varepsilon \tag{13.5-50}$$

and hence

$$\varepsilon = \frac{2}{b(b+2)} \tag{13.5-51}$$

Then we can replace Eq. 13.5-46 by

$$\text{Kramers (approximate):} \qquad \boldsymbol{\tau}_p = -\frac{nH\langle \boldsymbol{QQ} \rangle}{1-\langle Q^2/Q_0^2 \rangle} + (1-\varepsilon b)nkT\boldsymbol{\delta} \tag{13.5-52}$$

(b) Now to get an approximate constitutive equation, we have to eliminate all $\langle\ \rangle$ quantities appearing in Eqs. 13.5-47 and 13.5-52. To do this we take the trace of Eq. 13.5-52 and solve for $\langle Q^2/Q_0^2 \rangle$:

$$\left\langle \frac{Q^2}{Q_0^2} \right\rangle = 1 - Z^{-1} \tag{13.5-53}$$

where

$$Z = 1 + \frac{3}{b}\left((1-\varepsilon b) - \frac{\text{tr}\,\boldsymbol{\tau}_p}{3nkT}\right) \tag{13.5-54}$$

Then Eq. 13.5-52 can be rewritten

$$\text{Kramers (approximate):} \qquad \boldsymbol{\tau}_p = -nHZ\langle \boldsymbol{QQ} \rangle + (1-\varepsilon b)nkT\boldsymbol{\delta} \tag{13.5-55}$$

[17] R. B. Bird, P. J. Dotson, and N. L. Johnson [*J. Non-Newtonian Fluid Mech.*, **7**, 213-235 (1980)] did a similar analysis for $\varepsilon = 0$. In this paper Eq. 58 and all subsequent equations are in error.

Now we can form the convected derivative $(\tau_p/Z)_{(1)}$ from Eq. 13.5-55 and then use Eq. 13.5-47 to eliminate $\langle \boldsymbol{QQ} \rangle_{(1)}$. This leads after some rearrangement to[18]

$$\boxed{Z\boldsymbol{\tau}_p + \lambda_H \boldsymbol{\tau}_{p(1)} - \lambda_H[\boldsymbol{\tau}_p - (1 - \varepsilon b)nkT\boldsymbol{\delta}]\frac{D \ln Z}{Dt} = -(1 - \varepsilon b)nkT\lambda_H \boldsymbol{\gamma}_{(1)}} \tag{13.5-56}$$

which is an approximate constitutive equation.[19] Note that this equation is not linear in $\boldsymbol{\tau}_p$; it contains the parameters $\lambda_H = \zeta/4H$ (time constant), $b = HQ_0^2/kT$ (dimensionless), and nkT.

(c) For steady-state shear flow ($v_x = \dot{\gamma}y$) Eq. 13.5-56 becomes

$$Z\begin{pmatrix} \tau_{p,xx} & \tau_{p,xy} & \tau_{p,xz} \\ \tau_{p,xy} & \tau_{p,yy} & \tau_{p,yz} \\ \tau_{p,xz} & \tau_{p,yz} & \tau_{p,zz} \end{pmatrix} - \lambda_H \dot{\gamma} \begin{pmatrix} 2\tau_{p,xy} & \tau_{p,yy} & \tau_{p,yz} \\ \tau_{p,yy} & 0 & 0 \\ \tau_{p,yz} & 0 & 0 \end{pmatrix} = -(1 - \varepsilon b)nkT\lambda_H \dot{\gamma} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{13.5-57}$$

From this we find that $\tau_{p,yy} = \tau_{p,zz} = 0$, and we get a pair of algebraic equations for $\tau_{p,xy}$ and $\tau_{p,xx}$, from which we can extract the following equation for $\mathscr{S} = \tau_{p,xy}/[3nkT(1 - \varepsilon b)]$:

$$\mathscr{S}^3 + 3p\mathscr{S} + 2q = 0 \tag{13.5-58}$$

where

$$p = \frac{b}{54(1 - \varepsilon b)} + \frac{1}{18}; \qquad q = \frac{b\lambda_H \dot{\gamma}}{108(1 - \varepsilon b)} \tag{13.5-59}$$

The only real root of this equation is[20]

$$\mathscr{S} = -2p^{1/2} \sinh(\tfrac{1}{3} \operatorname{arcsinh} qp^{-3/2}) \tag{13.5-60}$$

From this $\eta(\dot{\gamma})$ can be obtained, and with $\varepsilon = 2/[b(b + 2)]$:

$$\text{For } \dot{\gamma} = 0: \quad \eta - \eta_s = nkT\lambda_H\left(\frac{b}{b + 5}\right) \tag{13.5-61}$$

$$\text{For } \dot{\gamma} \to \infty: \quad \eta - \eta_s \sim nkT\lambda_H\left(\frac{\sqrt{b/2}}{\lambda_H \dot{\gamma}} \frac{b}{b + 2}\right)^{2/3} \tag{13.5-62}$$

[18] An alternative formulation of the constitutive equation is

$$\boldsymbol{\tau}_p = nkT\lambda_H \boldsymbol{\alpha}_{(1)} \tag{13.5-56a}$$

where the "structure tensor" $\boldsymbol{\alpha} \equiv H\langle \boldsymbol{QQ} \rangle/kT$ is given by

$$(1 - b^{-1} \operatorname{tr} \boldsymbol{\alpha})^{-1}\boldsymbol{\alpha} + \lambda_H \boldsymbol{\alpha}_{(1)} = [b/(b + 2)]\boldsymbol{\delta} \tag{13.5-56b}$$

In the limit of very large b ("nearly Hookean dumbbells"), R. C. Armstrong and S. Ishikawa [*J. Rheol.*, **24**, 143-165 (1980)] found the following equation for $\boldsymbol{\alpha}$, *exact* to order $1/b$:

$$\boldsymbol{\alpha} + \lambda_H \boldsymbol{\alpha}_{(1)} + b^{-1}\{(\operatorname{tr} \boldsymbol{\alpha})\boldsymbol{\alpha} + 2\boldsymbol{\alpha} \cdot \boldsymbol{\alpha}\} = \boldsymbol{\delta} \tag{13.5-56c}$$

[see also R. C. Armstrong, S. K. Gupta, and O. Basaran, *Polym. Eng. Sci.*, **20**, 466-472 (1980), Eq. (9), for another equation for $\boldsymbol{\alpha}$, which provides a matching between Eq. 13.5-56c and Eq. 13.5-56 with $\varepsilon = 0$].

[19] The same equation (for $\varepsilon = 0$) was obtained by R. I. Tanner [*Trans. Soc. Rheol.*, **19**, 37-65 (1975)] by a different method (see Problem 13B.9).

[20] K. Rektorys, *Survey of Applicable Mathematics*, MIT Press, Cambridge, Mass. (1969), pp. 78-79 (in Table 1.1, the b in the third column should be q).

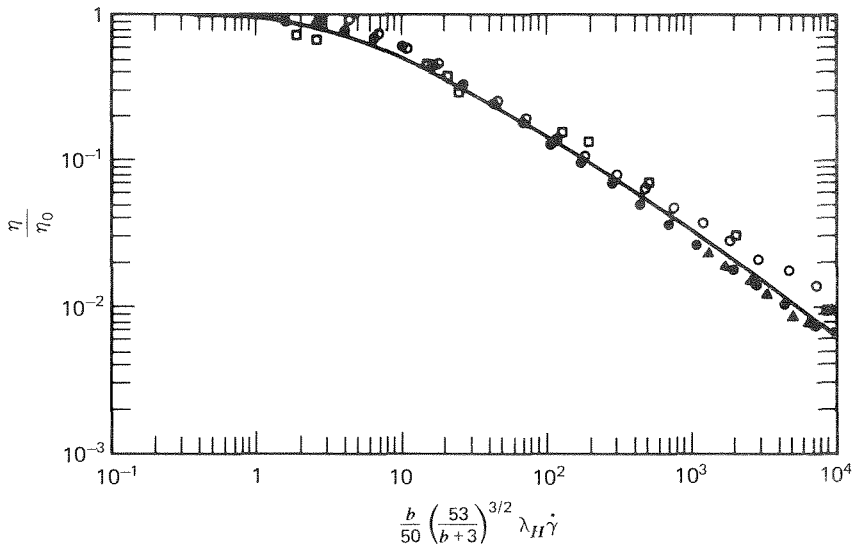


FIGURE 13.5-5. Comparison of Eq. 13.5-60 with experimental viscosity data for several nondilute polymer solutions. ○ polyacrylamide in glycerin; $\lambda_H = 510$ s. [P. J. Leider, *Ind. Eng. Chem. Fund.*, **13**, 342–346 (1974)], ● polyisobutylene in Oppanol-B-1; $\lambda_H = 1915$ s [P. J. Leider, *op. cit.*], □ hydroxyethylcellulose in glycerin/water; $\lambda_H = 2.91$ s [R. J. Grimm, *AIChE J.*, **24**, 427–439 (1978)], and ▲ polyethylene oxide in water; $\lambda_H = 9.23$ s [R. J. Grimm, *op. cit.*]. In making the data comparison b was taken to be 50 for all solutions, and ε is set equal to zero. Reprinted with permission from Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **9**, 157–178 (1981)].

The result for $\dot{\gamma} = 0$ agrees precisely with the exact expression in Eq. 13.5-24, and the simple power-law result for large $\dot{\gamma}$ has been shown to be in good agreement, between $b = 10$ and $b = 300$, with exact numerical calculations.[8] For a comparison of the $\eta(\dot{\gamma})$ curve from Eq. 13.5-60 with some experimental solution data, see Fig. 13.5-5. From Eq. 13.5-57 we can also get the result $\Psi_1 = 2(\eta - \eta_s)^2/[(1 - \varepsilon b)nkT]$.

(d) For steady elongational flow ($v_z = \dot{\varepsilon}z$, $v_x = -\frac{1}{2}\dot{\varepsilon}x$, $v_y = -\frac{1}{2}\dot{\varepsilon}y$), an analysis similar to that in **(c)** leads to

$$\text{For } \dot{\varepsilon} = 0: \qquad \bar{\eta} - 3\eta_s = 3nkT\lambda_H\left(\frac{b}{b+5}\right) \tag{13.5-63}$$

$$\text{For } \dot{\varepsilon} \to \infty: \qquad \bar{\eta} - 3\eta_s \sim 2nkT\lambda_H b$$

$$\text{For } \dot{\varepsilon} \to -\infty: \quad \bar{\eta} - 3\eta_s \sim \tfrac{1}{2}nkT\lambda_H b \tag{13.5-64}$$

These results agree precisely with the exact results given in Eqs. 13.5-45 and 13.5-44 respectively.

It has been further demonstrated that (for $\varepsilon = 0$) the constitutive equation in Eq. 13.5-56 gives qualitatively reasonable results for shear and normal stresses at sudden inception of shear flow, and for steady shear flow with superposed oscillatory motion.[21] The constitutive equation has, in addition, been used to solve several flow problems: the fast squeezing flow between two parallel disks[22] and the transient development of velocity profiles at the inception of Couette flow.[23] Once the flow field has been determined the information about molecular stretching can be obtained from Eq. 13.5-53; this has been done for a sudden-contraction flow, and the results have been compared with limited data on light scattering.[24]

[21] Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **9**, 179–184 (1981).
[22] Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **9**, 157–178 (1981).
[23] Y. Mochimaru, *J. Non-Newtonian Fluid Mech.*, **12**, 135–152 (1983).
[24] R. C. Armstrong, S. K. Gupta, and O. Basaran, *op. cit.*

Hence for the FENE-dumbbell model, it has been possible to go through almost the complete sequence of activities:[25]

Molecular model		
↓		
Constitutive equation	←	Use experimental data on material functions to determine constants in the constitutive equation.
↓		
Solution of fluid dynamics problem	⇆	Compare with experimental data on the flow system (velocity profiles, forces, torques, etc.).
↓		
Calculation of molecular stretching in the flow field	⇆	Compare with molecular stretching determined by light scattering.

The execution of such a sequence is one of the goals of polymer fluid dynamics.

§13.6 HYDRODYNAMIC INTERACTION

Thus far in our study of dumbbell kinetic theory we have assumed that the two beads of the dumbbell move through the solvent without disturbing the velocity field. In this section we wish to discuss a method for removing this "free-draining" assumption, at least approximately. We follow here the approach of Kirkwood and Riseman,[1] who seem to have been the first to introduce the idea of *hydrodynamic interaction* into polymer kinetic theory; they drew heavily on the earlier hydrodynamic studies of Burgers[2] and Oseen.[3]

We begin with Eqs. 13.2-1 through 13.2-4, let the friction tensor $\boldsymbol{\zeta}$ be isotropic ($\boldsymbol{\zeta} = \zeta\boldsymbol{\delta}$), and use the Maxwellian velocity distribution in the expression for the Brownian force. Then the bead equations of motion become

$$\mathbf{0} = -\zeta[[\dot{\boldsymbol{r}}_1]] - (\boldsymbol{v}_1 + \boldsymbol{v}'_1)] - kT\frac{\partial}{\partial \boldsymbol{r}_1}\ln\Psi + \boldsymbol{F}_1^{(\phi)} + \boldsymbol{F}_1^{(e)} \tag{13.6-1}$$

$$\mathbf{0} = -\zeta[[\dot{\boldsymbol{r}}_2]] - (\boldsymbol{v}_2 + \boldsymbol{v}'_2)] - kT\frac{\partial}{\partial \boldsymbol{r}_2}\ln\Psi + \boldsymbol{F}_2^{(\phi)} + \boldsymbol{F}_2^{(e)} \tag{13.6-2}$$

Next we need to specify $\boldsymbol{v}'_1$ and $\boldsymbol{v}'_2$.

[25] L. E. Wedgewood and R. B. Bird, in *Integration of Fundamental Polymer Science and Technology*, L. A. Kleintjens and P. J. Lemstra (Eds.), Elsevier, London (1986), pp. 337–345.

[1] J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565–573 (1948); **22**, 1626–1627 (1954); see also A. Peterlin, *J. Polym. Sci.*, **5**, 473–482 (1950).

[2] J. M. Burgers, *Verhandelingen Koninkl. Ned. Akad. Wetenschap.*, **16**, (Section 1, Chapter 3), 113–184 (1938).

[3] C. W. Oseen, *Ark. f. Mat. Astr. og Fys.*, **6**, No. 29, 1–20 (1910).

Recall that in Example 1.4-1 (part c) we obtained an expression for the velocity disturbance produced at a position $\boldsymbol{r}$ by a sphere moving through the origin as it exerts a hydrodynamic force $\boldsymbol{F}_s$ on the fluid; this expression is $\boldsymbol{v}'(\boldsymbol{r}) = [\boldsymbol{\Omega} \cdot \boldsymbol{F}_s] + O(a^3/r^3)$, where $\boldsymbol{\Omega}$ is the *Oseen-Burgers tensor* in Eq. 1.4-33 and a is the bead radius. If we apply this result (omitting the a^3/r^3 and smaller contributions), we find that the velocity disturbance at bead "1" owing to the movement of bead "2" is

$$\boldsymbol{v}'_1 = [\boldsymbol{\Omega} \cdot \{\zeta([\![\dot{\boldsymbol{r}}_2]\!] - (\boldsymbol{v}_2 + \boldsymbol{v}'_2))\}] \tag{13.6-3}$$

in which the quantity inside braces is the hydrodynamic force exerted by "2" on the solvent. Then, using Eq. 13.6-2, we get

$$\boldsymbol{v}'_1 = \left[\boldsymbol{\Omega} \cdot \left\{-kT \frac{\partial}{\partial \boldsymbol{r}_2} \ln \Psi + \boldsymbol{F}_2^{(\phi)} + \boldsymbol{F}_2^{(e)}\right\}\right] \tag{13.6-4}$$

The Oseen-Burgers tensor in the notation of the present discussion is

$$\boldsymbol{\Omega} = \frac{1}{8\pi\eta_s Q}\left[\boldsymbol{\delta} + \frac{\boldsymbol{QQ}}{Q^2}\right] \tag{13.6-5}$$

Then Eqs. 13.6-1 and 13.6-2 can be rewritten for the unperturbed homogeneous flow field $\boldsymbol{v} = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}]$:

$$\begin{aligned}[\![\dot{\boldsymbol{r}}_1]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_1] &+ \left[\boldsymbol{\delta} \cdot \left(-\frac{kT}{\zeta}\frac{\partial}{\partial \boldsymbol{r}_1} \ln \Psi + \frac{1}{\zeta}\boldsymbol{F}_1^{(\phi)} + \frac{1}{\zeta}\boldsymbol{F}_1^{(e)}\right)\right] \\ &+ \left[\zeta\boldsymbol{\Omega} \cdot \left(-\frac{kT}{\zeta}\frac{\partial}{\partial \boldsymbol{r}_2} \ln \Psi + \frac{1}{\zeta}\boldsymbol{F}_2^{(\phi)} + \frac{1}{\zeta}\boldsymbol{F}_2^{(e)}\right)\right]\end{aligned} \tag{13.6-6}$$

$$\begin{aligned}[\![\dot{\boldsymbol{r}}_2]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_2] &+ \left[\boldsymbol{\delta} \cdot \left(-\frac{kT}{\zeta}\frac{\partial}{\partial \boldsymbol{r}_2} \ln \Psi + \frac{1}{\zeta}\boldsymbol{F}_2^{(\phi)} + \frac{1}{\zeta}\boldsymbol{F}_2^{(e)}\right)\right] \\ &+ \left[\zeta\boldsymbol{\Omega} \cdot \left(-\frac{kT}{\zeta}\frac{\partial}{\partial \boldsymbol{r}_1} \ln \Psi + \frac{1}{\zeta}\boldsymbol{F}_1^{(\phi)} + \frac{1}{\zeta}\boldsymbol{F}_1^{(e)}\right)\right]\end{aligned} \tag{13.6-7}$$

Next we take two linear combinations of these equations to get the time rate of change of the connector vector $\boldsymbol{Q} = \boldsymbol{r}_2 - \boldsymbol{r}_1$, and the time rate of change of the center of mass location $\boldsymbol{r}_c = \frac{1}{2}(\boldsymbol{r}_1 + \boldsymbol{r}_2)$. We assume that $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, t) = n\psi(\boldsymbol{Q}, t)$ as was done earlier in Eq. 13.2-7; we also write $\boldsymbol{F}^{(c)} = +\boldsymbol{F}_1^{(\phi)} = -\boldsymbol{F}_2^{(\phi)}$ as before. Then we get

$$[\![\dot{\boldsymbol{Q}}]\!] = [\boldsymbol{\kappa} \cdot \boldsymbol{Q}] + \left[(\boldsymbol{\delta} - \zeta\boldsymbol{\Omega}) \cdot \left(-\frac{2kT}{\zeta}\frac{\partial}{\partial \boldsymbol{Q}} \ln \psi - \frac{2}{\zeta}\boldsymbol{F}^{(c)} + \frac{1}{\zeta}(\boldsymbol{F}_2^{(e)} - \boldsymbol{F}_1^{(e)})\right)\right] \tag{13.6-8}$$

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c] + \tfrac{1}{2}\left[\left(\frac{1}{\zeta}\boldsymbol{\delta} + \boldsymbol{\Omega}\right) \cdot (\boldsymbol{F}_1^{(e)} + \boldsymbol{F}_2^{(e)})\right] \tag{13.6-9}$$

From the last equation we see that, in the absence of external forces, the center of mass moves with the fluid. Equation 13.6-8 is the equation for the internal motion.

The inclusion of $\boldsymbol{\Omega}$ in Eq. 13.6-8 complicates the theory considerably. In most of the polymer literature it has been customary to replace $\boldsymbol{\Omega}$ by an "equilibrium-averaged" or "preaveraged" Oseen tensor, defined by[4]

$$\langle \boldsymbol{\Omega} \rangle_{eq} = \int \boldsymbol{\Omega} \psi_{eq} \, d\boldsymbol{Q} = \Omega \boldsymbol{\delta} \tag{13.6-10}$$

where ψ_{eq} is the normalized configurational distribution function at equilibrium. That the average will yield a scalar times the unit tensor is evident from the fact that the integral is isotropic. Then Eq. 13.6-8 becomes identical with Eq. 13.2-7, but with $1/\zeta$ being replaced by $(1/\zeta) - \Omega$, and the differential equation of ψ, in the absence of external forces, is the same as Eq. 13.2-13 with the same replacement.

The Kramers expression for the stress tensor in Eq. A of Table 13.3-1 is unaltered by the inclusion of hydrodynamic interaction. The Giesekus form, however, is obtained from the Kramers form by using an integral over the diffusion equation and, therefore, the final expression for the stress tensor for preaveraged hydrodynamic interaction is the same as that in Eq. D of Table 13.3-1 but with $1/\zeta$ replaced by $(1/\zeta) - \Omega$ (see Problem 13B.8 for Hookean dumbbells with no preaveraging). Also Eq. 13.4-4 is valid if λ_H is replaced by $\tilde{\lambda}_H$ where $\tilde{\lambda}_H = 1/[4H(\zeta^{-1} - \Omega)]$. Thus the inclusion of preaveraged hydrodynamic interaction presents no particular problems; the final results have the same form as those without hydrodynamic interaction. In other words, for Hookean dumbbells we once again get a shear-rate independent viscosity, and an elongational viscosity that increases to infinity at a finite elongation rate.

Inclusion of the non-preaveraged hydrodynamic interaction does lead to a shear-rate-dependent viscosity.[5,6] In recent years attention has shifted away from the use of the Oseen-Burgers hydrodynamic interaction tensor in favor of the Rotne-Prager-Yamakawa tensor,[7,8] since it was found that the Oseen-Burgers tensor can lead to negative values of the translational diffusivity in multibead models.[9,10] The Rotne-Prager-Yamakawa tensor is discussed in §14.6.

EXAMPLE 13.6-1 The Effect of Hydrodynamic Interaction on the Intrinsic Viscosity of a Suspension of Hookean Dumbbells

By using the equilibrium-averaged hydrodynamic interaction, obtain an expression for the intrinsic viscosity of a dilute suspension of Hookean dumbbells.

SOLUTION For this problem Eq. 13.6-10 can be written as follows:

$$\langle \boldsymbol{\Omega} \rangle_{eq} = \frac{\int (1/8\pi\eta_s Q)(\boldsymbol{\delta} + \boldsymbol{QQ}/Q^2) e^{-HQ^2/2kT} d\boldsymbol{Q}}{\int e^{-HQ^2/2kT} d\boldsymbol{Q}} = \Omega \boldsymbol{\delta} \tag{13.6-11}$$

[4] B. H. Zimm, *J. Chem. Phys.*, **24**, 269 278 (1956); J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).

[5] H. C. Öttinger [*J. Chem. Phys.*, **83**, 6535-6536 (1985); **84**, 4068-4073 (1986)] has developed a method of self-consistent averaging, which leads to $\Psi_2 \neq 0$ and viscometric functions that depend on shear rate.

[6] B. H. Zimm, *Ann. N. Y. Acad. Sci.*, **89**, 670-671 (1961).

[7] J. Rotne and S. Prager, *J. Chem. Phys.*, **50**, 4831-4837 (1969).

[8] H. Yamakawa, *J. Chem. Phys.*, **53**, 436-443 (1970).

[9] R. E. DeWames, W. F. Hall, and M. C. Shen, *J. Chem. Phys.*, **46**, 2782-2794 (1967).

[10] R. Zwanzig, J. Kiefer, and G. H. Weiss, *Proc. Nat. Acad. Sci.*, **60**, 381-386 (1968).

These integrals can be evaluated with the help of §E.3 to give

$$\langle \boldsymbol{\Omega} \rangle_{eq} = \sqrt{\frac{H}{2\pi kT}} \frac{1}{3\pi\eta_s} \boldsymbol{\delta} = \Omega\boldsymbol{\delta} \tag{13.6-12}$$

For Hookean dumbbells without hydrodynamic interaction, the intrinsic viscosity can be obtained from Eqs. 13.4-17 and D.5-4:

$$[\eta] = \frac{\tilde{N}kT\zeta}{4MH\eta_s} \tag{13.6-13}$$

where $\tilde{N}$ is Avogadro's number. Therefore for Hookean dumbbell solutions with preaveraged hydrodynamic interaction we have immediately

$$[\eta] = \frac{\tilde{N}kT\zeta}{4MH\eta_s(1 - \sqrt{H/2\pi kT}(\zeta/3\pi\eta_s))} \tag{13.6-14}$$

This shows that the effect of the hydrodynamic interaction is to increase the viscosity. However, with preaveraged hydrodynamic interaction, the viscosity does not decrease as the shear rate increases.

EXAMPLE 13.6-2 Translational Diffusivity of Hookean Dumbbells

The translational diffusivity D_{tr} is related to the friction coefficient Z for the entire molecule (in this case, the dumbbell) by the *Nernst–Einstein equation*[11]

$$D_{tr} = \frac{kT}{Z} \tag{13.6-15}$$

Obtain an expression for the translational diffusivity by considering the motion of the center of mass of the dumbbell as it moves through a quiescent fluid with a force $\boldsymbol{F}^{(e)} = \boldsymbol{F}_1^{(e)} = \boldsymbol{F}_2^{(e)}$ acting on each bead.

SOLUTION From Eq. 13.6-9, with $\boldsymbol{v}_0 = \boldsymbol{0}$ and $\boldsymbol{\kappa} = \boldsymbol{0}$, we get

$$[\![\dot{\boldsymbol{r}}_c]\!] = \frac{1}{\zeta}(\boldsymbol{\delta} + \zeta\boldsymbol{\Omega}) \cdot \boldsymbol{F}^{(e)} \tag{13.6-16}$$

When this equation is multiplied by ψ and integrated over all configurations, then we get

$$\langle \dot{\boldsymbol{r}}_c \rangle = \left[\frac{1}{\zeta}\int (\boldsymbol{\delta} + \zeta\boldsymbol{\Omega})\psi d\boldsymbol{Q}\right] \cdot \boldsymbol{F}^{(e)} \tag{13.6-17}$$

Since the fluid is at rest, we can replace ψ by ψ_{eq} to get

$$\langle \dot{\boldsymbol{r}}_c \rangle = \frac{1}{\zeta}(1 + \zeta\Omega)\boldsymbol{F}^{(e)} \tag{13.6-18}$$

[11] For a derivation of this equation from the general expression for the mass flux, see R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960), Eq. 18.4-14a on p. 568.

The dumbbell friction coefficient Z is defined by

$$2\boldsymbol{F}^{(e)} = Z\langle \dot{\boldsymbol{r}}_c \rangle \tag{13.6-19}$$

By combining Eqs. 13.6-15, 13.6-18, and 13.6-19 we get

$$D_{tr} = \frac{kT}{2\zeta}(1 + \zeta\Omega) \tag{13.6-20}$$

When hydrodynamic interaction is neglected, the term $\zeta\Omega$ does not appear; for the analogous result for the rotatory diffusivity, see Eq. 13.2-13b.

§13.7 ANISOTROPIC EFFECTS

We now wish to go back to Eqs. 13.2-2 and 13.2-3 and explore the consequences of allowing the hydrodynamic drag and the Brownian motion to be anisotropic. That is, we use Eq. 13.2-2 with the symmetric friction tensor $\boldsymbol{\zeta}$ (but without the hydrodynamic interaction perturbation $\boldsymbol{v}'_v$) and Eq. 13.2-3 in which the velocity-space average is taken with respect to a velocity distribution that is not isotropic. Specifically we replace Eq. 13.1-3 by

$$\Xi = \frac{\exp(-(m/2kT)\boldsymbol{\xi} : \sum_v (\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v}))}{\iint \exp(-(m/2kT)\boldsymbol{\xi} : \sum_v (\dot{\boldsymbol{r}}_v - \boldsymbol{v})(\dot{\boldsymbol{r}}_v - \boldsymbol{v}))d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2} \tag{13.7-1}$$

in which the tensor $\boldsymbol{\xi}$ may depend on the configuration coordinates and time; if $\boldsymbol{\xi}$ is the unit tensor this velocity distribution reduces to the Maxwellian distribution.

The velocity distribution in Eq. 13.7-1 should satisfy two conditions. First, we note that the temperature is defined by requiring that the kinetic energy of the beads of a dumbbell with respect to the mass-average velocity $\boldsymbol{v}$ be $3kT$. This requirement is satisfied if $\text{tr}\,\boldsymbol{\xi}^{-1} = 3$. Second, it should be noted that unless $\boldsymbol{\xi}$ reduces to the unit tensor in the limit of no velocity gradient, Eq. 13.7-1 is inconsistent with equilibrium statistical mechanics. The empiricism for $\boldsymbol{\xi}^{-1}$ in Eq. 13.7-7 below is inconsistent with the first requirement, but consistent with the second. The empiricism in Eq. 13.7-13 below satisfies the first requirement, but satisfies the second only if α and β are taken to be functions such that α and β both become unity as the velocity gradient goes to zero.

When Eq. 13.7-1 is used to evaluate the average value in Eq. 13.2-3 we get for the Brownian force on bead v

$$\boldsymbol{F}_v^{(b)} = -\frac{kT}{\Psi}\left[\frac{\partial}{\partial \boldsymbol{r}_v} \cdot \boldsymbol{\xi}^{-1}\Psi\right] \tag{13.7-2}$$

When these anisotropic effects are taken into account, the *diffusion equation* for $\psi(\boldsymbol{Q}, t)$ becomes[1]

$$\boxed{\frac{\partial \psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \left[\boldsymbol{\kappa} \cdot \boldsymbol{Q}\psi - 2kT\,\boldsymbol{\zeta}^{-1} \cdot \left[\frac{\partial}{\partial \boldsymbol{Q}} \cdot \boldsymbol{\xi}^{-1}\psi\right] - 2\boldsymbol{\zeta}^{-1} \cdot \boldsymbol{F}^{(c)}\psi\right]\right)} \tag{13.7-3}$$

[1] R. B. Bird and J. M. Wiest, *J. Rheol.*, **29**, 519–532 (1985); in this paper alternatives to the empiricism in Eq. 13.7-6 are suggested.

When this equation is multiplied by $\boldsymbol{QQ}$ and integrated over all orientations we get the *equation of change for* $\langle \boldsymbol{QQ} \rangle$:

$$\tfrac{1}{2}\langle \boldsymbol{QQ} \rangle_{(1)} = kT\left\langle \xi^{-1} : \left\{ \left(\frac{\partial}{\partial \boldsymbol{Q}} \zeta^{-1} \right) \boldsymbol{Q} + \left[\left(\frac{\partial}{\partial \boldsymbol{Q}} \zeta^{-1} \right) \boldsymbol{Q} \right]^{\dagger} \right\} \right\rangle$$
$$+ kT\langle \{ \zeta^{-1} \cdot \xi^{-1} \} + \{ \xi^{-1} \cdot \zeta^{-1} \} \rangle - \langle \{ \zeta^{-1} \cdot \boldsymbol{F}^{(c)} \boldsymbol{Q} \} + \{ \boldsymbol{Q} \boldsymbol{F}^{(c)} \cdot \zeta^{-1} \} \rangle \qquad (13.7\text{-}4)$$

When $\xi = \delta$ and $\zeta = \zeta\delta$, these last two equations simplify to Eqs. 13.2-13 and 13.2-17 respectively.

When the anisotropic velocity distribution in Eq. 13.7-1 is used to evaluate the last term in Eq. 13.3-14 we are led to[1]

$$\boxed{\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\langle \boldsymbol{Q}\boldsymbol{F}^{(c)} \rangle + 2nkT \langle \xi^{-1} \rangle} \qquad (13.7\text{-}5)$$

We now consider two special cases of the above results.

a. Empiricisms for the Anisotropy Tensors

We now explore the consequences of the following empirical expressions which give the anisotropy tensors ξ and ζ in terms of the macroscopic quantity $\boldsymbol{\tau}_p = \boldsymbol{\tau} - \boldsymbol{\tau}_s$:[2]

$$\zeta^{-1} = \frac{1}{\zeta}\left(\boldsymbol{\delta} - \frac{a}{nkT} \boldsymbol{\tau}_p \right) \qquad (13.7\text{-}6)$$

$$\xi^{-1} = \boldsymbol{\delta} - \frac{b}{nkT} \boldsymbol{\tau}_p \qquad (13.7\text{-}7)$$

where a and b are arbitrary parameters, that have to be determined a posteriori by fitting experimental data. When these expressions for the anisotropy tensors are substituted into Eq. 13.7-5, written for Hookean dumbbells [$\boldsymbol{F}^{(c)} = H\boldsymbol{Q}$], we then get

$$(1 + 2b)\boldsymbol{\tau}_p = -nH\langle \boldsymbol{QQ} \rangle + nkT\boldsymbol{\delta} \qquad (13.7\text{-}8)$$

Convected differentiation gives

$$(1 + 2b)\boldsymbol{\tau}_{p(1)} = -nH\langle \boldsymbol{QQ} \rangle_{(1)} - nkT\dot{\boldsymbol{\gamma}} \qquad (13.7\text{-}9)$$

These equations can be solved for $\langle \boldsymbol{QQ} \rangle$ and $\langle \boldsymbol{QQ} \rangle_{(1)}$ respectively, and these are then substituted into Eq. 13.7-4 after it has been written for Hookean dumbbells with the expressions for ξ^{-1} and ζ^{-1} given above. This leads to the constitutive equation for $\boldsymbol{\tau}_p$:

$$\boldsymbol{\tau}_p + \lambda'_H \boldsymbol{\tau}_{p(1)} - \frac{a}{nkT} \{ \boldsymbol{\tau}_p \cdot \boldsymbol{\tau}_p \} = -nkT\lambda''_H \dot{\boldsymbol{\gamma}} \qquad (13.7\text{-}10)$$

[2] H. Giesekus, *J. Non-Newtonian Fluid Mech.*, **11**, 69–109 (1982); **12**, 367–374 (1983); the idea of a non-isotropic Stokes' law was introduced earlier in H. Giesekus, *Rheol. Acta*, **5**, 29–36 (1966), fn. 11. Giesekus introduced a nonisotropic Brownian motion as we have done in Eq. 13.7-7, but with $b = a$.

where $\lambda'_H = [(1 + 2b)/(1 + b)](\zeta/4H) = (1 + 2b)\lambda''_H$. The constitutive equation can also be written in terms of $\boldsymbol{\tau}$:

$$\boldsymbol{\tau} + \lambda'_H \boldsymbol{\tau}_{(1)} - \frac{a}{nkT}\{\boldsymbol{\tau}\cdot\boldsymbol{\tau}\} - \frac{a\eta_s}{nkT}\{\boldsymbol{\tau}\cdot\boldsymbol{\gamma}_{(1)} + \boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\tau}\}$$
$$= -(\eta_s + nkT\lambda''_H)\boldsymbol{\gamma}_{(1)} + \frac{a\eta_s^2}{nkT}\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(1)}\} - \lambda'_H\eta_s\boldsymbol{\gamma}_{(2)} \tag{13.7-11}$$

It should be noted that the constitutive equation with $b = 0$ (for which $\operatorname{tr}\boldsymbol{\xi}^{-1} = 3$) is the same as Eqs. 13.7-10 and 13.7-11 but with λ'_H and λ''_H both equal to $\lambda_H = \zeta/4H$; for that case reasonably shaped curves were obtained for the material functions when a is in the range $0 \le a \le \frac{1}{2}$.

b. The Encapsulated Dumbbell Model

Bird and DeAguiar[3] developed a simple theory for concentrated solutions and melts by using the elastic dumbbell model. In a melt the molecules are crowded together, so that motion in the direction of the backbone may be easier than motion perpendicular to it. Hence it seems reasonable to introduce a modified Stokes' law that has different friction coefficients in the directions of dumbbell vibration and rotation. This is accomplished by letting

$$\boldsymbol{\zeta}^{-1} = \frac{1}{\zeta}[\sigma\boldsymbol{\delta} + (1 - \sigma)\boldsymbol{uu}] \tag{13.7-12}$$

in which ζ and σ are constants, and $\boldsymbol{u} = \boldsymbol{Q}/Q$ is the unit vector pointing from bead "1" to bead "2." In addition, we wish to explore the consequences of introducing anisotropy into the velocity distribution (and hence also into the Brownian force in the bead equation of motion and into the bead contribution to the stress tensor) by writing

$$\boldsymbol{\xi}^{-1} = \beta\boldsymbol{\delta} + (\alpha - \beta)\boldsymbol{uu} \tag{13.7-13}$$

Here α and β are constants; the requirement that $\operatorname{tr}\boldsymbol{\xi}^{-1} = 3$ implies that $\alpha + 2\beta = 3$. If β is in the range $1 \le \beta \le \frac{3}{2}$, $\boldsymbol{\xi}$ is positive definite.

For these choices for $\boldsymbol{\zeta}$ and $\boldsymbol{\xi}$, Eqs. 13.7-4 and 13.7-5 give

$$\langle\boldsymbol{QQ}\rangle_{(1)} = \frac{4kT}{\zeta}\sigma\beta\boldsymbol{\delta} - \frac{4}{\zeta}\langle\boldsymbol{QF}^{(c)}\rangle + \frac{4kT}{\zeta}(\alpha + 2\beta - 3\sigma\beta)\left\langle\frac{\boldsymbol{QQ}}{Q^2}\right\rangle \tag{13.7-14}$$

$$\boldsymbol{\tau}_p = -n\langle\boldsymbol{QF}^{(c)}\rangle + 2nkT(\alpha - \beta)\left\langle\frac{\boldsymbol{QQ}}{Q^2}\right\rangle + \tfrac{1}{3}nkT(-\alpha + 4\beta)\boldsymbol{\delta} \tag{13.7-15}$$

Bird and DeAguiar considered FENE dumbbells (cf. §13.5) and introduced these approximations:[4]

$$\left\langle\frac{H\boldsymbol{QQ}}{1 - (Q^2/Q_0^2)}\right\rangle \doteq \frac{H\langle\boldsymbol{QQ}\rangle}{1 - \langle Q^2/Q_0^2\rangle}; \qquad \left\langle\frac{\boldsymbol{QQ}}{Q^2}\right\rangle \doteq \frac{\langle\boldsymbol{QQ}\rangle}{\langle Q^2\rangle} \tag{13.7-16a,b}$$

[3] R. B. Bird and J. R. DeAguiar, *J. Non-Newtonian Fluid Mech.*, **13**, 149–160 (1983); J. R. DeAguiar, *ibid.*, 161–179 (1983).

[4] X. J. Fan, *J. Non-Newtonian Fluid Mech.*, **17**, 251–265 (1985), has solved the diffusion equation numerically for steady shear flow, thereby avoiding the approximations in Eq. 13.7-16.

Then, following the procedures used in §13.4 and Example 13.5-2, they eliminated the average values to get a constitutive equation for $\boldsymbol{\tau}_p$:

$$B_\tau \boldsymbol{\tau}_p + \lambda_H \boldsymbol{\tau}_{p(1)} = -(2\beta - 1)nkT\lambda_H \dot{\boldsymbol{\gamma}} + B_\delta \boldsymbol{\delta} \tag{13.7-17}$$

in which

$$B_\tau = \frac{(\sigma\beta - \mathscr{T})Z}{(2\beta - 1 - \mathscr{T})} - \lambda_H \frac{D \ln Z}{Dt} \tag{13.7-18}$$

$$B_\delta = \frac{(\sigma\beta - 2\beta + 1)\mathscr{T}Z}{3(2\beta - 1 - \mathscr{T})} - \frac{1}{3}\lambda_H(2\beta - 1)\frac{D \ln Z}{Dt} \tag{13.7-19}$$

$$Z = \frac{[1 + (3/b)(1 - \mathscr{T})](2\beta - 1 - \mathscr{T})}{1 - \mathscr{T}} \tag{13.7-20}$$

$$\mathscr{T} = \frac{\operatorname{tr} \boldsymbol{\tau}_p}{3nkT} \tag{13.7-21}$$

and, as before, $\lambda_H = \zeta/4H$, and the relation $\alpha + 2\beta = 3$ has been used to eliminate α. DeAguiar[3] found that values of λ_H, b, σ, and β could be obtained to fit experimental data on concentrated polymer solutions. Each of the four parameters is related to some physical aspect of the model: the time constant $\lambda_H = \zeta/4H$ describes the relaxation processes of the model; $b = HQ_0^2/kT$ is a measure of the nonlinearity of the spring; σ indicates the degree of anisotropy in the viscous drag; and β describes the deviation from the Maxwellian velocity distribution. In connection with the parameter β, it may be pointed out that the associated anisotropy in the Brownian motion is closely related to the notion of "reptation"; by the latter one means that the Brownian motion of a chainlike polymer is restricted to the direction along the polymer chain backbone.

PROBLEMS

13A.1 Test of FENE Dumbbell Model

a. From Eqs. 13.5-24 and 13.5-26 obtain the value of shear rate $\dot{\gamma}_0$ for which $\eta - \eta_s$ has dropped to 0.99 of its zero-shear-rate value, and the value of the frequency ω_0 for which $\eta' - \eta_s$ has dropped to 0.99 of its zero-frequency value. Show that

$$\frac{\dot{\gamma}_0}{\omega_0} = \sqrt{\frac{(b + 5)(2b + 11)}{2(4b + 17)}} \underset{b}{\overset{\text{large}}{\longrightarrow}} \frac{\sqrt{b}}{2} \tag{13A.1-1}$$

which was obtained by Graessley.[1]

b. Evaluate $\dot{\gamma}_0/\omega_0$ for $b = 10$, 100, and 1000.

c. Compare these results with some sample data shown in Chapter 3. Can any significant conclusions be drawn from the comparison?

13A.2 Molecular Stretching and Non-Newtonian Viscosity

a. Use the FENE dumbbell model to explore the relation between rheological behavior and molecular stretching in the flow field. Specifically use Eqs. 13.5-24 and 13C.4-1 to estimate how much the molecules have to be stretched beyond their equilibrium length in order for the viscosity η to deviate from η_0 by 1%.

[1] W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1–179 (1974), Eq. 8.19.

b. Use Eq. 13.5-53 to find out whether or not the molecules are stretched out to nearly their maximum length at a shear rate for which $\eta/\eta_0 = 0.01$.

13A.3 Estimation of Kinetic Theory Time Constant

In Fig. 13.5-3 a comparison is given between experimental and theoretical curves for $[\eta']$ and $[\eta'']$. The time constant λ_Q was determined by fitting the data to be $\lambda_Q = 4.215$s. The definition of λ_Q in terms of the model parameters ζ and Q_0^2 is given in Eq. 13.5-3. Use this formula to estimate λ_Q from the molecular weight of the polystyrene ($\bar{M}_w = 860{,}000$, $\bar{M}_w/\bar{M}_n = 1.15$), the structural formula for polystyrene (from which Q_0 can be inferred), and the solvent viscosity $\eta_s = 0.3$ Pa·s.

13B.1 Constitutive Equation for Hookean Dumbbells in Non-Isothermal Flow

The development leading to Eq. 11.3-20 makes it clear that the Hookean spring constant H in general depends on the temperature T. Show that when the development in Eqs. 13.4-1 to 13.4-4 is followed for $H = H(T)$ the following constitutive equation[2] is obtained for τ_p:

$$\boldsymbol{\tau}_p + \frac{\zeta}{4H}\left[\boldsymbol{\tau}_{p(1)} - (\boldsymbol{\tau}_p - nkT\boldsymbol{\delta})\frac{d\ln H}{d\ln T}\frac{D\ln T}{Dt} - nkT\boldsymbol{\delta}\,\frac{D\ln T}{Dt}\right] = -nkT\left(\frac{\zeta}{4H}\right)\dot{\boldsymbol{\gamma}} \tag{13B.1-1}$$

This emphasizes the fact that in nonisothermal systems one cannot simply replace the time constant λ_H in Eq. 13.4-4 by a temperature-dependent function.

13B.2 The Effective-Velocity-Gradient Assumption

In §13.6 the hydrodynamic interaction effect is accounted for by using the Oseen-Burgers tensor and then, because of mathematical complications, one replaces this tensor by its equilibrium-averaged value. An alternative procedure is to replace the fluid velocity at bead v (that is $\boldsymbol{v}_v = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_v]$ in Eq. 13.2-5) by

$$\boldsymbol{v}_v = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_v] - \tfrac{1}{2}\xi[\dot{\boldsymbol{\gamma}}\cdot(\boldsymbol{r}_v - \boldsymbol{r}_c)] \tag{13B.2-1}$$

where ξ is a small quantity[3] that accounts for the difference between the velocity gradient "seen" by the macromolecule and the velocity gradient imposed on the fluid by external forces.

a. Show how the introduction of ξ via Eq. 13B.2-1 changes the dumbbell kinetic theory in §§13.2 and 13.3.

b. Show that the constitutive equation for Hookean dumbbells becomes

$$\boldsymbol{\tau}_p + \lambda_H[\boldsymbol{\tau}_{p(1)} + \tfrac{1}{2}\xi\{\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\tau}_p + \boldsymbol{\tau}_p\cdot\dot{\boldsymbol{\gamma}}\}] = -nkT\lambda_H(1-\xi)\dot{\boldsymbol{\gamma}} \tag{13B.2-2}$$

This is a special case of the Oldroyd 6-constant model of Chapter 7 (see also Eq. D.4-5).

[2] G. Marrucci, *Trans. Soc. Rheol*, **16**, 321-330 (1972). Marrucci's equation was used by R. J. Fisher and M. M. Denn, *AIChE J.*, **23**, 23-28 (1977), to describe nonisothermal polymer-melt spinning.

[3] The parameter ξ was first introduced by R. J. Gordon and W. R. Schowalter, *Trans. Soc. Rheol.*, **16**, 79-97, (1972); see also N. Phan-Thien, O. Manero, and L. G. Leal, *Rheol. Acta*, **23**, 151-162 (1984), and M. W. Johnson, Jr., and D. Segalman, *J. Non-Newtonian Fluid Mech.*, **2**, 255-270 (1977). A relation between ξ and hydrodynamic interaction has been suggested by R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **5**, 1-12 (1979) and R. B. Bird and C. F. Curtiss, *ibid.*, **14**, 85-101 (1984).

c. Show that

$$\eta - \eta_s = \frac{nkT\lambda_H(1-\xi)}{1 + 2\xi(1-\tfrac{1}{2}\xi)(\lambda_H\dot{\gamma})^2} \tag{13B.2-3}$$

$$\Psi_1 = \frac{2nkT\lambda_H^2(1-\xi)}{1 + 2\xi(1-\tfrac{1}{2}\xi)(\lambda_H\dot{\gamma})^2} \tag{13B.2-4}$$

$$\Psi_2 = -\tfrac{1}{2}\xi\Psi_1 \tag{13B.2-5}$$

Are these results realistic as $\dot{\gamma} \to \infty$?

d. Show further that in steady shear flow

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{eq}} = 1 + \frac{2(1-\xi)^2}{3}\,\frac{(\lambda_H\dot{\gamma})^2}{1 + 2\xi(1-\tfrac{1}{2}\xi)(\lambda_H\dot{\gamma})^2} \tag{13B.2-6}$$

What is the value of this ratio in the limit of very large shear rates for some reasonable value of ξ?

13B.3 Configurational Distribution Function for Steady Shear Flow of a Dilute Solution of Hookean Dumbbells

a. Show that, for steady shear flow $v_x = \dot{\gamma}y$, the tensor $\boldsymbol{\alpha}$ in Eq. 13.4-13 is

$$\boldsymbol{\alpha} = \begin{pmatrix} 1 + 2\lambda_H^2\dot{\gamma}^2 & \lambda_H\dot{\gamma} & 0 \\ \lambda_H\dot{\gamma} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{13B.3-1}$$

b. Next show that Eq. 13.4-12 becomes[4]

$$\psi = \left(\frac{H}{2\pi kT}\right)^{3/2} \frac{1}{\sqrt{1+\lambda_H^2\dot{\gamma}^2}} \times \exp\left[-\frac{H}{2kT}\left\{\frac{X^2 - 2\lambda_H\dot{\gamma}XY + (1+2\lambda_H^2\dot{\gamma}^2)Y^2 + (1+\lambda_H^2\dot{\gamma}^2)Z^2}{1+\lambda_H^2\dot{\gamma}^2}\right\}\right] \tag{13B.3-2}$$

where $\lambda_H = \zeta/4H$ and X, Y, and Z are the components of $\boldsymbol{Q}$, which range from $-\infty$ to $+\infty$.

c. Verify that this $\psi(X, Y, Z)$ satisfies Eq. 13.2-13, when the latter is written for steady simple shear flow and for Hookean dumbbells.

d. Obtain the viscosity for the solution by using the Kramers expression for the stress tensor. First show that

$$\eta - \eta_s = \frac{nH}{\dot{\gamma}}\langle XY\rangle = \frac{nH}{\dot{\gamma}}\iiint \psi(X, Y, Z)XY\,dX\,dY\,dZ \tag{13B.3-3}$$

where $\psi(X, Y, Z)$ is the function given in Eq. 13B.3-2. The integrations are made easier by making the changes of variables:

$$\bar{X} = X - \lambda_H\dot{\gamma}Y; \qquad \bar{Y} = \sqrt{1+\lambda_H^2\dot{\gamma}^2}\,Y; \qquad \bar{Z} = \sqrt{1+\lambda_H^2\dot{\gamma}^2}\,Z \tag{13B.3-4}$$

[4] H. A. Kramers, as cited in footnote 8 of J. J. Hermans, *Physica*, **10**, 777-789 (1943); it seems to us that $\exp\mu^2[\ ]$ in that reference should be replaced by $\exp\tfrac{1}{2}\mu^2[\ ]$.

This leads to

$$\eta - \eta_s = \frac{nH}{\dot{\gamma}} \frac{\lambda_H \dot{\gamma}}{1 + \lambda_H^2 \dot{\gamma}^2} \frac{\int_{-\infty}^{+\infty} \bar{Y}^2 e^{-a\bar{Y}^2} d\bar{Y}}{\int_{-\infty}^{+\infty} e^{-a\bar{Y}^2} d\bar{Y}} \tag{13B.3-5}$$

where $a = (H/2kT)/(1 + \lambda_H^2 \dot{\gamma}^2)$. Show that this leads to Eq. 13.4-17.

e. Repeat part (**b**) using the Giesekus expression for the stress tensor (Eq. D of Table 13.3-1).

f. Next use Eq. 13B.3-2 to obtain the expression in Eq. 13.4-20 for the stretching of elastic dumbbells in a shear flow.

13B.4 Expansion of the Potential Flow Distribution Function

In Eq. 13.2-14 the exact distribution function for a dilute solution of elastic dumbbells in steady, homogeneous, potential flow is given. Here we consider how to expand this result to obtain Eq. 13.5-6.

a. Expand $\exp[(\zeta/4kT)(\boldsymbol{\kappa}:\boldsymbol{QQ})]$ as a power series in the argument $(\zeta/kT)(\boldsymbol{\kappa}:\boldsymbol{QQ})$.

b. Determine J/J_{eq} as a power series in $\dot{\gamma}$ by using the fact that ψ is normalized together with the power series expression developed in (**a**). Show that the result through second order is

$$\frac{J}{J_{eq}} = 1 + \frac{1}{15}\left(\frac{\zeta}{8kT}\right)^2 \langle Q^4 \rangle_{eq} (\dot{\gamma}:\dot{\gamma}) + \cdots \tag{13B.4-1}$$

The averages given in Eqs. E.7-4 and E.7-5 are useful in performing the averages over θ and ϕ, which must be done in order to obtain this equation.

c. Insert the expansions in (**a**) and (**b**) into $\psi = \psi_{eq}\phi_{fl}$ and obtain Eq. 13.5-6.

13B.5 Verification of Intermediate Step in Nonlinear Elastic Dumbbell Kinetic Theory

a. First simplify Eq. 13.2-13 for equilibrium and obtain

$$kT \frac{1}{Q^2}\frac{d}{dQ}\left(Q^2 \frac{d\psi_{eq}}{dQ}\right) + \frac{1}{Q^2}\frac{d}{dQ}[Q^2 F^{(c)} \psi_{eq}] = 0 \tag{13B.5-1}$$

To get this it has been recognized that ψ_{eq} is a function of Q alone and that $\boldsymbol{F}^{(c)}$ can also be written as its scalar magnitude $F^{(c)}$ multiplied by $\boldsymbol{Q}/Q$.

b. Substitute Eq. 13.5-5 into Eq. 13.2-13 and obtain

$$\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot \left\{[\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\psi_{eq}\sum\phi_k - \frac{kT}{2H\lambda_H}\frac{\partial}{\partial \boldsymbol{Q}}(\psi_{eq}\sum\phi_k) - \frac{1}{2H\lambda_H}\boldsymbol{F}^{(c)}\psi_{eq}\sum\phi_k\right\}\right) = 0 \tag{13B.5-2}$$

Differentiate the first term as a product of a scalar and a vector and show that one term vanishes; use Eq. 12.3-7 to combine the second two terms. This gives

$$\left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\frac{\partial}{\partial \boldsymbol{Q}}\psi_{eq}\sum\phi_k\right) - \left(\frac{\partial}{\partial \boldsymbol{Q}}\cdot\left(\frac{kT}{2H\lambda_H}\psi_{eq}\frac{\partial}{\partial \boldsymbol{Q}}\sum\phi_k\right)\right) = 0 \tag{13B.5-3}$$

Performing the differentiations and using Eq. 12.3-7 again then yields

$$\left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\left[-\frac{\boldsymbol{F}^{(c)}}{kT}\psi_{eq}\sum\phi_k+\psi_{eq}\frac{\partial}{\partial\boldsymbol{Q}}\sum\phi_k\right]\right)$$
$$-\frac{kT}{2H\lambda_H}\left(-\frac{\boldsymbol{F}^{(c)}}{kT}\psi_{eq}\cdot\frac{\partial}{\partial\boldsymbol{Q}}\sum\phi_k\right)-\frac{kT}{2H\lambda_H}\left(\psi_{eq}\frac{\partial}{\partial\boldsymbol{Q}}\cdot\frac{\partial}{\partial\boldsymbol{Q}}\sum\phi_k\right)=0 \qquad (13B.5\text{-}4)$$

The factor ψ_{eq} can now be removed. When this is done Eqs. 13.5-7, 13.5-8, and so on can be obtained by equating terms of the same order in the velocity gradients.

13B.6 Verification of First-Order Perturbation Solution in the Nonlinear Elastic Dumbbell Kinetic Theory

Verify that Eq. 13.5-10 does satisfy Eq. 13.5-7. Proceed as follows:

a. First show that Eq. 13.5-10 can also be written as

$$\phi_1=\frac{\zeta}{4kT}(\boldsymbol{\kappa}:\boldsymbol{QQ}) \qquad (13B.6\text{-}1)$$

b. Then show that

$$\frac{\partial}{\partial\boldsymbol{Q}}(\boldsymbol{\kappa}:\boldsymbol{QQ})=[\boldsymbol{\kappa}\cdot\boldsymbol{Q}]+[\boldsymbol{\kappa}^{\dagger}\cdot\boldsymbol{Q}] \qquad (13B.6\text{-}2)$$

c. Next show that

$$\left(\frac{\partial}{\partial\boldsymbol{Q}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\right)=0 \qquad (13B.6\text{-}3)$$

d. Use all the above results to complete the proof.

13B.7 The Second Normal Stress Coefficient

In Eq. 13.4-19 it was found that the second normal stress coefficient Ψ_2 is zero. Show that $\Psi_2=0$ is an immediate consequence of the molecular expression for the stress tensor by writing Eq. D of Table 13.3-1 for steady shear flow.

13B.8 Giesekus Form of the Stress Tensor for Hookean Dumbbells with Oseen–Burgers Hydrodynamic Interaction (No Preaveraging)

Show that for Hookean dumbbells Eq. D of Table 13.3-1 has to be replaced by

$$\boldsymbol{\tau}_p=\frac{n\zeta}{4}\langle\boldsymbol{QQ}\rangle_{(1)}+\frac{nkT\zeta}{8\pi\eta_s}\left\langle\frac{1}{Q}\boldsymbol{\delta}+\frac{1}{Q^3}\boldsymbol{QQ}\right\rangle-\frac{n\zeta H}{4\pi\eta_s}\left\langle\frac{1}{Q}\boldsymbol{QQ}\right\rangle \qquad (13B.8\text{-}1)$$

when complete Oseen–Burgers hydrodynamic interaction is taken into account.

13B.9 Approximate Constitutive Equation for FENE-Dumbbells

An interesting derivation of an approximate constitutive equation for nonlinear elastic dumbbells was suggested by Tanner.[5] The main idea is that we have to make a guess for the distribution function. A very simple proposition is that *all* dumbbells have exactly the same orientation and stretching, so that

$$\psi(\boldsymbol{Q}, t) = \delta(\boldsymbol{Q} - \boldsymbol{S}(t)) \tag{13B.9-1}$$

Substitute this rough guess for $\psi(\boldsymbol{Q}, t)$ into Eqs. 13.5-46 and 13.5-47. Follow the general procedure of Example 13.5-2 to eliminate $\boldsymbol{SS}$ and $\boldsymbol{S}^2$ from the two resulting equations. Show that Eq. 13.5-56, with $\varepsilon = 0$, is obtained as a constitutive equation. Can you suggest any other functions that might be better than that in Eq. 13B.9-1?

13B.10 Zero-Shear-Rate Viscosity of Fraenkel Dumbbells

Show that for Fraenkel dumbbells (see Table 11.5-1)

$$\eta_0 - \eta_s = \frac{n\zeta \int_0^\infty Q^4 \exp[-H(Q - Q_0)^2/2kT]dQ}{12 \int_0^\infty Q^2 \exp[-H(Q - Q_0)^2/2kT]dQ} \tag{13B.10-1}$$

Show that in the limit of $H \to \infty$, Eq. 13B.10-1 gives the *rigid dumbbell* result:

$$\eta_0 - \eta_s = nkT\lambda \tag{13B.10-2}$$

where $\lambda = \zeta Q_0^2/12kT$, and that for small HQ_0^2/kT one can obtain systematic deviations from the *Hookean dumbbell* result:

$$\eta_0 - \eta_s = nkT\lambda_H\left(1 + \frac{4}{3}\sqrt{\frac{HQ_0^2}{2\pi kT}} + \cdots\right) \tag{13B.10-3}$$

where $\lambda_H = \zeta/4H$.

13B.11 An Approximate Constitutive Equation for Modified Fraenkel Dumbbells

a. Apply the method of Problem 13B.9 to the modified Fraenkel dumbbell model in which Q_0/Q is replaced by $(Q_0/Q)^2$ in Eq. C of Table 11.5-1. Show that this leads to

$$Z\boldsymbol{\tau}_p + \lambda_H\boldsymbol{\tau}_{p(1)} - \lambda_H(\boldsymbol{\tau}_p - nkT\boldsymbol{\delta})\frac{D \ln Z}{Dt} = -nkT\lambda_H\dot{\gamma} \tag{13B.11-1}$$

in which $\lambda_H = \zeta/4H$, and $Z(\text{tr } \boldsymbol{\tau}_p)$ is given by

$$Z = \frac{1 - \mathscr{T}}{1 - \mathscr{T} + (b/3)} \tag{13B.11-2}$$

where $\mathscr{T} = (\text{tr } \boldsymbol{\tau}_p)/3nkT$ and $b = HQ_0^2/kT$.

b. Let H approach ∞ so that a rigid dumbbell of length Q_0 is produced. Show that a constitutive equation of the form of Eq. 13B.11-1 is obtained, but with λ_H replaced by $\lambda = \zeta Q_0^2/12kT$ and Z replaced by $Y = 1 - \mathscr{T}$. How well do the results of this approximate constitutive equation agree with the exact results in Chapter 14?

[5] R. I. Tanner, *Trans. Soc. Rheol.*, **19**, 37–65 (1975).

13C.1 Retarded-Motion-Expansion Constants for Hookean Dumbbell Solutions

Start with Eq. 13.4-9 and expand the finite strain tensor $\gamma_{[0]}(t, t')$ about $t' = t$; then perform the integration term by term. Compare the result with the retarded-motion expansion in Eq. 6.2-1 and obtain expressions for the coefficients in the expansion. Show that

$$b_1 = \eta_s + nkT\lambda_H \tag{13C.1-1}$$

$$b_k = (-1)^k nkT\lambda_H^k \tag{13C.1-2}$$

and that all other b's are zero. Compare these results with those in Eqs. 13.5-18 to 13.5-23.

13C.2 Dumbbells with "Internal Viscosity"

In this chapter we have discussed dumbbells in which the beads are joined together by some kind of linear or nonlinear spring. One could also invent other kinds of connectors that would account intuitively for other sorts of effects when the molecules are stretched. In one such connector, which has received considerable attention in the literature, the connector tension is represented as a Hookean spring and a linear dashpot in parallel.[6] That is, it is imagined that the molecule has some kind of "internal viscosity." We thus write

$$\boldsymbol{F}^{(c)} = H\boldsymbol{Q} + K\left(\frac{\boldsymbol{Q}}{Q}\right)\dot{Q} \tag{13C.2-1}$$

in which H and K are constants. This kind of force law presents a problem: since it involves non-conservative forces, we cannot use the methods of Chapter 12 to obtain the equilibrium configurational distribution function, and hence we do not have a proper starting point for doing the nonequilibrium kinetic theory.

The various publications on this subject[6] have essentially replaced $\dot{Q}$ in Eq. 13C.2-1 by $[\![\dot{Q}]\!]$. Show that this allows Eq. 13C.2-1 to be written as

$$\boldsymbol{F}^{(c)} = H\boldsymbol{Q} + K\left(\frac{\boldsymbol{QQ}}{Q^2}\right)\cdot[\![\dot{\boldsymbol{Q}}]\!] \tag{13C.2-2}$$

According to this equation the internal-viscosity contribution to $\boldsymbol{F}^{(c)}$ depends on the *average* rate of stretching of the dumbbells.

Next show that for the force law of Eq. 13C.2-2, the internal equation of motion corresponding to Eq. 13.2-7 is, in the absence of external forces,

$$[\![\dot{\boldsymbol{Q}}]\!] = \left[\left(\boldsymbol{\delta} - \frac{1}{(\zeta/2K)+1}\frac{\boldsymbol{QQ}}{Q^2}\right)\cdot\left([\boldsymbol{\kappa}\cdot\boldsymbol{Q}] - \frac{2kT}{\zeta}\frac{\partial}{\partial\boldsymbol{Q}}\ln\psi - \frac{2}{\zeta}H\boldsymbol{Q}\right)\right] \tag{13C.2-3}$$

This has to be substituted into Eq. 13.2-12 to get the differential equation for ψ; the solution of this equation is not easy. Booij and van Wiechen[7] give a solution in powers of a dimensionless parameter

[6] W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **28**, 1533-1579 (1945); **29**, 71-94 (1946); R. Cerf, *Adv. in Polym. Phys.* **1**, 382-450 (1959); A. Peterlin, *J. Polym. Sci.*, **A2**, **5**, 179-193 (1967); A. Peterlin and C. Reinhold, *Trans. Soc. Rheol.*, **11**, 15-37 (1967); E. R. Bazúa and M. C. Williams, *J. Chem. Phys.*, **59**, 2858-2868 (1973); *J. Polym. Sci. (Phys.)*, **A2**, **12**, 825-848 (1974); M. C. Williams, *AIChE J.*, **21**, 1-25 (1975); C. W. Manke and M. C. Williams, *Macromolecules*, **18**, 2045-2051 (1985); *J. Non-Newtonian Fluid Mech.*, **30**, 19-28 (1986); G. G. Fuller and L. G. Leal, *J. Non-Newtonian Fluid Mech.*, **8**, 271-310 (1981); N. Phan-Thien, J. D. Atkinson, and R. I. Tanner [*J. Non-Newtonian Fluid Mech.*, **3**, 309-330 (1978) have used a Langevin approach to do the kinetic theory for a nonlinear dumbbell, with a frictional coefficient that depends on Q, and internal viscosity.

[7] H. C. Booij and P. H. van Wiechen, *J. Chem. Phys.*, **52**, 5056-5068 (1970).

containing K. Their results show that this model (with no "hydrodynamic interaction" included) gives a shear-rate-dependent viscosity, a finite limiting value for $\eta'(\omega)$ as $\omega \to \infty$, and a partial description of the flow experiment in which small amplitude oscillations are superposed on steady shear flow.

13C.3 Energy Dissipation in Hookean Dumbbell Solutions[8]

a. Form the double-dot product of Eq. A of Table 13.3-1 (with the external-force terms omitted) with $\dot{\gamma}$, and then specialize to Hookean dumbbells to get

$$-(\tau:\dot{\gamma}) = \eta_s(\dot{\gamma}:\dot{\gamma}) + nH(\dot{\gamma}:\langle \boldsymbol{QQ}\rangle) \tag{13C.3-1}$$

b. For steady shear flow we know that τ can be represented by the CEF equation in Eq. 9.6-18 (or Eq. D.4-4). Show that the introduction of this expression into Eq. 13C.3-1 leads to

$$\eta(\dot{\gamma}:\dot{\gamma}) = \eta_s(\dot{\gamma}:\dot{\gamma}) + nH(\dot{\gamma}:\langle \boldsymbol{QQ}\rangle) \tag{13C.3-2}$$

Note that Ψ_1 and Ψ_2 have dropped out. Interpret the result.

c. Specialize to the flow $v_x = \dot{\gamma}y$ with $\dot{\gamma}$ = constant and show that this leads directly to $\eta - \eta_s = (nH/\dot{\gamma})\langle XY\rangle$, in which X and Y are Cartesian components of $\boldsymbol{Q}$.

d. Next show how to derive the result in (**c**) by making dissipation arguments at the molecular level. That is, obtain an expression for the viscosity by considering the viscous dissipation associated with the bead movement through the fluid; this method then avoids going through any of the development in §13.3. The energy dissipated by the motion of a bead through the fluid equals the product of the velocity of the bead relative to that of the fluid multiplied by the hydrodynamic drag force acting on the bead. Therefore in a solution

$$E_v = \text{energy dissipation} = n\zeta \sum_{\nu=1}^{2} \langle (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}_\nu)\cdot(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}_\nu)\rangle \tag{13C.3-3}$$

Now replace the second $(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}_\nu)$ by the sum of the Brownian motion and spring terms using Eq. 13.2-5. Show that the integration over velocities then leads to

$$E_v = n\left\langle \sum_{\nu=1}^{2} [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu]\cdot\left(kT\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln\Psi - \boldsymbol{F}_\nu^{(\phi)}\right)\right\rangle \tag{13C.3-4}$$

or

$$E_v = n\left\langle [\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot kT\frac{\partial}{\partial \boldsymbol{Q}}\ln\psi + [\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\cdot\boldsymbol{F}^{(c)}\right\rangle \tag{13C.3-5}$$

Show that the Brownian motion term is zero, and that for Hookean dumbbells and for steady simple shear flow $v_x = \dot{\gamma}y$ the remaining term can be simplified to give

$$E_v = nH\dot{\gamma}\langle XY\rangle \tag{13C.3-6}$$

Then obtain the result in (**c**) by equating this to the appropriate macroscopic expression.

[8] This problem is based on a discussion by J. Riseman and J. G. Kirkwood, in *Rheology*, F. R. Eirich (Ed.), Academic Press, New York (1956), Vol. 1, Chapter 13, pp. 495–523; see particularly Section III.

13C.4 Stretching of FENE Dumbbells in Steady-State Shear Flow

Show that the FENE dumbbell analog of Eq. 13.4-20 is

$$\frac{\langle Q^2\rangle}{Q_0^2} = \frac{3}{b+5}\left[1 + \frac{2b^2(b+2)}{3(b+5)(b+7)(b+9)}(\lambda_H\dot{\gamma})^2 + \cdots\right] \tag{13C.4-1}$$

13C.5 Stretching of Hookean Dumbbells in Flow Associated with a Line Sink

In Problem 6B.5 the flow of a third-order fluid near a line sink is discussed; in Example 8.4-1 the same flow is considered for a convected Jeffreys (the "Oldroyd-B") model.

a. Use the results of Problem 6B.5 and the third-order fluid constants for Hookean dumbbells in Problem 13C.1 to find the molecular stretching in the flow $v_r = C/r$, $v_\theta = 0$, $v_z = 0$:

$$\frac{\langle Q^2\rangle}{\langle Q^2\rangle_{eq}} = 1 + \frac{2}{3}\left(\frac{2C\lambda_H}{r^2}\right)^2 + 2\left(\frac{2C\lambda_H}{r^2}\right)^3 \tag{13C.5-1}$$

Interpret the result.

b. Next obtain the components of the $\gamma_{[0]}$ tensor for the line source (or sink) flow, and then use the second line of Eq. 13.4-11 to get the result in Eq. 13C.5-1.

c. Show how to use Eqs. 13.4-12 and 13.4-13 to get the configuration-space distribution function at all points in the flow field.

13C.6 Use of Dumbbell Models in Nondilute Solutions[9]

In §13.6 we show how hydrodynamic interaction can be included in the modeling of dilute polymer solutions. As the polymer concentration is increased the hydrodynamic interaction becomes less important because of the "shielding" of distant parts of a single polymer owing to the fact that other molecules are interposed. Wang and Zimm,[9] using some results from the theory of flow through porous media, obtain an expression for Ω that is different from that in Eq. 13.6-11, namely:

$$\Omega = \frac{1}{6\pi\eta_s}\frac{4\pi\int_0^\infty Q\exp(-2\psi_0\sqrt{HQ^2/2kT})\exp(-HQ^2/2kT)dQ}{(2\pi kT/H)^{3/2}} \tag{13C.6-1}$$

where $\psi_0 = \sqrt{nkT\zeta/H\eta_s}$ is a "shielding coefficient." Show that this can be integrated to give

$$\Omega = \frac{1}{3\pi\eta_s}\sqrt{\frac{H}{2\pi kT}}(1-\Delta) \tag{13C.6-2}$$

where

$$\Delta = \sqrt{\pi}\psi_0(\text{erfc }\psi_0)(\exp\psi_0^2) \tag{13C.6-3}$$

Note that in the limit of infinite dilution ($n \to 0$), both ψ_0 and Δ go to zero. Finally obtain for the viscosity

$$\eta - \eta_s = \frac{nkT\lambda_H}{1 - \sqrt{H/2\pi kT}\,(\zeta/3\pi\eta_s)(1-\Delta)} \tag{13C.6-4}$$

[9] F. W. Wang and B. H. Zimm, *J. Polym. Sci., Polymer Physics Edition* **12**, 1619–1637 (1974); the Wang–Zimm paper deals with bead-spring chains rather than with dumbbells.

In the limit of $n \to 0$, Eq. 13C.6-4 becomes the same as Eq. 13.6-14. The value of ψ_0 for the "free draining result" is obtained setting $\Delta = 1$ in Eq. 13C.6-3. This theory of hydrodynamic shielding describes the transition from "Zimm-like" behavior (infinite dilution) to "Rouse-like" behavior (solution sufficiently concentrated that hydrodynamic effects are unimportant).

13C.7 Thermodynamic Quantities for Flowing Dilute Polymer Solutions (Hookean Dumbbell Model)

To get the *internal energy* of a polymer solution one must add up all the kinetic energies and potential energies of interaction in the system. If we model the polymer as a bead-spring chain, then the polymer contribution to the internal energy is the sum of the kinetic energies of the beads and the potential energies associated with the springs. The polymer contribution to the internal energy (per unit volume) of a flowing polymer solution, with the macromolecules modeled as Hookean dumbbells, is then[10]

$$U_{\text{flow}} = \iiiint \left(\frac{1}{2} HQ^2 + \sum_{\nu=1}^{2} \frac{1}{2} m\dot{r}_\nu^2 \right) F(\boldsymbol{r}_1, \boldsymbol{r}_2, \dot{\boldsymbol{r}}_1, \dot{\boldsymbol{r}}_2) d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2$$

$$= n \int \frac{1}{2} HQ^2\, \psi(\boldsymbol{Q}, t) d\boldsymbol{Q} + \text{const.} \tag{13C.7-1}$$

The constant arises from integrating the kinetic energy over all velocity space, with Eq. 13.1-3 being used for the velocity space distribution; because of the assumption of equilibration in momentum space (Eq. 13.1-3) this constant is independent of the flow field.

a. Use Eqs. 13C.7-1 and 13.4-12 [$\psi(\boldsymbol{Q}, t)$ for any flow field] to get for the *internal energy*:

$$U_{\text{flow}} = \tfrac{1}{2} nkT \operatorname{tr} \boldsymbol{\alpha} + \text{const.} \tag{13C.7-2}$$

Show that the change of internal energy from equilibrium to steady-state shear flow with shear rate $\dot{\gamma}$ is

$$\Delta U = U_{\text{flow}} - U_{\text{eq}} = nkT\, \lambda_H^2 \dot{\gamma}^2 \tag{13C.7-3}$$

Does this agree with your intuition?

b. The *entropy* (per unit volume) of the polymer solution in a flow situation is[11]

$$S_{\text{flow}} = -k \iiiint F \ln F\, d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, d\dot{\boldsymbol{r}}_1\, d\dot{\boldsymbol{r}}_2 + \text{const.}$$

$$= -nk \int \psi \ln \psi\, d\boldsymbol{Q} + \text{const.} \tag{13C.7-4}$$

in which F is the distribution function of Eq. 13.1-1, and ψ is that of Eq. 13.1-2. Show that the use of Eq. 13.4-12 leads to

$$\Delta S = S_{\text{flow}} - S_{\text{eq}} = nk \ln \sqrt{\det \boldsymbol{\alpha}} \tag{13C.7-5}$$

or that for steady-state shear flow

$$\Delta S = nk \ln \sqrt{1 + \lambda_H^2 \dot{\gamma}^2} \tag{13C.7-6}$$

[10] See H. C. Booij, *J. Chem. Phys.*, **80**, 4571-4572 (1984); G. Marrucci, *Trans. Soc. Rheol.*, **16**, 321-330 (1972); G. C. Sarti and G. Marrucci, *Chem. Eng. Sci.*, **28**, 1053-1059 (1973).

[11] See, for example, R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, London (1938), or L. Landau and E. M. Lifshitz, *Statistical Physics*, Addison-Wesley, Reading, MA (1958).

That is, as the shear rate increases, the dumbbells tend to become more and more aligned, and the entropy *increases*.

Does this agree with your intuition?

c. The *Helmholtz free energy*, $A = U - TS$, can now be obtained. Show that

$$\Delta A = \tfrac{1}{2} nkT[\mathrm{tr}(\boldsymbol{\alpha} - \boldsymbol{\delta}) - \ln(\det \boldsymbol{\alpha})] \tag{13C.7-7}$$

in agreement with Eq. 10 in the paper by Booij.[10]

For an extension of the ideas in this problem to more general molecular models with constraints see Problem 16C.6.

CHAPTER 14

THE RIGID DUMBBELL AND MULTIBEAD-ROD MODELS

In the preceding chapter we showed how rheological properties of flexible macromolecules, such as polyethylene, polystyrene, and polyisobutylene, can be described approximately by means of elastic dumbbell models. These models account for the orientation and stretching of the individual polymer molecules in the fluid. Admittedly the models are drastic oversimplifications of the true system, but by using these models we can illustrate many problem-solving techniques.

In this chapter we turn to macromolecules that are rodlike, such as isotactic polypropylene, poly-*n*-butylisocyanate, proteins in helical forms, DNA in its helix configuration, and tobacco mosaic virus (see Fig. 11.5-2). Here we use the rigid dumbbell as the simplest mechanical model for these molecules. This model accounts for the orientability of the polymer molecules in flow fields and ignores the less important molecular stretching and bending motions, which are undoubtedly of minor importance in the rheological properties.

Many of the results of this chapter can be generalized rather easily to multibead rod models just by appropriate changes in notation. We indicate in this chapter how these generalizations can be performed, but the justification is postponed until Chapter 16 where the equations for general bead-spring-rod models are given. The notation for the dumbbell and associated multibead-rod models is given in §14.1.

The main kinetic theory equations are presented in §14.2 and 14.3, where the diffusion equation for the orientational distribution function and the expression for the stress tensor are given. In §14.4 we show how to solve the diffusion equation for several simple flows and how to use the results for obtaining the rheological properties. In the next section, §14.5, the analysis is extended to arbitrary, time-dependent, homogeneous flows, and the constitutive equation is expressed in the form of the first several terms of a memory-integral expansion. In the final section, §14.6, we include the hydrodynamic interaction in the modeling of the rodlike macromolecules.

An important reason for including rigid dumbbells immediately after elastic dumbbells is to enable us to compare and contrast the key kinetic theory equations for the two models. Since the rigid dumbbell model has a constraint (i.e., the interbead distance is held constant), we are forced to work in a two-dimensional configuration space and it is convenient to use the two polar angles as the generalized coordinates for the system. As a result the diffusion equation and the stress-tensor expression have forms that are different from the analogous equations for elastic dumbbells. Similar differences occur later in the book between bead-spring chain and bead-rod chain models.

In this chapter we consider only the bead-rod models, but it must be recognized that there is a vast literature on the hydrodynamics of rigid particles, such as ellipsoids, rigid rods, and other bodies of revolution.[1]

§14.1 MODELING OF SOLUTIONS OF RODLIKE POLYMERS

The mechanical model to be used throughout most of this chapter is the rigid dumbbell model shown in Fig. 14.1-1. This model consists of two point masses ("beads") joined by a massless rod, and the interaction with the solvent is presumed to take place only at the beads. We label the beads "-1" and "1" since this enables some equations to be written in a more compact form. Also it is then possible to generalize the rigid dumbbell results rather easily to the multibead rod models of Fig. 14.1-2; such generalizations will be pointed out from time to time during this chapter. Hence, although the chapter is written primarily in terms of the simple rigid dumbbell model, the techniques introduced here apply to a more general class of mechanical models.

As in §13.1 we take the flow field of the polymer solution to be homogeneous, and we use $\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^\dagger$ to describe the velocity gradients in the fluid. We replace the phase-space distribution function $f(\boldsymbol{r}_c, \theta, \phi, \boldsymbol{p}_c, P_\theta, P_\phi, t)$ by the corresponding distribution function in the position-generalized-velocity space $F(\boldsymbol{r}_c, \theta, \phi, \dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, t)$. Then we define the distribution function $\Xi(\dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, \boldsymbol{r}_c, \theta, \phi, t)$ by[1]

$$\begin{aligned} F(\boldsymbol{r}_c, \theta, \phi, \dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, t) \\ &= \Psi(\boldsymbol{r}_c, \theta, \phi, t)\Xi(\dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, \boldsymbol{r}_c, \theta, \phi, t) \\ &\doteq n\psi(\theta, \phi, t)\Xi_{eq}(\dot{\boldsymbol{r}}_c, \dot{\theta}, \dot{\phi}, \theta) \end{aligned} \tag{14.1-1}$$

Because of the constraint in the system (the rigid-rod connector) the configuration is specified by giving just two configuration coordinates, namely the polar angles θ and ϕ, or alternatively the unit vector $\boldsymbol{u}$ pointing from bead "-1" to bead "1." The fraction of dumbbells that at time t are in the orientation range θ, ϕ to $\theta + d\theta, \phi + d\phi$ is then given by $\psi(\theta, \phi, t)d\theta\, d\phi$, where $0 \leq \theta < \pi$ and $0 \leq \phi < 2\pi$. For many purposes it is convenient to use a different configurational distribution function, $f(\boldsymbol{u}, t) = (1/\sin\theta)\psi(\theta, \phi, t)$. At equilibrium the configurational distribution functions ψ and f are given by

$$\psi_{eq}(\theta, \phi) = \frac{\sin\theta}{4\pi}; \qquad f_{eq} = \frac{1}{4\pi} \tag{14.1-2}$$

[1] The pioneering work on rigid ellipsoids includes G. B. Jeffery, *Proc. Roy. Soc.*, **A102**, 161-179 (1922); J. M. Burgers, *Kon. Ned. Akad. Wet. Verhand.* (Eerste Sectie), **16**, 113-184 (1938); A. Peterlin and H. A. Stuart, *Z. Phys.*, **112**, 1-19. 129-147 (1939); N. Saitō, *J. Phys. Soc. Japan*, **6**, 297-301, 302-304 (1951); H. A. Scheraga, *J. Chem. Phys.*, **23**, 1526-1532 (1955); and H. Giesekus, *Rheol. Acta*, **2**, 50-62 (1962). In the Giesekus publication it is reported that $-\Psi_2/\Psi_1$ is $\frac{2}{7}$ for extremely flat (oblate) ellipsoids and $\frac{1}{7}$ for extremely elongated (prolate) ellipsoids. For extensive reviews of suspension rheology see H. Brenner, *Int. J. Multiphase Flow*, **1**, 195-341 (1974); H. Brenner, *Chem. Eng. Sci.*, **27**, 1069-1107 (1972); H. Brenner and D.W. Condiff, *J. Coll. Interface Sci.*, **47**, 199-264 (1974). Exact hydrodynamic analyses of the dumbbell models have been given by S. Wakiya, *J. Phys. Soc. Japan*, **31**, 1581-1587 (1971) and by A. Nir and A. Acrivos, *J. Fluid Mech.*, **59**, 209-223 (1973), the latter for the osculating dumbbell. Analytical results for many limiting cases have been worked out by E. J. Hinch and L. G. Leal, *J. Fluid Mech.*, **52**, 683-712 (1972), **56**, 803-813 (1972), **57**, 753-767 (1973); L. G. Leal and E. J. Hinch, *ibid.*, **46**, 685-703 (1971), **55**, 745-765 (1972).

[1] It is customary to replace the velocity-space distribution function Ξ by its equilibrium expression Ξ_{eq} which is:

$$\Xi_{eq} \propto \exp\left(-\frac{m}{2kT}[2(\dot{\boldsymbol{r}}_c - \boldsymbol{v})^2 + \tfrac{1}{2}L^2\dot{\boldsymbol{u}}^2]\right) \tag{14.1-1a}$$

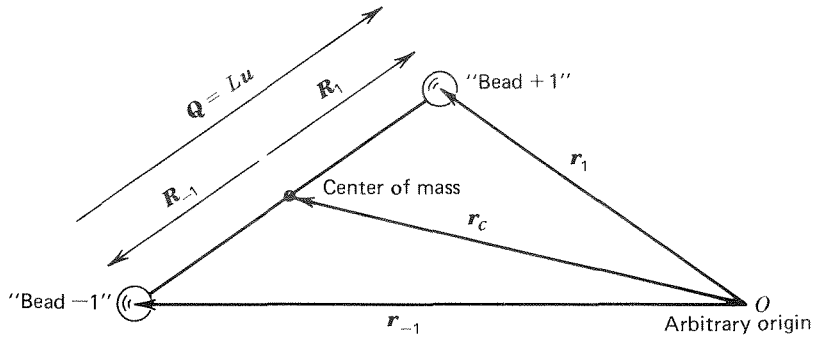


FIGURE 14.1-1. Rigid dumbbell model, with two point masses connected by a massless rigid rod of length L. The unit vector $\boldsymbol{u}$ points in the direction from bead "-1" to bead "$+1$."

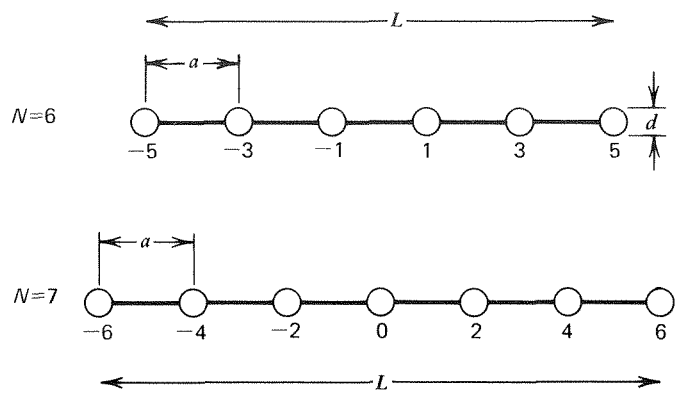


FIGURE 14.1-2. Multibead rods of length L with N evenly spaced beads; note that $L = (N-1)a$. When N is even, beads are numbered $\nu = \pm 1, \pm 3, \ldots$; when N is odd, beads are numbered $\nu = 0, \pm 2, \pm 4, \ldots$. The unit vector $\boldsymbol{u}$ gives the direction from $-\nu$ to $+\nu$, and $\boldsymbol{R}_\nu = (L\nu/2(N-1))\boldsymbol{u} = (\nu a/2)\boldsymbol{u}$ gives the location of bead ν with respect to the center of mass of the rod. The ratio d/a is called ξ, with $0 \le \xi \le 1$. When $\xi = 1$ the beads are just touching, and such a multibead rod is called an "osculating multibead rod."

These equations just state that all orientations are equally likely.

The distribution functions are normalized thus:

$$\iint \psi(\theta, \phi, t)d\theta\, d\phi = 1; \qquad \int f(\boldsymbol{u}, t)d\boldsymbol{u} = 1 \tag{14.1-3}$$

in which $\int \cdots d\boldsymbol{u}$ is exactly the same as $\iint \cdots \sin\theta\, d\theta\, d\phi$. In addition, average values of quantities that depend only on the configuration of the dumbbells are obtained as follows:

$$\langle B \rangle = \iint B(\theta, \phi)\psi(\theta, \phi, t)d\theta\, d\phi \tag{14.1-4a}$$

$$\langle B \rangle = \int B(\boldsymbol{u})f(\boldsymbol{u}, t)d\boldsymbol{u} \tag{14.1-4b}$$

As in the previous chapters the double brackets $[\![\ ]\!]$ are used to indicate averages in momentum (or velocity) space.

In setting up the force balance we proceed as in Chapter 13, except that there is now no intramolecular force. The force balance therefore includes only the hydrodynamic force (the resistance experienced by the bead as it moves through the solution), the Brownian force (a suitably time-smoothed force accounting for the force due to thermal motions), and the external force. The exact form of the Brownian force in a system with constraints is derived in Chapter 18, and in this chapter we take over the results of this later derivation.

It is convenient in this chapter to present most of the formal development by using the orientation vector $\boldsymbol{u}$ rather than the angles θ and ϕ. In so doing we use some shorthand notation, such as $d\boldsymbol{u} = \sin\theta\, d\theta\, d\phi$ already introduced. We also use an operator

$$\frac{\partial}{\partial \boldsymbol{u}} = \boldsymbol{s}\frac{\partial}{\partial\theta} + \boldsymbol{t}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} \tag{14.1-5}$$

in which $\boldsymbol{s}$ and $\boldsymbol{t}$ are the unit vectors described in §11.6 and whose components and derivatives are summarized in §E.5. It should be noted that the $\partial/\partial\boldsymbol{u}$ operator does not obey the usual rules of calculus for the $\partial/\partial\boldsymbol{r}$ (or ∇) operator. Some useful relations involving the $\partial/\partial\boldsymbol{u}$ operator are given in §E.6 in Appendix E.

Finally the time derivative of the orientation vector $\boldsymbol{u}$ is

$$\dot{\boldsymbol{u}} = \boldsymbol{s}\dot{\theta} + \boldsymbol{t}\dot{\phi}\sin\theta \tag{14.1-6}$$

With this and other relations given above we can go back and forth between relations written explicitly in terms of the angles θ and ϕ and those written formally in terms of the orientation vector $\boldsymbol{u}$.

§14.2 THE "DIFFUSION EQUATION" FOR THE CONFIGURATIONAL DISTRIBUTION FUNCTION

We begin by writing the equation of motion for the center of mass of the dumbbell and also that for the internal (i.e., rotatory) motion. The latter may be combined with an equation of continuity in the configuration space to obtain the second-order differential equation for the distribution function $f(\boldsymbol{u}, t)$. The pattern of the development is not quite parallel to that in §13.2 for elastic dumbbells because of the constraint of fixed interbead distance in the rigid dumbbell.

a. The Equations of Motion for the Beads of the Dumbbell

The usual statement of Newton's law of motion as "mass times acceleration equals the sum of the forces" is valid only when there are no constraints in the system. As a consequence we *cannot* write, by analogy with Eq. 13.2-1, a force balance of the form $\boldsymbol{F}_{\nu}^{(h)} + \boldsymbol{F}_{\nu}^{(b)} + \boldsymbol{F}_{\nu}^{(e)} = \boldsymbol{0}$ (here there is no spring force $\boldsymbol{F}_{\nu}^{(\phi)}$, and, as in §13.2, we assume that inertial forces can be neglected). That is, in a molecular model with constraints, we cannot set the sum of the forces on each bead equal to zero.

To get the equation of motion (i.e., force balance) for the entire molecular model we can, however, set the sum of the forces acting on the center of mass equal to zero; this is equivalent to writing

$$\sum_{v} [\boldsymbol{F}_v^{(h)} + \boldsymbol{F}_v^{(b)} + \boldsymbol{F}_v^{(e)}] = \boldsymbol{0} \tag{14.2-1}$$

where the sum is over the two terms $v = 1$ and $v = -1$. This equation describes the translational motion of the molecular model as a whole; the forces acting on the center of mass sum to zero, since there are no constraints on the location of the center of mass.

To get the equation of motion for the internal degrees of freedom of the rigid dumbbell model (that is, the motion in the θ- and ϕ-directions), we add up the differences of the various types of forces $\boldsymbol{F}_1^{(\ )} - \boldsymbol{F}_{-1}^{(\ )}$ and then "project out" the θ- and ϕ-components by multiplying the sum by $(\boldsymbol{\delta} - \boldsymbol{uu})$:

$$[(\boldsymbol{\delta} - \boldsymbol{uu}) \cdot ((\boldsymbol{F}_1^{(h)} - \boldsymbol{F}_{-1}^{(h)}) + (\boldsymbol{F}_1^{(b)} - \boldsymbol{F}_{-1}^{(b)}) + (\boldsymbol{F}_1^{(e)} - \boldsymbol{F}_{-1}^{(e)}))] = \boldsymbol{0} \tag{14.2-2}$$

Keep in mind that $\boldsymbol{\delta} - \boldsymbol{uu} = \boldsymbol{ss} + \boldsymbol{tt}$, so that $[(\boldsymbol{\delta} - \boldsymbol{uu}) \cdot \boldsymbol{F}] = \boldsymbol{s}F_\theta + \boldsymbol{t}F_\phi$, the latter containing the θ- and ϕ-components of the vector $\boldsymbol{F}$. The rigid dumbbell just has two internal degrees of freedom, described by the configuration coordinates, θ and ϕ, and there is one equation of motion corresponding to each of these two degrees of freedom. The systematic approach for obtaining the equations of motion for arbitrary models with constraints is given in Chapters 16–18.

In order to implement Eqs. 14.2-1 and 14.2-2 above, we need expressions for the various forces acting on the beads:

$$\boldsymbol{F}_v^{(b)} = -v \frac{kT}{L} \frac{\partial}{\partial \boldsymbol{u}} \ln f \qquad (v = \pm 1) \tag{14.2-3}$$

$$\begin{aligned} \boldsymbol{F}_v^{(h)} &= -\zeta([\![\dot{\boldsymbol{r}}_v]\!] - \boldsymbol{v}_v) \\ &= -\zeta([\![\dot{\boldsymbol{r}}_c]\!] + \tfrac{1}{2}vL[\![\dot{\boldsymbol{u}}]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c] - \tfrac{1}{2}vL[\boldsymbol{\kappa} \cdot \boldsymbol{u}]) \qquad (v = \pm 1) \end{aligned} \tag{14.2-4}$$

Here the Brownian motion expression is similar in form to the $-kT(\partial \ln \Psi / \partial \boldsymbol{r}_v)$ term in Eq. 13.2-5 and is consistent with the assumption of a Maxwellian velocity distribution. The Stokes' law expression assumes that the hydrodynamic drag is isotropic, and it is further assumed that the fluid velocity field is homogeneous so that $\boldsymbol{v}_v = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_v]$.

When these expressions for the forces are substituted into Eq. 14.2-1 we get the average velocity for the dumbbell center of mass:

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c] + \frac{1}{2\zeta}(\boldsymbol{F}_1^{(e)} + \boldsymbol{F}_{-1}^{(e)}) \tag{14.2-5}$$

This states that the centers of mass of the dumbbells on the average move with the fluid velocity if no external forces are present.

When the force expressions are substituted into Eq. 14.2-2 we obtain the average time rate of change of the orientation vector $\boldsymbol{u}$:

$$[\![\dot{\boldsymbol{u}}]\!] = [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] - \frac{1}{6\lambda} \frac{\partial}{\partial \boldsymbol{u}} \ln f - \frac{1}{\zeta L}[(\boldsymbol{\delta} - \boldsymbol{uu}) \cdot (\boldsymbol{F}_1^{(e)} - \boldsymbol{F}_{-1}^{(e)})] \tag{14.2-6}$$

in which $\lambda = \zeta L^2/12kT$ is the time constant for the rigid dumbbell. It should be emphasized that this equation contains only a θ- and ϕ-component. Keep in mind that $[\![\dot{\boldsymbol{u}}]\!] = s[\![\dot{\theta}]\!] + \boldsymbol{t}[\![\dot{\phi}]\!] \sin\theta$; that $[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu}]$ is the same as $s[\boldsymbol{\kappa}\cdot\boldsymbol{u}]_\theta + \boldsymbol{t}[\boldsymbol{\kappa}\cdot\boldsymbol{u}]_\phi$; and that $\partial/\partial\boldsymbol{u} = s\,\partial/\partial\theta + \boldsymbol{t}\,(\sin\theta)^{-1}\,\partial/\partial\phi$ is a two-dimensional analog of a ∇-operator (see §E.6). In the ensuing discussion we let $[(\boldsymbol{\delta} - \boldsymbol{uu})\cdot(\boldsymbol{F}_1^{(e)} - \boldsymbol{F}_{-1}^{(e)})] = (2/L)\partial\phi^{(e)}/\partial\boldsymbol{u}$, where $\phi^{(e)}$ is the external potential; it is assumed that $\phi^{(e)}$ does not depend on the center of mass location (that is, on $\boldsymbol{r}_c$).

b. The Equation of Continuity for $f(\boldsymbol{u}, t)$

The equation of continuity for $f(\boldsymbol{u}, \mathrm{t})$ is a conservation statement regarding the orientations of an ensemble of rigid dumbbells. The main idea is that dumbbells leaving one orientation must end up in another. Mathematically this is expressed by the following relation:

$$\frac{\partial}{\partial t} f = -\left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\![\dot{\boldsymbol{u}}]\!] f\right) \tag{14.2-7}$$

This is a two-dimensional analog of the equation of continuity obtained in Eq. 13.2-12 for elastic dumbbells.

c. The "Diffusion Equation" for $f(\boldsymbol{u}, t)$

Substitution of the expression for $[\![\dot{\boldsymbol{u}}]\!]$ from Eq. 14.2-6 into the equation of continuity above gives the diffusion equation:

$$\boxed{\frac{\partial}{\partial t} f = \frac{1}{6\lambda}\left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} f\right) - \frac{\partial}{\partial \boldsymbol{u}} \cdot \left([\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu}] f - \frac{1}{6kT\lambda}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)} f\right)} \tag{14.2-8}$$

This is the differential equation that indicates the way in which the distribution of rigid dumbbell orientations changes with time when the imposed time-dependent, homogeneous velocity field is described by $\boldsymbol{\kappa}(t)$. The distribution function must be periodic in ϕ.

No general solution of Eq. 14.2-8 is available. For steady-state homogeneous, potential flow in the absence of external forces the solution is

$$f = \frac{1}{J} e^{3\lambda(\boldsymbol{\kappa}:\boldsymbol{uu})} \tag{14.2-9}$$

as may be shown by substitution into the differential equation; J is the normalization factor.

To conclude this section we obtain the equation of change for any function of dumbbell orientation $B(\boldsymbol{u})$ that is periodic in ϕ. This is done by multiplying Eq. 14.2-8 by B and integrating over all the configuration space, using the integral expressions given in §E.7:

$$\frac{d}{dt}\langle B\rangle = \frac{1}{6\lambda}\left\langle \frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} B \right\rangle + \left\langle \boldsymbol{\kappa}:\boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}} B \right\rangle - \frac{1}{6kT\lambda}\left\langle \left[\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right] \cdot \frac{\partial}{\partial \boldsymbol{u}} B \right\rangle \tag{14.2-10}$$

A similar equation can be obtained for a tensor of any order. In particular for the tensor $\mathbf{B} = \boldsymbol{uu}$ we can specialize Eq. 14.2-10 to

$$\langle \boldsymbol{uu} \rangle_{(1)} = \frac{1}{3\lambda}\boldsymbol{\delta} - \frac{1}{\lambda}\langle \boldsymbol{uu} \rangle - 2\{\boldsymbol{\kappa} : \langle \boldsymbol{uuuu} \rangle\} - \frac{1}{6kT\lambda}\left\langle \left[\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right]\boldsymbol{u} + \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)} \right\rangle \quad (14.2\text{-}11)$$

in which the subscript (1) indicates a convected derivative. This result is used presently.

§14.3 EXPRESSIONS FOR THE STRESS TENSOR

In §13.3 we presented a simple kinetic theory derivation for the stress tensor for a dilute solution of polymer molecules modeled as elastic dumbbells. This led directly to the "Kramers expression" for the stress tensor, given in Eq. A of Table 13.3-1; this expression contains three terms: the solvent contribution, the spring contribution, and the bead momentum-transport contribution. It was then shown that the stress tensor can be transformed into several other forms, in particular the Kramers–Kirkwood and the Giesekus expressions, neither one of which contains the spring force law explicitly.

The derivation for elastic dumbbells in §13.3 is not applicable to rigid dumbbells because the rigid dumbbell contains a constraint. However, it turns out that the stress-tensor expressions in Table 13.3-1 that do not contain the spring force law explicitly can be applied to the rigid dumbbell model. This is certainly not obvious, and proof of this must be postponed to Chapter 18 where the general expression for the stress tensor is derived from first principles using a complete phase-space kinetic theory. Suffice it to say at this point that the Kramers–Kirkwood expression can be used for rigid dumbbells even when hydrodynamic interaction is included, and that the Giesekus expression is valid when hydrodynamic interaction is neglected.

In Table 14.3-1 we summarize the various expressions for the stress tensor for dilute solutions of rodlike polymers modeled as rigid dumbbells. A name has been attached to each expression in order to emphasize the one-to-one correspondence with the formulas of Table 13.3-1. In Example 14.3-1 we show how to go from the Kramers–Kirkwood expression (Eq. C of Table 14.3-1) to the other expressions.

SPECIAL NOTE ON EXTENSION TO MULTIBEAD-ROD MODELS
(without hydrodynamic interaction)

To adapt the equation for $f(\boldsymbol{u}, t)$ in Eq. 14.2-8 and the stress tensor formulas in Eqs. A and D of Table 14.3-1 to multibead rods with N beads distributed uniformly along a rod of length L (see Fig. 14.1-2) replace the rigid dumbbell time constant $\lambda = \zeta L^2/12kT$ by the multibead-rod time constant

$$\lambda_N = \frac{\zeta L^2 N(N+1)}{72(N-1)kT} \quad (14.3\text{-}1)$$

All results in §§14.4 and 14.5 may be generalized to multibead rods in this way.

TABLE 14.3-1

Expressions for the Stress Tensor for Dilute Solutions of Rodlike Polymers Modeled as Rigid Dumbbells[a,b] (Maxwellian velocity distribution assumed)

Kramers:[c]

$$\tau = -\eta_s\dot{\gamma} - 3nkT\langle \boldsymbol{uu}\rangle - 6nkT\lambda\boldsymbol{\kappa}:\langle \boldsymbol{uuuu}\rangle + nkT\boldsymbol{\delta} - n\left\langle \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right\rangle \tag{A}$$

Modified Kramers:

$$\tau = -\eta_s\dot{\gamma} - 3nkT\left(\frac{2}{L^2}\right)\sum_{\substack{\nu=-1\\ \nu\neq 0}}^{+1}\langle \boldsymbol{R}_\nu\boldsymbol{R}_\nu\rangle - 6nkT\lambda\boldsymbol{\kappa}:\left(\frac{8}{L^4}\right)\sum_{\substack{\nu=-1\\ \nu\neq 0}}^{+1}\langle \boldsymbol{R}_\nu\boldsymbol{R}_\nu\boldsymbol{R}_\nu\boldsymbol{R}_\nu\rangle + nkT\boldsymbol{\delta} - n\left\langle \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right\rangle \tag{B}$$

Kramers-Kirkwood:[d]

$$\tau = -\eta_s\dot{\gamma} - n\sum_{\substack{\nu=-1\\ \nu\neq 0}}^{+1}\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)}\rangle \tag{C}$$

Giesekus:[e]

$$\tau = -\eta_s\dot{\gamma} + 3nkT\lambda\langle \boldsymbol{uu}\rangle_{(1)} + \frac{1}{2}n\left\langle\left(\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right)\boldsymbol{u} - \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right\rangle \tag{D}$$

[a] R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1–90 (1971). H. Giesekus, *Kolloid-Z.*, **147–149**, 29–45 (1956); erratum: *Rheol. Acta*, **1**, 404 (1961), fn. 18.

[b] R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **14**, 85–101 (1984); *J. Polym. Sci.: Polym. Symp.*, **73**, 187–199 (1985).

[c] This form of the stress tensor was given first by S. Prager, *Trans. Soc. Rheol.*, **1**, 53–62 (1957).

[d] H. A. Kramers, *Physica*, **11**, 1–19 (1944); J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281–283 (1951); J. G. Kirkwood and R. J. Plock, *ibid.*, **24**, 665–669 (1956); for a multicomponent generalization, see C. F. Curtiss and R. B. Bird, *Physica*, **118A**, 191–204 (1983), Eq. (36). In this table, only Eq. C can be used when hydrodynamic interaction effects are included (see §14.6).

[e] A simplified form of this expression, valid for steady-state flows, was first given by S. Prager, *loc. cit.*

EXAMPLE 14.3-1. Interrelation of Stress Tensor Formulas

Show how to get the Kramers and Giesekus stress tensor expressions from the Kramers-Kirkwood formula; neglect external forces.

SOLUTION (a) In Eq. C of Table 14.3-1 we replace $\boldsymbol{R}_\nu$ by $\frac{1}{2}\nu L\boldsymbol{u}$ and $\boldsymbol{F}_\nu^{(h)}$ by $-\zeta([\![\dot{\boldsymbol{r}}_\nu]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu])$; this gives for $\tau_p = \tau - \tau_s = \tau + \eta_s\dot{\gamma}$:

$$\begin{aligned}\tau_p &= \tfrac{1}{2}n\zeta L\langle \boldsymbol{u}([\![\dot{\boldsymbol{r}}_1]\!] - \boldsymbol{\kappa}\cdot\boldsymbol{r}_1] - [[\![\dot{\boldsymbol{r}}_{-1}]\!] - \boldsymbol{\kappa}\cdot\boldsymbol{r}_{-1}])\rangle \\ &= \tfrac{1}{2}n\zeta L^2\langle \boldsymbol{u}[[\![\dot{\boldsymbol{u}}]\!] - \boldsymbol{\kappa}\cdot\boldsymbol{u}]\rangle\end{aligned} \tag{14.3-2}$$

Then use Eq. 14.2-6 and neglect the external force terms to get

$$\begin{aligned}\tau_p &= -\tfrac{1}{2}n\zeta L^2\boldsymbol{\kappa}:\langle \boldsymbol{uuuu}\rangle - nkT\left\langle \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\ln f\right\rangle \\ &= -6nkT\lambda\boldsymbol{\kappa}:\langle \boldsymbol{uuuu}\rangle - 3nkT\langle \boldsymbol{uu}\rangle + nkT\boldsymbol{\delta}\end{aligned} \tag{14.3-3}$$

The details for performing the integral involving $\ln f$ are as follows:

$$\left\langle \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\ln f\right\rangle = \iint \boldsymbol{us}\frac{\partial f}{\partial\theta}\sin\theta\, d\theta\, d\phi + \iint \boldsymbol{ut}\frac{\partial f}{\partial\phi}\, d\theta\, d\phi$$

$$= -\iint f(\boldsymbol{ss} - \boldsymbol{uu} + \boldsymbol{us}\cot\theta)\sin\theta\, d\theta\, d\phi$$

$$-\iint f(\boldsymbol{tt} - \boldsymbol{uu} - \boldsymbol{us}\cot\theta)\sin\theta\, d\theta\, d\phi$$

$$= -\iint f(\boldsymbol{ss} + \boldsymbol{tt} + \boldsymbol{uu} - 3\boldsymbol{uu})\sin\theta\, d\theta\, d\phi \qquad (14.3\text{-}4)$$

In going from the first to the second line, integration by parts has been used as well as the periodicity of f in the variable ϕ. In addition the rules for differentiation of the unit vectors in Table E.5-2 have been used.

(**b**) To get the Giesekus expression multiply Eq. 14.2-11 by $3nkT\lambda$ and subtract from Eq. 14.3-3 to get Eq. D of Table 14.3-1.

§14.4 SOLUTION OF THE KINETIC THEORY EQUATIONS FOR SPECIAL FLOWS[1]

In this section we illustrate the solution to the diffusion equation and the calculation of the stress tensor for simple flows in the absence of external forces. The flows considered here are simple shear and elongation, because of their wide use in rheological characterizations. Detailed derivations for other flows are given elsewhere.[1]

a. Simple Shearing Flows of Rigid Dumbbell Solutions

For simple shear flow, $v_x = \dot\gamma(t)y$ the only nonzero component of the tensor $\boldsymbol{\kappa}$ is $\kappa_{xy} = \dot\gamma$, and the diffusion equation given in Eq. 14.2-8 may be written as

$$6\lambda\frac{\partial f}{\partial t} = \left[\frac{1}{S}\frac{\partial}{\partial\theta}\left(S\frac{\partial f}{\partial\theta}\right) + \frac{1}{S^2}\frac{\partial^2 f}{\partial\phi^2}\right] - (6\lambda\dot\gamma)\left[\frac{sc}{S}\frac{\partial}{\partial\theta}(S^2Cf) - \frac{\partial}{\partial\phi}(s^2 f)\right]$$

$$\equiv \Lambda f - (6\lambda\dot\gamma)\Omega_s f \qquad (14.4\text{-}1)$$

where Λ and Ω_s are linear operators; we use the abbreviations $S = \sin\theta$, $C = \cos\theta$, $s = \sin\phi$, and $c = \cos\phi$.

[1] In this section we have drawn heavily from R. B. Bird, H. R. Warner, Jr., and D. C. Evans [*Adv. in Polym. Sci.*, **8**, 1-90 (1971)] where detailed results are given for many material functions. In addition Table 3 gives an extensive summary of rigid and Hookean dumbbell results.

Next we simplify the Giesekus expression for the stress tensor to simple shearing flows. The three combinations of stress components that are of interest for shearing flow are:

$$\tau_{yx} - \tau_{yx,s} = \tfrac{1}{2}nkT\lambda\left[\frac{\partial}{\partial t}\langle P_2^2 s_2\rangle - \dot\gamma(t)\langle 2(P_0^0 - P_2^0)c_0 - P_2^2 c_2\rangle\right] \tag{14.4-2}$$

$$\tau_{xx} - \tau_{yy} = nkT\lambda\left[\frac{\partial}{\partial t}\langle P_2^2 c_2\rangle - \dot\gamma(t)\langle P_2^2 s_2\rangle\right] \tag{14.4-3}$$

$$\tau_{yy} - \tau_{zz} = -nkT\lambda\left[\frac{\partial}{\partial t}\langle 3P_2^0 c_0 + \tfrac{1}{2}P_2^2 c_2\rangle\right] \tag{14.4-4}$$

In these expressions we have rewritten S, C, s, and c in terms of spherical harmonics $P_n^m s_m$ and $P_n^m c_m$. In addition, we have introduced the abbreviations $s_k = \sin k\phi$ and $c_k = \cos k\phi$. Use of the spherical harmonics[2] facilitates the solution of the equation for f and the subsequent evaluation of the stress tensor components.

The Λ-operator of Eq. 14.4-1 acting on a spherical harmonic gives the same spherical harmonic multiplied by the constant $-n(n+1)$:

$$\begin{aligned}\Lambda P_n^m s_m &= -n(n+1)P_n^m s_m\\ \Lambda P_n^m c_m &= -n(n+1)P_n^m c_m\end{aligned} \tag{14.4-5}$$

Furthermore, the result of Ω_s operating on the spherical harmonics can be expressed as a linear combination of spherical harmonics

$$\begin{aligned}\Omega_s P_n^m s_m &= \sum_{j=m-2}^{m+2}\sum_{k=n-2}^{n+2} a_{nk}^{mj} P_k^j c_j \qquad (m > 0)\\ \Omega_s P_n^m c_m &= -\sum_{j=m-2}^{m+2}\sum_{k=n-2}^{n+2} a_{nk}^{mj} P_k^j s_j \qquad (m \geq 0)\end{aligned} \tag{14.4-6}$$

where the a_{nk}^{mj} are given in Table 14.4-1. In particular note that $\Omega_s 1 = \Omega_s P_0^0 c_0 = -\frac{1}{2}P_2^2 s_2$. In applying Eq. 14.4-6 and Table 14.4-1, keep in mind that Table 14.4-1 is valid only for $m \geq 0$, and that $P_n^m = 0$ if $m > n$.

EXAMPLE 14.4-1 Steady Shear Flow[1,3,4,5,6,7]

By means of a perturbation calculation obtain the solution to Eq. 14.4-1 for the flow $v_x = \dot\gamma y$, $v_y = 0$, $v_z = 0$ with $\dot\gamma$ being a constant (the "shear rate"). Obtain expressions for the viscometric functions as a power series in $\dot\gamma$.

[2] See §E.8 for information on spherical harmonics and Legendre polynomials.
[3] H. Giesekus, *Kolloid-Z.*, **147-149**, 29–45 (1956); Erratum: *Rheol. Acta*, **1**, 404 (1961), footnote 18.
[4] J. G. Kirkwood and R. J. Plock, *J. Chem. Phys.*, **24**, 665–669 (1956).
[5] S. Prager, *Trans. Soc. Rheol.*, **1**, 53–62 (1957).
[6] T. Kotaka, *J. Chem. Phys.*, **30**, 1566–1567 (1959).
[7] S. Kim and X. J. Fan, *J. Rheol.*, **28**, 117–122 (1984).

TABLE 14.4-1[a]

Tabulation of the a_{nk}^{mj} of Eq. 14.4-6

$$a_{n,n-2}^{m,m-2} = \frac{(n-2)(n+m)(n+m-1)(n+m-2)(n+m-3)(1-\delta_{m0})}{4(2n+1)(2n-1)}$$

$$a_{n,n}^{m,m-2} = \frac{3(n+m)(n+m-1)(n-m+1)(n-m+2)(1-\delta_{m0})}{4(2n-1)(2n+3)}$$

$$a_{n,n+2}^{m,m-2} = -\frac{(n+3)(n-m+1)(n-m+2)(n-m+3)(n-m+4)(1-\delta_{m0})}{4(2n+1)(2n+3)}$$

$$a_{nn}^{mm} = -\frac{m}{2}$$

$$a_{n,n-2}^{m,m+2} = -\frac{(n-2)(1+\delta_{m0})}{4(2n+1)(2n-1)}$$

$$a_{n,n}^{m,m+2} = -\frac{3(1+\delta_{m0})}{4(2n-1)(2n+3)}$$

$$a_{n,n+2}^{m,m+2} = \frac{(n+3)(1+\delta_{m0})}{4(2n+1)(2n+3)}$$

All other a_{nk}^{mj} are zero.

[a] R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1 90 (1971), Table 1 on p. 23.

SOLUTION **(a)** Solution for the Distribution Function

Since we are considering only flows that are not far from equilibrium we expand $f(\theta, \phi)$ in a power series:

$$f(\theta, \phi) = \frac{1}{4\pi}[1 + (6\lambda\dot{\gamma})\phi_1 + (6\lambda\dot{\gamma})^2\phi_2 + \cdots] \tag{14.4-7}$$

Since f is normalized to unity (Eq. 14.1-3) the $\phi_k(\theta, \phi)$ must satisfy the relations

$$\int_0^{2\pi}\int_0^{\pi} \phi_k(\theta, \phi) S \, d\theta \, d\phi = \int_0^{2\pi}\int_0^{\pi} \phi_k P_0^0 c_0 S \, d\theta \, d\phi$$
$$= 0 \qquad (k = 1, 2, 3, \ldots) \tag{14.4-8}$$

Substitution of Eq. 14.4-7 into Eq. 14.4-1 with $\partial f/\partial t = 0$ for steady state gives

$$\Lambda[1 + (6\lambda\dot{\gamma})\phi_1 + (6\lambda\dot{\gamma})^2\phi_2 + \cdots] = (6\lambda\dot{\gamma})\Omega_s[1 + (6\lambda\dot{\gamma})\phi_1 + (6\lambda\dot{\gamma})^2\phi_2 + \cdots] \tag{14.4-9}$$

Equating coefficients of equal powers of $(6\lambda\dot{\gamma})$ gives a series of differential equations for the ϕ_k:

$$\begin{aligned} \Lambda\phi_1 &= \Omega_s 1 = -\tfrac{1}{2}P_2^2 s_2 \\ \Lambda\phi_2 &= \Omega_s\phi_1 \\ &\vdots \qquad\quad \vdots \\ \Lambda\phi_k &= \Omega_s\phi_{k-1} \end{aligned} \tag{14.4-10}$$

Using the first member of Eqs. 14.4-10 and 14.4-5 we see that

$$\phi_1 = \tfrac{1}{12} P_2^2 s_2 \tag{14.4-11}$$

Note that we could add a constant to the ϕ_1 given above and still satisfy the differential equation; however, the normalization condition Eq. 14.4-8 requires that this constant be zero. Similarly the integration constants that arise in determining all the other ϕ_k are equal to zero.

Next we use the ϕ_1 just found, together with Eq. 14.4-10 for ϕ_2, to get

$$\begin{aligned} \Lambda\phi_2 = \Omega_s\phi_1 &= \tfrac{1}{12}\Omega_s(P_2^2 s_2) \\ &= \tfrac{1}{12}\left[\tfrac{6}{7}P_2^0 c_0 - P_2^2 c_2 - \tfrac{6}{7}P_4^0 c_0 + \tfrac{1}{28}P_4^4 c_4\right] \end{aligned} \tag{14.4-12}$$

Here we have used Eq. 14.4-6 and Table 14.4-1. Once again, the information about the Λ-operator in Eq. 14.4-5 is used with the differential equation for ϕ_2. The result is

$$\phi_2 = -\frac{1}{84}P_2^0 c_0 + \frac{1}{72}P_2^2 c_2 + \frac{1}{280}P_4^0 c_0 - \frac{1}{6720}P_4^4 c_4 \tag{14.4-13}$$

Similarly, we find that

$$\phi_3 = -\frac{19}{7560}P_2^2 s_2 - \frac{1}{18480}P_4^2 s_2 + \frac{1}{221760}P_6^2 s_2 + \frac{1}{25200}P_4^4 s_4 - \frac{1}{15966720}P_6^6 s_6 \tag{14.4-14}$$

This procedure can be continued to get the coefficients in the higher ϕ_k.

(b) Evaluation of the Stress Tensor Components.

To compute the stress components we now substitute the series expansion for the distribution function into Eqs. 14.4-2, 14.4-3, and 14.4-4 written for steady state:

$$\begin{aligned} \tau_{yx} - \tau_{yx,s} = -\frac{nkT\lambda\dot\gamma}{8\pi}\int_0^{2\pi}\int_0^{\pi}\Big[2(P_0^0 - P_2^0)c_0 - P_2^2 c_2\Big] \\ \times\Big[P_0^0 c_0 + (6\lambda\dot\gamma)\Big(\frac{1}{12}P_2^2 s_2\Big) + (6\lambda\dot\gamma)^2\Big(-\frac{1}{84}P_2^0 c_0 + \frac{1}{72}P_2^2 c_2 \\ + \frac{1}{280}P_4^0 c_0 - \frac{1}{6720}P_4^4 c_4\Big) + \cdots\Big] S\,d\theta\,d\phi \end{aligned} \tag{14.4-15}$$

$$\begin{aligned} \tau_{xx} - \tau_{yy} = -\frac{nkT\lambda\dot\gamma}{4\pi}\int_0^{2\pi}\int_0^{\pi} P_2^2 s_2\Big[P_0^0 c_0 + (6\lambda\dot\gamma)\Big(\frac{1}{12}P_2^2 s_2\Big) \\ + (6\lambda\dot\gamma)^2\Big(-\frac{1}{84}P_2^0 c_0 + \frac{1}{72}P_2^2 c_2 + \frac{1}{280}P_4^0 c_0 - \frac{1}{6720}P_4^4 c_4\Big) + \cdots\Big] S\,d\theta\,d\phi \end{aligned} \tag{14.4-16}$$

$$\tau_{yy} - \tau_{zz} = 0 \tag{14.4-17}$$

All of the integrals above are easily evaluated using Eq. E.8-7. According to the orthogonality conditions the dashed-underlined terms contribute nothing to the stresses. Evaluation of the

remaining terms, including those arising from ϕ_3, ϕ_4, and ϕ_5 gives the following viscometric functions[1,3,4,5,6] defined in Eqs. D.5-1, 2, and 3:

$$\eta - \eta_s = nkT\lambda\left[1 - \frac{18}{35}(\lambda\dot{\gamma})^2 + \frac{1326}{1925}(\lambda\dot{\gamma})^4 - \cdots\right] \tag{14.4-18}$$

$$\Psi_1 = \frac{6}{5}nkT\lambda^2\left[1 - \frac{38}{35}(\lambda\dot{\gamma})^2 + \frac{38728}{25025}(\lambda\dot{\gamma})^4 - \cdots\right] \tag{14.4-19}$$

$$\Psi_2 = 0 \tag{14.4-20}$$

Kim and Fan[7] have obtained the coefficients in the expansions up to $(\lambda\dot{\gamma})^{40}$ and have determined that the series converge for $\lambda\dot{\gamma} < 0.81$; they also extended their solution to about $\lambda\dot{\gamma} = 1.2$ by analytic continuation and obtained excellent agreement with earlier numerical calculations.[8] The expressions above, including the $(\lambda\dot{\gamma})^4$ term are good to within 1% only up to about $\lambda\dot{\gamma} = 0.46$. In the limit of very large shear rates Stewart and Sørensen obtained "power law" limiting expressions using numerical methods (see Example 14.6-2):

$$\eta - \eta_s \doteq 0.678\, nkT\lambda(\lambda\dot{\gamma})^{-1/3} \tag{14.4-21}$$

$$\Psi_1 \doteq 1.20\, nkT\lambda^2(\lambda\dot{\gamma})^{-4/3} \tag{14.4-22}$$

these expressions being good approximations for $\lambda\dot{\gamma}$ greater than about 5.

The time constant λ contains ζ and L, which are not experimentally measurable. Hence for making comparisons with experimental data one can determine λ from the zero-shear-rate viscosity in Eq. 14.4-18:

$$\lambda = \frac{\eta_0 - \eta_s}{nkT} = \frac{[\eta]_0\eta_s M}{\tilde{N}kT} \tag{14.4-23}$$

where $[\eta]_0$ is the zero-shear-rate intrinsic viscosity (Eq. D.5-4) and $\tilde{N}$ is Avogadro's number. When this is substituted into Eqs. 14.4-18 and 14.4-19, relations are obtained among measurable quantities (e.g., η, η_s, M, T, and $\dot{\gamma}$).

Figures 14.4-1 and 14.4-2 show comparisons between experimental data for rigid, rodlike macromolecules and the rigid dumbbell results. In Fig. 14.4-1 we show the data of Wada[9] for tobacco mosaic virus in water; the time constant in this case was chosen to give a reasonable fit of the data. The poor agreement may be due to the model itself, to the neglect of hydrodynamic interaction, or to association effects. In Fig. 14.4-2 are given the data of Yang[10] on poly-γ-benzyl-L-glutamate in *m*-cresol, reinterpreted as non-Newtonian intrinsic viscosity; two calculated curves are shown, illustrating two different ways of determining the time constant. Note that the time constant determined from the η versus $\dot{\gamma}$ curve differs from that calculated from $[\eta]_0$, η_s, M, and T using Eq. 14.4-23 only by a factor of 3.5. This is rather good agreement in view of the crudeness of the model and the neglect of hydrodynamic interaction. The $\dot{\gamma}^{-1/3}$ dependence predicted by Eq. 14.4-21 seems to be borne out by the data comparison in Fig. 14.4-2.

b. Elongational Flows of Rigid Dumbbell Solutions

A second class of flows for which we illustrate the use of the kinetic theory equations for rigid dumbbells is simple elongation $v_z = \dot{\varepsilon}(t)z$, $v_x = -\frac{1}{2}\dot{\varepsilon}(t)x$, $v_y = -\frac{1}{2}\dot{\varepsilon}(t)y$. For these

[8] W. E. Stewart and J. P. Sørensen, *Trans. Soc. Rheol.*, **16**, 1-13 (1972).
[9] E. Wada, *J. Polym. Sci.*, **14**, 305-307 (1954); *J. Sci. Res. Inst.*, **47**, 168-170 (Dec. 1953).
[10] J. T. Yang, *J. Amer. Chem. Soc.*, **80**, 1783-1788 (1958); **81**, 3902-3907 (1959).

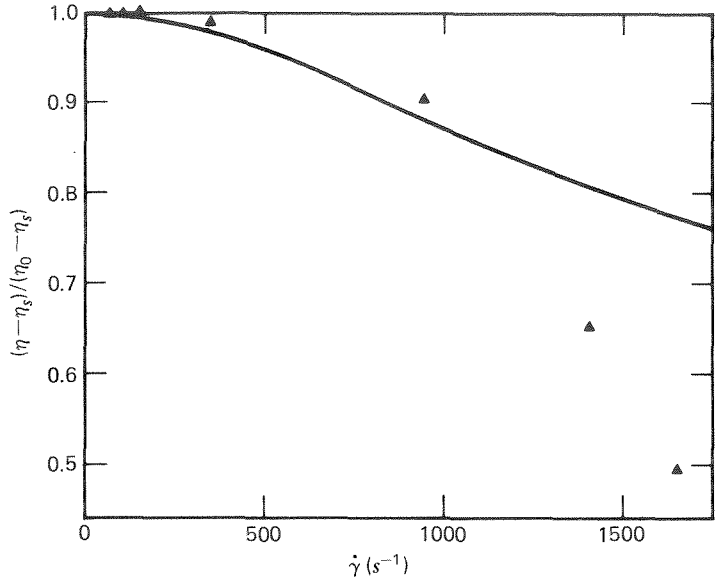


FIGURE 14.4-1. Plot of the ratio $(\eta - \eta_s)/(\eta_0 - \eta_s)$ versus the shear rate $\dot{\gamma}$. The solid triangles are data for tobacco mosaic virus in water at a concentration of 1.14×10^{-3} g/cm^3. The solid curve is a plot of Eq. 14.4-18 or Fig. 14.6-1 (with $h = 0$) for the rigid dumbbell model with the time constant λ chosen to be 6×10^{-4} s, which represents the best fit of the data. Data of E. Wada, *J. Sci. Res. Inst.*, **47**, 168-170 (Dec. 1953). The authors are indebted to Professor J. S. Dahler for correspondence regarding this data comparison; see also A. R. Altenberger and J. S. Dahler, *Macromolecules*, **18**, 1700-1710 (1985).

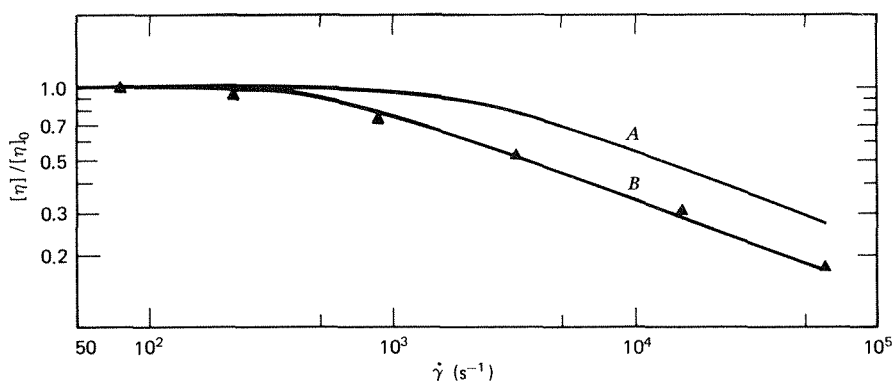


FIGURE 14.4-2. Plot of the ratio $[\eta]/[\eta]_0$ versus the shear rate $\dot{\gamma}$. The solid triangles are data for poly-γ-benzyl-*L*-glutamate ($\bar{M}_w = 2.08 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 1.3$) in *m*-cresol (helix structure) extrapolated to infinite dilution. The solid curves are based on the rigid-dumbbell calculations of Stewart and Sørensen as given in Fig. 14.6-1. Curve A was obtained by getting the time constant ($\lambda = 2.94 \times 10^{-4}$ s) from $\lambda = [\eta]_0 \eta_s M/\tilde{N}kT$ (cf. Eq. 14.4-23) with M taken to be the experimentally determined $\bar{M}_w$ and by assuming that the solution is monodisperse ($\bar{M}_w/\bar{M}_n = 1$). Curve B was obtained by choosing the time constant λ to be 1.04×10^{-3} s, which represents the best fit of the data. Data of J. T. Yang, *J. Am. Chem. Soc.*, **80**, 1783-1788 (1958). [R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1-90 (1971).]

flows $\kappa_{zz} = \dot{\varepsilon}$, $\kappa_{xx} = \kappa_{yy} = -\frac{1}{2}\dot{\varepsilon}$ and all other $\kappa_{ij} = 0$. Substitution of these components of $\boldsymbol{\kappa}$ into Eq. 14.2-8 gives the diffusion equation for elongational flow:

$$6\lambda \frac{\partial}{\partial t} f = \Lambda f + \tfrac{3}{2}(6\lambda\dot{\varepsilon}) \frac{1}{S} \frac{\partial}{\partial \theta} (S^2 C f)$$

$$= \Lambda f + \tfrac{3}{2}(6\lambda\dot{\varepsilon})\Omega_e f \tag{14.4-24}$$

Here Λ is the same as the operator used for shear flow in Eq. 14.4-1; Ω_e is an operator for elongational flows. The elongation rate $\dot{\varepsilon}$ is in general a function of time.

The stress difference related to the elongational viscosity is found from the Giesekus expression for the stress tensor to be

$$\tau_{xx} - \tau_{zz} = 3\eta_s\dot{\varepsilon}(t) + 6nkT\lambda\dot{\varepsilon}(t)$$

$$+ 3nkT\lambda\left[\frac{\partial}{\partial t}\langle(P_0^0 - P_2^0) + \tfrac{1}{6}P_2^2 c_2\rangle - \dot{\varepsilon}(t)\langle(P_0^0 - P_2^0) - \tfrac{1}{6}P_2^2 c_2\rangle\right] \tag{14.4-25}$$

In solving kinetic theory problems for elongational flow we need the information on the Λ-operator and orthogonality conditions given earlier. In addition we need to know how the Ω_e operator affects the P_n^0 (the Legendre polynomials):

$$\Omega_e P_n^0 = -\frac{n(n-1)(n-2)}{(2n+1)(2n-1)} P_{n-2}^0$$

$$+ \left[2 + \frac{n(n+1)^2 - 3(n+1)(n+2)}{(2n+3)(2n+1)} - \frac{n^2(n+1) + 3n(n-1)}{(2n+1)(2n-1)}\right] P_n^0$$

$$+ \frac{(n+1)(n+2)(n+3)}{(2n+1)(2n+3)} P_{n+2}^0 \tag{14.4-26}$$

Note that $\Omega_e 1 = \Omega_e P_0^0 = 2P_2^0$.

EXAMPLE 14.4-2 Steady Elongational Flow[11]

Determine the distribution function for a steady simple elongational flow. Then find the elongational viscosity for a rigid dumbbell suspension.

SOLUTION **(a)** Solution for the Distribution Function

Because of the symmetry of the flow about the z-axis we expect the distribution function to depend on θ alone. Hence we write the diffusion equation as

$$0 = \frac{1}{S}\frac{d}{d\theta}\left(S\frac{d}{d\theta}f\right) + 9\lambda\dot{\varepsilon}\frac{1}{S}\frac{d}{d\theta}(S^2 C f) \tag{14.4-27}$$

Integrating this equation once gives

$$\frac{d}{d\theta} f = -9\lambda\dot{\varepsilon} S C f \tag{14.4-28}$$

[11] R. B. Bird, M. W. Johnson, Jr., and J. F. Stevenson in *Proc. 5th International Congress on Rheology*, S. Onogi (Ed.), University of Tokyo Press, Tokyo (1970), Vol. 4, pp. 159–168.

The integration constant in Eq. 14.4-28 has been set equal to zero because cylindrical symmetry requires that $(df/d\theta) = 0$ at $\theta = 0$ and π. A second integration gives

$$f = \frac{1}{J} e^{(9/2)\lambda\dot{\varepsilon}C^2} \tag{14.4-29}$$

where J is the normalization constant. Note that this result can also be deduced from Eq. 14.2-9, which gives f for any steady-state, homogeneous potential flow.

(b) Evaluation of the Elongational Viscosity

From the definition of the elongational viscosity in Eq. D.5-14 and the normal-stress difference expression in Eq. 14.4-25, we obtain

$$\bar{\eta} - 3\eta_s = 6nkT\lambda - 3nkT\lambda\langle S^2(1 + s^2)\rangle \tag{14.4-30}$$

Then introduction of the distribution function from Eq. 14.4-29 gives

$$\bar{\eta} - 3\eta_s = 6nkT\lambda - 3nkT\lambda \frac{\int_0^{2\pi}\int_0^{\pi} \exp[(9/2)\lambda\dot{\varepsilon}C^2]S^2(1 + s^2)S\, d\theta\, d\phi}{\int_0^{2\pi}\int_0^{\pi} \exp[(9/2)\lambda\dot{\varepsilon}C^2]S\, d\theta\, d\phi} \tag{14.4-31}$$

The integrals over ϕ can be performed, and then the integrals over θ can be rewritten using the change of variable $\xi = \sqrt{X}\cos\theta$ where $X = (9/2)\lambda|\dot{\varepsilon}|$. This gives

$$\begin{aligned}\frac{\bar{\eta} - 3\eta_s}{3nkT\lambda} &= \frac{1}{2} + \frac{3}{2X}\frac{\int_0^{\sqrt{X}} y^2 \exp(\pm y^2)dy}{\int_0^{\sqrt{X}} \exp(\pm y^2)\, dy} \\ &= \frac{1}{2} \mp \frac{3}{4X} \pm \frac{3}{4\sqrt{X}}\frac{\exp(\pm X)}{\int_0^{\sqrt{X}} \exp(\pm y^2)dy}\end{aligned} \tag{14.4-32}$$

TABLE 14.4-2

Elongational Viscosity for Rigid Dumbbells[a]

	$(\bar{\eta} - 3\eta_s)/3nkT\lambda$	
$\lambda\|\dot{\varepsilon}\|$	Positive $\dot{\varepsilon}$	Negative $\dot{\varepsilon}$
0	1.00	1.00
0.01	1.01	0.98
0.1	1.06	0.94
0.2	1.13	0.83
0.5	1.33	0.77
1.0	1.61	0.66
3.0	1.88	0.56
10.0	1.99	0.52
∞	2.00	0.50

[a] Values for positive $\dot{\varepsilon}$ are taken from R. B. Bird, M. W. Johnson, Jr., and J. F. Stevenson, *Proc. 5th International Congress on Rheology*, S. Onogi, (Ed.), University of Tokyo Press (1970), Vol. 4, pp. 159–168.

in which the upper signs are to be used when $\dot{\varepsilon}$ is positive and the lower for $\dot{\varepsilon}$ negative. To get the second line of Eq. 14.4-32 the integral in the numerator of the first line is integrated by parts. The integral in the denominator is $(\sqrt{\pi}/2)\,\mathrm{erf}\,\sqrt{X}$ if the minus sign is used; with the plus sign it is closely related[12] to "Dawson's integral." Values of the quantity $(\bar{\eta} - 3\eta_s)/3nkT\lambda$ are shown in Table 14.4-2. It is evident that for rigid dumbbells $\bar{\eta}$ is a far less sensitive function of $\dot{\varepsilon}$ than it is for elastic dumbbells. No experimental data are available for comparison with the theory.

§14.5 SOLUTION OF THE KINETIC THEORY EQUATIONS FOR GENERAL FLOWS

In the foregoing section we showed how to obtain a perturbation expansion for steady-shear flow valid for small shear rates; for steady elongational flow we were able to get a complete solution to the equation for the orientational distribution function. In this section we show how to develop the stress tensor in a "memory-integral expansion" (Eqs. D.4-1 and 9.6-12) valid for a rather wide class of flows.[1] This is done by performing the perturbation expansion of §14.4(a) to get $f(\boldsymbol{u}, t)$ for an arbitrary irrotational, time-dependent, homogeneous flow. With the distribution function thus obtained we can then obtain the stress tensor as a series of integrals, and from the latter it is possible to determine the first few kernel functions in a memory-integral expansion; this expansion can then be used to solve flow problems that are not irrotational. It has been proven that for a wide class of fluids the response to arbitrary irrotational flows is sufficient to determine completely the rheological behavior of the fluid.[2]

We now attempt to solve Eq. 14.2-8, which we write as

$$6\lambda \frac{\partial f}{\partial t} = \Lambda f - 6\lambda \Omega f \tag{14.5-1}$$

where

$$\Lambda f = \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} \right) f \tag{14.5-2}$$

$$\Omega f = \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] f \right) \tag{14.5-3}$$

with Λ and Ω being operators. Since the fluid is incompressible, $\boldsymbol{\kappa}$ is traceless, and since we are restricting the derivation to irrotational flow, $\boldsymbol{\kappa}$ is symmetric so that $\boldsymbol{\kappa} = \frac{1}{2}\dot{\boldsymbol{\gamma}}$; the tensor $\boldsymbol{\kappa}$ may depend on the time t.

We postulate a solution of the form

$$f = \frac{1}{4\pi} \sum_{k=0}^{\infty} (6\lambda)^k \phi_k \tag{14.5-4}$$

[12] M. Abramowitz and I. A. Stegun (Eds.), *Handbook of Mathematical Functions*, Nat. Bur. of Standards, Washington, D. C. (1964), p. 692, Section 19.14.5.

[1] This method was first given by R. B. Bird and R. C. Armstrong, *J. Chem. Phys.*, **56**, 3680-3682 (1972) and further developed by R. C. Armstrong and R. B. Bird [*J. Chem. Phys.*, **58**, 2715-2723 (1973); erratum: in Eq. 22, replace 27/280 by 27/980]. Later the memory-integral expansion developed through third order by these authors was put into the form of a corotational memory-integral expansion by S. I. Abdel-Khalik, O. Hassager, and R. B. Bird [*J. Chem. Phys.*, **61**, 4312-4316 (1974); erratum: in Eq. 14 change 1/70 to 1/35]. The presentation here in terms of surface spherical harmonics was developed by R. C. Armstrong (unpublished).

[2] B. D. Coleman and C. Truesdell, *ZAMM*, **45**, 547-551 (1965).

in which $\phi_k(\boldsymbol{u}, t)$ is of kth order in κ; furthermore $\phi_0 \equiv 1$. Since f is normalized to unity the ϕ_k must satisfy the constraints

$$\int \phi_k(\boldsymbol{u}, t) d\boldsymbol{u} = 0 \qquad (k = 1, 2, 3, \ldots) \tag{14.5-5}$$

Substitution of the series solution of Eq. 14.5-4 into the differential equation of Eq. 14.5-1 gives a set of equations for the ϕ_k:

$$6\lambda \frac{\partial}{\partial t} \phi_1 = \Lambda \phi_1 - \Omega 1 \tag{14.5-6}$$

$$6\lambda \frac{\partial}{\partial t} \phi_2 = \Lambda \phi_2 - \Omega \phi_1 \tag{14.5-7}$$

$$\vdots$$

$$6\lambda \frac{\partial}{\partial t} \phi_k = \Lambda \phi_k - \Omega \phi_{k-1} \tag{14.5-8}$$

The main problem in this section is to solve Eqs. 14.5-6 to 14.5-8. This is done by using the surface spherical harmonics defined in Eq. E.10-1.

We start by noting that Eq. 14.5-6 may be written as

$$\begin{aligned} 6\lambda \frac{\partial}{\partial t} \phi_1 &= \Lambda \phi_1 - \boldsymbol{\kappa} : (\boldsymbol{\delta} - 3\boldsymbol{uu}) \\ &= \Lambda \phi_1 + \tfrac{1}{2}(\dot{\boldsymbol{\gamma}} : \mathbf{S}_2) \end{aligned} \tag{14.5-9}$$

To get the last term in this equation we had to evaluate $\Omega 1$, making use of the differential operations in §E.6, as well as Eq. E.10-3. Because of the way in which Λ operates on the surface spherical harmonics, we try a solution of the form

$$\phi_1 = (\boldsymbol{\alpha}(t) : \mathbf{S}_2) \tag{14.5-10}$$

where $\boldsymbol{\alpha}$ is a second-order, symmetric tensor. Note that we could have also included a term $A(t)\mathbf{S}_0$ in the postulated solution. However, it can be shown that the normalization condition, Eq. 14.5-5, requires that the coefficient of $\mathbf{S}_0$ be zero. When the postulated solution is inserted into the differential equation for ϕ_1 we obtain

$$\left(\left\{ 6\lambda \frac{d}{dt} \boldsymbol{\alpha} + 6\boldsymbol{\alpha} - \tfrac{1}{2}\dot{\boldsymbol{\gamma}} \right\} : \mathbf{S}_2 \right) = 0 \tag{14.5-11}$$

In order for this to be satisfied for all θ and ϕ, the coefficient of $\mathbf{S}_2$ must be identically zero. This leads to the following first-order, ordinary differential equation for $\boldsymbol{\alpha}$:

$$\frac{d}{dt} \boldsymbol{\alpha} + \frac{1}{\lambda} \boldsymbol{\alpha} = \frac{1}{12\lambda} \dot{\boldsymbol{\gamma}} \tag{14.5-12}$$

which can be solved to give

$$\boldsymbol{\alpha} = \frac{1}{12\lambda} \int_{-\infty}^{t} e^{-(t-t')/\lambda} \dot{\boldsymbol{\gamma}}' \, dt' \tag{14.5-13}$$

in which $\dot{\gamma}' = \dot{\gamma}(t')$. Substituting these results into the postulated form for ϕ_1 and using Eq. E.10-3 for $\mathbf{S}_2$ gives

$$\phi_1 = \frac{1}{4\lambda}\int_{-\infty}^{t} e^{-(t-t')/\lambda}(\dot{\gamma}' : \boldsymbol{uu})dt' \tag{14.5-14}$$

since tr $\dot{\gamma} = 0$ for an incompressible fluid

Next we proceed to Eq. 14.5-7 for $\phi_2(\boldsymbol{u}, t)$:

$$\begin{aligned} 6\lambda\frac{\partial}{\partial t}\phi_2 &= \Lambda\phi_2 - 3\Omega(\boldsymbol{\alpha} : \boldsymbol{uu}) \\ &= \Lambda\phi_2 - (\dot{\gamma}\boldsymbol{\alpha} : (3\boldsymbol{u\delta u} - \tfrac{15}{2}\,\boldsymbol{uuuu})) \\ &= \Lambda\phi_2 + \tfrac{3}{7}(\{\dot{\gamma}\cdot\boldsymbol{\alpha}\} : \mathbf{S}_2) + \tfrac{1}{14}(\dot{\gamma}\boldsymbol{\alpha} \vdots \mathbf{S}_4) \end{aligned} \tag{14.5-15}$$

In getting the second line we have made use of the tracelessness and symmetry of the $\dot{\gamma}$ tensor; to get the third line we used the expressions for the $\mathbf{S}_k$ given in §E.10. An appropriate postulate for the solution of the ϕ_2 equation is then

$$\phi_2 = (\boldsymbol{\beta}(t) : \mathbf{S}_2) + (\mathbf{B}(t) \vdots \mathbf{S}_4) \tag{14.5-16}$$

When this is put into the differential equation for ϕ_2 in Eq. 14.5-15 and the coefficients multiplying similar surface spherical harmonics equated, we obtain

$$\frac{d}{dt}\boldsymbol{\beta} + \frac{1}{\lambda}\boldsymbol{\beta} = \frac{1}{14\lambda}\{\dot{\gamma}\cdot\boldsymbol{\alpha}\} \tag{14.5-17}$$

$$\frac{d}{dt}\mathbf{B} + \frac{10}{3\lambda}\mathbf{B} = \frac{1}{84\lambda}\dot{\gamma}\boldsymbol{\alpha} \tag{14.5-18}$$

These may be integrated to give

$$\boldsymbol{\beta} = \frac{1}{168\lambda^2}\int_{-\infty}^{t}\int_{-\infty}^{t'} e^{-(t-t'')/\lambda}\{\dot{\gamma}'\cdot\dot{\gamma}''\}dt''dt' \tag{14.5-19}$$

$$\mathbf{B} = \frac{1}{1008\lambda^2}\int_{-\infty}^{t}\int_{-\infty}^{t'} e^{-(7/3)(t-t')/\lambda}e^{-(t-t'')/\lambda}\,\dot{\gamma}'\dot{\gamma}''\,dt''\,dt' \tag{14.5-20}$$

The final expression for ϕ_2 is obtained by putting these expressions into Eq. 14.5-16:

$$\begin{aligned} \phi_2 = \frac{1}{\lambda^2}\int_{-\infty}^{t}\int_{-\infty}^{t'}&\left(-\frac{1}{168}(\dot{\gamma}' : \dot{\gamma}'') + \frac{1}{56}(\{\dot{\gamma}'\cdot\dot{\gamma}''\} : \boldsymbol{uu})\right)e^{-(t-t'')/\lambda}\,dt''\,dt' \\ + \frac{1}{\lambda^2}\int_{-\infty}^{t}\int_{-\infty}^{t'}&\left(+\frac{1}{168}(\dot{\gamma}' : \dot{\gamma}'') - \frac{5}{84}(\{\dot{\gamma}'\cdot\dot{\gamma}''\} : \boldsymbol{uu})\right. \\ &\left. + \frac{5}{48}(\dot{\gamma}' : \boldsymbol{uu})(\dot{\gamma}'' : \boldsymbol{uu})\right)e^{-(7/3)(t-t')/\lambda}e^{-(t-t'')/\lambda}\,dt''\,dt' \end{aligned} \tag{14.5-21}$$

Higher ϕ_k can be found by continuing the process.

Now that the first few terms in the series for $f(\boldsymbol{u}, t)$ have been found, we can substitute f from Eq. 14.5-4 into the Giesekus expression for the stress tensor (Eq. D of Table 14.3-1) and perform the necessary integrations over $\boldsymbol{uu}$, $\boldsymbol{uuuu}$, and so on, to get:

$$\begin{aligned}
\boldsymbol{\tau} &= -\eta_s\dot{\boldsymbol{\gamma}} + 3nkT\lambda\langle\boldsymbol{uu}\rangle_{(1)} \\
&= -\eta_s\dot{\boldsymbol{\gamma}} + 3nkT\lambda\left[\int\frac{1}{4\pi}\sum_{k=0}^{\infty}(6\lambda)^k\phi_k\boldsymbol{uu}\,d\boldsymbol{u}\right]_{(1)} \\
&= -(\eta_s + \tfrac{2}{5}nkT\lambda)\dot{\boldsymbol{\gamma}} - \tfrac{3}{5}nkT\int_{-\infty}^{t}\dot{\boldsymbol{\gamma}}'e^{-(t-t')/\lambda}\,dt' \\
&\quad - \tfrac{6}{35}nkT\lambda\int_{-\infty}^{t}\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}' + \dot{\boldsymbol{\gamma}}'\cdot\dot{\boldsymbol{\gamma}}\}e^{-(t-t')/\lambda}\,dt' \\
&\quad - \tfrac{9}{70}nkT\int_{-\infty}^{t}\int_{-\infty}^{t'}\{\dot{\boldsymbol{\gamma}}'\cdot\dot{\boldsymbol{\gamma}}'' + \dot{\boldsymbol{\gamma}}''\cdot\dot{\boldsymbol{\gamma}}'\}e^{-(t-t'')/\lambda}\,dt''\,dt' - \cdots \qquad (14.5\text{-}22) \\
&\quad + \text{isotropic terms containing integrals of } \dot{\boldsymbol{\gamma}}
\end{aligned}$$

In order to put this expression for $\boldsymbol{\tau}$ in the form of a memory integral expansion, we insert the expansion (from Eq. 9D.1-6 with $\boldsymbol{\omega} = \boldsymbol{0}$):

$$\dot{\boldsymbol{\gamma}}' = \boldsymbol{\gamma}'_{[1]} - \frac{1}{2}\int_{t'}^{t}\{\boldsymbol{\gamma}'_{[1]}\cdot\boldsymbol{\gamma}''_{[1]} + \boldsymbol{\gamma}''_{[1]}\cdot\boldsymbol{\gamma}'_{[1]}\}\,dt'' + \cdots \qquad (14.5\text{-}23)$$

Then if we abbreviate the integrand of this last integral by $\{\ \ \}$, we get[3]:

$$\begin{aligned}
\boldsymbol{\tau} &= -(\eta_s + \tfrac{2}{5}nkT\lambda)\dot{\boldsymbol{\gamma}} - \tfrac{3}{5}nkT\int_{-\infty}^{t}\boldsymbol{\gamma}'_{[1]}e^{-(t-t')/\lambda}\,dt' \\
&\quad + \tfrac{3}{10}nkT\int_{-\infty}^{t}\int_{t'}^{t}\{\ \ \}e^{-(t-t')/\lambda}\,dt''\,dt' \\
&\quad - \tfrac{6}{35}nkT\lambda\int_{-\infty}^{t}\int_{-\infty}^{t}\{\ \ \}2\delta(t-t'')e^{-(t-t')/\lambda}\,dt''\,dt' \\
&\quad - \tfrac{9}{70}nkT\int_{-\infty}^{t}\int_{-\infty}^{t'}\{\ \ \}e^{-(t-t'')/\lambda}\,dt''\,dt' - \cdots \\
&\quad + \text{isotropic terms} \qquad (14.5\text{-}24)
\end{aligned}$$

Next the following operations are performed in order to combine the three double integrals: in the first two integrals interchange t' and t''; then in the first integral change the order of integration so that the inner integral over t'' goes from $-\infty$ to t'; finally change the upper limit of the inner integral in the first and third double integral from t' to t and include in the integrand a factor

$$g(t, t', t'') = \begin{cases} 1 & \text{for } -\infty < t'' \le t' \\ 0 & \text{for } t' < t'' \le t \end{cases} \qquad (14.5\text{-}25)$$

[3] See §E.4 for the definition of the Dirac δ-function.

This then yields a *memory-integral expansion*[4]

$$\boxed{\begin{aligned}\tau = &-\int_{-\infty}^{t} G_1(t-t')\gamma'_{[1]}\,dt' \\ &-\int_{-\infty}^{t}\int_{-\infty}^{t} G_2(t-t', t-t'')\{\gamma'_{[1]}\cdot\gamma''_{[1]} + \gamma''_{[1]}\cdot\gamma'_{[1]}\}dt''\,dt' \\ &-\cdots + \text{isotropic terms}\end{aligned}} \tag{14.5-26}$$

in which

$$\boxed{G_1 = (2\eta_s + \tfrac{4}{5}nkT\lambda)\delta(t-t') + \tfrac{3}{5}nkT\,e^{-(t-t')/\lambda}} \tag{14.5-27}$$

$$\boxed{G_2 = nkT[\tfrac{12}{35}\lambda\delta(t-t') - \tfrac{6}{35}]g(t, t', t'')e^{-(t-t'')/\lambda}} \tag{14.5-28}$$

The third-order contributions to the memory-integral expansion have also been worked out.[1] The function G_1 is the "relaxation modulus" G of linear viscoelasticity (see §5.2), from which all linear viscoelastic material functions can be obtained. Figure 14.5-1 shows how the rigid dumbbell results for $\eta'(\omega) = \int_0^\infty G(s)\cos\omega s\,ds$ and $\eta''(\omega) = \int_0^\infty G(s)\sin\omega s\,ds$ compare with experimental data for tobacco mosaic virus; it can be seen that the predicted shapes of the curves are very nearly correct.

Once the kernel functions $G_1, G_2, \ldots$ are known the retarded-motion expansion (Eq. D.4-3) can be obtained by expanding the kinematic tensor $\gamma_{[1]}$ about $t' = t$ and then designating the resulting integrals over the kernel functions by the constants $b_1, b_2, b_{11}, \ldots$ (see §9.6). When this is done the following constants are obtained:[5]

$$\begin{cases} b_1 = \eta_s + nkT\lambda \\ b_2 = -\tfrac{3}{5}nkT\lambda^2 \\ b_{11} = 0 \end{cases} \qquad \begin{cases} b_3 = \tfrac{3}{5}nkT\lambda^3 \\ b_{12} = \tfrac{12}{35}nkT\lambda^3 \\ b_{1:11} = \tfrac{3}{35}nkT\lambda^3 \end{cases} \tag{14.5-29}$$

Note that $|b_2| > |b_{11}|$ and that $b_3 > b_{12} > b_{1:11}$, the same inequalities having also been found for FENE dumbbells in §13.5. The fourth-order constants have also been obtained for rigid dumbbells.[5] Another way to get the retarded motion expansion constants[6] is to solve Eq. 14.2-8 for a general homogeneous, steady-state flow using the perturbation method of §13.5.

[4] It is also possible to present the rigid-dumbbell results in terms of a "corotational memory-integral expansion" [S. I. Abdel-Khalik, O. Hassager, and R. B. Bird, *J. Chem. Phys.*, **61**, 4312–4316 (1974)]. The first three terms of the corotational expansion represent the rigid dumbbell η, Ψ_1, and $\bar{\eta}$ curves far better than the first three terms of Eq. 14.5-26.

[5] R. C. Armstrong, Ph.D. Thesis, University of Wisconsin-Madison (1973); see also R. C. Armstrong and R. B. Bird, *op. cit.*

[6] H. Giesekus, *Kolloid-Z.*, **147–149**, 29–45 (1956); *Rheol. Acta*, **3**, 59–71 (1963); S. Prager, *Trans. Soc. Rheol.*, **1**, 53–62 (1957).

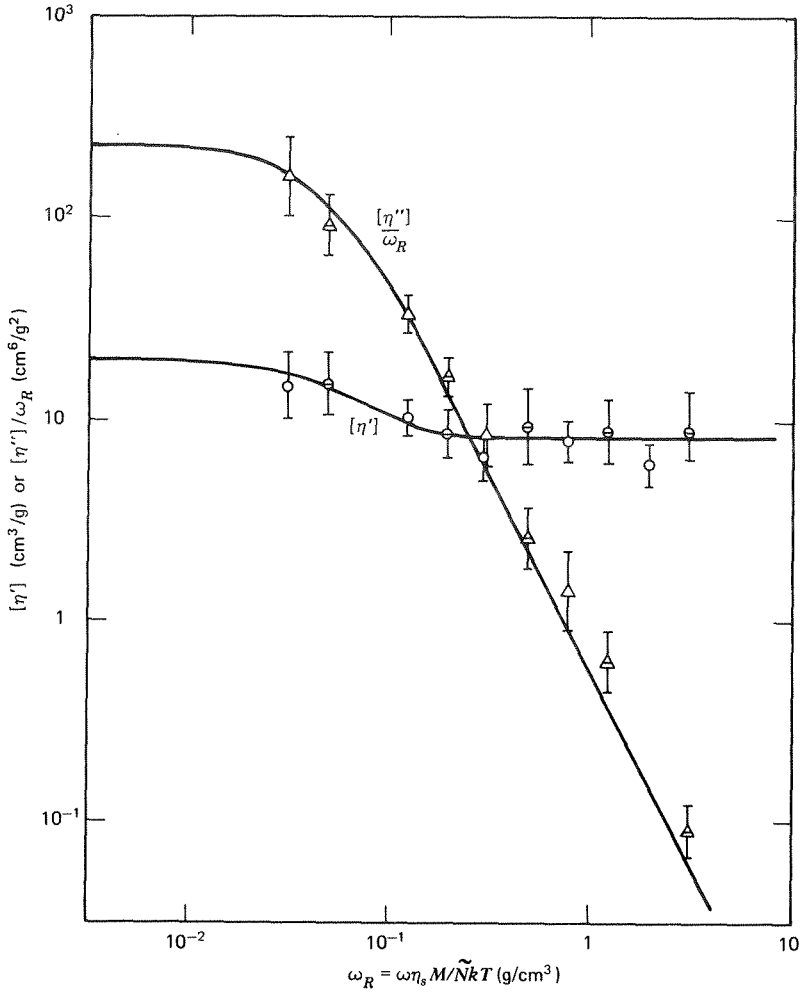


FIGURE 14.5-1. Comparison of the intrinsic complex viscosity predicted by the rigid dumbbell model with experimental data. Both $[\eta']$ (circles) and $[\eta'']/\omega_R$ (triangles) are plotted as functions of reduced frequency $\omega_R = \omega\eta_s M/\tilde{N}kT$. The data are for solutions of tobacco mosaic virus ($M = 3.9 \times 10^7$ g/mol) in a mixture of glycerol and water containing EDTA. Empty symbols represent data taken at 310.0 K; dashed symbols, at 298.2 K. The solvent viscosity at the two temperatures is 3.43×10^{-3} and 5.16×10^{-3} Pa·s, respectively. The rigid dumbbell predictions were computed by using a value $[\eta]_0 = 20$ cm^3/g, which was chosen to provide a best fit with the data. This choice corresponds to choosing λ by Eq. 14.4-23. Furthermore this value for $[\eta]_0$ is of the correct order of magnitude; Nemoto, Schrag, Ferry, and Fulton estimate from literature values that $[\eta]_0 = 27$ cm^3/g. [Data from N. Nemoto, J. L. Schrag, J. D. Ferry, and R. W. Fulton, *Biopolymers*, **14**, 407–417 (1975).]

§14.6 HYDRODYNAMIC INTERACTION[1,2]

Up to this point in the discussion of rigid-dumbbell kinetic theory we have ignored hydrodynamic interaction. We now return to the force balance equations in Eqs. 14.2-1 and 14.2-2 and make a modification in the hydrodynamic force terms to account for the fluid perturbation resulting from the bead motion. After this has been done the diffusion equation and the stress tensor formula are discussed.

a. The Hydrodynamic Interaction Tensor and Stokes' Law

We begin by modifying Eq. 14.2-4 to include the fluid velocity perturbation $\boldsymbol{v}'_v$ resulting from bead $-v$ (where, as in §14.2, $v = +1$ or -1):

$$\boldsymbol{F}_v^{(h)} = -\zeta([\![\dot{\boldsymbol{r}}_v]\!] - \boldsymbol{v}_v - \boldsymbol{v}'_v) \tag{14.6-1}$$

where $\boldsymbol{v}'_v = -[\boldsymbol{\Omega} \cdot \boldsymbol{F}_{-v}^{(h)}]$, in which $\boldsymbol{\Omega}$ is the hydrodynamic interaction tensor (cf. Eq. 13.6-3). We could use the Oseen-Burgers tensor introduced in §13.6, but instead we use the somewhat more general Rotne-Prager-Yamakawa hydrodynamic interaction tensor[3] which for the rigid dumbbell is

$$\boldsymbol{\Omega} = \frac{1}{8\pi\eta_s L}(A\boldsymbol{\delta} + B\boldsymbol{uu}) \tag{14.6-2}$$

where $A = 1 + \frac{1}{6}\xi^2$ and $B = 1 - \frac{1}{2}\xi^2$. The quantity $\xi = d/L$ is the ratio of the bead diameter to the distance between bead centers: when $\xi = 0$ the beads are point masses and Eq. 14.6-2 becomes the Oseen-Burgers tensor, and when $\xi = 1$ the beads are osculating. The Rotne-Prager-Yamakawa tensor accounts approximately for the finite size of the beads and is preferable when many-bead models are used. In fact this improved hydrodynamic interaction tensor was developed because it had been found that for many-bead rods the Oseen-Burgers' tensor led to negative values of the translational diffusivity.[4]

When Eqs. 14.6-1 and 14.6-2 are combined, and when $\boldsymbol{v}_v$ is replaced by $\boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_v]$, the following expression is obtained for the hydrodynamic force on bead v:

$$\boldsymbol{F}_v^{(h)} = -\boldsymbol{J} - \zeta(\tfrac{1}{2}vL[\![\boldsymbol{u}]\!] - \tfrac{1}{2}vL[\boldsymbol{\kappa} \cdot \boldsymbol{u}]) - h[(A\boldsymbol{\delta} + B\boldsymbol{uu}) \cdot \boldsymbol{F}_{-v}^{(h)}] \tag{14.6-3}$$

where $h = \zeta/8\pi\eta_s L$ is the *hydrodynamic interaction parameter* and

$$\boldsymbol{J} = \zeta([\![\dot{\boldsymbol{r}}_c]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c]) \tag{14.6-4}$$

[1] R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **14**, 85-101 (1984).

[2] The first work on rigid dumbbells with hydrodynamic interaction was that of H. Giesekus, *Rheol. Acta*, **2**, 50-62 (1962); some of this work was later duplicated by R. B. Bird and H. R. Warner, Jr., *Trans. Soc. Rheol.*, **15**, 741-750 (1971). Much earlier J. G. Kirkwood and P. L. Auer [*J. Chem. Phys.*, **19**, 281-283 (1951)] derived an expression for the complex viscosity for a multibead dumbbell, and T. Kotaka [*J. Chem. Phys.*, **30**, 1566-1567 (1959)] developed the theory for viscosity and normal-stress functions.

[3] J. Rotne and S. Prager, *J. Chem. Phys.*, **50**, 4831-4837 (1969); H. Yamakawa, *J. Chem. Phys.*, **53**, 436-443 (1970).

[4] R. E. DeWames, W. F. Hall, and M. C. Shen, *J. Chem. Phys.*, **46**, 2782-2794 (1967); R. Zwanzig, J. Kiefer, and G. H. Weiss, *Proc. Natl. Acad. Sci.*, **60**, 381-386 (1968).

We now split $\boldsymbol{F}_v^{(h)}$ into two vectors, one having only a component in the $\boldsymbol{u}$ direction, and another having components only in the $\boldsymbol{s}$ and $\boldsymbol{t}$ directions:

$$[\boldsymbol{uu}\cdot\boldsymbol{F}_v^{(h)}] = -[\boldsymbol{uu}\cdot\boldsymbol{J}] + \tfrac{1}{2}v\zeta L[\boldsymbol{\kappa}:\boldsymbol{uuu}] - (A+B)h[\boldsymbol{uu}\cdot\boldsymbol{F}_{-v}^{(h)}] \tag{14.6-5}$$

$$[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{F}_v^{(h)}] = -[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{J}] - \tfrac{1}{2}v\zeta L([\![\dot{\boldsymbol{u}}]\!] - [\boldsymbol{\kappa}\cdot\boldsymbol{u}] + [\boldsymbol{\kappa}:\boldsymbol{uuu}]) - Ah[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{F}_{-v}^{(h)}] \tag{14.6-6}$$

If these equations are written for the ith Cartesian component and if each equation is divided by the factor multiplying the "$\frac{1}{2}v$" then both equations are found to have the form

$$\phi_v + \alpha\phi_{-v} + C = \tfrac{1}{2}v \qquad (v = \pm 1) \tag{14.6-7}$$

where $\alpha = (A+B)h$ in the first equation and $\alpha = Ah$ in the second. Equation 14.6-7 may be solved to give

$$\phi_v = \frac{v}{2(1-\alpha)} - \frac{C}{1+\alpha} \qquad (v = \pm 1) \tag{14.6-8}$$

Consequently Eqs. 14.6-5 and 6 can also be solved:

$$[\boldsymbol{uu}\cdot\boldsymbol{F}_v^{(h)}] = \frac{v\zeta L[\boldsymbol{\kappa}:\boldsymbol{uuu}]}{2[1-(A+B)h]} - \frac{[\boldsymbol{uu}\cdot\boldsymbol{J}]}{1+(A+B)h} \tag{14.6-9}$$

$$[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{F}_v^{(h)}] = \frac{-v\zeta L[[\![\dot{\boldsymbol{u}}]\!] - \boldsymbol{\kappa}\cdot\boldsymbol{u} + \boldsymbol{\kappa}:\boldsymbol{uuu}]}{2(1-Ah)} - \frac{[(\boldsymbol{\delta}-\boldsymbol{uu})\cdot\boldsymbol{J}]}{1+Ah} \tag{14.6-10}$$

These equations are used in lieu of Eq. 14.2-4.

b. The Diffusion Equation for $f(\boldsymbol{u}, t)$

We omit the external force terms in the force balance in Eq. 14.2-1. In this balance the Brownian forces $\boldsymbol{F}_v^{(b)}$ are given by Eq. 14.2-3, and the hydrodynamic forces $\boldsymbol{F}_v^{(h)}$ can be obtained by adding together Eqs. 14.6-9 and 14.6-10. Then when the sum on v in Eq. 14.2-1 is performed, we find that $\boldsymbol{J}$ must be zero. Hence from Eq. 14.6-4 we conclude that

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_c] \tag{14.6-11}$$

That is, the center of mass moves, on the average, with the fluid.

Next, from Eqs. 14.2-2, 14.6-9, and 14.6-10 we get, in the absence of external forces

$$[\![\dot{\boldsymbol{u}}]\!] = [\boldsymbol{\kappa}\cdot\boldsymbol{u}] - [\boldsymbol{\kappa}:\boldsymbol{uuu}] - \frac{2kT(1-Ah)}{\zeta L^2}\frac{\partial}{\partial\boldsymbol{u}}\ln f \tag{14.6-12}$$

When this is substituted into the equation of continuity for $f(\boldsymbol{u}, t)$ (Eq. 14.2-7) we obtain the *diffusion equation*

$$\boxed{\frac{\partial}{\partial t} f = \frac{1}{6\lambda_2^{(1)}} \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} f \right) - \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] f \right)} \tag{14.6-13}$$

in which $\lambda_2^{(1)}(h, \xi) = (\zeta L^2/12kT)[1 - h(1 + \frac{1}{6}\xi^2)]^{-1}$ is a time constant for the two-bead rod (i.e., rigid dumbbell). This partial differential equation differs from Eq. 14.2-8 only in the definition of the time constant; hence all the solutions to Eq. 14.2-8 given in §14.4 and §14.5 can be taken over at once for rigid dumbbells with hydrodynamic interaction.

c.. The Stress Tensor

It is proven later—in Chapter 18—that Eq. C of Table 14.3-1 is the correct expression to use for the stress tensor when hydrodynamic interaction is included. In terms of the $\boldsymbol{u}$ vector this formula becomes

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} - \tfrac{1}{2} nL \langle \boldsymbol{u}(\boldsymbol{F}_1^{(h)} - \boldsymbol{F}_{-1}^{(h)}) \rangle \tag{14.6-14}$$

The $\boldsymbol{F}_v^{(h)}$ for $v = \pm 1$ may be obtained by adding together Eqs. 14.6-9 and 14.6-10, with $\boldsymbol{J} = \boldsymbol{0}$; we also eliminate $[\![\boldsymbol{\dot{u}}]\!]$ from the second of these equations by using Eq. 14.6-12. This gives

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} - \tfrac{1}{2} nL \left\langle \boldsymbol{u} \left(\frac{\zeta L [\boldsymbol{\kappa} : \boldsymbol{uuu}]}{1 - (A + B)h} + \frac{2kT}{L} \frac{\partial}{\partial \boldsymbol{u}} \ln f \right) \right\rangle \tag{14.6-15}$$

The integral involving $(\partial/\partial \boldsymbol{u}) \ln f$ can be performed (see Eq. 14.3-4) and we get finally

$$\boxed{\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} - 6nkT\lambda_2^{(2)} \{\boldsymbol{\kappa} : \langle \boldsymbol{uuuu} \rangle\} - 3nkT \langle \boldsymbol{uu} \rangle + nkT\boldsymbol{\delta}} \tag{14.6-16}$$

where $\lambda_2^{(2)}(h, \xi) = (\zeta L^2/12kT)[1 - 2h(1 - \frac{1}{6}\xi^2)]^{-1}$. This has the same form as Eq. A of Table 14.3-1; only the time constant is different. Note that in the differential equation for $f(\boldsymbol{u}, t)$ the time constant $\lambda_2^{(1)}(h, \xi)$ appears, whereas in the stress tensor it is $\lambda_2^{(2)}(h, \xi)$ that comes in; note further that $\lambda_2^{(2)}(h, \xi)$ may be obtained from $\lambda_2^{(1)}(h, \xi)$ by replacing h by $2h$, and ξ^2 by $-\xi^2$. The stress tensor can also be put in the "Giesekus form":

$$\boxed{\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + 3nkT\lambda_2^{(2)} \langle \boldsymbol{uu} \rangle_{(1)} - \left[1 - \frac{\lambda_2^{(2)}}{\lambda_2^{(1)}} \right] (3nkT \langle \boldsymbol{uu} \rangle - nkT\boldsymbol{\delta})} \tag{14.6-17}$$

which can be compared with Eq. D of Table 14.3-1. When there is no hydrodynamic interaction $\lambda_2^{(1)} = \lambda_2^{(2)} = \lambda = \zeta L^2/12kT$.

SPECIAL NOTE ON EXTENSION TO MULTIBEAD-ROD MODELS
(with hydrodynamic interaction)

To extend Eqs. 14.6-13, 14.6-16, and 14.6-17 to multibead rods with N beads distributed uniformly over a rod of length L with bead centers separated by the distance a (see Fig. 14.1-2), replace $\lambda_2^{(1)}$ by $\lambda_N^{(1)}$, and $\lambda_2^{(2)}$ by $\lambda_N^{(2)}$ where

$$\lambda_N^{(1)}(h, \xi) = \frac{\zeta a^2}{12kT}\left(\sum_{\nu=-(N-1)}^{N-1} \nu\phi_\nu(h, \xi^2, N)\right) \tag{14.6-18a}$$

$$\lambda_N^{(2)}(h, \xi) = \frac{\zeta a^2}{12kT}\left(\sum_{\nu=-(N-1)}^{N-1} \nu\phi_\nu(2h, -\xi^2, N)\right) \tag{14.6-18b}$$

and

$$\phi_\nu(\alpha, \beta, N) + 2\alpha\sum_{\mu}{}' \left(\frac{1}{|\nu-\mu|} + \frac{2}{3}\beta\frac{1}{|\nu-\mu|^3}\right)\phi_\mu(\alpha, \beta, N) = \tfrac{1}{2}\nu \tag{14.6-19}$$

Here $\sum_\mu'$ is a sum from $-(N-1)$ *to* $+(N-1)$, omitting the term $\mu = \nu$, and using even (odd) values of μ if N is odd (even). For multibead dumbbells h is redefined as $h = \zeta/8\pi\eta_s a$. In addition, some sample values of $\lambda_N^{(k)}$ are given in Table 14.6-1. (For detailed discussions of the multibead-rod model, see Examples 16.1-1, 16.2-1, 16.3-1, and 16.4-1.)

EXAMPLE 14.6-1 The Viscometric Functions for Multibead Rods[1]

Obtain the small shear rate expansion of the viscometric functions for a dilute solution of rodlike polymers modeled as multibead rods including hydrodynamic interaction. Find $\Psi_{2,0}/\Psi_{1,0}$ for the model in which the beads are just touching each other.

SOLUTION **(a)** First one has to solve Eq. 14.6-13, with $\lambda_2^{(1)}(h, \xi)$ replaced by $\lambda_N^{(1)}(h, \xi)$, for steady-shear flow. This solution can be immediately taken over from Eqs. 14.4-7, 14.4-11, 14.4-13, and 14.4-14 with λ replaced by $\lambda_N^{(1)}(h, \xi)$. Then we use Eq. 14.6-17 for the stress tensor, appropriately modified for N beads; for steady shear flow this gives for the stress components

$$\tau_{yx} - \tau_{yx,s} = -\tfrac{1}{2}nkT\lambda_N^{(2)}\dot{\gamma}\langle 2(P_0^0 - P_2^0)c_0 - P_2^2c_2\rangle - \left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right](\tfrac{1}{2}nkT\langle P_2^2 s_2\rangle), \tag{14.6-20}$$

$$\tau_{xx} - \tau_{yy} = -nkT\lambda_N^{(2)}\dot{\gamma}\langle P_2^2 s_2\rangle - \left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right](nkT\langle P_2^2 c_2\rangle), \tag{14.6-21}$$

$$\tau_{yy} - \tau_{zz} = \left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right](3nkT\langle \tfrac{1}{6}P_2^2 c_2 + P_2^0 c_0\rangle) \tag{14.6-22}$$

When the averaged values are evaluated using the expansion for $f(\boldsymbol{u}, t)$, the following series are obtained for the viscometric functions:

$$\eta - \eta_s = nkT\lambda_N^{(2)}\left\{1 - \frac{18}{35}[\lambda_N^{(2)}\dot{\gamma}]^2 + \cdots\right\}$$
$$+ \frac{3}{5}nkT\lambda_N^{(1)}\left\{1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right\}\left\{1 - \frac{38}{35}[\lambda_N^{(1)}\dot{\gamma}]^2\cdots\right\} \tag{14.6-23}$$

$$\Psi_1 = \frac{6}{5} nkT\lambda_N^{(2)}\lambda_N^{(1)}\left\{1 - \frac{38}{35}[\lambda_N^{(1)}\dot{\gamma}]^2 + \cdots\right\}$$
$$+ \frac{6}{5} nkT\lambda_N^{(1)2}\left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right]\left\{1 - \frac{46}{35}[\lambda_N^{(1)}\dot{\gamma}]^2 + \cdots\right\} \quad (14.6\text{-}24)$$

$$\Psi_2 = -\frac{12}{35} nkT\lambda_N^{(1)2}\left[1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right]\left\{1 - \frac{157}{110}[\lambda_N^{(1)}\dot{\gamma}]^2 + \cdots\right\} \quad (14.6\text{-}25)$$

When hydrodynamic interaction is neglected $h = 0$, and then the time constants become $\lambda_N^{(1)}(h, \xi) = \lambda_N^{(2)}(h, \xi) = \zeta L^2 N(N+1)/72(N-1)kT$, so that Eqs. 14.4-18, 14.4-19, and 14.4-20 are recovered for $N = 2$.

TABLE 14.6-1

Information Required to Obtain $\lambda_N^{(1)}(h, \xi)$ and $\lambda_N^{(2)}(h, \xi)$ for Solutions of Multibead Rods (with Osculating Spheres and Rotne–Prager–Yamakawa Hydrodynamic Interaction)[a]

Number of beads N	$\frac{\lambda_N^{(1)}(\frac{3}{8}, 1)}{(\zeta a^2/6kT)}$	$\frac{\lambda_N^{(2)}(\frac{3}{8}, 1)}{(\zeta a^2/6kT)}$	$1 - \frac{\lambda_N^{(2)}(\frac{3}{8}, 1)}{\lambda_N^{(1)}(\frac{3}{8}, 1)}$
2	0.8889E + 00	0.1333E + 01	−0.50000
3	0.2485E + 01	0.3122E + 01	−0.25810
4	0.5185E + 01	0.5969E + 01	−0.15120
5	0.9121E + 01	0.9842E + 01	−0.07912
6	0.1449E + 02	0.1490E + 02	−0.02842
7	0.2147E + 02	0.2125E + 02	0.01022
8	0.3022E + 02	0.2899E + 02	0.04076
9	0.4091E + 02	0.3822E + 02	0.06570
10	0.5369E + 02	0.4905E + 02	0.08652
11	0.6873E + 02	0.6156E + 02	0.10425
12	0.8617E + 02	0.7587E + 02	0.11956
13	0.1062E + 03	0.9205E + 02	0.13295
14	0.1289E + 03	0.1102E + 03	0.14479
15	0.1544E + 03	0.1304E + 03	0.15535
16	0.1829E + 03	0.1528E + 03	0.16484
17	0.2146E + 03	0.1774E + 03	0.17344
18	0.2495E + 03	0.2043E + 03	0.18136
19	0.2879E + 03	0.2336E + 03	0.18842
20	0.3297E + 03	0.2654E + 03	0.19501
25	0.5970E + 03	0.4648E + 03	0.22148
30	0.9727E + 03	0.7386E + 03	0.24071
35	0.1473E + 04	0.1097E + 04	0.25548
40	0.2113E + 04	0.1548E + 04	0.26737
45	0.2908E + 04	0.2102E + 04	0.27697
50	0.3872E + 04	0.2768E + 04	0.28512
55	0.5021E + 04	0.3554E + 04	0.29210
60	0.6368E + 04	0.4469E + 04	0.29816
65	0.7928E + 04	0.5522E + 04	0.30349
70	0.9714E + 04	0.6720E + 04	0.30823

[a] "E + 04" means "$\times 10^4$."

(b) From Eqs. 14.6-24 and 14.6-25, in the limit as $\dot{\gamma} \to 0$, we get

$$\frac{\Psi_{2,0}}{\Psi_{1,0}} = -\frac{2}{7}\left(1 - \frac{\lambda_N^{(2)}}{\lambda_N^{(1)}}\right) \tag{14.6-26}$$

For the model with osculating dumbbells the bead diameter d is the same as the distance between the bead centers a, so that $\xi = d/a = 1$. The hydrodynamic interaction parameter $h = \zeta/8\pi\eta_s L$ can be estimated by using the Stokes' law expression for ζ, namely $\zeta = 3\pi\eta_s d$; hence $h = \frac{3}{8}$. Values of $\lambda_N^{(1)}(h, \xi)$ and $\lambda_N^{(2)}(h, \xi)$ for $\xi = 1$ and $h = \frac{3}{8}$ are given in Table 14.6-1. It can be seen from the table that

$$\frac{\Psi_{2,0}}{\Psi_{1,0}} > 0 \quad \text{for } N \leq 6; \qquad \frac{\Psi_{2,0}}{\Psi_{1,0}} < 0 \quad \text{for } N \geq 7 \tag{14.6-27}$$

This emphasizes the sensitivity of the second normal stress difference to details of structure. We know of no experimental data on rigid rodlike molecules that corroborate these theoretical results.

EXAMPLE 14.6-2 Steady Shear Flow Properties of Rigid Dumbbell Suspensions at Arbitrary Shear Rates[5] (Numerical Calculation)

Determine the viscometric functions for a dilute suspension of rigid dumbbells, including complete hydrodynamic interaction, for arbitrarily large shear rates. The velocity field is $v_x = \dot{\gamma}y$, $v_y = v_z = 0$. Use Oseen-Burgers hydrodynamic interaction.

SOLUTION The differential equation for $f(\boldsymbol{u})$ is the same as Eq. 14.4-1 except that λ is replaced with $\lambda_2^{(1)}(h, 0) = \lambda/(1 - h) \equiv \lambda_h$

$$\Lambda f = (6\lambda_h\dot{\gamma})\Omega_s f \tag{14.6-28}$$

The distribution function f is normalized to unity. As in Example 14.4-1 we solve Eq. 14.6-28 by expanding f in terms of the spherical harmonics. Here we do not use these functions as coefficients in a power series expansion in shear rate, as before. Instead we use all spherical harmonics of the first $M + 1$ kinds to construct an Mth order approximation to f, denoted by $f^{(M)}$, for any shear rate:

$$f^{(M)} = \sum_{n=0}^{M} \sum_{m=0}^{n} (A_n^m P_n^m c_m + B_n^m P_n^m s_m) \tag{14.6-29}$$

The coefficients A_n^m and B_n^m are functions of the dimensionless shear rate $\lambda_h\dot{\gamma}$ and are to be determined for each approximation $f^{(M)}$ so as to make it close to the actual f in some sense. The quantity multiplying B_n^0 is zero and, hence, these coefficients do not actually enter. However, for convenience we write the sum on m from 0 to n.

To find the coefficients at the Mth level of approximation, we insert Eq. 14.6-29 into Eq. 14.6-28 and use the relations for the Λ and Ω_s operators presented in §14.4:

$$\sum_{n=0}^{M} \sum_{m=0}^{n} n(n+1)(A_n^m P_n^m c_m + B_n^m P_n^m s_m)$$

$$- (6\lambda_h\dot{\gamma}) \sum_{n=0}^{M} \sum_{m=0}^{n} \sum_{j=m-2}^{m+2} \sum_{k=n-2}^{n+2} a_{nk}^{mj}(A_n^m P_k^j s_j - B_n^m P_k^j c_j) \equiv F^{(M)} \tag{14.6-30}$$

The residual function $F^{(M)}$ then tells how nearly the trial function satisfies the differential equation. If we had guessed the correct solution, $F^{(M)}$ would be zero. The coefficients are now determined by

[5] This example is patterned after W. E. Stewart and J. P. Sørensen, *Trans. Soc. Rheol.*, **16**, 1-13 (1972).

applying Galerkin's method.[6] This method requires that when $F^{(M)}$ is multiplied by a function of θ and ϕ and integrated over all possible orientations, the result is zero; in other words a weighted mean value of $F^{(M)}$ is forced to be zero. Since we have $(M+1)(M+2)$ coefficients to evaluate, we use the $(M+1)(M+2)$ linearly independent spherical harmonics in $f^{(M)}$ as weighting functions. Because the spherical harmonics form a complete set of functions, these integral requirements will force $f^{(M)}$ to satisfy Eq. 14.6-28 as M approaches infinity. Equivalently, we set $F^{(M)}$ orthogonal to each of the $(M+1)(M+2)$ spherical harmonics:

$$\int_0^{2\pi}\int_0^{\pi} F^{(M)} P_q^p \begin{Bmatrix} s_p \\ c_p \end{Bmatrix} S \, d\theta \, d\phi = 0 \qquad \begin{matrix} (p = 0, 1, \ldots, q) \\ (q = 0, 1, \ldots, M) \end{matrix} \tag{14.6-31}$$

where the integral must be zero for both s_p and c_p. It is in the above sense that we require $f^{(M)}$ to be close to f. Insertion of Eq. 14.6-30 for $F^{(M)}$ into Eq. 14.6-31 and application of the orthogonality condition Eq. E.8-7 gives

$$\begin{aligned} q(q+1)A_q^p + (6\lambda_h\dot{\gamma}) \sum_{n=0}^{M} \sum_{m=0}^{n} a_{nq}^{mp} B_n^m = 0, \\ q(q+1)B_q^p - (6\lambda_h\dot{\gamma}) \sum_{n=0}^{M} \sum_{m=0}^{n} a_{nq}^{mp} A_n^m = 0, \end{aligned} \qquad \begin{matrix} (p = 0, 1, \ldots, q) \\ (q = 0, 1, \ldots, M) \end{matrix} \tag{14.6-32}$$

No information is obtained from the above equations for $q = 0$, because they are then identically satisfied. These two equations should give information about A_0^0 and B_0^0. The lost condition on A_0^0 can be replaced by a relation obtained from substituting $f^{(M)}$ into the normalization condition:

$$A_0^0 = 1 \tag{14.6-33}$$

The lost condition on B_0^0 does not need to be replaced, since none of the coefficients B_n^0 are required.

Symmetry requirements can be used to simplify the problem further. The problem description is unchanged by reflections through the xy-plane. Hence the distribution function must be unchanged by replacement of θ with $\pi - \theta$. This means that all A_n^m and B_n^m are zero if n is odd. In addition, a combined rotation through $\phi = 180°$ plus a reflection through the xy-plane is equivalent to a single rotation through $\phi = 360°$. Thus A_n^m and B_n^m must also be zero if m is odd. The problem is thus to determine the remaining $(\frac{1}{2}M + 1)^2$ coefficients from the same number of conditions contained in Eqs. 14.6-32 and 14.6-33.

As an example, we show how to find the coefficients that go with $f^{(2)}$. For $M = 2$, the unknowns are A_0^0, A_2^0, A_2^2, and B_2^2, and from Eqs. 14.6-32 and 14.6-33 they must be solutions to

$$\begin{gathered} A_0^0 = 1; \quad 6A_2^0 + (\tfrac{36}{7})(\lambda_h\dot{\gamma})B_2^2 = 0; \quad -6A_2^2 + (6\lambda_h\dot{\gamma})B_2^2 = 0; \\ 3\lambda_h\dot{\gamma}A_0^0 - \tfrac{3}{7}\lambda_h\dot{\gamma}A_2^0 - 6\lambda_h\dot{\gamma}A_2^2 - 6B_2^2 = 0 \end{gathered} \tag{14.6-34}$$

From this system of equations it is easy to show that

$$f^{(2)} = 1 - \frac{21(\lambda_h\dot{\gamma})P_2^0}{[49 + 46(\lambda_h\dot{\gamma})^2]} + \frac{49(\lambda_h\dot{\gamma})((\lambda_h\dot{\gamma})P_2^2 c_2 + P_2^2 s_2)}{2[49 + 46(\lambda_h\dot{\gamma})^2]} \tag{14.6-35}$$

Once the distribution function has been found, the stresses may be calculated from Eq. 14.6-20, 14.6-21, and 14.6-22. If $f^{(M)}$ is used to compute the ensemble averages in those relations, we

[6] F. B. Hildebrand, *Methods of Applied Mathematics*, Prentice-Hall, Englewood Cliffs, NJ (1965), 2nd ed., p. 286.

can express the viscometric functions in terms of the coefficients of the spherical harmonics. Insertion of Eq. 14.6-29 into Eqs. 14.6-20, 14.6-21, and 14.6-22 gives for $M \geq 2$:

$$\frac{\eta - \eta_s}{nkT\lambda_h} = \left(\frac{1-h}{1-2h}\right)[1 - \tfrac{1}{5}A_2^0 - \tfrac{6}{5}A_2^2] - \frac{6}{5\lambda_h\dot{\gamma}}\frac{h}{(1-2h)}B_2^2 \tag{14.6-36}$$

$$\frac{\Psi_1}{nkT\lambda_h^2} = \frac{12}{5\lambda_h\dot{\gamma}}\left(\frac{1-h}{1-2h}\right)B_2^2 - \frac{12}{5(\lambda_h\dot{\gamma})^2}\frac{h}{(1-2h)}A_2^2 \tag{14.6-37}$$

$$\frac{\Psi_2}{nkT\lambda_h^2} = \frac{3}{5(\lambda_h\dot{\gamma})^2}\frac{h}{(1-2h)}(A_2^0 + 2A_2^2) \tag{14.6-38}$$

Numerical values for these material functions can be obtained over a wide range of dimensionless shear rates. At any given value of $\lambda_h\dot{\gamma}$, the coefficients in $f^{(M)}$ are determined for successively larger values of M until the stress components converge to four digits. Convergence occurs for $M \leq 22$ provided that $\lambda_h\dot{\gamma} \leq 20$. For $\lambda_h\dot{\gamma} \geq 30$, M is always taken to be 22. Figure 14.6-1 shows the viscometric functions found in this way for the maximum and minimum value of the hydrodynamic interaction parameter h. At high shear rates a power-law region is clearly discernable for all three functions. The power-law asymptotes for $\lambda_h\dot{\gamma} \to \infty$ are given by

$$\frac{\eta - \eta_s}{nkT\lambda_h} \doteq 0.678\left(\frac{1-h}{1-2h}\right)(\lambda_h\dot{\gamma})^{-1/3} \tag{14.6-39}$$

$$\frac{\Psi_1}{nkT\lambda_h^2} \doteq 1.20\left(\frac{1-h}{1-2h}\right)(\lambda_h\dot{\gamma})^{-4/3} \tag{14.6-40}$$

$$\frac{\Psi_2}{nkT\lambda_h^2} \doteq 0.93\left(\frac{h}{1-2h}\right)(\lambda_h\dot{\gamma})^{-7/3} \tag{14.6-41}$$

Note that the effect of hydrodynamic interaction on the steady-shear flow properties is dramatic only for Ψ_2. As found in the perturbation calculation, Ψ_2 is positive when hydrodynamic interaction is included.

Now that the distribution function has been determined, it is of interest to see how the orientations of the dumbbells are affected by the shear flow. In Fig. 14.6-2 we show f for several values of the reduced shear rate. Note that as the shear rate is increased the dumbbells spend a greater fraction of their time nearer to the xz-plane. Most of the dumbbells are found to point just above the x-axis; once a dumbbell has been kicked below the x-axis by Brownian fluctuations, it quickly rotates toward the preferred orientation because of the hydrodynamic forces.

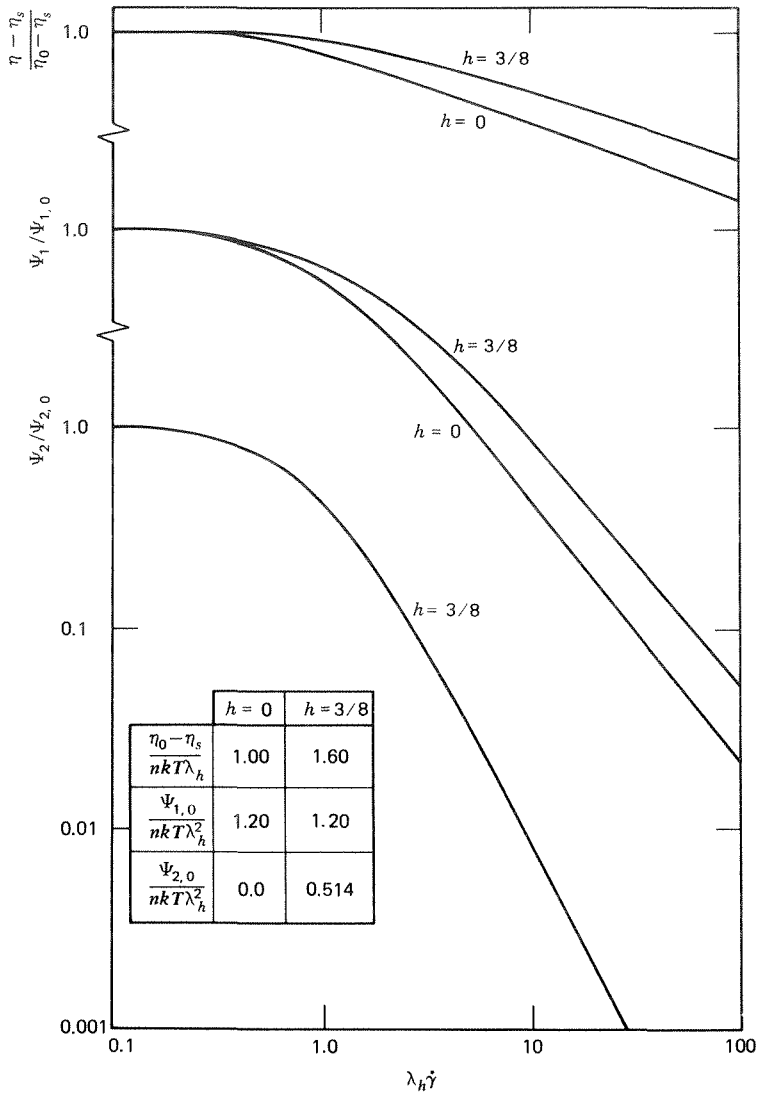
EXAMPLE 14.6-3 Translational Diffusivity of Rigid Dumbbells in Dilute Solution[7]

Obtain an expression for D_{tr} for rigid dumbbell solutions using Rotne-Prager-Yamakawa hydrodynamic interaction.

SOLUTION Start with Eq. 14.2-1—the force balance on the center of mass—and use Eq. 14.2-3 for $\boldsymbol{F}_v^{(b)}$ and Eqs. 14.6-9 and 14.6-10 for $\boldsymbol{F}_v^{(h)}$. This leads directly to

$$\frac{[\boldsymbol{uu}\cdot\boldsymbol{J}]}{1 + (A+B)h} + \frac{[(\boldsymbol{\delta} - \boldsymbol{uu})\cdot\boldsymbol{J}]}{1 + Ah} = \tfrac{1}{2}[\boldsymbol{F}_1^{(e)} + \boldsymbol{F}_{-1}^{(e)}] \tag{14.6-42}$$

[7] For multibead rods with hydrodynamic interaction D_{tr} has been obtained by J. Riseman and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 512–516 (1950); see also H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 280.



	$h = 0$	$h = 3/8$
$\frac{\eta_0-\eta_s}{nkT\lambda_h}$	1.00	1.60
$\frac{\Psi_{1,0}}{nkT\lambda_h^2}$	1.20	1.20
$\frac{\Psi_{2,0}}{nkT\lambda_h^2}$	0.0	0.514

FIGURE 14.6-1. Viscometric functions for a dilute suspension of rigid dumbbells with complete hydrodynamic interaction. The quantity h is a hydrodynamic interaction parameter: $h = 0$ represents no hydrodynamic interaction, and $h = 3/8$ represents maximum hydrodynamic interaction. It is interesting to note that the η-curve approaches its asymptote from above, crossing it at $\lambda_h\dot{\gamma} = 0.3$, and is 13% higher than its asymptote at $\lambda_h\dot{\gamma} = 1$ (for the $h = 0$ curve). The normal-stress-coefficient curves approach their asymptotes from below. [W. E. Stewart and J. P. Sørensen, *Trans. Soc. Rheol.*, **16**, 1–13 (1972)].

If the external force acting on both beads is the same, so that $\boldsymbol{F}_1^{(e)} = \boldsymbol{F}_{-1}^{(e)} = \boldsymbol{F}^{(e)}$, then the solution of Eq. 14.6-42 for $\boldsymbol{J}$ is

$$\boldsymbol{J} = [1 + (A + B)h][\boldsymbol{uu} \cdot \boldsymbol{F}^{(e)}] + (1 + Ah)[(\boldsymbol{\delta} - \boldsymbol{uu}) \cdot \boldsymbol{F}^{(e)}] \tag{14.6-43}$$

According to Eq. 14.6-4, for a system at rest $\boldsymbol{J} = \zeta[\![\dot{\boldsymbol{r}}_c]\!]$. When Eq. 14.6-43 is multiplied by $(1/\zeta)f_{\text{eq}}$ and integrated over all $\boldsymbol{u}$ we get $\langle \dot{\boldsymbol{r}}_c \rangle_{\text{eq}}$, which is the average velocity of the center of mass that results from

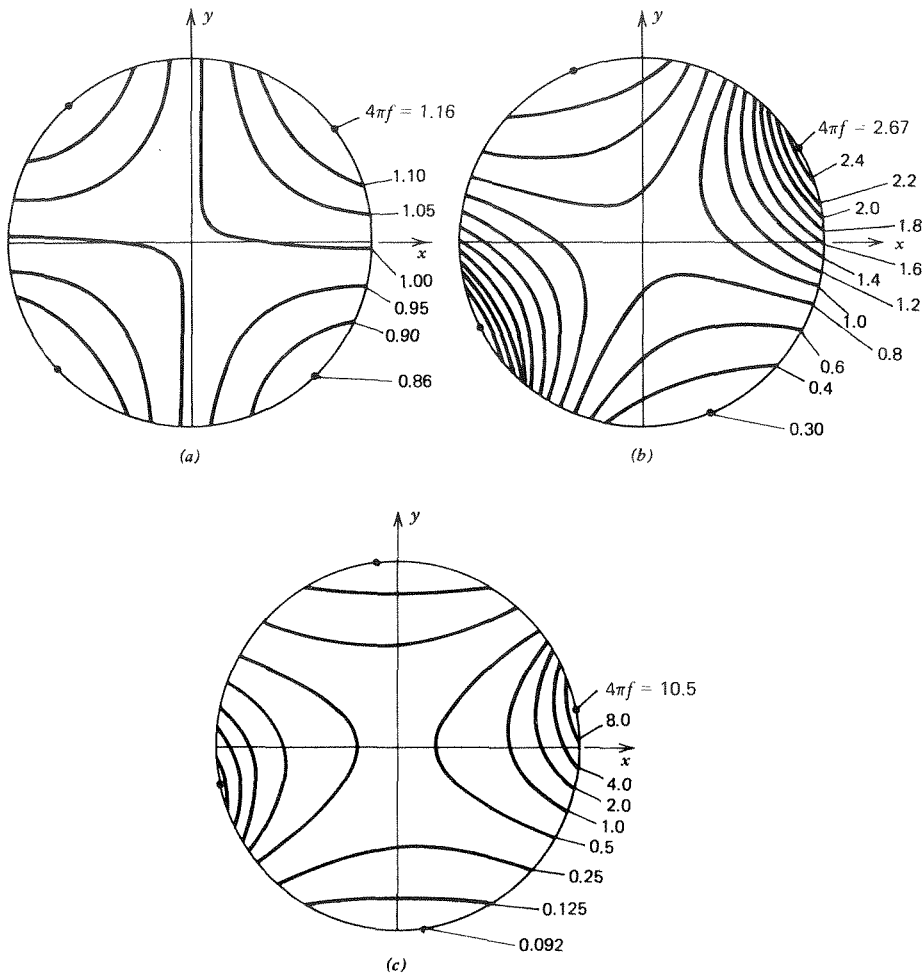


FIGURE 14.6-2. The distribution function f (multiplied by 4π) for a rigid dumbbell suspension undergoing steady shear flow. Contours of constant f are plotted on a unit sphere, and the resulting diagram projected onto the xy-plane (the unit sphere is viewed along the z-axis from infinity). Plots are shown for three different shear shear rates: (*a*) $\lambda_h\dot{\gamma} = 0.1$, (*b*) $\lambda_h\dot{\gamma} = 1.0$, and (*c*) $\lambda_h\dot{\gamma} = 10.0$. Notice that the peak in f at $\phi = 90°$ and $\theta \doteq$ (*a*) 40°, (*b*) 27°, and (*c*) 13° approaches the x-axis as $\lambda_h\dot{\gamma}$ increases. If there were no flow ($\lambda_h\dot{\gamma} = 0$), then f would be $1/4\pi$ everywhere on the surface of the unit sphere. [W. E. Stewart and J. P. Sørensen, *Trans. Soc. Rheol.*, **16**, 1-13 (1972)].

an applied external force. The result is

$$\langle \dot{\boldsymbol{r}}_c \rangle_{\text{eq}} = \frac{1}{\zeta}[1 + (A + \tfrac{1}{3}B)h]\boldsymbol{F}^{(e)} \tag{14.6-44}$$

But the friction coefficient Z for the dumbbell is defined by $2\boldsymbol{F}^{(e)} = Z\langle \dot{\boldsymbol{r}}_c \rangle$ (Eq. 13.6-19) and the translational diffusivity is related to Z by $D_{\text{tr}} = kT/Z$ (Eq. 13.6-15), so that for Rotne-Prager-Yamakawa hydrodynamic interaction

$$D_{\text{tr}} = \frac{kT}{2\zeta}[1 + (A + \tfrac{1}{3}B)h] = \frac{kT}{2\zeta}(1 + \tfrac{4}{3}h) \tag{14.6-45}$$

In obtaining this result we have used the equilibrium value of $\langle \dot{r}_c \rangle$ since the fluid as a whole is very nearly in a state of rest. We have also used the values of A and B given just below Eq. 14.6-2. For Oseen–Burgers hydrodynamic interaction ($A = B = 1$) the same result is obtained; for no hydrodynamic interaction D_{tr} is just $kT/2\zeta$.

PROBLEMS

14A.1 Viscosity of a Tobacco Mosaic Virus Solution

For the tobacco mosaic virus solution shown in Fig. 14.4-1, the zero-shear-rate intrinsic viscosity is $[\eta]_0 = 28\ \text{cm}^3/\text{g}$. Compute the viscosity of a $5.1 \times 10^{-4}\ \text{g/cm}^3$ aqueous solution of tobacco mosaic virus at a temperature of 300 K and at a shear rate $\dot{\gamma} = 0.15\ \text{s}^{-1}$. Compare the size of the macromolecule contribution to τ_{yx} to the magnitude of the solvent contribution.

14A.2 Distribution Function for Steady Shear Flow

a. A dilute suspension of rodlike macromolecules is undergoing steady shear flow. Using the perturbation solution for the distribution function given in Eqs. 14.4-7, 14.4-11, and 14.4-13, construct a plot showing contours of constant f for a dimensionless shear rate $\lambda\dot{\gamma} = 0.1$. The graph should be patterned after Fig. 14.6-2. Compare the plot from the perturbation solution to that based on the exact numerical solution, Fig. 14.6-2*a*. How well does the perturbation expansion describe the dumbbell suspension at these low shear rates?

b. Next use the terms through ϕ_3 in the perturbation solution to locate a few points on Fig. 14.6-2*b* for which $f = 1.4$ and $\lambda\dot{\gamma} = 1.0$. How well does the expansion do at the higher shear rate?

14A.3 Elongational Viscosity of a Poly-γ-benzyl-L-glutamate Solution

It is desired to estimate the behavior of the solution of poly-γ-benzyl-L-glutamate in *m*-cresol shown in Fig. 14.4-2 in an elongational flow. Pertinent data for the solution are $[\eta]_0 = 2.90\ \text{dL/g}$; $T = 293\ K$; $\bar{M}_w = 208{,}000$; $c = 0.51\ \text{g/dL}$.

a. What is the zero-elongation-rate elongational viscosity for this solution?

b. What is the slope of the $\bar{\eta}$ versus $\dot{\varepsilon}$ curve at $\dot{\varepsilon} = 0$?

c. What is the maximum value of $\bar{\eta}$ at large elongation rates (see Problem 14B.3)?

d. At a reduced elongation rate $\lambda\dot{\varepsilon} = \frac{1}{2}$, what is the value of $\bar{\eta}$? Compare this result with the prediction of the Hookean dumbbell.

14B.1 Stress Tensor for Steady, Homogeneous Potential Flow

Show that for rigid dumbbells in a fluid undergoing steady, homogeneous potential flow

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - 3nkT\lambda \frac{\int_0^{2\pi}\int_0^{\pi} \{\boldsymbol{\kappa}\cdot\boldsymbol{uu} + \boldsymbol{uu}\cdot\boldsymbol{\kappa}\} \exp(3\lambda\boldsymbol{\kappa}:\boldsymbol{uu}) \sin\theta\, d\theta\, d\phi}{\int_0^{2\pi}\int_0^{\pi} \exp(3\lambda\boldsymbol{\kappa}:\boldsymbol{uu}) \sin\theta\, d\theta\, d\phi} \qquad \text{(14B.1-1)}$$

What is the corresponding result for elastic dumbbells?

14B.2 Obtaining Rigid Dumbbell Results from an Elastic Dumbbell Model

Show that the stress tensor for rigid dumbbell suspensions undergoing steady, homogeneous irrotational flow (Eq. 14B.1-1) may be obtained from the corresponding result for Fraenkel dumbbells by taking the limit as $H \to \infty$. (HINT: see Eq. E.4-1.) What is the physical significance of this limiting process? Although this procedure works for dumbbell models it does not for three-bead, two-spring (rod) systems. (See §16.5.)

14B.3 Elongational Viscosity by Viscous Dissipation Arguments[1]

The limiting value of the elongational viscosity for a rigid dumbbell suspension at high elongation rates may be evaluated using a simple viscous dissipation argument. This is possible because in the limit as $\dot{\varepsilon} \to \infty$, all of the dumbbells will have a fixed orientation parallel to the z-axis (see Fig. 14B.3).

a. By computing the rate at which a bead does work on the solvent moving past it, show that the rate of viscous dissipation due to the presence of the dumbbells is $\frac{1}{2}n\zeta L^2\dot{\varepsilon}^2$, if there are n dumbbells per unit volume.

b. Next show that the rate of energy dissipation in the solvent flow field is $3\eta_s\dot{\varepsilon}^2$. In doing this it is assumed that the solvent flow field is not disturbed by the presence of the dumbbells.

c. Use Eq. 9.6-21 to obtain the rate of viscous dissipation in a viscoelastic continuum undergoing an elongational flow in terms of the components of the solution stress tensor and the velocity gradient tensor; then use Eq. D.5-14 to rewrite this result in terms of the elongational viscosity $\bar{\eta}$ and the elongation rate $\dot{\varepsilon}$. Equate this result to the sum of the dissipation rates in (a) and (b) and show that

$$\bar{\eta}(\infty) = 3\eta_s + 6nkT\lambda \tag{14B.3-1}$$

d. Show that Eq. 14B.3-1 is in agreement with $\bar{\eta}(\infty)$ found from Eq. 14.4-32.

14B.4 Oldroyd Model and Rigid Dumbbell Solution

a. Insert the expressions in Eq. 14.5-29 for the b's into the corresponding expression for the six-constant Oldroyd model given in Table 6.2-2. Show that the Oldroyd model constants are given in terms of the rigid-dumbbell kinetic theory parameters by:

$$\eta_0 = \eta_s + nkT\lambda \tag{14B.4-1}$$

$$\lambda_1 = \lambda \tag{14B.4-2}$$

$$\lambda_2 = \lambda\left(1 - \frac{3}{5}\frac{nkT\lambda}{\eta_s + nkT\lambda}\right) \tag{14B.4-3}$$

$$\lambda_3 = \tfrac{8}{7}\lambda \tag{14B.4-4}$$

$$\lambda_4 = \tfrac{8}{7}\lambda \tag{14B.4-5}$$

$$\lambda_5 = -\tfrac{2}{7}\lambda \tag{14B.4-6}$$

b. Show that when the above constants are substituted into Eq. A of Table 7.3-3 we get

$$\frac{\eta - \eta_s}{nkT\lambda} = \frac{1 + (124/245)(\lambda\dot{\gamma})^2}{1 + (50/49)(\lambda\dot{\gamma})^2} \tag{14B.4-7}$$

How does this compare with the exact numerical calculations of Stewart and Sørensen (§14.6)?

c. Compare Eq. 14B.4-7 with Eq. 14.4-18. [NOTE: The six-constant Oldroyd model with the constants given in (a) describes the steady shear flow properties through the third order in $\lambda\dot{\gamma}$ exactly

[1] R. I. Tanner and W. Stehrenberger, *J. Chem. Phys.*, **55**, 1958-1964 (1971).

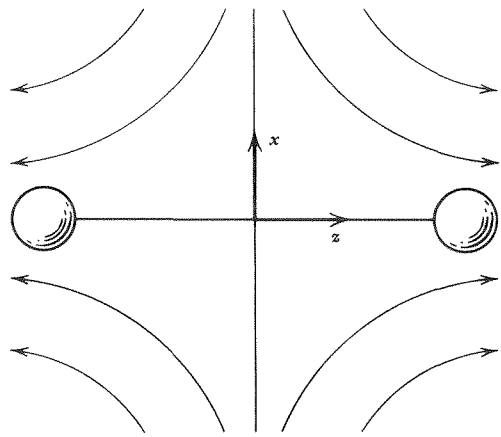


FIGURE 14B.3. Orientation of a dumbbell in an elongational flow as $\dot{\varepsilon} \to \infty$.

and almost all transient phenomena through the second order; in order to get a complete second-order description it is necessary to include additional nonlinear terms[2] in Eq. 7.3-2].

d. Use the six-constant Oldroyd model parameters determined above together with Eq. F of Table 7.3-3 to show that

$$\frac{\bar{\eta} - 3\eta_s}{3nkT\lambda} = \frac{1 + (26/35)\lambda\dot{\varepsilon} + (104/245)(\lambda\dot{\varepsilon})^2}{1 + (1/7)\lambda\dot{\varepsilon} + (4/49)(\lambda\dot{\varepsilon})^2} \tag{14B.4-8}$$

Compare this result with the exact solution for $\bar{\eta}$ with regard to predictions at both low and high elongation rates.

14B.5 Stress Relaxation after Cessation of Steady Shear Flow[3]

A dilute solution of rigid dumbbells undergoes a steady shear flow, $v_x = \dot{\gamma}_0 y$, $v_y = v_z = 0$, for $t < 0$. Then at time $t = 0$, the flow is suddenly stopped. We wish to use the formalism of §14.4 to develop expressions for the decaying shear and normal stresses after the fluid is brought to rest.

a. For $t < 0$, we denote the flow contribution to the distribution function by $f(t < 0) \equiv f^<(\theta, \phi)$. What is $f^<$ for this problem?

b. Likewise, $f(t \geq 0) \equiv f^>(\theta, \phi, t)$. Show that the differential equation for $f^>$ is

$$6\lambda \frac{\partial f^>}{\partial t} = \Lambda f^> \tag{14B.5-1}$$

What are the initial and final conditions that $f^>$ must satisfy?

[2] This has been attempted by R. B. Bird, *Zeits. für angew. Math. u. Phys.*, **23**, 157–159 (1972), but the resulting viscosity equation is less realistic than Eq. 14B.4-7 [see note added in proof in S. I. Abdel-Khalik, O. Hassager, and R. B. Bird, *J. Chem. Phys.*, **61**, 4312–4316 (1974)].

[3] This flow was first analyzed by H. Giesekus, *Rheol. Acta*, **1**, 2–20 (1958). Many other time dependent flow problems are discussed by R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1–90 (1971); the coefficient 4/7 in Eq. 14B.5-4 is given incorrectly as 15/14 in this review.

c. Verify that the solution to Eq. 14B.5-1 is

$$f^{>}(\theta, \phi, t) = \sum_{n=0}^{\infty} \sum_{m=0}^{n} P_n^m (A_{mn} c_m + B_{mn} s_m) e^{-n(n+1)t/6\lambda} \tag{14B.5-2}$$

where the A_{mn} and B_{mn} are constants that may depend on the shear rate.

d. Apply the initial condition to show that up through third-order terms $f^{>}$ is given by

$$\begin{aligned} 4\pi f^{>}(\theta, \phi, t) = 1 &+ (6\lambda\dot{\gamma}_0)\left[\frac{1}{12} P_2^2 s_2 e^{-t/\lambda}\right] + (6\lambda\dot{\gamma}_0)^2\left[\left(-\frac{1}{84} P_2^0 + \frac{1}{72} P_2^2 c_2\right)e^{-t/\lambda}\right. \\ &\left. + \left(\frac{1}{280} P_4^0 - \frac{1}{6720} P_4^4 c_4\right)e^{-10t/3\lambda}\right] + (6\lambda\dot{\gamma}_0)^3\left[\left(-\frac{19}{7560} P_2^2 e^{-t/\lambda} - \frac{1}{18480} P_4^2 e^{-10t/3\lambda}\right.\right. \\ &\left.\left. + \frac{1}{221760} P_6^2 e^{-7t/\lambda}\right)s_2 + \frac{1}{25200} P_4^4 s_4 e^{-10t/3\lambda} - \frac{1}{15966720} P_6^6 s_6 e^{-7t/\lambda}\right] + \cdots \end{aligned} \tag{14B.5-3}$$

e. Finally use $f^{>}$ to determine the following time-dependent stress components (actually, with $f^{>}$ known through terms of order $(\lambda\dot{\gamma}_0)^3$, the terms of order $(\lambda\dot{\gamma}_0)^2$ in Ψ_1^- and Ψ_2^- cannot be obtained):

$$\frac{\eta^-}{\eta(\dot{\gamma}_0) - \eta_s} = \frac{3}{5}\left[1 - \frac{4}{7}(\lambda\dot{\gamma}_0)^2 + \cdots\right]e^{-t/\lambda} \tag{14B.5-4}$$

$$\frac{\Psi_1^-}{\Psi_1(\dot{\gamma}_0)} = \left[1 - \frac{8}{35}(\lambda\dot{\gamma}_0)^2 + \cdots\right]e^{-t/\lambda} \tag{14B.5-5}$$

$$\Psi_2^- = -\frac{12}{35} nkT\lambda^2\left[1 - \frac{157}{110}(\lambda\dot{\gamma}_0)^2 + \cdots\right]e^{-t/\lambda} \tag{14B.5-6}$$

where the functions η^-, Ψ_1^-, and Ψ_2^- are defined in Eqs. D.5-11, D.5-12, and D.5-13, and $\eta(\dot{\gamma}_0)$ and $\Psi_1(\dot{\gamma}_0)$ are the steady shear flow values of η and Ψ_1 for a shear rate $\dot{\gamma}_0$. Comment on the qualitative shapes of these functions.

f. Verify that the rigid dumbbell results above satisfy

$$(\tau_{xx} - \tau_{yy})^{<} = 2\dot{\gamma}_0 \int_0^{\infty} \tau_{yx}^{>} dt \tag{14B.5-7}$$

See Problem 14C.1 for a derivation of this equation.

14B.6 Vortex Inhibition[4]

In this problem we wish to investigate the effect of dilute polymer solutions in vortex inhibition (see §2.5(g)). The following procedure is suggested:

a. The flow in the draining tank is assumed to be

$$\boldsymbol{v} = -\frac{\dot{\varepsilon}}{2} r\boldsymbol{\delta}_r + \frac{\Omega}{r}\boldsymbol{\delta}_\theta + \dot{\varepsilon} z\boldsymbol{\delta}_z \tag{14B.6-1}$$

[4] R. C. Armstrong, Ph.D. Thesis, University of Wisconsin, Madison (1973). A more detailed description of the vortex flow, including numerical simulations and measurements of velocity fields, is given by S. Ishikawa, Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge (1979). Also given here are numerical computations of stretching of nonlinear elastic dumbbells (cf. Eq. 13.5-56c) in the bottom boundary layer region of the vortex flow.

when referred to cylindrical coordinates. The coordinate system is chosen so that the z-axis coincides with the centerline of the tank, the positive direction being in the direction of the exiting fluid. For our purposes we can assume that the free surface is at $z = 0$ and that the level in the tank remains constant. This velocity seems reasonable for small values of r, the region of interest in vortex inhibition. Show that the assumed profile satisfies the continuity equation.

b. Assuming that the dilute polymer solution is adequately described by the second-order fluid model Eq. D.4-3, determine the normal stress differences $(\tau_{rr} - \tau_{zz})$ and $(\tau_{\theta\theta} - \tau_{rr})$ for the postulated flow in terms of the expansion coefficients b_1, b_2, and b_{11}.

c. Using the b's for rigid dumbbells, find the normal stresses.

d. In order to see the effects of these stresses in inhibiting vortex formation, use the radial component of the equation of motion together with the answer in **(c)** to find the pressure distribution over the fluid required to keep a level surface.

$$\text{Answer:} \quad p = -\frac{2b_2\Omega^2}{r^4} + \text{constant} \qquad \text{(for small } r\text{)}$$

The result **(d)** says that in order to maintain a flat fluid surface, which we assumed we would have, the pressure over the solution must be unbounded at $r = 0$ and decrease as r^{-4} near the center. In an actual experiment, of course, the pressure above the fluid is simply atmospheric pressure. If we remove the required pressure distribution, we would expect the liquid to "bulge out" at $r = 0$ rather than "dip in" as occurs in the vortex.

14B.7 Steady Elongational Viscosity for Multibead Dumbbells with Hydrodynamic Interaction

Show that Eq. 14.4-32 can be modified for multibead dumbbells as follows:

$$\frac{\bar{\eta} - 3\eta_s}{3nkT\lambda_N^{(2)}} = \left[\frac{1}{2} \mp \frac{3}{4X} \pm \frac{3}{4}\frac{\exp(\pm X)}{\sqrt{X}\int_0^{\sqrt{X}} \exp(\pm y^2)dy}\right] \tag{14B.7-1}$$

in which $X = (9/2)\lambda_N^{(1)}|\dot{\varepsilon}|$.

14B.8 Rigid-Dumbbell Diffusion Equation for Shear Flows

Show how to obtain Eq. 14.4-1 from Eq. 14.2-8. Information in §§E.5 and E.6 may be helpful. Also note that for the shear flow being considered in §14.4(a), $\boldsymbol{\kappa} = \boldsymbol{\delta}_x\boldsymbol{\delta}_y\dot{\gamma}$. Use Appendix A to show that this tensor can also be written as

$$\begin{aligned}\boldsymbol{\kappa} = &(\sin\theta\cos\phi\,\boldsymbol{u} + \cos\theta\cos\phi\,\boldsymbol{s} \\ &- \sin\phi\,\boldsymbol{t})(\sin\theta\sin\phi\,\boldsymbol{u} + \cos\theta\sin\phi\,\boldsymbol{s} + \cos\phi\,\boldsymbol{t})\dot{\gamma}\end{aligned} \tag{14B.8-1}$$

14C.1 A Theorem for Stress Relaxation[5]

Consider the problem of stress relaxation in a dilute suspension of rigid dumbbells after cessation of a steady homogeneous flow. Before $t = 0$ we take the transpose of the velocity gradient tensor to be a constant $\boldsymbol{\kappa} = \boldsymbol{\kappa}_0$; for $t \geq 0$, $\boldsymbol{\kappa} = \mathbf{0}$. If the stress tensor for $t < 0$ and $t \geq 0$ is denoted by $\boldsymbol{\tau}^<$ and $\boldsymbol{\tau}^>$, respectively, then show that

$$\boldsymbol{\tau}^< + (\eta_s + nkT\lambda)(\boldsymbol{\kappa}_0 + \boldsymbol{\kappa}_0^\dagger) = \left\{\boldsymbol{\kappa}_0 \cdot \int_0^\infty \boldsymbol{\tau}^> dt + \int_0^\infty \boldsymbol{\tau}^> dt \cdot \boldsymbol{\kappa}_0^\dagger\right\} \tag{14C.1-1}$$

[5] O. Hassager and R. B. Bird, *J. Chem. Phys.*, **56**, 2498–2501 (1972).

Furthermore, show that if the flow for $t < 0$ is a simple shear flow with $v_x = \dot{\gamma}_0 y$, $v_y = v_z = 0$, then the above simplifies to Eq. 14B.5-7.

14C.2 Properties of Mixtures of Rigid Dumbbells

In the text we have taken the rigid dumbbell suspension to be monodisperse, since we have assumed all dumbbells have the same length L Here we extend the results for the steady-shear-flow material functions to polydisperse solutions by allowing the suspension to contain dumbbells of m different lengths.

a. Show that if the fraction of dumbbells of length L_j is x_j, then

$$(\eta - \eta_s)_{\text{mix}} = nkT \sum_{j=1}^{m} x_j \lambda_j \left[1 - \frac{18}{35} (\lambda_j \dot{\gamma})^2 + \frac{1326}{1925} (\lambda_j \dot{\gamma})^4 - \cdots \right] \tag{14C.2-1}$$

$$\Psi_{1\,\text{mix}} = \tfrac{6}{5} nkT \sum_{j=1}^{m} x_j \lambda_j^2 \left[1 - \frac{38}{35} (\lambda_j \dot{\gamma})^2 + \cdots \right] \tag{14C.2-2}$$

where $\lambda_j = \zeta L_j^2 / 12kT$.

b. We now restrict our attention to mixtures for which the zero-shear-rate viscosity is the same as for a monodisperse solution of dumbbells of length L. With this additional restriction show that the above results can be written

$$\left(\frac{\eta - \eta_s}{\eta_0 - \eta_s} \right)_{\text{mix}} = \sum_{j=1}^{m} x_j \left(\frac{L_j}{L} \right)^2 \left[1 - \frac{18}{35} \left(\frac{L_j}{L} \right)^4 (\lambda \dot{\gamma})^2 + \frac{1326}{1925} \left(\frac{L_j}{L} \right)^8 (\lambda \dot{\gamma})^4 - \cdots \right] \tag{14C.2-3}$$

$$\left(\frac{\Psi_1}{\Psi_{1,0}} \right)_{\text{mix}} = \frac{\sum_{j=1}^{m} x_j (L_j/L)^4 [1 - \frac{38}{35} (L_j/L)^4 (\lambda \dot{\gamma})^2 + \cdots]}{\sum_{j=1}^{m} x_j (L_j/L)^4} \tag{14C.2-4}$$

Figures 14C.2 *a* and *b* show the viscometric functions of the mixture found using the scheme outlined here but computed numerically following the procedure of Example 14.6-2.

14D.1 Time-Dependent Elongational Flows of Rigid Dumbbell Suspensions[6]

Consider the unsteady elongational flow field $v_z = \dot{\varepsilon} z$, $v_x = -(\dot{\varepsilon}/2)x$, and $v_y = -(\dot{\varepsilon}/2)y$, where $\dot{\varepsilon} = \dot{\varepsilon}_0 f(t)$. Here $\dot{\varepsilon}_0$ is a constant used to order results, and $f(t)$ specifies the time dependence of the velocity field.

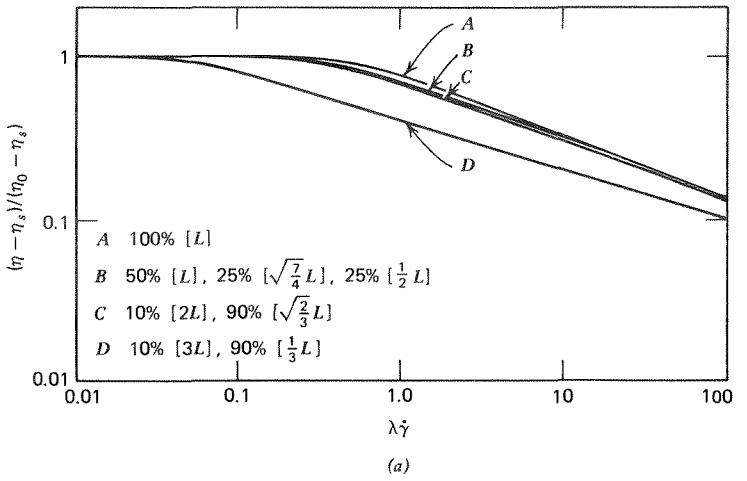
a. Show that the distribution function for this flow is

$$\begin{aligned} f = \frac{1}{4\pi} \Bigg\{ 1 &+ (6\lambda\dot{\varepsilon}_0) \left[\frac{1}{2} P_2^0(1; t) \right] + (6\lambda\dot{\varepsilon}_0)^2 \left[\frac{1}{28} P_2^0(0, 1; t) + \frac{3}{14} P_4^0\left(\frac{7}{3}, 1; t \right) \right] \\ &+ (6\lambda\dot{\varepsilon}_0)^3 \left[P_2^0\left(\frac{1}{392} (0, 0, 1; t) - \frac{1}{49} \left(-\frac{7}{3}, \frac{7}{3}, 1; t \right) \right) \right. \\ &\left. + \text{terms containing } P_4^0 \text{ and } P_6^0 \right] + \cdots \Bigg\} \end{aligned} \tag{14D.1-1}$$

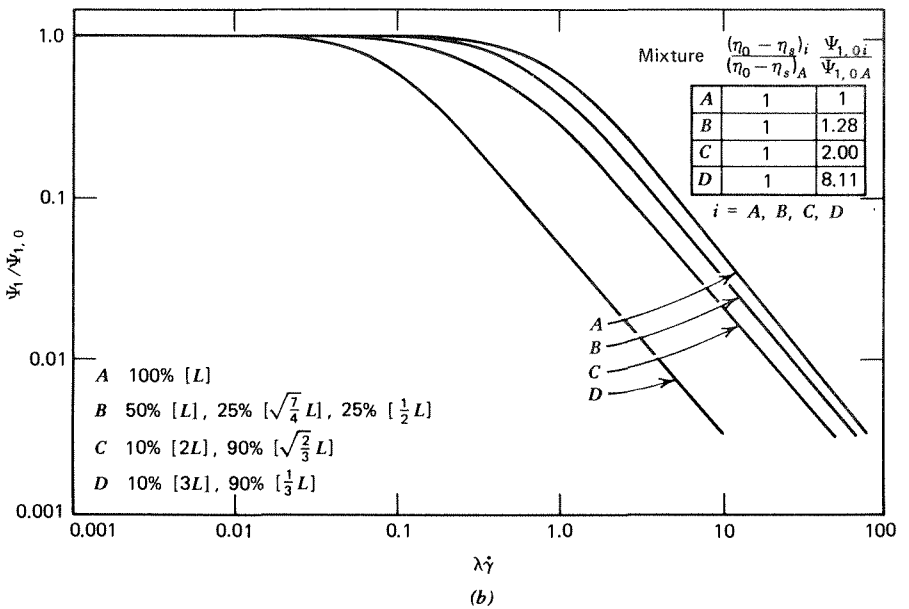
We have used the abbreviated notation $(a, b, c, \ldots; t)$ which is illustrated by

$$(a, b, c; t) = \frac{1}{\lambda^3} \int_{-\infty}^{t} \int_{-\infty}^{t'} \int_{-\infty}^{t''} e^{-a(t-t')/\lambda} e^{-b(t-t'')/\lambda} e^{-c(t-t''')/\lambda} f(t') f(t'') f(t''') \, dt''' \, dt'' \, dt' \tag{14D.1-2}$$

[6] R. B. Bird and R. C. Armstrong, *J. Chem. Phys.*, **56**, 3680–3682 (1972).



(a)



(b)

FIGURE 14C.2. (*a*) Viscosity and (*b*) first normal stress coefficient for various mixtures of rigid dumbbells. For a rigid linear molecule, the molecular weight is proportional to the length. Thus, the mixtures shown here have $\bar{M}_w/\bar{M}_n$ equal to A, 1; B, 1.093; C, 1.145; and D, 2.780. From these curves we see that (i) the shapes and displacements are sensitive to $\bar{M}_w/\bar{M}_n$ (ii) that the displacements are governed primarily by the length of the longest dumbbell in the mixture, and (iii) the first normal stress coefficient is more affected than viscosity by polydispersity. [R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1-90 (1971)].

b. Use the result in **(a)** to find

$$\left(\frac{\tau_{xx}-\tau_{zz}}{nkT}\right)-\left(\frac{3\eta_s\dot{\varepsilon}}{nkT}\right)=(\lambda\dot{\varepsilon}_0)\left[\frac{9}{5}(1;t)+\frac{6}{5}f(t)\right]$$
$$+(\lambda\dot{\varepsilon}_0)^2\left[\frac{27}{35}(0,1;t)+\frac{36}{35}f(t)(1;t)\right]$$
$$+(\lambda\dot{\varepsilon}_0)^3\left[\frac{81}{245}(0,0,1;t)+\frac{108}{245}f(t)(0,1;t)\right.$$
$$\left.-\frac{648}{245}\left(-\frac{7}{3},\frac{7}{3},1;t\right)+\frac{648}{245}f(t)\left(\frac{7}{3},1;t\right)\right]+\cdots \qquad (14D.1\text{-}3)$$

c. Show that the kernels G_1 and G_2 for the memory integral expansion can be obtained from D.1-3.

CHAPTER 15

THE BEAD-SPRING CHAIN MODELS

In Chapter 13 the kinetic theory of polymers was introduced by using the elastic dumbbell models to describe the polymer molecule. These models are the simplest ones for flexible macromolecules and contain the main physical ideas normally incorporated in dilute-solution theories. The dumbbell models are, of course, oversimplified models, accounting for polymer-solvent interaction only at two points. We now consider the more realistic chain models composed of N beads and $N - 1$ springs connected linearly; this model was introduced in §11.4, and some of the equilibrium properties of the model were examined in Chapter 12. In the Rouse and Zimm models the springs are taken to be Hookean. When hydrodynamic interaction is neglected the bead-spring chain model is called the Rouse model,[1] and when hydrodynamic interaction is included it is referred to as the Zimm model.[2]

The Rouse and Zimm models have been widely used by polymer chemists for interpreting linear viscoelastic measurements and have had considerable influence on the direction of experimental programs.[3] They are mathematically more complicated than the dumbbell models because they have N beads instead of two. Consequently much of this chapter has to deal with questions of coordinate transformations and normal coordinates;[4,5,6] this requires the use of some elementary notions from the theory of matrices.

The two principal parts of the kinetic theory are given in the first two sections: the diffusion equation for the chain distribution function is given in §15.1, and the expression for the stress tensor is given in §15.2. Then in §15.3 we specialize to chains with Hookean springs and obtain the constitutive equation; from the latter we obtain expressions for some of the rheological properties. Up to this point the development does not include hydrodynamic interaction; that is, we are concerned with the Rouse theory for "freely draining" chains. In §15.4 we consider the Zimm theory for chains with equilibrium averaged hydrodynamic interaction.

It must be emphasized that neither the Rouse nor the Zimm theory describes the decrease of viscosity with increasing shear rate. The models have been used primarily in the description of linear viscoelastic phenomena. The Rouse and Zimm theories illustrate the

[1] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272–1280 (1953); R. Takserman-Krozer, *J. Polym. Sci.*, **C16**, 2855–2865 (1967).

[2] B. H. Zimm, *J. Chem. Phys.*, **24**, 269–278 (1956); errors in Zimm's paper have been pointed out by M. C. Williams [*J. Chem. Phys.*, **42**, 2988–2989 (1965)], who also obtained expressions for the normal stresses.

[3] J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 3rd ed. (1980).

[4] A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539–553 (1971).

[5] P. H. van Wiechen and H. C. Booij, *J. Eng. Math.*, **5**, 89–98 (1971).

[6] D. H. King and D. F. James, *J. Chem. Phys.*, **78**, 4743-4748, 4749-4754 (1983); see also H. C. Booij, *ibid.*, **80**, 4571-4572 (1984).

use of normal coordinates in coupled mechanical systems, and in addition provide useful background for the study of the chapters that follow.

§15.1 THE "DIFFUSION EQUATION" FOR THE CONFIGURATION-SPACE DISTRIBUTION FUNCTION

The discussion of §13.1 on modeling of polymer solutions can be taken over directly in this chapter, except that there are now N beads rather than 2. We make the same assumption regarding the factoring of the single-molecule phase-space distribution function that we made in Eq. 13.1-1, and we assume that the velocity distribution is Maxwellian about the fluid velocity at the center of mass of the polymer chain, exactly as we did in Eq. 13.1-3. We now obtain the partial differential equation for the configuration-space distribution function by combining the force balances on the beads with the equation of continuity in configuration space.

a. The Equations of Motion for the Beads of the Chain

If the acceleration terms in the equations of motion are omitted then these reduce to force balances, one for each bead; these are generalizations of Eqs. 13.2-1 to 13.2-4 with $\nu = 1, 2$ being replaced by $\nu = 1, 2, \ldots, N$. When we use Stokes' law with a scalar friction coefficient and a Maxwellian velocity distribution in the Brownian force term, the equations of motion for the beads become (cf. Eq. 13.2-5):

$$-\zeta([\![\dot{\boldsymbol{r}}_\nu]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu]) - kT\frac{\partial}{\partial \boldsymbol{r}_\nu}\ln\Psi + \boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)} = \boldsymbol{0} \qquad (\nu = 1, 2, \ldots, N) \quad (15.1\text{-}1)$$

These equations of motion for the N beads can be transformed into equations of motion for the center of mass $\boldsymbol{r}_c = (1/N)\sum_\nu \boldsymbol{r}_\nu$ and for the connector vectors $\boldsymbol{Q}_k = \boldsymbol{r}_{k+1} - \boldsymbol{r}_k$ by using the relations in Table 15.1-1. In this way we obtain (see Problem 15B.5)

$$[\![\dot{\boldsymbol{r}}_c]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_c] + \frac{1}{N\zeta}\sum_\nu \boldsymbol{F}_\nu^{(e)} \quad (15.1\text{-}2)$$

$$[\![\dot{\boldsymbol{Q}}_j]\!] = [\boldsymbol{\kappa}\cdot\boldsymbol{Q}_j] - \frac{1}{\zeta}\sum_k A_{jk}\left(kT\frac{\partial}{\partial \boldsymbol{Q}_k}\ln\psi + \boldsymbol{F}_k^{(c)}\right) + \frac{1}{\zeta}\sum_\nu \bar{B}_{j\nu}\boldsymbol{F}_\nu^{(e)} \quad (15.1\text{-}3)$$

Here $\boldsymbol{F}_k^{(c)} = -\sum_\nu B_{\nu k}\boldsymbol{F}_\nu^{(\phi)}$ is the tension in the kth connector, and the A_{jk} are the elements of the Rouse matrix defined in Eq. 11.6-8. Clearly the equations of motion for the $\boldsymbol{Q}_j$ are coupled, the motion of each link depending on the movement of the adjacent links in the chain.

b. Equation of Continuity for $\psi(\boldsymbol{Q}^{N-1}, t)$

By means of a derivation similar to that in §13.2(b) we obtain for the bead-spring chain model

$$\frac{\partial\Psi}{\partial t} = -\sum_\nu\left(\frac{\partial}{\partial \boldsymbol{r}_\nu}\cdot[\![\dot{\boldsymbol{r}}_\nu]\!]\Psi\right) \quad (15.1\text{-}4)$$

TABLE 15.1-1[a]

Relations Involving $\bar{B}_{kv}$ and B_{vk}

Algebraic relations

$$\sum_{v} \bar{B}_{kv} = 0 \tag{A}$$

$$\sum_{v} B_{vk} = 0 \tag{B}$$

$$\sum_{v} \bar{B}_{jv} B_{vk} = \delta_{jk} \tag{C}$$

$$\sum_{k} B_{vk} \bar{B}_{k\mu} = \delta_{v\mu} - \frac{1}{N} \tag{D}$$

$$B_{v+1,k} - B_{vk} = \delta_{vk} \tag{E}$$

Derivatives of arbitrary functions of the configurational vectors $f(\boldsymbol{r}_c, \boldsymbol{Q}_1, \boldsymbol{Q}_2, \ldots, \boldsymbol{Q}_{N-1}) = g(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$:

$$\frac{\partial f}{\partial \boldsymbol{r}_c} = \sum_{v} \frac{\partial g}{\partial \boldsymbol{r}_v}; \quad \frac{\partial f}{\partial \boldsymbol{Q}_k} = \sum_{v} B_{vk} \frac{\partial g}{\partial \boldsymbol{r}_v} \tag{F}$$

$$\frac{\partial g}{\partial \boldsymbol{r}_v} = \frac{1}{N} \frac{\partial f}{\partial \boldsymbol{r}_c} + \sum_{k} \bar{B}_{kv} \frac{\partial f}{\partial \boldsymbol{Q}_k} \tag{G}$$

Jacobian relation for the configurational vectors

$$\left| \frac{\partial(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)}{\partial(\boldsymbol{r}_c, \boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_{N-1})} \right| = 1 \tag{H}$$

Relations between the net spring force $\boldsymbol{F}_v^{(\phi)}$ acting on bead v and the force $\boldsymbol{F}_k^{(c)}$ on bead $v = k$ due to the tension in the kth connector.

$$\boldsymbol{F}_v^{(\phi)} = -\sum_{k} \bar{B}_{kv} \boldsymbol{F}_k^{(c)} = -\frac{\partial \phi}{\partial \boldsymbol{r}_v} \tag{I}$$

$$\boldsymbol{F}_k^{(c)} = -\sum_{v} B_{vk} \boldsymbol{F}_v^{(\phi)} = +\frac{\partial \phi}{\partial \boldsymbol{Q}_k} \tag{J}$$

[a] For additional information on chain geometry and the definitions of the Rouse matrix (A_{ij}) and the Kramers matrix (C_{ij}) see §11.6.

By applying the chain rule of partial differentiation and using the relations in Table 15.1-1 we get

$$\frac{\partial \Psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{r}_c} \cdot [\![\dot{\boldsymbol{r}}_c]\!]\Psi\right) - \sum_j \left(\frac{\partial}{\partial \boldsymbol{Q}_j} \cdot [\![\dot{\boldsymbol{Q}}_j]\!]\Psi\right) \tag{15.1-5}$$

Next we use Eq. 15.1-2, the fact that there are no concentration gradients, and the fact that $\boldsymbol{\kappa}$ is traceless (a consequence of $(\nabla \cdot \boldsymbol{v}) = 0$) in order to simplify Eq. 15.1-5 to

$$\frac{\partial \psi}{\partial t} = -\sum_j \left(\frac{\partial}{\partial \boldsymbol{Q}_j} \cdot [\![\dot{\boldsymbol{Q}}_j]\!]\psi\right) \tag{15.1-6}$$

Note that we do not evaluate the average in velocity space appearing in this equation.

c. The Diffusion Equation for $\psi(\boldsymbol{Q}^{N-1}, t)$

We now substitute $[\![\dot{\boldsymbol{Q}}_j]\!]$ from Eq. 15.1-3 into the equation of continuity to get the diffusion equation:

$$\boxed{\frac{\partial \psi}{\partial t} = -\sum_j \left(\frac{\partial}{\partial \boldsymbol{Q}_j} \cdot \left\{[\boldsymbol{\kappa} \cdot \boldsymbol{Q}_j]\psi - \frac{1}{\zeta}\sum_k A_{jk}\left[kT\frac{\partial}{\partial \boldsymbol{Q}_k}\psi + \boldsymbol{F}_k^{(c)}\psi\right] + \frac{1}{\zeta}\sum_\nu \bar{B}_{j\nu}\boldsymbol{F}_\nu^{(e)}\psi\right\}\right)} \tag{15.1-7}$$

This equation has to be solved to get the distribution function. For the Rouse model, for which $\boldsymbol{F}_j^{(c)} = H\boldsymbol{Q}_j$, the solution is known for any choice of the flow field (i.e., for any choice of $\boldsymbol{\kappa}(t)$), as is shown in §15.3. For steady-state, homogeneous, potential flow of a dilute solution of bead-spring chains with any kind of spring force law and no external forces, the diffusion equation has a solution similar to that shown in Eq. 13.2-14:

$$\psi(\boldsymbol{Q}^{N-1}) = \frac{1}{J}\exp[-\phi(\boldsymbol{Q}^{N-1})/kT]\exp\left[(\zeta/2kT)(\boldsymbol{\kappa} : \sum_i \sum_j C_{ij}\boldsymbol{Q}_i\boldsymbol{Q}_j)\right] \tag{15.1-8}$$

where J is a normalization constant, and $\phi(\boldsymbol{Q}^{N-1})$ is the total potential energy of the bead-spring chain. This can be used for getting the distribution of orientations in elongational flow, for example.

Next we derive an equation of change for the average value of any scalar function of the connector vectors, $B(\boldsymbol{Q}^{N-1})$. We multiply the diffusion equation, Eq. 15.1-7, by B and then integrate over the entire configuration space. This leads to the following relation:[1]

$$\begin{aligned}\frac{d}{dt}\langle B\rangle = &\left(\boldsymbol{\kappa} : \left\langle \sum_j \boldsymbol{Q}_j \frac{\partial}{\partial \boldsymbol{Q}_j} B\right\rangle\right) + \frac{kT}{\zeta}\left\langle \sum_j \sum_k A_{jk}\left(\frac{\partial}{\partial \boldsymbol{Q}_k} \cdot \frac{\partial}{\partial \boldsymbol{Q}_j} B\right)\right\rangle \\ &- \frac{1}{\zeta}\left\langle \sum_j \sum_k A_{jk}\left(\boldsymbol{F}_k^{(c)} \cdot \frac{\partial}{\partial \boldsymbol{Q}_j} B\right)\right\rangle + \frac{1}{\zeta}\sum_j \sum_\nu \bar{B}_{j\nu}\left\langle\left(\boldsymbol{F}_\nu^{(e)} \cdot \frac{\partial}{\partial \boldsymbol{Q}_j} B\right)\right\rangle\end{aligned} \tag{15.1-9}$$

[1] O. Hassager and R. B. Bird, *J. Chem. Phys.*, **56**, 2498–2501 (1972), erratum, *ibid.*, **57**, 1368 (1972).

A similar relation is valid for any tensor function of the $\boldsymbol{Q}_j$. In particular we let $\mathbb{B}(\boldsymbol{Q}^{N-1})$ be the second-order tensor $\sum_j \sum_k C_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k$, where the C_{jk} are the elements of the Kramers matrix defined in Eq. 11.6-7. When this choice is made one gets:[1]

$$\left\langle \sum_j \sum_k C_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k \right\rangle_{(1)} = \frac{2kT}{\zeta}(N-1)\boldsymbol{\delta} - \frac{2}{\zeta}\left\langle \sum_k \boldsymbol{F}_k^{(c)}\boldsymbol{Q}_k \right\rangle + \frac{1}{\zeta}\sum_\nu \sum_k B_{\nu k}\left\langle \boldsymbol{F}_\nu^{(e)}\boldsymbol{Q}_k + \boldsymbol{Q}_k\boldsymbol{F}_\nu^{(e)} \right\rangle \tag{15.1-10}$$

which is the analog of Eq. 13.2-17 for elastic dumbbells. The subscript (1) denotes the convected time derivative. Finally we note that at equilibrium ($\boldsymbol{\kappa} = \mathbf{0}$), Eq. 15.1-10 gives

$$\sum_k \langle \boldsymbol{F}_k^{(c)}\boldsymbol{Q}_k \rangle_{\text{eq}} = (N-1)kT\boldsymbol{\delta} \tag{15.1-11}$$

a result that we need in the next section.

§15.2 EXPRESSIONS FOR THE STRESS TENSOR

In §13.3 we derived an expression for the stress tensor for a dilute polymer solution in which the polymers were modeled as elastic dumbbells. In getting the polymer contribution to the stress tensor, we accounted for three major effects: the contribution resulting from the tensions in the springs, that resulting from external forces, and that associated with the momentum transport by the beads. These elementary physical arguments led us to the expression for the stress tensor in Eq. 13.3-14. An analogous derivation for the bead-spring chain model would lead us to the following expressions for the stress tensor, one in terms of the tensions in the connectors, and the other in terms of the hydrodynamic forces:

$$\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\sum_{k=1}^{N-1}\langle \boldsymbol{Q}_k\boldsymbol{F}_k^{(c)} \rangle + n\sum_{\nu=1}^{N}\sum_{k=1}^{N-1} B_{\nu k}\langle \boldsymbol{Q}_k\boldsymbol{F}_\nu^{(e)} \rangle + nm\sum_{\nu=1}^{N}\langle (\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}) \rangle$$

Solvent contribution	Contribution of intramolecular forces	Contribution of external forces	Contribution of the bead motion

(15.2-1)

$$\boldsymbol{\pi} = \boldsymbol{\pi}_s - n\sum_{\nu=1}^{N}\langle \boldsymbol{R}_\nu\boldsymbol{F}_\nu^{(h)} \rangle + Nnm\langle (\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v}) \rangle \tag{15.2-2}$$

The only assumption made in going from Eq. 15.2-1 to Eq. 15.2-2 is that the velocity distribution function is an even function of $(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})$. Both of these equations are applicable whether or not hydrodynamic interaction is included, and whether the friction coefficient is a second-order tensor or a scalar.

In most kinetic theories of polymers it is assumed that the velocity distribution is Maxwellian; in this chapter we adopt this same assumption henceforth, so that the last term of Eq. 15.2-1 becomes $NnkT\boldsymbol{\delta}$, and the last term of Eq. 15.2-2 becomes $nkT\boldsymbol{\delta}$. Then the stress

TABLE 15.2-1

Expressions for the Stress Tensor for Bead-Spring Chains[a,b] (Maxwellian Velocity Distribution Assumed)

Kramers:[c]

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\sum_{k=1}^{N-1}\langle \underline{Q}_k \underline{F}_k^{(c)}\rangle + n\sum_{v=1}^{N}\sum_{k=1}^{N-1} B_{vk}\langle \underline{Q}_k \underline{F}_v^{(e)}\rangle + (N-1)nkT\boldsymbol{\delta} \tag{A}$$

Modified Kramers:

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + n\sum_{v=1}^{N}\langle \boldsymbol{R}_v(\boldsymbol{F}_v^{(\phi)} + \boldsymbol{F}_v^{(e)})\rangle + (N-1)nkT\boldsymbol{\delta} \tag{B}$$

Kramers-Kirkwood:[d]

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} - n\sum_{v=1}^{N}\langle \boldsymbol{R}_v \boldsymbol{F}_v^{(h)}\rangle \tag{C}$$

Giesekus:[e]

$$\boldsymbol{\tau} = -\eta_s\dot{\boldsymbol{\gamma}} + \tfrac{1}{2}n\zeta\left\langle \sum_{j=1}^{N-1}\sum_{k=1}^{N-1} C_{jk}\underline{Q}_j\underline{Q}_k\right\rangle_{(1)}$$

$$+ \tfrac{1}{2}n\sum_{v=1}^{N}\sum_{k=1}^{N-1} B_{vk}\langle \underline{Q}_k \underline{F}_v^{(e)} - \underline{F}_v^{(e)}\underline{Q}_k\rangle \tag{D}$$

[a] R. B. Bird and C. F. Curtiss, *J. Polym. Sci.: Polym. Symp.*, **73**, 187-199 (1985).
[b] See §15.4 for inclusion of hydrodynamic interaction.
[c] H. A. Kramers, *Physica*, **11**, 1-19 (1944).
[d] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).
[e] H. Giesekus, *Rheol. Acta*, **2**, 50-62 (1962); O. Hassager and R. B. Bird, *J. Chem. Phys.*, **56**, 2498-2501 (1972).

tensor may be expressed in terms of $\boldsymbol{\tau}$ by subtracting the corresponding expression at equilibrium. This leads to the expressions in Table 15.2-1. Once again we attach names to these various forms for the stress tensor in order to distinguish among them. Equations A and B in this table are obtained directly from Eq. 15.2-1, and Eq. C is a simplification of Eq. 15.2-2; Eq. D is obtained from Eq. A by making use of Eq. 15.1-10 to eliminate the spring force law.

§15.3 THE BEAD-SPRING CHAIN WITH HOOKEAN SPRINGS (ROUSE MODEL)

The first two sections of this chapter apply to bead-spring chains with any kind of spring force law. In this section we specialize the results for chains with Hookean springs (the Rouse chain). First we obtain a solution to the diffusion equation for any kind of flow pattern. Then we obtain the constitutive equation for the fluid.

a. Introduction of Normal Coordinates

In the diffusion equation, Eq. 15.1-7, we note that there is coupling among the various connector vectors because of the Rouse matrix. This coupling can be removed by

introducing a new set of variables called "normal coordinates".[1] Specifically we introduce the $\boldsymbol{Q}'_k$ (the Cartesian components Q'_{kn} with $n = 1, 2, 3$ are the normal coordinates) by

$$\boldsymbol{Q}_j = \sum_k \Omega_{jk} \boldsymbol{Q}'_k \tag{15.3-1}$$

Here the Ω_{jk} are the elements of an $(N-1) \times (N-1)$ orthogonal matrix ($\Omega^{-1}_{jk} = \Omega_{kj}$) chosen to diagonalize the Rouse matrix. That is, the Ω_{ij} have the following properties:[2]

$$\sum_i \Omega_{ij}\Omega_{ik} = \delta_{jk} \tag{15.3-2}$$

$$\sum_j \sum_k \Omega_{ji} A_{jk} \Omega_{kl} = a_l \delta_{il} \tag{15.3-3}$$

where the $a_l = 4 \sin^2(l\pi/2N)$ are the eigenvalues of the Rouse matrix (see Eq. 11.6-9). The elements of the rotation matrix Ω_{jk} are known to be[3]

$$\Omega_{jk} = \sqrt{\frac{2}{N}} \sin \frac{jk\pi}{N} \tag{15.3-4}$$

In addition it can be shown that the derivatives transform as follows:

$$\frac{\partial}{\partial \boldsymbol{Q}_j} = \sum_k \Omega_{jk} \frac{\partial}{\partial \boldsymbol{Q}'_k} \tag{15.3-5}$$

by using the relation among the coordinates, Eq. 15.3-1, and the orthogonality property of the Ω_{jk}.

When the diffusion equation in Eq. 15.1-7 is now written in terms of the normal coordinates, it becomes

$$\frac{\partial \psi}{\partial t} = -\sum_j \left(\frac{\partial}{\partial \boldsymbol{Q}'_j} \cdot \left\{ [\boldsymbol{\kappa} \cdot \boldsymbol{Q}'_j]\psi - \frac{a_j}{\zeta} \left[kT \frac{\partial}{\partial \boldsymbol{Q}'_j} \psi + H \boldsymbol{Q}'_j \psi \right] \right\} \right) \tag{15.3-6}$$

This form of the diffusion equation is somewhat simpler inasmuch as only a single summation appears on the right side.

b. Separation of Variables in the Transformed Diffusion Equation[4,5,6]

Next we postulate that Eq. 15.3-6 has a solution of the form

$$\psi(\boldsymbol{Q}'^{N-1}, t) = \prod_{k=1}^{N-1} \psi_k(\boldsymbol{Q}'_k, t) \tag{15.3-7}$$

[1] For an elementary discussion of normal coordinates in polymer kinetic theory see B. H. Zimm, in F. R. Eirich, ed., *Rheology*, Vol. 3, Academic Press, New York (1960), Chapter 1, pp. 1–16.

[2] Note that Eqs. 15.3-2 and 15.3-3 are sufficient to determine all the Ω_{jk} (of which there are $(N-1) \times (N-1)$) and the a_j (of which there are $N-1$), that is a total of $N(N-1)$ unknowns. The relations in Eq. 15.3-2 are a set of $(1/2)N(N-1)$ equations, and, since the A_{jk} are symmetric, Eq. 15.3-3 contains $(1/2)N(N-1)$ equations.

[3] P. H. Verdier, *J. Chem. Phys.*, **45**, 2118–2121 (1966); J. Kovac and M. Fixman, *ibid.*, **63**, 935–941 (1975); D. H. King and D. F. James, *ibid.*, **78**, 4743–4748 (1983).

[4] A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539–553 (1971).

[5] P. H. van Wiechen and H. C. Booij, *J. Eng. Math.*, **5**, 89–98 (1971).

[6] D. H. King and D. F. James, *J. Chem. Phys.*, **78**, 4743–4748, 4749–4754 (1983); erratum: *ibid.* **80**, 4573 (1984). See also H. C. Booij, *J. Chem. Phys.*, **80**, 4571–4572 (1984).

with $\int \psi_k(\boldsymbol{Q}'_k, t)d\boldsymbol{Q}'_k = 1$ giving the normalization. Substitution of this postulated solution into Eq. 15.3-6 then gives

$$\sum_j \left(\prod_{\substack{k=1 \\ k\neq j}}^{N-1} \psi_k \right) \frac{\partial \psi_j}{\partial t} = -\sum_j \left(\left(\prod_{\substack{k=1 \\ k\neq j}}^{N-1} \psi_k \right) \frac{\partial}{\partial \boldsymbol{Q}'_j} \cdot \left\{ [\boldsymbol{\kappa} \cdot \boldsymbol{Q}'_j]\psi_j - \frac{a_j}{\zeta} \left[kT \frac{\partial}{\partial \boldsymbol{Q}'_j} \psi_j + H\boldsymbol{Q}'_j \psi_j \right] \right\} \right) \tag{15.3-8}$$

Next we divide by $\prod_k \psi_k = \psi_1 \psi_2 \cdots \psi_{N-1}$, and this gives us terms containing only $\boldsymbol{Q}'_1$, terms containing only $\boldsymbol{Q}'_2$, and so on. The only way that this equation can be satisfied is if each of these groups of terms is equal to $E_j(t)$, a function of t (with $\sum_j E_j(t) = 0$). That is,

$$\frac{\partial \psi_j}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}'_j} \cdot \left\{ [\boldsymbol{\kappa} \cdot \boldsymbol{Q}'_j]\psi_j - \frac{a_j}{\zeta} \left[kT \frac{\partial}{\partial \boldsymbol{Q}'_j} \psi_j + H\boldsymbol{Q}'_j \psi_j \right] \right\} \right) + E_j(t)\psi_j \tag{15.3-9}$$

If this equation is integrated over all $\boldsymbol{Q}'_j$, then according to the normalization condition the left side is zero; the first term on the right side is also zero, because of the vanishing of ψ_j as $\boldsymbol{Q}'_j \to \infty$. We conclude, therefore, that all the $E_j(t)$ must be zero. Then Eq. 15.3-9, for the jth normal mode, has the same form as the elastic dumbbell equation in Eq. 13.2-13 (with $\boldsymbol{F}^{(c)}$ set equal to $H\boldsymbol{Q}$). We also point out that when Eq. 15.3-9 is multiplied by $\boldsymbol{Q}'_j\boldsymbol{Q}'_j$ and integrated over all $\boldsymbol{Q}'_j$, we get

$$\langle \boldsymbol{Q}'_j\boldsymbol{Q}'_j \rangle_{(1)} = \frac{2a_j}{\zeta} (kT\boldsymbol{\delta} - H\langle \boldsymbol{Q}'_j\boldsymbol{Q}'_j \rangle) \tag{15.3-10}$$

a result that we need presently.

c. Development of the Constitutive Equation

Next we specialize Eq. A of Table 15.2-1 for Hookean springs by inserting $\boldsymbol{F}_j^{(c)} = H\boldsymbol{Q}_j$; then we write both Eqs. A and D in terms of the normal coordinates. Note that the spring contribution in the Kramers expression can be written thus:

$$\begin{aligned} -nH \sum_i \langle \boldsymbol{Q}_i\boldsymbol{Q}_i \rangle &= -nH \sum_i \sum_k \sum_l \Omega_{ik}\Omega_{il} \langle \boldsymbol{Q}'_k\boldsymbol{Q}'_l \rangle \\ &= -nH \sum_k \langle \boldsymbol{Q}'_k\boldsymbol{Q}'_k \rangle \end{aligned} \tag{15.3-11}$$

and that the polymer contribution in the Giesekus expression can be transformed as follows:

$$\begin{aligned} \frac{n\zeta}{2} \sum_i \sum_j C_{ij} \langle \boldsymbol{Q}_i\boldsymbol{Q}_j \rangle_{(1)} &= \frac{n\zeta}{2} \sum_i \sum_j \sum_k \sum_l C_{ij}\Omega_{ik}\Omega_{jl} \langle \boldsymbol{Q}'_k\boldsymbol{Q}'_l \rangle_{(1)} \\ &= \frac{n\zeta}{2} \sum_k c_k \langle \boldsymbol{Q}'_k\boldsymbol{Q}'_k \rangle_{(1)} \end{aligned} \tag{15.3-12}$$

in which $c_k = 1/a_k$ is the kth eigenvalue of the Kramers matrix. As a result the Kramers and Giesekus expressions can be written finally as

$$\boldsymbol{\tau} = -\eta_s \dot{\boldsymbol{\gamma}} + \sum_j \boldsymbol{\tau}_j \tag{15.3-13}$$

with

$$\text{Kramers:} \quad \tau_j = -nH\langle \boldsymbol{Q}'_j \boldsymbol{Q}'_j \rangle + nkT\boldsymbol{\delta} \tag{15.3-14}$$

$$\text{Giesekus:} \quad \tau_j = +\frac{n\zeta c_j}{2}\langle \boldsymbol{Q}'_j \boldsymbol{Q}'_j \rangle_{(1)} \tag{15.3-15}$$

Then because of Eq. 15.3-10 we can obtain the following differential equation for the jth contribution to the stress tensor:

$$\tau_j + \lambda_j \tau_{j(1)} = -nkT\lambda_j \dot{\gamma} \tag{15.3-16}$$

in which the quantities $\lambda_j = \zeta/2Ha_j = \zeta c_j/2H$ are the time constants. Hence we have demonstrated that each of the partial stress tensors satisfies a constitutive equation that is exactly of the same form as the equation satisfied by the polymer contribution to the stress tensor of a Hookean dumbbell. That is, each of the "normal modes" is given by a convected Maxwell model (see Table 7.3-2). Therefore, the constitutive equation can be put into an integral form, thus:[4]

$$\boxed{\tau = -\eta_s \dot{\gamma} + \int_{-\infty}^{t} \left\{ nkT \sum_j \frac{1}{\lambda_j} e^{-(t-t')/\lambda_j} \right\} \gamma_{[0]}(t, t')dt'} \tag{15.3-17}$$

[7]

in which $\gamma_{[0]}$ is the finite strain tensor discussed in §8.1 and §9.2 (see also Appendix D); the quantity within the braces is called the "memory function." We have thus succeeded in getting the complete constitutive equation for the dilute solution of Hookean chains without actually getting the solution to the diffusion equation.

Any flow problem for a solution of Rouse chains can be solved (at least in principle) by using Eq. 15.3-17 and the hydrodynamic equations of continuity and motion. Furthermore, when the flow field is specified [i.e., $\gamma_{[0]}(t, t')$ is known] the expression for $\tau + \eta_s\dot{\gamma}$ for the Rouse model is just a linear superposition of similar results for the Hookean dumbbells (see Eq. 13.4-9) with relaxation times given by

$$\lambda_j = \frac{\zeta c_j}{2H} = \frac{\zeta/2H}{4\sin^2(j\pi/2N)} = \frac{3M[\eta]\eta_s}{2(N^2-1)\tilde{N}kT\sin^2(j\pi/2N)} \tag{15.3-18}$$

In the last line we have eliminated ζ and H by using the expression for intrinsic viscosity given ahead in Eq. 15.3-28. We note further that for large N and small j (i.e., the largest time constants)[8]

$$\lambda_j \sim \frac{\zeta/2H}{4(j\pi/2N)^2} = \frac{6[\eta]M\eta_s}{\pi^2\tilde{N}kT}\left(\frac{1}{j^2}\right) \tag{15.3-19}$$

[7] Note that Eq. 15.3-17 has the same form as the first term in Eq. D.4-1.

[8] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272–1280 (1953), Eq. 33.

d. Solution to the Diffusion Equation

For many purposes it is desirable to have the complete solution to the diffusion equation. This means we have to go back and solve Eq. 15.3-9 (with $E_j(t)$ set equal to zero). This can be done by taking the three-dimensional Fourier transform[6,9] of this equation:

$$\frac{\partial \bar{\psi}_j}{\partial t} = \left(\boldsymbol{\kappa} : \left(\frac{\partial \bar{\psi}}{\partial \boldsymbol{P}}\boldsymbol{P}\right)\right) - \frac{a_j H}{\zeta}\left[\frac{kT}{H}(\boldsymbol{P}\cdot\boldsymbol{P})\bar{\psi}_j + \left(\boldsymbol{P}\cdot\frac{\partial}{\partial \boldsymbol{P}}\bar{\psi}_j\right)\right] \tag{15.3-20}$$

We now try a solution of the form

$$\bar{\psi}_j = \exp\left[-\frac{kT}{2H}(\boldsymbol{\alpha}_j : \boldsymbol{P}\boldsymbol{P})\right] \tag{15.3-21}$$

When this is substituted into the preceding equation we get

$$\boldsymbol{\alpha}_j + \lambda_j \boldsymbol{\alpha}_{j(1)} = \boldsymbol{\delta} \tag{15.3-22}$$

for the differential equation for $\boldsymbol{\alpha}_j$. We note, however, that this is just the same differential equation as that for $\langle H\boldsymbol{Q}_j'\boldsymbol{Q}_j'/kT\rangle$ as may be seen from Eq. 15.3-10. Therefore, from Eqs. 15.3-14, 15.3-16, and 15.3-17 we see that[4]

$$\boldsymbol{\alpha}_j = \boldsymbol{\delta} - \frac{1}{\lambda_j}\int_{-\infty}^{t} e^{-(t-t')/\lambda_j}\boldsymbol{\gamma}_{[0]}(t, t')dt' \tag{15.3-23}$$

[9] We follow the conventions of A. Erdélyi (Ed.), *Tables of Integral Transforms*, Vol. I, McGraw-Hill, New York (1954) and define

$$\bar{\psi}(\boldsymbol{P}, t) \equiv \mathscr{F}\{\psi(\boldsymbol{Q}, t)\} = \int_{-\infty}^{+\infty}\psi(\boldsymbol{Q}, t)\exp[-i(\boldsymbol{P}\cdot\boldsymbol{Q})]d\boldsymbol{Q} \tag{15.3-20a}$$

$$\psi(\boldsymbol{Q}, t) \equiv \mathscr{F}^{-1}\{\bar{\psi}(\boldsymbol{P}, t)\} = (2\pi)^{-3}\int_{-\infty}^{+\infty}\bar{\psi}(\boldsymbol{P}, t)\exp[+i(\boldsymbol{P}\cdot\boldsymbol{Q})]d\boldsymbol{P} \tag{15.3-20b}$$

With these conventions we can derive the following relations:

$$\mathscr{F}\left\{\frac{\partial}{\partial \boldsymbol{Q}}\psi\right\} = i\boldsymbol{P}\bar{\psi} \tag{15.3-20c}$$

$$\mathscr{F}\{\boldsymbol{Q}\psi\} = i\frac{\partial}{\partial \boldsymbol{P}}\bar{\psi} \tag{15.3-20d}$$

$$\mathscr{F}\left\{\boldsymbol{Q}\frac{\partial}{\partial \boldsymbol{Q}}\psi\right\} = -\left(\frac{\partial}{\partial \boldsymbol{P}}\bar{\psi}\right)\boldsymbol{P} - \boldsymbol{\delta}\bar{\psi} \tag{15.3-20e}$$

$$\mathscr{F}\left\{\frac{\partial}{\partial \boldsymbol{Q}}\frac{\partial}{\partial \boldsymbol{Q}}\psi\right\} = -\boldsymbol{P}\boldsymbol{P}\bar{\psi} \tag{15.3-20f}$$

These are used to get Eq. 15.3-20.

When Eq. 15.3-21 is inverted and ψ_j is normalized to unity, we get the solution of Eq. 15.3-9 as[4,5]

$$\psi_j(\mathbf{Q}'_j, t) = \frac{(H/2\pi kT)^{3/2}}{\sqrt{\det \boldsymbol{\alpha}_j}} e^{-(H/2kT)(\boldsymbol{\alpha}_j^{-1}:\mathbf{Q}_j\mathbf{Q}_j)} \tag{15.3-24}$$

Equations 15.3-24 and 15.3-23, along with Eq. 15.3-7, then give the configuration-space distribution function for the Rouse chain with Hookean springs. This result is a generalization of that given in Eqs. 13.4-12 and 13.4-13 for Hookean dumbbells. As in Chapter 13 we note that, since the combination $\boldsymbol{\delta} - \boldsymbol{\gamma}_{[0]}$ is positive definite, the $\boldsymbol{\alpha}_j^{-1}$ all exist.

EXAMPLE 15.3-1 Material Functions from the Rouse Model

Obtain the material functions for the Rouse model for (**a**) steady-state shear flow, and (**b**) small-amplitude oscillatory shearing motion. Show that the Rouse model gives $[\eta]$ proportional to molecular weight (Staudinger's rule). Show further how the Rouse theory suggests a way to plot η' data taken at different temperatures so that all the data fall on a single curve (the method of reduced variables).

SOLUTION (**a**) Steady-State Shear Flow

In Eqs. 13.4-17 to 13.4-19 we obtained the steady-state shear flow material functions for the elastic dumbbell with a Hookean spring connector. A superposition of solutions then gives for the Rouse model

$$\eta - \eta_s = nkT \sum_{j=1}^{N-1} \lambda_j = nkT\left(\frac{\zeta}{4H}\right)\left[\frac{N^2 - 1}{3}\right] \tag{15.3-25}$$

$$\Psi_1 = 2nkT \sum_{j=1}^{N-1} \lambda_j^2 = 2nkT\left(\frac{\zeta}{4H}\right)^2\left[\frac{(N^2 - 1)(2N^2 + 7)}{45}\right] \tag{15.3-26}$$

$$\Psi_2 = 0 \tag{15.3-27}$$

in which use has been made of the sums in Eqs. 11.6-10 and 11.6-12 and the definitions of the material functions in Eqs. D.5-1 to D.5-3. The quantities in brackets are both unity for $N = 2$. We note that none of the material functions depend on the shear rate.[10]

[10] F. Bueche, *J. Chem. Phys.*, **22**, 1570–1576 (1954), using the Rouse model (but with the springs restricted to being aligned in the *x*-, *y*-, and *z*-directions) obtained a result analogous to Eq. 15.3-25, in which, however, the viscosity decreases dramatically with increasing shear rate. This result, which has often been quoted and used, is incorrect, probably because the kinetic theory was improperly formulated in a corotating coordinate frame. Other polymer researchers have expressed doubts about Bueche's expression for steady-shear flow viscosity, for example, H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 316, and A. Peterlin, *Adv. Macr. Chem.*, **1**, 225–281 (1968), p. 252.

In another paper [*J. Chem. Phys.*, **22**, 603–609 (1954)] Bueche derived expressions for η' and η'' which are not in agreement with the Rouse results in Eqs. 15.3-29 and 30. R. E. DeWames, W. F. Hall, and M. C. Shen, *J. Chem. Phys.*, **46**, 2782–2794 (1961) reported that they could resolve the discrepancy between Bueche and Rouse by correcting an error in the Bueche paper. For further discussion, see M. C. Williams, *AIChE J.*, **21**, 1–25 (1975), p. 6, footnote.

From Eq. 15.3-25 we can get the dependence of the intrinsic viscosity $[\eta]$ on molecular weight M, if we recognize that the number of beads is related to the molecular weight and bead mass by $N = M/m$. Then for large N we get

$$[\eta] = \lim_{c \to 0} \frac{(\eta - \eta_s)}{c\eta_s} = \lim_{n \to 0} \frac{(\eta - \eta_s)\tilde{N}}{n\eta_s M}$$

$$= \frac{kT}{\eta_s} \frac{\zeta \tilde{N}}{12Hm^2} M \tag{15.3-28}$$

where $\tilde{N}$ is Avogadro's number and c is the mass concentration. The proportionality of $[\eta]_0$ to M is known as the Staudinger rule.[11] However for most dilute polymer solutions it is found[12] that $[\eta]_0 = K'M^a$, where a is in the range from 0.5 to 0.8 (see §3.6). In §15.4 we shall find that the inclusion of hydrodynamic interaction does indeed provide a more realistic relation between $[\eta]_0$ and M; it also leads to a more accurate portrayal of the shapes of the $[\eta']$ and $[\eta'']$ curves.

(b) Small-Amplitude Oscillatory Shearing

By superposing the results given for Hookean dumbbells in Eqs. 13.4-21 and 13.4-22 we get directly

$$\eta' - \eta_s = nkT \sum_{j=1}^{N} \frac{\lambda_j}{1 + (\lambda_j \omega)^2} \tag{15.3-29}$$

$$\eta'' = nkT \sum_{j=1}^{N-1} \frac{\lambda_j^2 \omega}{1 + (\lambda_j \omega)^2} \tag{15.3-30}$$

According to the Rouse theory η' should approach η_s in the limit of very high frequencies, but experimental data indicate that the high frequency limit is higher than η_s. If the approximate expression for λ_j in Eq. 15.3-19 is used, then Eqs. 15.3-29 and 15.3-30 give η' and η'' in terms of molecular weight, (zero-shear-rate) intrinsic viscosity, and temperature. The model parameters ζ, H, and N, all difficult to relate precisely to molecular structure, have thus been eliminated.

It can be seen from Eq. 15.3-18 that all the λ_j have the same dependence on temperature. One can therefore define a function $a_T(T_0)$ by

$$a_T(T_0) = \frac{\lambda_j(T)}{\lambda_j(T_0)} \tag{15.3-31}$$

where T_0 is some arbitrary reference temperature. One can then show from Eq. 15.3-29 that data taken at various temperatures plotted as

$$\frac{\eta' - \eta_s}{a_T} \frac{T_0 n_0}{Tn} \quad \text{versus} \quad a_T \omega \tag{15.3-32}$$

should superpose on the curve corresponding to T_0. Here n_0 is the number density of macromolecules at T_0. Hence if a_T is known, then an $\eta'(\omega)$ curve over a wide frequency range at temperature T_0 can be

[11] H. Staudinger and W. Heuer, Ber. der deutschen chem. Gesellschaft, **63**, 222-234 (1930); see also F. W. Billmeyer, Jr., *Textbook of Polymer Science*, Wiley Interscience, New York (1984), 3rd ed.

[12] P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York (1953), pp. 310-314; W. R. Krigbaum and P. J. Flory, *J. Polym. Sci.*, **11**, 37-51 (1953); M. Kurata and W. H. Stockmayer, *Adv. Polym. Sci.*, **3**, 196-312 (1963).

generated by taking η' data at various temperatures over a modest frequency range. The above procedure is known as the *method of reduced variables*[13] (the term *time-temperature superposition principle* is also widely used). The function $a_T(T_0)$ has been successfully fitted by the empirical WLF equation:[14]

$$\log a_T = \frac{-c_1^0(T - T_0)}{c_2^0 + (T - T_0)} \tag{15.3-33}$$

in which T_0 is an arbitrary reference temperature, and c_1^0 and c_2^0 are experimentally determined constants. Although the method of reduced variables was developed empirically, it is useful to see how the molecular approach justifies the method.

EXAMPLE 15.3-2 Chain Extension in Steady Shear Flow[15]

In Example 11.4-1 we obtained $\langle r^2\rangle_{eq}$, the average value of the square of the end-to-end distance of a Rouse chain in a dilute solution at equilibrium. Obtain the analogous expression for a Rouse chain in an arbitrary flow field; then obtain $\langle r^2\rangle$ for a steady-state shear flow $v_x = \dot{\gamma}y$, $v_y = v_z = 0$.

SOLUTION First we express $\langle r^2\rangle$ in terms of the normal coordinates introduced in Eq. 15.3-1:

$$\begin{aligned}\langle r^2\rangle &= \langle (\boldsymbol{r}_N - \boldsymbol{r}_1)^2\rangle \\ &= \mathrm{tr}\sum_j\sum_k \langle \boldsymbol{Q}_j\boldsymbol{Q}_k\rangle \\ &= \mathrm{tr}\sum_{jkmn} \Omega_{jm}\Omega_{kn}\langle \boldsymbol{Q}'_m\boldsymbol{Q}'_n\rangle\end{aligned} \tag{15.3-34}$$

From Eq. 15.3-24 we see that

$$\mathrm{tr}\langle \boldsymbol{Q}'_m\boldsymbol{Q}'_n\rangle = \delta_{mn}\,\mathrm{tr}\langle \boldsymbol{Q}'_m\boldsymbol{Q}'_m\rangle \tag{15.3-35}$$

and from Eq. 15.3-14 we get

$$\mathrm{tr}\langle \boldsymbol{Q}'_m\boldsymbol{Q}'_n\rangle = \delta_{mn}\left(\frac{3kT}{H} - \frac{1}{nH}\,\mathrm{tr}\,\boldsymbol{\tau}_m\right) \tag{15.3-36}$$

Next it follows from the integral of Eq. 15.3-16 that $\boldsymbol{\tau}_m$ is given in terms of the flow field by

$$\boldsymbol{\tau}_m = nkT\int_{-\infty}^{t}\frac{1}{\lambda_m}e^{-(t-t')/\lambda_m}\boldsymbol{\gamma}_{[0]}(t, t')dt' \tag{15.3-37}$$

[13] J. D. Ferry, *J. Amer. Chem. Soc.*, **72**, 3746–3752 (1950).

[14] M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701–3707 (1955); for an extensive discussion of the WLF equation see J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York (1980), 3rd ed., Chapter 11, Sections B and C, pp. 273–290. It has been found that for many polymer solutions, if T_0 is taken to be the glass-transition temperature T_g, then $c_1^0 = 17.44$ and $c_2^0 = 51.6$; these constants should not be used above $T_g + 100$.

[15] R. B. Bird, H. H. Saab, P. J. Dotson, and X. J. Fan, *J. Chem. Phys.*, **79**, 5729–5730 (1983).

For steady shear flow $\text{tr}\,\tau_m = -2nkT\lambda_m^2\dot{\gamma}^2$ (see Eq. 13.4-15) so that

$$\begin{aligned}\frac{\langle r^2\rangle}{\langle r^2\rangle_{\text{eq}}} &= 1 - \frac{1}{3(N-1)nkT}\sum_{jkm}\Omega_{jm}\Omega_{km}\,\text{tr}\,\tau_m \\ &= 1 + \frac{2}{3(N-1)}\left(\sum_{jkm}\Omega_{jm}\Omega_{km}\lambda_m^2\right)\dot{\gamma}^2 \\ &= 1 + \frac{2}{3(N-1)}\left(\frac{\zeta}{2H}\right)^2\left(\sum_{jkm}\Omega_{jm}\Omega_{km}c_m^2\right)\dot{\gamma}^2 \\ &= 1 + \frac{2}{3(N-1)}\left(\frac{\zeta}{2H}\right)^2\left(\sum_{ijk}C_{ik}C_{kj}\right)\dot{\gamma}^2 \\ &= 1 + \frac{1}{45}N(N+1)(N^2+1)\lambda_H^2\dot{\gamma}^2 \end{aligned} \tag{15.3-38}$$

where $\lambda_H = \zeta/4H$; here Eq. 11.6-13 has been used, as well as a relation for C_{jk} and c_j similar to Eq. 15.3-3 (see Problem 15D.3). Equation 15.3-38 has been used to check Brownian-dynamics simulations.[16]

§15.4 THE BEAD-SPRING CHAIN WITH HOOKEAN SPRINGS AND EQUILIBRIUM-AVERAGED HYDRODYNAMIC INTERACTION (ZIMM MODEL)

Up to this point in this chapter we have considered "free draining" chains—that is, we have not included the hydrodynamic interactions among the various beads in one chain. In this section we show how this hydrodynamic interaction can be accounted for approximately, by using the equilibrium-averaged Oseen–Burgers tensor, as was originally done by Zimm[1] who was guided by the formalism developed earlier by Kirkwood and collaborators.[2]

We begin by modifying the equations of motion for the beads (Eq. 15.1-1) by including an extra contribution $\boldsymbol{v}'_\nu$ to the fluid velocity at bead ν:

$$-\zeta([\![\dot{\boldsymbol{r}}_\nu]\!] - \boldsymbol{v}_0 - [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu] - \boldsymbol{v}'_\nu) - kT\frac{\partial}{\partial\boldsymbol{r}_\nu}\ln\Psi + \boldsymbol{F}_\nu^{(\phi)} + \boldsymbol{F}_\nu^{(e)} = \boldsymbol{0} \tag{15.4-1}$$

The hydrodynamic interaction contribution $\boldsymbol{v}'_\nu$ is presumed to depend linearly on the hydrodynamic forces acting on all the other beads in the chain, the coefficients being the hydrodynamic interaction tensors $\boldsymbol{\Omega}_{\nu\mu}$:

$$\begin{aligned}\boldsymbol{v}'_\nu &= -\sum_\mu[\boldsymbol{\Omega}_{\nu\mu}\cdot\boldsymbol{F}_\mu^{(h)}] \\ &= \sum_\mu\left[\boldsymbol{\Omega}_{\nu\mu}\cdot\left\{-kT\frac{\partial}{\partial\boldsymbol{r}_\mu}\ln\Psi + \boldsymbol{F}_\mu^{(\phi)} + \boldsymbol{F}_\mu^{(e)}\right\}\right]\end{aligned} \tag{15.4-2}$$

[16] P. J. Dotson, *J. Chem. Phys.*, **79**, 5730–5731 (1983); H. H. Saab and P. J. Dotson, Univ. of Wisconsin Rheology Research Center Rept. No. 97 (Nov. 1984).

[1] B. H. Zimm, *J. Chem. Phys.*, **24**, 269–278 (1956); for a tabulation of the errata in this paper see J. J. Hermans (Ed.), *Polymer Solutions Properties, Part II, Hydrodynamics and Light Scattering*, Dowdon, Hutchinson, and Ross, Stroudsburg, PA (1978), pp. 83–84.

[2] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967).

In the Zimm theory the $\boldsymbol{\Omega}_{\nu\mu}$ are taken to be the Oseen–Burgers tensors:

$$\boldsymbol{\Omega}_{\nu\mu} = \frac{1}{8\pi\eta_s r_{\mu\nu}}\left(\boldsymbol{\delta} + \frac{\boldsymbol{r}_{\mu\nu}\boldsymbol{r}_{\mu\nu}}{r_{\mu\nu}^2}\right) \text{ for } \mu \neq \nu;\ \boldsymbol{\Omega}_{\nu\nu} = \mathbf{0} \tag{15.4-3}$$

Note that the indices on $\boldsymbol{\Omega}_{\nu\mu}$ are labels for the pairs of beads, whose relative locations are given by the vectors $\boldsymbol{r}_{\mu\nu} = \boldsymbol{r}_\nu - \boldsymbol{r}_\mu$. Equations 15.4-1 to 15.4-3 are generalizations of the equations for elastic dumbbells given in Eqs. 13.6-1, 13.6-2, 13.6-4, and 13.6-5.

Combination of the above three equations then gives for the velocity of the νth bead

$$[\![\dot{\boldsymbol{r}}_\nu]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu] + \frac{1}{\zeta}\sum_\mu\left[\boldsymbol{\Upsilon}_{\nu\mu}\cdot\left(-kT\frac{\partial}{\partial\boldsymbol{r}_\mu}\ln\Psi + \boldsymbol{F}_\mu^{(\phi)} + \boldsymbol{F}_\mu^{(e)}\right)\right] \tag{15.4-4}$$

in which we have introduced[3] the *dimensionless diffusion tensors* $\boldsymbol{\Upsilon}_{\nu\mu}$:

$$\boldsymbol{\Upsilon}_{\nu\mu} = \delta_{\nu\mu}\boldsymbol{\delta} + \zeta\boldsymbol{\Omega}_{\nu\mu} \tag{15.4-5}$$

Note that both $\boldsymbol{\Omega}_{\nu\mu}$ and $\boldsymbol{\Upsilon}_{\nu\mu}$ are symmetric tensors and in addition symmetric with respect to the indices ν and μ.

The discussion here is restricted to the use of equilibrium-averaged Oseen–Burgers tensors. That is, in Eq. 15.4-5 we replace $\boldsymbol{\Omega}_{\nu\mu}$ by

$$\langle\boldsymbol{\Omega}_{\nu\mu}\rangle_{\text{eq}} = \frac{\int\boldsymbol{\Omega}_{\nu\mu}\Psi_{\text{eq}}\,d\boldsymbol{r}^N}{\int\Psi_{\text{eq}}\,d\boldsymbol{r}^N} = \frac{1-\delta_{\nu\mu}}{6\pi\eta_s}\left\langle\frac{1}{r_{\mu\nu}}\right\rangle_{\text{eq}}\boldsymbol{\delta} \tag{15.4-6}$$

Then the dimensionless diffusion tensors become $\boldsymbol{\Upsilon}_{\nu\mu} = H_{\nu\mu}\boldsymbol{\delta}$, where

$$H_{\nu\mu} = \delta_{\nu\mu} + (1-\delta_{\nu\mu})\zeta\frac{1}{6\pi\eta_s}\left\langle\frac{1}{r_{\mu\nu}}\right\rangle_{\text{eq}} \tag{15.4-7}$$

are the components of the $N \times N$ *Zimm hydrodynamic interaction matrix*, which is symmetric and nonsingular. The use of equilibrium averaging then allows us to rewrite the expressions for the bead velocities as

$$[\![\dot{\boldsymbol{r}}_\nu]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_\nu] + \frac{1}{\zeta}\sum_\mu H_{\nu\mu}\left[-kT\frac{\partial\ln\Psi}{\partial\boldsymbol{r}_\mu} + \boldsymbol{F}_\mu^{(\phi)} + \boldsymbol{F}_\mu^{(e)}\right] \tag{15.4-8}$$

This equation is more complicated than the corresponding "free draining" equation (Eq. 15.1-1), because now the velocity of the νth bead depends on the various forces acting on all of the beads in the chain. This extra coupling can, however, be taken care of without too much difficulty.

[3] The *diffusion tensors* are generally defined as $\boldsymbol{D}_{\nu\mu} = (kT/\zeta)\boldsymbol{\Upsilon}_{\nu\mu}$ but we prefer to use the dimensionless quantities defined in Eq. 15.4-5.

We now want to transform the N equations for the bead velocities to $N-1$ equations for the connector vectors and an additional equation for the motion of the bead-spring chain as a whole (cf. Eqs. 15.1-2 and 15.1-3). The situation is somewhat more complicated than that in §15.1, since when hydrodynamic interaction is included it is found that the center of mass moves relative to the solvent even when there are no external forces acting. Hence, it is conventional to introduce a "(hydrodynamic) center of resistance,"[4] $\boldsymbol{r}_h$, which is defined as that weighted mean of the bead position vectors that has no relative motion with respect to the solvent when there are no external forces. That is, we define:

$$\boldsymbol{r}_h = \sum_v l_v \boldsymbol{r}_v \qquad \left(\sum_v l_v = 1\right) \tag{15.4-9}$$

and then determine the weight factors l_v so that $\boldsymbol{r}_h$ satisfies the definition above. Clearly $l_v = 1/N$ when hydrodynamic interaction is neglected.

We now replace Eqs. 11.6-3 and 11.6-4 by

$$\boldsymbol{Q}_k = \sum_v \bar{B}_{kv} \boldsymbol{r}_v \tag{15.4-10}$$

$$\boldsymbol{r}_v - \boldsymbol{r}_h = \sum_k \tilde{B}_{vk} \boldsymbol{Q}_k \tag{15.4-11}$$

where

$$\bar{B}_{kv} = \delta_{k+1,v} - \delta_{kv} \tag{15.4-12}$$

$$\tilde{B}_{vk} = \begin{cases} \sum_{\mu=1}^{k} l_\mu & k < v \\ -\sum_{\mu=k+1}^{N} l_\mu & k \geq v \end{cases} \tag{15.4-13}$$

Various relations involving the $\bar{B}_{kv}$ and $\tilde{B}_{vk}$ are given in Table 15.4-1. In addition to the above quantities we shall need the $(N-1) \times (N-1)$ modified Kramers and Rouse matrices whose components are

$$\tilde{C}_{ij} = \sum_v \sum_\mu \tilde{B}_{vi} H_{v\mu}^{-1} \tilde{B}_{\mu j} \tag{15.4-14}$$

$$\tilde{A}_{ij} = \sum_v \sum_\mu \bar{B}_{iv} H_{v\mu} \bar{B}_{j\mu} \tag{15.4-15}$$

These matrices become identical to the Kramers and Rouse matrices of Eqs. 11.6-7 and 8 when hydrodynamic interaction is neglected. They are not, however, inverse to one another until we make a particular choice for the l_v after Eq. 15.4-17.

[4] A. S. Lodge and Y. Wu, *Rheol. Acta*, **10**, 539–553 (1971); O. Hassager and R. B. Bird, *J. Chem. Phys.*, **56**, 2498–2501 (1972). In §16.1 and §18.4 a more general discussion is given in which a set of tensors $\boldsymbol{\lambda}_v$ plays a role somewhat related to that of the l_v here.

TABLE 15.4-1[a]

Relations Involving $\bar{B}_{kv}$ and $\tilde{B}_{vk}$

Algebraic relations

$$\sum_v \bar{B}_{kv} = 0 \tag{A}$$

$$\sum_v l_v \tilde{B}_{vk} = 0 \tag{B}$$

$$\sum_v \bar{B}_{jv} \tilde{B}_{vk} = \delta_{jk} \tag{C}$$

$$\sum_k \tilde{B}_{vk} \bar{B}_{k\mu} = \delta_{v\mu} - l_\mu \tag{D}$$

Derivatives of arbitrary functions of the configurational vectors $f(\boldsymbol{r}_h, \boldsymbol{Q}_1, \boldsymbol{Q}_2, \ldots, \boldsymbol{Q}_{N-1}) = g(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$:

$$\frac{\partial f}{\partial \boldsymbol{r}_h} = \sum_v \frac{\partial g}{\partial \boldsymbol{r}_v}; \qquad \frac{\partial f}{\partial \boldsymbol{Q}_k} = \sum_v \tilde{B}_{vk} \frac{\partial g}{\partial \boldsymbol{r}_v} \tag{E}$$

$$\frac{\partial g}{\partial \boldsymbol{r}_v} = l_v \frac{\partial f}{\partial \boldsymbol{r}_h} + \sum_k \bar{B}_{kv} \frac{\partial f}{\partial \boldsymbol{Q}_k} \tag{F}$$

Jacobian relation for the configurational vectors

$$\left| \frac{\partial(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)}{\partial(\boldsymbol{r}_h, \boldsymbol{Q}_1, \ldots, \boldsymbol{Q}_N)} \right| = 1 \tag{G}$$

Relations between the net spring force $\boldsymbol{F}_v^{(\phi)}$ acting on bead v and the force $\boldsymbol{F}_k^{(c)}$ on bead $v = k$ due to the tension in the kth connector.

$$\boldsymbol{F}_v^{(\phi)} = -\sum_k \bar{B}_{kv} \boldsymbol{F}_k^{(c)} = -\frac{\partial \phi}{\partial \boldsymbol{r}_v} \tag{H}$$

$$\boldsymbol{F}_k^{(c)} = -\sum_v \tilde{B}_{vk} \boldsymbol{F}_v^{(\phi)} = +\frac{\partial \phi}{\partial \boldsymbol{Q}_k} \tag{I}$$

[a] For the definitions of the modified Rouse matrix $(\tilde{A}_{ij})$ and the modified Kramers matrix $(\tilde{C}_{ij})$ see Eqs. 15.4-14 and 15.4-15.

With the above definitions and with the help of Table 15.4-1 we may now get an expression for the velocity of the center of resistance and the time rate change of the connector vectors:

$$[\![\dot{\boldsymbol{r}}_h]\!] = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}_h] - \frac{kT}{\zeta}\sum_\mu\sum_\nu l_\mu l_\nu H_{\nu\mu}\frac{\partial}{\partial \boldsymbol{r}_h}\ln\Psi$$
$$-\frac{1}{\zeta}\sum_k\left\{\sum_\mu\sum_\nu l_\nu H_{\nu\mu}\bar{B}_{k\mu}\right\}\left[kT\frac{\partial}{\partial \boldsymbol{Q}_k}\ln\Psi + \boldsymbol{F}_k^{(c)}\right] + \frac{1}{\zeta}\sum_\nu\sum_\mu l_\nu H_{\nu\mu}\boldsymbol{F}_\mu^{(e)} \quad (15.4\text{-}16)$$

$$[\![\dot{\boldsymbol{Q}}_j]\!] = [\boldsymbol{\kappa}\cdot\boldsymbol{Q}_j] - \frac{kT}{\zeta}\left\{\sum_\mu\sum_\nu l_\mu H_{\nu\mu}\bar{B}_{j\nu}\right\}\frac{\partial}{\partial \boldsymbol{r}_h}\ln\Psi$$
$$-\frac{1}{\zeta}\sum_k\tilde{A}_{jk}\left[kT\frac{\partial}{\partial \boldsymbol{Q}_k}\ln\Psi + \boldsymbol{F}_k^{(c)}\right] + \frac{1}{\zeta}\sum_\nu\sum_\mu H_{\nu\mu}\bar{B}_{j\nu}\boldsymbol{F}_\mu^{(e)} \quad (15.4\text{-}17)$$

In these equations the derivatives with respect to $\boldsymbol{Q}_k$ are understood to be taken at constant $\boldsymbol{r}_h$. Since it is assumed that $\Psi(\boldsymbol{r}^N, t) = n\psi(\boldsymbol{Q}^{N-1}, t)$, the derivatives with respect to $\boldsymbol{r}_h$ in the above equations vanish. Then in order that the center of resistance move with the fluid in the absence of any external forces, it is necessary to select the l_ν in such a way that the quantity inside the braces { } in Eq. 15.4-16 be zero for all values of the index k. With this choice for the l_ν the modified Kramers and Rouse matrices become inverse to one another. The dashed-underlined terms in Eqs. 15.4-16 and 15.4-17 can now be omitted.

The equation of continuity for the distribution function, Eq. 15.1-4, may also be rewritten in terms of the variables $\mathbf{r}_h$ and $\boldsymbol{Q}_k$:

$$\frac{\partial\Psi}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{r}_h}\cdot[\![\dot{\boldsymbol{r}}_h]\!]\Psi\right) - \sum_j\left(\frac{\partial}{\partial \boldsymbol{Q}_j}\cdot[\![\dot{\boldsymbol{Q}}_j]\!]\Psi\right) \quad (15.4\text{-}18)$$

The term involving the derivative with respect to $\boldsymbol{r}_h$ can be omitted as explained above.

When $[\![\dot{\boldsymbol{Q}}_j]\!]$ from Eq. 15.4-17 is now substituted into Eq. 15.4-18 we obtain the diffusion equation; if we omit the external force terms we get

$$\boxed{\frac{\partial}{\partial t}\psi = -\sum_j\left(\frac{\partial}{\partial \boldsymbol{Q}_j}\cdot\left\{[\boldsymbol{\kappa}\cdot\boldsymbol{Q}_j]\psi - \frac{1}{\zeta}\sum_k\tilde{A}_{jk}\left(kT\frac{\partial}{\partial \boldsymbol{Q}_k}\psi + \boldsymbol{F}_k^{(c)}\psi\right)\right\}\right)} \quad (15.4\text{-}19)$$

This equation is the same as Eq. 15.1-7 except that the Rouse matrix elements A_{jk} have been replaced by the corresponding modified Rouse matrix elements $\tilde{A}_{jk}$ that contain information about the hydrodynamic interaction between the beads.

When the diffusion equation is multiplied by $\sum_j\sum_k\tilde{C}_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k$ and integrated over all the connector vectors $\boldsymbol{Q}_j$, we obtain

$$\left\langle\sum_j\sum_k\tilde{C}_{jk}\boldsymbol{Q}_j\boldsymbol{Q}_k\right\rangle_{(1)} = \frac{2kT}{\zeta}(N-1)\boldsymbol{\delta} - \frac{2}{\zeta}\left\langle\sum_k\boldsymbol{F}_k^{(c)}\boldsymbol{Q}_k\right\rangle \quad (15.4\text{-}20)$$

which is analogous to Eq. 15.1-10. Up to this point no assumption has been made regarding the spring force law.

All of the development in §15.3 for the free-draining Rouse chains can now be taken over just by replacing the Rouse and Kramers matrices by the corresponding modified matrices in Eqs. 15.4-14 and 15.4-15, and by making similar replacements for the eigenvalues of the matrices. As a consequence the constitutive equation for the chain with Hookean springs and equilibrium-averaged hydrodynamic interaction can be obtained by making a slight modification of Eq. 15.3-17:[4]

$$\boxed{\tau = -\eta_s\dot{\gamma} + \int_{-\infty}^{t} \left\{ nkT \sum_j \frac{1}{\tilde{\lambda}_j} e^{-(t-t')/\tilde{\lambda}_j} \right\} \gamma_{[0]}(t, t')dt'} \tag{15.4-21}$$

in which the modified time constants are

$$\tilde{\lambda}_j = \frac{\zeta \tilde{c}_j}{2H} = \frac{\zeta}{2H\tilde{a}_j} \tag{15.4-22}$$

the $\tilde{c}_j$ and $\tilde{a}_j$ being the eigenvalues of the modified Kramers and Rouse matrices respectively.

The only remaining problem is then that of evaluating the eigenvalues of the matrix in Eq. 15.4-15, which in turn contains the Zimm hydrodynamic interaction matrix $H_{\nu\mu}$. From the definition in Eq. 15.4-7 and the expression for $\langle 1/r_{\nu\mu}\rangle_{eq}$ worked out in Eq. 12.5-11 we have

$$H_{\mu\nu} = \delta_{\mu\nu} + (1 - \delta_{\mu\nu})h^* \sqrt{\frac{2}{|\mu - \nu|}} \tag{15.4-23}$$

in which h^* is the dimensionless hydrodynamic interaction parameter[5] given by

$$h^* = \frac{\zeta}{\eta_s}\sqrt{\frac{H}{36\pi^3 kT}} \tag{15.4-24}$$

Next we have to use the above expression for $H_{\nu\mu}$ and the definition of the $\bar{B}_{k\nu}$ from Eq. 15.4-12 in order to construct the elements of the modified matrix $\tilde{A}_{jk}$. Then we have to determine the eigenvalues of this matrix. For $N = 2$ and 3 the eigenvalues can be found analytically (see Problem 15B.2):

$$\begin{aligned} N = 2: \quad & \tilde{a}_1 = 2(1 - \sqrt{2}h^*) \\ N = 3: \quad & \tilde{a}_1 = 1 - h^* \\ & \tilde{a}_2 = 3 + (1 - 4\sqrt{2})h^* \end{aligned} \tag{15.4-25}$$

[5] This h^*, first used by G. B. Thurston and A. Peterlin [*J. Chem. Phys.*, **46**, 4881–4885 (1967)] is related to Zimm's h by $h = \sqrt{N-1}\,h^*$.

For higher values of N the eigenvalues are given in tabular form for various values of N and h^*; for example, for $N = 5$:

$h^* = 0.075$	$h^* = 0.150$	$h^* = 0.250$
$\tilde{a}_1 = 0.375$	0.367	0.357
$\tilde{a}_2 = 1.274$	1.166	1.022
$\tilde{a}_3 = 2.333$	2.047	1.667
$\tilde{a}_4 = 3.170$	2.722	2.125

(15.4-26)

Several groups of investigators have compiled eigenvalue tables,[6] the most extensive table being that of Sammler, Schrag, and Lodge.[7] For some purposes it is convenient to have available an approximate expression for the eigenvalues, such as Thurston's equation,[8] which reproduces the exact numerical values to within 10% or better:

$$\tilde{a}_j = a_j b \left(\frac{j}{N}\right)^{\sigma} \tag{15.4-27}$$

in which

$$b = 1 - 1.66h^{*0.78} \tag{15.4-28}$$

$$\sigma = -1.40h^{*0.78} \tag{15.4-29}$$

and the a_j are the eigenvalues for the Rouse model given in Eq. 11.6-9.

The inclusion of the equilibrium-averaged hydrodynamic interaction still leads to the method of reduced variables, and furthermore it gives $[\eta] = K'M^a$ with a less than unity in agreement with experimental data (see Problem 15A.2). This noticeable improvement over the Rouse theory is taken as one bit of evidence to support the notion that hydrodynamic interaction is an important effect in the kinetic theory of macromolecular solutions. Other evidence of the importance of hydrodynamic interaction is in the comparison between the Zimm theory and experimental linear viscoelastic data as shown[9] in Fig. 15.4-1. It can be seen that the Zimm theory gives curves that have the same shapes as the curves obtained experimentally. In addition, the inclusion of hydrodynamic interaction gives nearly the correct dependence of translational diffusivity on molecular weight (see Example 15.4-2).

There seems to be general agreement among polymer chemists that the measured oscillatory linear viscoelastic material functions (G' and G'', or η' and η'') have shapes very similar to those computed by the Zimm theory for very dilute solutions in poor solvents. However, as the concentration or solvent power increases, the measured material functions acquire shapes that are more nearly of the form given by the Rouse theory (even though the Rouse theory was intended for dilute solutions). The reason for this unexpected success of

[6] B. H. Zimm, G. M. Roe, and L. F. Epstein, *J. Chem. Phys.*, **24**, 279-280 (1956); G. B. Thurston and J. D. Morrison, *Polymer*, **10**, 421-438 (1969); K. Osaki, *Adv. Polym. Phys.*, **12**, 1-64 (1973); *Macromolecules*, **5**, 141-144 (1972); A. S. Lodge and Y. Wu, University of Wisconsin Rheology Research Center Report No. 16 (1972); A. S. Lodge, University of Wisconsin Rheology Research Center Report No. 19 (1972).

[7] R. L. Sammler, J. L. Schrag, and A. S. Lodge, "Exact Eigenvalue Spectra for Calculation of Dynamic Functions for Dilute Polymer Solutions Based on the Bead-Spring Model: Part I. Linear Homopolymers," Univ. of Wisconsin Rheology Research Center Report No. 82, June 1982.

[8] G. B. Thurston, *Polymer*, **15**, 569-572 (1974).

[9] K. Osaki, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 144-147 (1972).

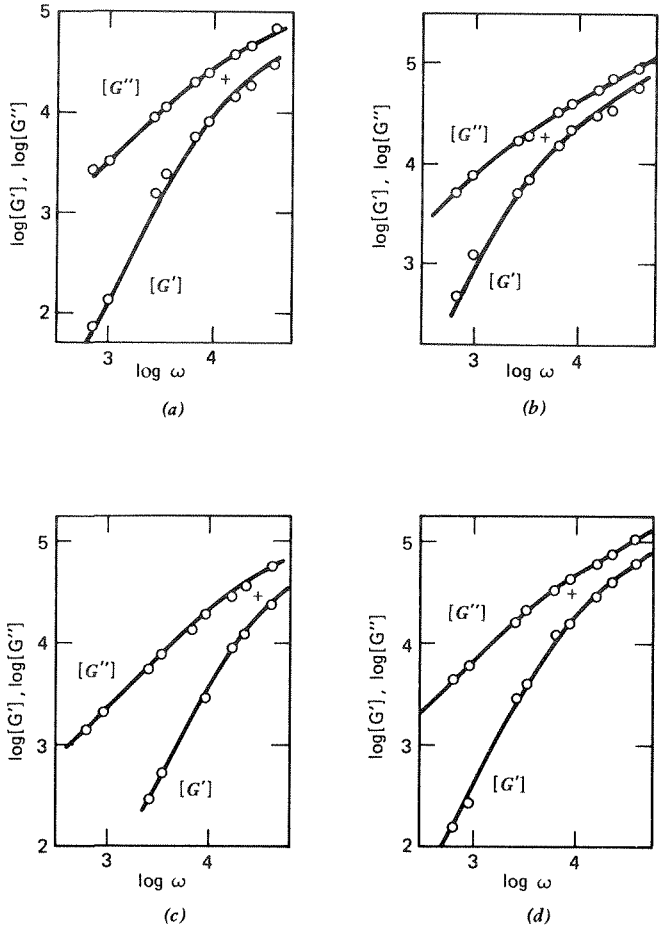


FIGURE 15.4-1. Comparison of the Zimm theory (Eqs. 15.3-29 and 30, with λ_j replaced by the $\tilde{\lambda}_j$ of Eq. 15.4-22) with experimental data. The data are presented in terms of $[G'] = \omega\eta_s[\eta'']$ and $[G''] = \omega\eta_s[\eta']$. In each case N is taken to be 200. The data in (*a*) and (*b*) are those of K. Osaki, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **3**, 144–147 (1972); those in (*c*) and (*d*) were taken from R. M. Johnson, J. L. Schrag, and J. D. Ferry, *Polymer J.*, **1**, 742–749 (1970). On each graph the + sign corresponds to the coordinates λ_1^{-1}, $\tilde{N}kT/M$. The theoretical curves were calculated from the eigenvalues computed by Lodge and Wu.[6] [Reprinted with permission from K. Osaki, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 144–147 (1972). Copyright by the American Chemical Society.]

Graph	Solute	Solvent	Temperature	h^*
(a)	Poly-α-methylstyrene ($M = 1.43 \times 10^6$)	Decalin	298°K	0.2
(b)	Poly-α-methylstyrene ($M = 1.43 \times 10^6$)	α-chloro-naphthalene	298°K	0.1
(c)	Polystyrene ($M = 8.6 \times 10^5$)	Decalin	289°K	0.2
(d)	Polystyrene ($M = 8.6 \times 10^5$)	α-chloro-naphthalene	298°K	0.15

the Rouse theory in concentrated solutions may be because the various parts of one chain are "shielded" from each other by the surrounding polymer molecules.[10]

There have been many modifications of the Rouse–Zimm theory, which are outside the scope of this text. The reviews of Yamakawa,[11] Osaki,[9] Fixman and Stockmayer,[12] and Williams[13] provide convenient guides to the research literature. We just mention here some of the refinements that have been considered:

1. Elimination of the assumption of preaveraging the Oseen tensor.[14,15]
2. Inclusion of the "excluded volume effect.[15,16,17]
3. Modification for polymers that are not chainlike, for example branched polymers[18,19] and ring-shaped polymers.[20,21,22,23,24]
4. Inclusion of "stiffness" by adding a term to the chain potential energy that describes a resistance against the bending of two adjacent links.[25]
5. Inclusion of "internal viscosity" by incorporating dashpots into the molecular model.[5,26,27,28]
6. Inclusion of nonlinear springs in the chain.[29]

[10] K. F. Freed and S. F. Edwards, *J. Chem. Phys.*, **61**, 3626–3633 (1974); F. W. Wang and B. H. Zimm, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1619–1637 (1974).

[11] H. Yamakawa, *Modern Theories of Polymer Solutions*, Harper and Row, New York (1971); *Ann. Revs. Phys. Chem.*, **25**, 179–200 (1974).

[12] M. Fixman and W. H. Stockmayer, *Ann. Revs. Phys. Chem.*, **21**, 407–428 (1970).

[13] M. C. Williams, *AIChE J.*, **21**, 1–25 (1975).

[14] This work has been done primarily by Fixman and collaborators: M. Fixman, *J. Chem. Phys.*, **45**, 785–792, 793–803 (1966); C. W. Pyun and M. Fixman, *J. Chem. Phys.*, **42**, 3838–3844 (1965), **44**, 2107–2115 (1966); H. D. Stidham and M. Fixman, *J. Chem. Phys.*, **48**, 3092–3095 (1968). A comparison of theory with experiment has been presented by H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 317; Yamakawa concludes that the Fixman theory underestimates the shear rate dependence of the viscosity. Another comparison between theory and experiment has been given by G. C. Berry and E. F. Casassa, *Macromolecular Reviews*, **4**, 1–66 (1970), pp. 36–38.

[15] R. H. Shafer [*Macromolecules*, **9**, 895–898 (1976)] calculated the normal stress differences in steady shear flow, without preaveraging the Oseen–Burgers tensors, and found that $\Psi_2 = -0.01\,\Psi_1$; this should be compared with the relation $\Psi_2 = -(1/7)\Psi_1$ obtained for rigid rods [T. Kotaka, *J. Chem. Phys.*, **30**, 1566–1567 (1959); see also §16.4]. Experimental data of M. Keentok, A. G. Georgescu, A. A. Sherwood, and R. I. Tanner [*J. Non-Newtonian Fluid Mech.*, **6**, 303–324 (1980)] for 0.2%–7% (by weight) polydisperse polymer solutions give values of $-\Psi_2/\Psi_1$ between 0.065 and 0.30.

[16] A. Peterlin, *J. Chem. Phys.*, **23**, 2464–2465 (1955).

[17] N. W. Tschoegl, *J. Chem. Phys.*, **40**, 473–479 (1964).

[18] J. S. Ham, *J. Chem. Phys.*, **26**, 625–633 (1957).

[19] B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, **37**, 19–42 (1959).

[20] B. H. Zimm and W. H. Stockmayer, *J. Chem. Phys.*, **17**, 1301–1314 (1949); V. Bloomfield and B. H. Zimm, *J. Chem. Phys.*, **44**, 315–323 (1966).

[21] J. M. Wiest, S. R. Burdette, T. W. Liu, and R. B. Bird, *J. Non-Newtonian Fluid Mech.* (1987).

[22] M. Kurata, *Bull. Inst. Chem. Res. Kyōto Univ.*, **44**, 150–154 (1966); M. Fukatsu, *loc. cit.*, **43**, 156–166 (1965); M. Fukatsu and M. Kurata, *J. Chem. Phys.*, **44**, 4539–4545 (1966).

[23] G. Tanaka and H. Yamakawa, *Polym. Journal*, **4**, 446–451 (1973).

[24] S. Imai, *J. Chem. Phys.*, **51**, 1732–1741 (1969).

[25] R. A. Harris and J. E. Hearst, *J. Chem. Phys.*, **44**, 2595–2602 (1966); J. E. Hearst, R. A. Harris, and E. Beals, *J. Chem. Phys.*, **45** 3106–3113 (1966). I. Noda and J. E. Hearst, *J. Chem. Phys.*, **54**, 2342–2354 (1971).

[26] R. Cerf, *Adv. Polym. Phys.*, **1**, 382–450 (1959).

[27] A. Peterlin, *J. Polym. Sci.*, **A2**, **5**, 179–193 (1967); A. Peterlin and C. Reinhold, *Trans. Soc. Rheol.*, **11**, 15–37 (1967).

[28] E. R. Bazúa and M. C. Williams, *J. Chem. Phys.*, **59**, 2858–2868 (1973); *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 825–848 (1974).

[29] R. B. Bird, P. J. Dotson, and N. L. Johnson, *J. Non-Newtonian Fluid Mech.*, **7**, 213–235 (1980); errata: *ibid.* (1984) Eq. 58 is incorrect, and all subsequent results are in error; A. Peterlin, *Pure Appl. Chem.*, **12**, 563–586 (1966).

Some of these modifications are taken into account only approximately, and there are points of controversy regarding the nature of the assumptions. These points of disagreement are discussed in the review articles cited earlier. All of the above modifications of the basic theory introduce additional parameters and, consequently, better fitting of the experimental data is claimed. It is probably not possible at the present time to decide whether the alleged more accurate description is a result of a fundamental improvement in the model or simply a result of the greater flexibility of the theoretical functions.

EXAMPLE 15.4-1 Stress Relaxation after Cessation of Steady Homogeneous Flows (Non-Hookean Springs)[4]

Consider a flow system for which $\boldsymbol{v}_0 = \boldsymbol{0}$ and

$$\begin{aligned} \boldsymbol{\kappa} &= \boldsymbol{\kappa}_0 \qquad t \leq 0 \\ \boldsymbol{\kappa} &= \boldsymbol{0} \qquad t > 0 \end{aligned} \tag{15.4-30}$$

Obtain the Hassager-Bird relation between the stresses prior to $t = 0$ and an integral over the stresses from $t = 0$ to $t = \infty$.

SOLUTION We start with Eq. D of Table 15.2-1 with C_{ij} replaced by $\tilde{C}_{ij}$. For $t > 0$ this simplifies to

$$\boldsymbol{\tau} = \frac{n\zeta}{2} \frac{\partial}{\partial t} \left\langle \sum_i \sum_j \tilde{C}_{ij} \boldsymbol{Q}_i \boldsymbol{Q}_j \right\rangle \tag{15.4-31}$$

When the latter is integrated with respect to time from $t = 0$ to $t = \infty$ we get

$$\int_0^\infty \boldsymbol{\tau}\, dt = -\frac{n\zeta}{2} \left\langle \sum_i \sum_j \tilde{C}_{ij} \boldsymbol{Q}_i \boldsymbol{Q}_j \right\rangle_{t=0} + A\boldsymbol{\delta} \tag{15.4-32}$$

in which A is a constant. The isotropic term arises from the evaluation of the $\langle\ \rangle$ quantity at $t = \infty$. Then for $t \leq 0$, Eq. D of Table 15.2-1 gives

$$\boldsymbol{\tau} = -\eta_s(\boldsymbol{\kappa}_0 + \boldsymbol{\kappa}_0^\dagger) - \frac{n\zeta}{2} \left\{ \boldsymbol{\kappa}_0 \cdot \left\langle \sum_i \sum_j \tilde{C}_{ij} \boldsymbol{Q}_i \boldsymbol{Q}_j \right\rangle_{t=0} + \left\langle \sum_i \sum_j \tilde{C}_{ij} \boldsymbol{Q}_i \boldsymbol{Q}_j \right\rangle_{t=0} \cdot \boldsymbol{\kappa}_0^\dagger \right\} \tag{15.4-33}$$

Since the distribution function is continuous at $t = 0$, the $\langle\ \rangle_{t=0}$ expressions are equal in Eqs. 15.4-32 and 15.4-33. Therefore,

$$(\boldsymbol{\tau})_{t\leq 0} + (\eta_s + A)(\boldsymbol{\kappa}_0 + \boldsymbol{\kappa}_0^\dagger) = \left\{ \boldsymbol{\kappa}_0 \cdot \int_0^\infty \boldsymbol{\tau}(t)dt + \int_0^\infty \boldsymbol{\tau}(t)dt \cdot \boldsymbol{\kappa}_0^\dagger \right\} \tag{15.4-34}$$

For the shearing flow $v_x = \dot{\gamma}_0 y$ between two parallel planes, Eq. 15.4-34 yields[30]

$$(\tau_{xx} - \tau_{yy})_{t\leq 0} = 2\dot{\gamma}_0 \int_0^\infty \tau_{yx}(t)dt \tag{15.4-35}$$

[30] B. D. Coleman and H. Markovitz, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 2195-2207 (1974), have shown by continuum mechanics arguments that Eq. 15.4-35 is valid for any incompressible, simple fluid with fading memory, within an error of $O(\dot{\gamma}_0^4)$.

Note that no assumptions have been made about the nature of the spring force $\boldsymbol{F}_k^{(c)}$; hence the springs could be nonlinear. Equation 15.4-35 has not been tested experimentally for dilute polymer solutions.[31]

EXAMPLE 15.4-2 Translational Diffusion for Bead-Spring Chains

Obtain an expression for the average velocity of the center of mass of a polymer molecule moving under the influence of an external force in a fluid that is otherwise at rest. Use the Nernst-Einstein equation to obtain the expression for the translational diffusivity of a bead-spring chain.

SOLUTION Begin by summing Eq. 15.4-8, with $\boldsymbol{\kappa} = \boldsymbol{0}$ and $\boldsymbol{v}_0 = \boldsymbol{0}$ over all beads, and then divide by the total number of beads in the chain to get

$$[\![\dot{\boldsymbol{r}}_c]\!] = \frac{1}{N\zeta}\sum_{\nu}\sum_{\mu} H_{\nu\mu}\left[-kT\frac{\partial \ln \Psi}{\partial \boldsymbol{r}_\mu} + \boldsymbol{F}_\mu^{(\phi)} + \boldsymbol{F}^{(e)}\right] \tag{15.4-36}$$

Here all the forces $\boldsymbol{F}_\mu^{(e)}$ are taken to be the same and equal to $\boldsymbol{F}^{(e)}$. Next use Eqs. G and I of Table 15.1-1 to get

$$[\![\dot{\boldsymbol{r}}_c]\!] = \frac{1}{N\zeta}\sum_{\nu}\sum_{\mu} H_{\nu\mu}\left[-kT\sum_k \bar{B}_{k\mu}\frac{\partial \ln \Psi}{\partial \boldsymbol{Q}_k} - \sum_k \bar{B}_{k\mu}\boldsymbol{F}_k^{(c)} + \boldsymbol{F}^{(e)}\right] \tag{15.4-37}$$

where $\boldsymbol{F}_k^{(c)}$ is a function of the scalar Q_k multiplied by the vector $\boldsymbol{Q}_k$. Then average over all configurations using the distribution function for a system at equilibrium; when this is done the terms involving the connector vectors $\boldsymbol{Q}_k$ drop out, and we are left with

$$\langle \dot{\boldsymbol{r}}_c \rangle_{eq} = \frac{1}{N\zeta}\sum_{\nu}\sum_{\mu} H_{\nu\mu}\boldsymbol{F}^{(e)} \tag{15.4-38}$$

If we now define the friction coefficient Z for the entire polymer chain by

$$N\boldsymbol{F}^{(e)} = Z\langle \dot{\boldsymbol{r}}_c \rangle_{eq} \tag{15.4-39}$$

then use of the Nernst-Einstein equation (Eq. 13.6-15) and the equations for $H_{\nu\mu}$ (Eq. 15.4-7) gives for any spring law:

$$\boxed{D_{tr} = \frac{kT}{N^2\zeta}\sum_{\nu}\sum_{\mu} H_{\nu\mu} = \frac{kT}{N\zeta}\left[1 + \frac{\zeta}{6\pi\eta_s N}\sum_{\substack{\nu \\ \nu\neq\mu}}\sum_{\mu}\left\langle\frac{1}{r_{\mu\nu}}\right\rangle_{eq}\right]} \tag{15.4-40}$$

[31] E. K. Harris, Jr., Ph.D. Thesis, University of Wisconsin, Madison (1970), found that the experimental values of the right side of Eq. 15.4-35 were 20-100% larger than the experimental values of the left side for 7.5% solutions of polystyrene of various molecular weights in Aroclor. Later measurements on polystyrene melts and concentrated solutions of polyisobutylene in a mineral oil by P. Attane, P. LeRoy, J. M. Pierrard, and G. Turrel [*J. Non-Newtonian Fluid Mech.*, **3**, 1-12 (1977)] and for concentrated solutions of polystyrene in *n*-butylbenzene by H. W. Gao, S. Ramachandran, and E. B. Christiansen [*J. Rheol.*, **25**, 213-235 (1981)] show average deviations from Eq. 15.4-35 of about 5%.

TABLE 15.4-2

Molecular Weight Dependence of Diffusion Coefficient for Very Dilnte Solntions[a,b]

Reference	System	Comments	Exponent b in $D_{tr} \propto M^{-b}$
1.	Polystyrene in cyclohexane	Θ-condition	0.497 ± 0.006
2.	Polystyrene in cyclohexane	Θ-condition	0.49
3.	Polystyrene in benzene	Good solvent	0.55 ± 0.02
4.	Polystyrene in tetrahydrofuran	Good solvent	0.564 ± 0.004
5.	Polystyrene in toluene	Good solvent	0.577
6.	Polystyrene in tetrahydrofuran	Good solvent	0.58
7.	Polystyrene in 2-butanone	Good solvent	0.53 ± 0.02
8.	Polystyrene in tetrahydrofuran	Good solvent	0.533[c]
9.	Poly-α-methylstyrene in toluene and benzene	Good solvent	0.59 ± 0.01

[a] The molecular weight in $D_{tr} \propto M^{-b}$ is the weight-averaged molecular weight.
[b] For a general survey see D. W. Schaefer and C. C. Han, "Quasielastic Light Scattering from Dilute and Semidilute Polymer Solutions", in R. Pecora, ed., *Dynamic Light Scattering: Applications of Photon Spectroscopy*, Plenum Press, New York (1984).
[c] See Problem 15A.3.

1. T. A. King, A. Knox, W. I. Lee, and J. D. G. McAdam, *Polymer*, **14**, 151–155 (1973).
2. H. J. Cantow, *Makromol. Chemie*, **30**, 169–188 (1959).
3. M. Adam and M. Delsanti, *Macromolecules*, **10**, 1229–1237 (1977).
4. W. Mandema and H. Zeldenrust, *Polymer*, **18**, 835–839 (1977).
5. P. N. Pusey, J. M. Vaughan, and G. Williams, *J. Chem. Soc., Faraday Trans. II*, **70**, 1696–1704 (1974).
6. M. E. McDonnell and A. M. Jamieson, *J. Macromol. Sci.-Phys.*, **B13**, 67–88 (1977).
7. N. C. Ford, F. E. Karasz, and J. E. M. Owen, *Disc. Faraday Soc.*, **49**, 228–237 (1970).
8. B. Appelt and G. Meyerhoff, *Macromolecules*, **13**, 657–662 (1980).
9. T. L. Yu, H. Reihanian, and A. M. Jamieson, *Macromolecules*, **13**, 1590–1594 (1980).

This is the Kirkwood expression for the translational diffusivity of chainlike polymers in dilute solution.[32] For very large values of N and Hookean springs it may be shown (see Problem 15D.2) that the translational diffusivity becomes proportional to $N^{-1/2}$. Some sample experimental results are shown in Table 15.4-2. Generalizations of Eq. 15.4-40 are developed in §18.4c.

PROBLEMS

15A.1 Slope of $\log(\eta' - \eta_s)$ vs. $\log \omega$ Curves for Rouse and Zimm Models

Review the discussion leading up to Eqs. 5.3-8 and 9, and the use of Eqs. 5.2-16 and 5.2-17 to give the high-frequency expressions in Eqs. 5.3-14 and 5.3-15.

a. Use the appropriate time constants from the Rouse theory (in Eq. 15.3-19) in Eq. 15.3-29 and obtain the slope of the $\log(\eta' - \eta_s)$ vs. $\log \omega$ curve at high frequency.

b. Use the approximate eigenvalues for the Zimm theory (in Eq. 15.4-27) in Eq. 15.3-29 to obtain the high-frequency slope of the $\log(\eta' - \eta_s)$ vs. $\log \omega$ curve. What value is obtained for $h^* = 0.25$?

[32] J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967), pp. 13, 25, 41, 76–77, 95, 101–102; see also H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), pp. 261–262, 273–280. An equation for D_{tr} different from that in Eq. 15.4-40 was obtained by P. Brunn, *J. Chem. Phys.*, **80**, 5821–5826 (1984).

c. Compare the results in **(a)** and **(b)** with the data on $[G'']$ in Fig. 15.4-1 and with η' data for dilute and concentrated solutions in Chapter 3. What do you conclude?

Answers: a. Slope $= -\frac{1}{2}$
b. Slope $= -(1+\sigma)/(2+\sigma)$; approximately $-\frac{1}{3}$

15A.2 Hydrodynamic Interaction and Deviations from Staudinger's Rule

a. Show that use of Thurston's eigenvalue expression in Eq. 15.4-27 (with a_j given by Eq. 11.6-9) in the Zimm formula for $[\eta]$ (i.e., Eq. 15.3-28 with λ_j replaced by $\tilde{\lambda}_j$) leads to

$$[\eta] = \left(\frac{\zeta \tilde{N} kT}{2\pi^2 H \eta_s b m^{\sigma+2}} \sum_j \frac{1}{j^{2+\sigma}}\right) M^{\sigma+1} \tag{15A.2-1}$$

b. Show that as h^* varies from 0 to 0.25 the molecular-weight dependence[1] of $[\eta]$ varies from M to $\sqrt{M}$. Compare this with Osaki's result[1] that $[\eta] \propto \sqrt{M}$ as $M \to \infty$ for all $h^* > 0$.

15A.3 Molecular Weight Dependence of Translational Diffusivity

The following experimental data[2] were obtained by quasi-elastic light scattering for the translational diffusivity of linear polystyrenes in dilute solutions of tetrahydrofuran at 30°C:

Molecular Weight	D_{tr} ($cm^2 s^{-1}$)
1.8×10^5	3.25×10^{-7}
3.9×10^5	2.48×10^{-7}
3.0×10^6	8.13×10^{-8}
1.0×10^7	4.35×10^{-8}

From these data obtain a power-law expression for diffusivity as a function of molecular weight. Compare the exponent so obtained with that obtained from Eq. 15.4-40.

15B.1 The Configurational Matrices for $N = 3$

a. In §11.6 a number of relations involving matrix elements were given. For the special case that $N = 3$ show that

$$\bar{B}_{kv} = \begin{pmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \end{pmatrix} \tag{15B.1-1}$$

$$B_{vk} = \begin{pmatrix} -\frac{2}{3} & -\frac{1}{3} \\ \frac{1}{3} & -\frac{1}{3} \\ \frac{1}{3} & \frac{2}{3} \end{pmatrix} \tag{15B.1-2}$$

Then verify that Eqs. 11.6-3 through 11.6-15 are correct for $N = 3$, and that all entries in Table 15.1-1 are valid for $N = 3$.

[1] In θ-solvents $[\eta]$ has been found to be proportional to $\sqrt{M}$. For better solvents $[\eta] \propto M^a$ where $a > 0.5$. See the references cited after Eq. 15.3-28 and also I. Noda, K. Mizutani, T. Kato, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 787–794 (1970) and K. Osaki, *Macromolecules*, **5**, 141–144 (1972).

[2] T. L. Yu, H. Reihanian, and A. M. Jamieson, *Macromolecules*, **13**, 1590–1594 (1980).

b. Then show that for $N = 3$

$$\tilde{B}_{vk} = \begin{pmatrix} -l_2 - l_3 & -l_3 \\ l_1 & -l_3 \\ l_1 & l_1 + l_2 \end{pmatrix} \tag{15B.1-3}$$

Show that Eq. D of Table 15.4-1 is valid for $N = 3$. Then show that $\sum_k \tilde{A}_{ik}\tilde{C}_{kj} = \delta_{ij}$ if the $\{\ \}$-factor in Eq. 15.4-16 is zero.

15B.2 Calculation of the Time Constants and Viscosity in the Zimm Model for a Chain with Three Beads

a. Calculate the $\tilde{\lambda}_j$ of Eq. 15.4-22 for the chain with $N = 3$. Use the result in Eq. 15B.1-1 to find

$$(\tilde{A}_{ij}) = \begin{pmatrix} 2(1 - \sqrt{2}h^*) & (2\sqrt{2} - 1)h^* - 1 \\ (2\sqrt{2} - 1)h^* - 1 & 2(1 - \sqrt{2}h^*) \end{pmatrix} \tag{15B.2-1}$$

Then obtain the eigenvalues $\tilde{a}_j$ of this matrix and use them to find the time constants $\tilde{\lambda}_1$ and $\tilde{\lambda}_2$.

b. Are these time constants larger or smaller than the corresponding quantities for the Rouse model where hydrodynamic interaction is neglected? Can one get the Rouse results by setting $h^* = 0$? Is this a legitimate operation?

c. Obtain the expression for the viscosity of a three-bead chain with hydrodynamic interaction in terms of ζ, H, and h^*.

d. Obtain an expression for $\eta'(\omega)$ in terms of $[\eta]$, η_s, M, $\tilde{N}kT$, and h^*.

15B.3 Estimation of Maximum Value of h^* in the Zimm Theory[3]

In the expression for h^* given in Eq. 15.4-24, ζ can be estimated by using Stokes' law $\zeta = 6\pi\eta_s a$, where a is the bead radius. Show further that from the expression in Eq. 11.4-2, the average extension b of a single spring will be approximately $\sqrt{3kT/H}$; what restrictions are placed on this result? Show then that the introduction of a and b into the expression for h^* gives

$$h^* = 0.977(a/b) \tag{15B.3-1}$$

Next require $a < \frac{1}{2}b$ (where does this come from?), and thus obtain an approximate upper limit for the magnitude of h^*.

15B.4 Equilibrium-Averaged Hydrodynamic Interaction and the Hydrodynamic Interaction Center of Resistance

The hydrodynamic interaction center of resistance is defined in Eq. 15.4-9. The l_v are determined just after Eq. 15.4-17. That is the l_v must satisfy

$$\sum_v l_v = 1 \tag{15B.4-1}$$

$$\sum_\mu \sum_v l_v H_{v\mu} \bar{B}_{jv} = 0 \tag{15B.4-2}$$

[3] This problem is based on an analysis given by K. Osaki, J. L. Schrag, and J. D. Ferry, *Macromolecules*, **5**, 144–147 (1972).

Verify that this set of N equations is satisfied by

$$l_\nu = \frac{\sum_\mu H^{-1}_{\mu\nu}}{\sum_\mu \sum_\eta H^{-1}_{\mu\eta}} \tag{15B.4-3}$$

15B.5 Transformation of the Force-Balance Equations

The equation of motion for bead ν (or force-balance equation) is given in Eq. 15.1-1.

a. Use Eq. 15.1-1 to get Eq. 15.1-2 for the mean motion of the center of mass by summing on ν and dividing by N. This leads directly to the $[\![\dot{r}_c]\!]$, v_0, $[\kappa \cdot r_c]$, and external force terms in Eq. 15.1-2. The Brownian motion terms drop out by the use of $\Psi = n\psi$ and Eqs. A and G of Table 15.1-1. Why do the $F_\nu^{(\phi)}$ terms drop out?

b. Next in Eq. 15.1-1 substitute $r_\nu = r_c + \sum_k B_{\nu k} Q_k$ and use Eqs. G and I of Table 15.1-1. This gives after using the result of (**a**):

$$\sum_k B_{\nu k}[\![\dot{Q}_k]\!] = \left[\kappa \cdot \sum_k B_{\nu k} Q_k\right] - \frac{1}{\zeta}\sum_k \bar{B}_{k\nu}\left[kT\frac{\partial \ln \psi}{\partial Q_k} + F_k^{(c)}\right] + \frac{1}{\zeta}F_\nu^{(e)} - \frac{1}{N\zeta}\sum_\nu F_\nu^{(e)} \tag{15B.5-1}$$

Then multiply by $\bar{B}_{j\nu}$ and sum on ν to get Eq. 15.1-3, after using Eq. 11.6-8 and Eq. C of Table 15.1-1.

15C.1 Derivation of the Flory–Fox Equation from the Zimm Model

For many polymer-solvent systems the Flory–Fox relation[4]

$$[\eta]_0 = \Phi\frac{\langle r^2\rangle_{eq}^{3/2}}{M} \tag{15C.1-1}$$

holds, provided that $M > 10^6$. The constant Φ is nearly a universal constant, equal to about 2.5×10^{23} or $0.42\,\tilde{N}$ (where $\tilde{N}$ is Avogadro's number), when the root-mean-square end-to-end distance $\langle r^2\rangle^{1/2}$ is given in cm and $[\eta_0]$ is in cm^3/g.

Show that the Flory–Fox equation can be obtained from the bead-spring chain model of Zimm if h^* is taken to be 0.267. To do this use Eq. 15.3-25 with the λ_j of Eq. 15.4-22, and Eq. 15.4-27 describing the $\tilde{a}_j$. If the exact Zimm eigenvalues are used (instead of Eq. 15.4-27), then it can be shown[5] that $\Phi \doteq 0.474\tilde{N}$ for all values of h^* in the limit as $M \to \infty$.

15D.1 Single-Link Distribution Function for the Rouse Chain[6]

a. The configurational distribution function $\psi(Q^{N-1}, t)$ for a Rouse chain is given by Eqs. 15.3-7, 15.3-23, and 15.3-24. By integrating as described in Eq. 12.5-2 obtain the single-link distribution function $\psi_j(Q, t)$ for link j:

$$\psi_j(Q, t) = \frac{(H/2\pi kT)^{3/2}}{\sqrt{\det \sigma_j}}\exp\left[-\left(\frac{H}{2kT}\right)(\sigma_j^{-1} : QQ)\right] \tag{15D.1-1}$$

[4] P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904–1908 (1951); P. J. Flory, *op. cit.*, pp. 616–620; W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1–179 (1974); H. Yamakawa, *Modern Theories of Polymer Solutions*, Harper and Row, New York (1971), p. 365.

[5] H. C. Öttinger, to be published (1987).

[6] H. H. Saab, X. J. Fan, P. J. Dotson, and R. B. Bird, University of Wisconsin Rheology Research Center Report No. 97 (November 1984).

where

$$\sigma_j = \sum_k \Omega_{jk}^2 \alpha_k \tag{15D.1-2}$$

and α_k is given in terms of the finite strain tensor in Eq. 15.3-23. *Caution*: The distribution function $\psi_j(\mathbf{Q}, t)$ is not to be confused with the $\psi_j(\mathbf{Q}'_j, t)$ introduced in Eq. 15.3-7.

b. How do the results in (**a**) simplify at equilibrium?

c. Use (**a**) to get an expression for the average value of the square of the end-to-end distance of link j.

15D.2 Derivation of the Molecular-Weight Dependence of the Translational Diffusivity

Verify the statement after Eq. 15.4-40 that the Zimm theory predicts that the translational diffusivity is inversely proportional to the square root of the molecular weight. Use Eq. 12.5-11 for $\langle 1/r_{\mu\nu}\rangle_{eq}$ and then replace the double sum in Eq. 15.4-40 by a double integral. Consider chains with very large N, and retain only the terms containing the highest powers of N. Show that this leads to

$$\sum_\nu \sum_\mu \left\langle \frac{1}{r_{\mu\nu}} \right\rangle_{eq} \doteq \frac{8}{3}\sqrt{\frac{2H}{\pi kT}}\, N^{3/2} \tag{15D.2-1}$$

and that $D_{tr} \propto M^{-1/2}$.

15D.3 Relations Involving Matrices and Eigenvalues

Verify that for the Kramers matrix (C_{ij}) with eigenvalues c_j:

$$\sum_j C_{jj} = \sum_j c_j \tag{15D.3-1}$$

$$\sum_j C_{ij} C_{jk} = \sum_j c_j^2 \Omega_{ij} \Omega_{jk}^{-1} \tag{15D.3-2}$$

To get the second of these write Eq. 15.3-3 (in terms of C_{jk} and c_j) twice: once for free indices ip, and once for iq. When the two equations are multiplied together one gets

$$\sum_j \sum_k \sum_m \sum_n \Omega_{ij}^{-1} C_{jk} \Omega_{kp} \Omega_{im}^{-1} C_{mn} \Omega_{nq} = c_i^2 \delta_{ip} \delta_{iq} \tag{15D.3-3}$$

Perform the sum on i; then multiply by $\Omega_{rp}\Omega_{qs}^{-1}$ and sum on p and q to get the desired result. Equation 15D.3-2 is used in Eq. 15.3-38.

CHAPTER 16

GENERAL BEAD-ROD-SPRING MODELS

In Chapter 13 we set up the kinetic theory equations for elastic dumbbells, explaining thoroughly the origins of the terms in the diffusion equation for the configurational distribution function as well as the various forms for the stress-tensor expression. In Chapter 15 the kinetic theory was extended to linear bead-spring chains, the main new idea being the introduction of normal coordinates; the latter was systematized by the introduction of several sets of matrices that facilitated coordinate transformations and other operations. In Chapter 14 we dealt with the kinetic theory of rigid dumbbells and multibead-rods; we did not show in detail how to set up the kinetic theory equations, pointing out only that since the models in that chapter involved constraints (fixed interbead distances), special techniques would have to be developed later (in Chapters 17 and 18) to handle such models.

We have thus seen examples of models with and without constraints. In each of these chapters we have also seen modeling both with and without hydrodynamic interaction (the latter having received attention in §§13.6, 14.6, and 15.4). Most of the time we took the Stokes' law friction coefficient to be a scalar, but in §13.7 we examined the possibility of tensor friction coefficients. In the preceding three chapters we took the beads to be identical (as to mass and friction coefficient), but an obvious generalization would be to allow each bead in the model to have a different mass m_ν and friction coefficient ζ_ν. Thus far we have considered only linear arrangements of beads, and we have considered fluids containing only one polymer species, which, in addition, is monodisperse.

In Chapters 17 and 18 we set up the kinetic theory equations for mixtures and we include polydispersity. We allow for much more general models, with beads different, nonlinear bead arrangements, tensor friction coefficients, and beads of finite size in space; we also allow for hydrodynamic interaction. The development of the kinetic theory to that degree of generality is a long and arduous process. Since some readers will not wish to work through the details, we give in this chapter some of the key kinetic theory results for dilute solutions including (a) arbitrary bead-rod-spring models, (b) mixtures, (c) hydrodynamic interactions, and (d) structureless beads (i.e., point masses) that may have different masses and (scalar) friction coefficients. That is, the kinetic theory results we cite here are somewhat less general than those developed in Chapters 17 and 18 but much more general than those of the preceding three chapters. All of the key kinetic theory equations—diffusion equations and stress tensor expressions—given for the simple models of Chapters 13-15 (except for §13.7) are special cases of general equations summarized here.

In §16.1 we begin by systematizing the notation that we need in this chapter for handling complex molecular models and for including hydrodynamic interaction. In §§16.2 and 3 we present, respectively, the diffusion equation and the stress-tensor expressions. Then in §16.4 we show how to get the second-order fluid constants for arbitrary bead-rod-spring models (with and without hydrodynamic interaction). Next, in §§16.5 and 6, we

discuss the two important bead-rod-chain models: the freely jointed (Kramers) chain and the freely rotating (Kirkwood–Riseman) chain. Finally in §16.7 we discuss other kinds of bead-rod models.

§16.1 SUMMARY OF NOTATION

In this section we deal with three types of notational problems: (a) the development of systematic notation appropriate for describing the geometry of bead-rod-spring models when the first three generalized coordinates are the Euler angles, which specify the overall orientation of the model in space; (b) the presentation of some matrices and tensors that facilitate the formulation of kinetic theory equations for bead-rod-spring models including hydrodynamic interaction (complete or equilibrium averaged); and (c) the notation for various kinds of forces—generalized, effective, and true forces—that will be used in Chapters 17–19 and that allow some kinetic theory results to be written in more concise forms.

a. Use of Euler Angles

As discussed in §12.1, the configuration of an arbitrary molecular model made up of mass points may be described by a set of generalized coordinates Q_s. The number of coordinates required is determined by the model, but the particular choice of coordinates is arbitrary. For some molecular models the evaluation of the base vectors $\boldsymbol{b}_{vs}$, defined by Eq. 12.1-6, and the matrix components g_{st}, defined by Eq. 12.1-7, can be simplified somewhat by treating the overall orientation in space separately. To do this we introduce a coordinate system embedded in the model in an arbitrary but well-defined manner, with a set of orthogonal unit vectors $\check{\boldsymbol{\delta}}_1, \check{\boldsymbol{\delta}}_2, \check{\boldsymbol{\delta}}_3$ in the directions of the axes $\check{x}, \check{y}, \check{z}$ of the embedded frame. The orientation of this frame with respect to the fixed frame with unit vectors $\boldsymbol{\delta}_1, \boldsymbol{\delta}_2, \boldsymbol{\delta}_3$ is described by

$$\check{\boldsymbol{\delta}}_m = \sum_n \Omega_{mn} \boldsymbol{\delta}_n \tag{16.1-1}$$

where the Ω_{mn} are given in terms of the Euler angles α, β, γ in matrix form as follows:

$$(\Omega_{mn}) = \begin{pmatrix} cC\not{c} - s\$ & sC\not{c} + c\$ & -S\not{c} \\ -cC\$ - s\not{c} & -sC\$ + c\not{c} & S\$ \\ cS & sS & C \end{pmatrix} \tag{16.1-2}^{1}$$

with $s, S, \$$ denoting $\sin\alpha, \sin\beta, \sin\gamma$ and $c, C, \not{c}$ denoting $\cos\alpha, \cos\beta, \cos\gamma$. The geometrical interpretation of the Euler angles is discussed in §E.11.

The Euler angles may then be taken to be the first three generalized coordinates. If this is done, then, $Q_1 = \alpha, Q_2 = \beta, Q_3 = \gamma$ describe the orientation of the model in space and $Q_4, Q_5, Q_6, \ldots, Q_d$ are the remaining coordinates needed to specify the configuration of the model in the embedded coordinate system. The bead locations are then given by the three

[1] Note that the Ω_{mn} are the components of a 3×3 matrix describing rotations in a 3-dimensional space, whereas the Ω_{jk} of Eq. 15.3-1 are the components of an $(N-1) \times (N-1)$ matrix. Note further that the $\boldsymbol{\Omega}_{\nu\mu}$ of Eq. 15.4-2 form an $N \times N$ matrix of tensors (the "hydrodynamic interaction tensors"); when these tensors are equilibrium averaged, we write $\langle \boldsymbol{\Omega}_{\nu\mu} \rangle_{eq} = \Omega_{\nu\mu} \boldsymbol{\delta}$, where the $\Omega_{\nu\mu}$ form an $N \times N$ matrix of scalars.

Euler angles and the components R_{vm}, of $\boldsymbol{R}_v$, with respect to the embedded frame defined by $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$, so that

$$\boldsymbol{R}_v = \sum_m R_{vm} \check{\boldsymbol{\delta}}_m \tag{16.1-3}$$

and thus

$$\boldsymbol{R}_v = \sum_m \sum_n R_{vm} \Omega_{mn} \boldsymbol{\delta}_n \tag{16.1-4}$$

Note that the Ω_{mn} are functions only of Q_1, Q_2, and Q_3, whereas the R_{vm} depend only on Q_4, Q_5, Q_6, ... It is this separation that is important.

The systematization of the formulas for the various configurational quantities is then made possible by the introduction of the (Λ_{ut}) matrix defined by:[2]

$$\Lambda_{ut} = \begin{cases} \frac{1}{2} \sum_m \sum_n \sum_p \varepsilon_{umn} \Omega_{np} \dfrac{\partial \Omega_{mp}}{\partial Q_t} & t, u \leq 3 \\ \delta_{ut} & t, u \geq 4 \\ 0 & \text{otherwise} \end{cases} \tag{16.1-5}$$

This matrix and its inverse are given as follows[3] in terms of the Euler angles β and γ:

$$(\Lambda_{ut}) = \left(\begin{array}{ccc:ccc} -S\not{c} & \$ & 0 & & & \\ S\$ & \not{c} & 0 & & 0 & \\ C & 0 & 1 & & & \\ \hdashline & & & 1 & 0 & 0 \quad \cdots \\ & 0 & & 0 & 1 & 0 \quad \cdots \\ & & & 0 & 0 & 1 \quad \cdots \\ & & & \vdots & \vdots & \vdots \end{array}\right) \tag{16.1-6}$$

$$(\Lambda_{ut}^{-1}) = \left(\begin{array}{ccc:ccc} -S^{-1}\not{c} & S^{-1}\$ & 0 & & & \\ \$ & \not{c} & 0 & & 0 & \\ S^{-1}C\not{c} & -S^{-1}C\$ & 1 & & & \\ \hdashline & & & 1 & 0 & 0 \quad \cdots \\ & 0 & & 0 & 1 & 0 \quad \cdots \\ & & & 0 & 0 & 1 \quad \cdots \\ & & & \vdots & \vdots & \vdots \end{array}\right) \tag{16.1-7}$$

[2] The permutation symbol ε_{mnp} is 1 if mnp is a cyclic permutation of 123; -1 if mnp is a cyclic permutation of 321; and 0 otherwise. See §A.2 for additional information.

[3] Λ_{ut} means the ut-component of the matrix, and (Λ_{ut}) stands for the matrix. Λ_{ut}^{-1} means the ut-component of the inverse matrix.

The (Λ_{ut})-matrix may now be used to develop a formula for the vectors $\boldsymbol{b}_{vt}$

$$
\begin{aligned}
\boldsymbol{b}_{vt} &= \sqrt{m_v}\frac{\partial}{\partial Q_t}\boldsymbol{R}_v \\
&= \sqrt{m_v}\frac{\partial}{\partial Q_t}\sum_m\sum_n R_{vm}\Omega_{mn}\boldsymbol{\delta}_n \\
&= \begin{cases} \sqrt{m_v}\sum_m\sum_n R_{vm}\left(\dfrac{\partial \Omega_{mn}}{\partial Q_t}\right)\boldsymbol{\delta}_n & t \le 3 \\ \sqrt{m_v}\sum_m\sum_n \left(\dfrac{\partial R_{vm}}{\partial Q_t}\right)\Omega_{mn}\boldsymbol{\delta}_n & t \ge 4 \end{cases} \\
&= \begin{cases} \sqrt{m_v}\sum_m\sum_n R_{vm}\left(\sum_p\sum_u \varepsilon_{mpu}\Lambda_{ut}\Omega_{pn}\right)\boldsymbol{\delta}_n & t \le 3 \\ \sqrt{m_v}\sum_m\sum_n\sum_u \Lambda_{ut}\left(\dfrac{\partial R_{vm}}{\partial Q_u}\right)\Omega_{mn}\boldsymbol{\delta}_n & t \ge 4 \end{cases} \\
&= \begin{cases} \sum_m\sum_n\sum_u \Lambda_{ut}\left[\sqrt{m_v}\sum_p R_{vp}\varepsilon_{pmu}\right]\Omega_{mn}\boldsymbol{\delta}_n & t \le 3 \\ \sum_m\sum_n\sum_u \Lambda_{ut}\left[\sqrt{m_v}\left(\dfrac{\partial R_{vm}}{\partial Q_u}\right)\right]\Omega_{mn}\boldsymbol{\delta}_n & t \ge 4 \end{cases} \\
&= \sum_m\sum_n\sum_u \Lambda_{ut}b^{vum}\Omega_{mn}\boldsymbol{\delta}_n
\end{aligned}
\tag{16.1-8}
$$

where

$$
b^{vum} = \begin{cases} \sqrt{m_v}\sum_p R_{vp}\varepsilon_{pmu} & u \le 3 \\ \sqrt{m_v}\left(\dfrac{\partial R_{vm}}{\partial Q_u}\right) & u \ge 4 \end{cases}
\tag{16.1-9}
$$

Note that Λ_{ut} and Ω_{mn} depend only on the Euler angles, that is, Q_1, Q_2, Q_3, whereas the b^{vum} depend only on $Q_4, Q_5, Q_6, \ldots$. It may then be shown that

$$
g_{tu} = \sum_v\sum_w \Lambda_{vt}\Gamma_{vw}\Lambda_{wu}
\tag{16.1-10}
$$

where

$$
\Gamma_{uv} = \sum_v\sum_m b^{vum}b^{vvm}
\tag{16.1-11}
$$

are the elements of a generalized moment of inertia matrix. From this expression it follows that

$$
G_{tu} = \sum_v\sum_w \Lambda^{-1}_{tv}\Gamma^{-1}_{vw}\Lambda^{-1}_{uw}
\tag{16.1-12}
$$

where the Λ_{tv}^{-1} are the elements of the inverse matrix given by Eq. 16.1-7 and the Γ_{vw}^{-1} are the elements of the inverse of the generalized moment of inertia matrix. For some molecular models one may choose the embedded "body-fixed" coordinate system so that this (Γ_{vw}) matrix is diagonal and thus easily inverted. In the use of these models it is then particularly convenient to use the Euler angles as generalized coordinates.

In Table 16.1-1 we summarize the notation presented here; the general expressions are given, and also the special expressions when Q_1, Q_2, Q_3 are taken to be α, β, γ. The symbols in Table 16.1-1 are used to describe geometrical properties of a particular molecular species. Whenever it is necessary to distinguish among various species in a mixture, Greek superscripts are appended; for example, we write $\boldsymbol{R}_v^\alpha$, $\boldsymbol{b}_{vs}^\alpha$, g_{st}^α, and so on, for species α.

b. Hydrodynamic Interaction

The *hydrodynamic interaction tensors* $\boldsymbol{\Omega}_{v\mu}$ were introduced in Eq. 15.4-2 for bead-spring chains (and also earlier in Eq. 13.6-3 and below Eq. 14.6-1 for dumbbells). Specific forms for these tensors were also introduced: the Oseen–Burgers tensors, in Eqs. 13.6-5 and 15.4-3; and the Rotne–Prager–Yamakawa tensors, in Eq. 14.6-2. In §15.4 we also defined the dimensionless diffusion tensors $\boldsymbol{\Upsilon}_{v\mu}$, the Zimm hydrodynamic interaction matrix $H_{v\mu}$, and the weight factors l_v. In this section we define generalizations of these three quantities and some additional symbols that are helpful in systematizing the setting up of kinetic theory equations for mixtures, for more complex models, and for models with hydrodynamic interaction. The detailed development that leads to the notation summarized here is given in Chapters 17 and 18, and hence occasionally we refer ahead to equations where a fuller discussion is provided.

In the development of the kinetic theory the "hydrodynamic" force, $\boldsymbol{F}_v^{(h)\alpha}$, on bead v of a molecule of solute species α due to the surrounding solvent molecules is approximated by an expression similar to Stokes' law (Eq. 18.2-1) involving a set of friction tensors $\boldsymbol{\zeta}_v^\alpha$. In this chapter the beads are taken to be mass points, and consequently we take these friction tensors to be isotropic, so that $\boldsymbol{\zeta}_v^\alpha = \zeta_v^\alpha \boldsymbol{\delta}$. In the expression for the hydrodynamic force, the effect of hydrodynamic interaction is described by a set of tensors, $\boldsymbol{\Omega}_{v\mu}^\alpha$. In the "free-draining" approximation (i.e., no hydrodynamic interaction) these tensors are taken to be the null tensor.

The *dimensionless diffusion tensors* are defined (Eq. 18.2-4, see also Eq. 15.4-5) as

$$\boldsymbol{\Upsilon}_{v\mu}^\alpha = \delta_{v\mu}\boldsymbol{\delta} + \zeta_v^\alpha \boldsymbol{\Omega}_{v\mu}^\alpha \tag{16.1-13}$$

and the *dimensionless mobility tensors*, $\mathbf{B}_{v\mu}^\alpha$, are defined by the condition that

$$\sum_\mu (\mathbf{B}_{v\mu}^\alpha \cdot \boldsymbol{\Upsilon}_{\mu\eta}^\alpha) = \delta_{v\eta}\boldsymbol{\delta} \tag{16.1-14}$$

The tensors $\boldsymbol{\Omega}_{v\mu}^\alpha$ and $\mathbf{B}_{v\mu}^\alpha$ are symmetric tensors and also invariant under the permutation of the subscripts. In the approximation that the hydrodynamic interaction tensors are equilibrium averaged, $\boldsymbol{\Omega}_{v\mu}^\alpha$ is replaced by $\langle \boldsymbol{\Omega}_{v\mu}^\alpha \rangle_{\text{eq}} = \Omega_{v\mu}^\alpha \boldsymbol{\delta}$, that defines the scalar quantities

TABLE 16.1-1

Notation for Coordinates and Related Quantities for Bead-Rod-Spring Models

m_v = mass of vth bead
$\boldsymbol{r}_v$ = position of vth bead
$\boldsymbol{r}_c$ = position vector of center of mass $= \sum_v m_v \boldsymbol{r}_v / \sum_v m_v$
$\boldsymbol{R}_v = \boldsymbol{r}_v - \boldsymbol{r}_c$ = position vector of vth bead with respect to the center of mass (with components X_{vn} in an arbitrary space-fixed coordinate system, and R_{vn} in an embedded coordinate system).
Q_s = sth generalized coordinate
Λ_{st} = components of the matrix defined in Eq. 16.1-5
Ω_{mn} = components of the matrix defined in Eq. 16.1-2

Quantity	General Expressions	Special Expressions When Q_1, Q_2, Q_3 Are Taken to be the Euler Angles α, β, γ
Position vectors	$\boldsymbol{R}_v = \sum_n X_{vn} \boldsymbol{\delta}_n$ (A)	$\boldsymbol{R}_v = \sum_m \sum_n R_{vm} \Omega_{mn} \boldsymbol{\delta}_n$ (F)
Base vectors	$\boldsymbol{b}_{vs} = \sqrt{m_v}\, \dfrac{\partial}{\partial Q_s} \boldsymbol{R}_v$ (B)	$\boldsymbol{b}_{vs} = \sum_m \sum_n \sum_t \Lambda_{ts} b^{vtm} \Omega_{mn} \boldsymbol{\delta}_n$ (G)
Configurational matrix components	...	$b^{vtm} = \begin{cases} \sqrt{m_v} \sum_n R_{vn} \varepsilon_{nmt} & t \le 3 \\ \sqrt{m_v}\, \dfrac{\partial}{\partial Q_t} R_{vm} & t \ge 4 \end{cases}$ (H)
Covariant metric matrix components	$g_{st} = \sum_v (\boldsymbol{b}_{vs} \cdot \boldsymbol{b}_{vt})$ (C)	$g_{st} = \sum_u \sum_v \Lambda_{us}\, \Gamma_{uv} \Lambda_{vt}$ (I)
Generalized moment of inertia tensor components	...	$\Gamma_{uv} = \sum_v \sum_n b^{vun} b^{vvn}$ (J)
Contravariant metric matrix components	$G_{st} = g_{st}^{-1}$ (D)	$G_{st} = \sum_u \sum_v \Lambda_{su}^{-1} \Gamma_{uv}^{-1} \Lambda_{tv}^{-1}$ (K)
Determinant of the covariant metric matrix	$g = \det(g_{st})$ (E)	$g = \sin^2\beta \det(\Gamma_{uv})$ (L)

Note: Λ_{st}^{-1} means the st-component of the matrix inverse to the matrix (Λ_{st}).

$\Omega^{\alpha}_{\nu\mu}$. Thus when equilibrium averaging is used, the dimensionless diffusion and mobility tensors are isotropic:

$$\text{Equilibrium Averaged H.I.: } \boldsymbol{\Upsilon}^{\alpha}_{\nu\mu} = (\delta_{\nu\mu} + \zeta^{\alpha}_{\nu}\Omega^{\alpha}_{\nu\mu})\boldsymbol{\delta} = H^{\alpha}_{\nu\mu}\boldsymbol{\delta} \tag{16.1-15}$$

$$\text{Equilibrium Averaged H.I.: } \mathbf{B}^{\alpha}_{\nu\mu} = B^{\alpha}_{\nu\mu}\boldsymbol{\delta} \tag{16.1-16}$$

in which $(H^{\alpha}_{\nu\mu})$ is the *Zimm hydrodynamic interaction matrix* and $(B^{\alpha}_{\nu\mu})$ is the *dimensionless mobility matrix*. These matrices are inverse to one another; when hydrodynamic interaction is neglected, both of these matrices become the $N \times N$ unit matrix $(\delta_{\nu\mu})$. Note that in Eq. 16.1-13 we have written ζ^{α}_{ν}, indicating that the bead friction coefficients may depend on the bead number ν and the species α.

When complete hydrodynamic interaction is included the appropriate generalization of the scalar weight factors l_{ν} is a set of *weight tensors* $\boldsymbol{\lambda}^{\alpha}_{\nu}$ (Eq. 18.2-7) defined by

$$\boldsymbol{\lambda}^{\alpha}_{\nu} = \left\{(\mathbf{Z}^{\alpha})^{-1} \cdot \sum_{\mu} \boldsymbol{\zeta}^{\alpha}_{\mu\nu}\right\} \tag{16.1-17}$$

where $\mathbf{Z}^{\alpha}$ is the *total effective friction tensor*

$$\mathbf{Z}^{\alpha} = \sum_{\nu}\sum_{\mu} \boldsymbol{\zeta}^{\alpha}_{\nu\mu} = \sum_{\nu}\sum_{\mu} \zeta^{\alpha}_{\mu}\mathbf{B}^{\alpha}_{\nu\mu} \tag{16.1-18}$$

and the $\boldsymbol{\zeta}^{\alpha}_{\nu\mu}$ are the *effective friction tensors*. These quantities are summarized in Table 16.1-2, and simplified forms for equilibrium-averaged hydrodynamic interaction and no hydrodynamic interaction are given. In the table the species index α is omitted.

Along toward the end of Table 16.1-2 we give modifications of the metric matrix components g_{st} and G_{st} (see Table 16.1-1) that enable us to include hydrodynamic interaction formally in the diffusion equation. These *modified metric matrix components* $\tilde{g}^{\alpha}_{st}$ and $\tilde{G}^{\alpha}_{st}$ are given in terms of the *modified effective friction tensors* $\tilde{\boldsymbol{\zeta}}^{\alpha}_{\nu\mu}$. The latter quantities are also useful for obtaining a compact formula for the *coupling tensors* $\mathbf{M}^{\alpha}_{s}$, which, in the diffusion equation, appear "coupled" with the $\boldsymbol{\kappa}$-tensor through a double-dot product.

The notation summarized in Table 16.1-2 is very compact, and in §§16.2 and 16.3 it permits us to present some very general kinetic theory equations in an efficient way. Simplified equations for equilibrium-averaged or no hydrodynamic interaction are easily obtained by using the last two columns of Table 16.1-2. We conclude this discussion with two examples to illustrate the use of Table 16.1-1; Table 16.1-2 is used in Example 16.2-1.

EXAMPLE 16.1-1 Calculations of Configurational Quantities for the Multibead-Rod Model

Obtain the quantities listed in Eqs. A–E of Table 16.1-1 for the rigid multibead-rod model shown in Fig. 14.1-2. We need some of these quantities in Examples 16.2-1 and 16.3-1.

SOLUTION As generalized coordinates we take Q_1 and Q_2 to be θ and ϕ, the angles describing the direction of the unit vector along the rod. Then, as indicated in Fig. 14.1-2, the locations of the N beads are given by the following position vectors with respect to the center of mass:

$$\boldsymbol{R}_{\nu} = \tfrac{1}{2}a\nu\boldsymbol{u} \qquad (\nu = -(N-1), -(N-3), -(N-5), \ldots, +(N-1)) \tag{16.1-19}$$

Diffusion and Mobility Tensors and Related Quantites (With Complete Hydrodynamic Interaction and Equilibrium-Averaged Hydrodynamic Interaction)

The dimensionless diffusion and mobility tensors are related by $\sum_\eta \{\mathbf{B}_{\nu\eta} \cdot \boldsymbol{\Upsilon}_{\eta\mu}\} = \delta_{\nu\mu}\boldsymbol{\delta}$; the hydrodynamic interaction matrix and the mobility matrix are related by $\sum_\eta B_{\nu\eta}H_{\eta\mu} = \delta_{\nu\mu}$; and the modified metric matrix components are related by $\sum_t \tilde{g}_{st}\tilde{G}_{tu} = \delta_{su}$.

Quantity	Symbol	With Complete Hydrodynamic Interaction		With Equilibrium-Averaged Hydrodynamic Interaction		With no Hydrodynamic Interaction and Identical Beads	
Dimensionless diffusion tensors	$\boldsymbol{\Upsilon}_{\nu\mu}$	$\delta_{\nu\mu}\boldsymbol{\delta} + \zeta_\nu \boldsymbol{\Omega}_{\nu\mu}$	(A)	$(\delta_{\nu\mu} + \zeta_\nu \Omega_{\nu\mu})\boldsymbol{\delta} = H_{\nu\mu}\boldsymbol{\delta}$	(I)	$\delta_{\nu\mu}\boldsymbol{\delta}$	(R)
Dimensionless mobility tensors	$\mathbf{B}_{\nu\mu}$	Definition given implicitly above		$B_{\nu\mu}\boldsymbol{\delta}$	(J)	$\delta_{\nu\mu}\boldsymbol{\delta}$	(S)
Effective friction tensors	$\boldsymbol{\zeta}_{\nu\mu}$	$\zeta_\mu \mathbf{B}_{\nu\mu}$	(B)	$\zeta_\mu B_{\nu\mu}\boldsymbol{\delta}$	(K)	$\zeta\delta_{\nu\mu}\boldsymbol{\delta}$	(T)
Total effective friction tensor	$\mathbf{Z}$	$\sum_\nu \sum_\mu \boldsymbol{\zeta}_{\nu\mu}$	(C)	$\sum_\nu \sum_\mu \zeta_\mu B_{\nu\mu}\boldsymbol{\delta} \equiv Z\boldsymbol{\delta}$	(L)	$N\zeta\boldsymbol{\delta}$	(U)
Weight tensors	$\boldsymbol{\lambda}_\nu$	$\left\{\mathbf{Z}^{-1} \cdot \sum_\mu \boldsymbol{\zeta}_{\mu\nu}\right\}$	(D)	$\dfrac{\sum_\mu \zeta_\mu B_{\nu\mu}}{\sum_\nu \sum_\mu \zeta_\mu B_{\nu\mu}}\boldsymbol{\delta} \equiv l_\nu\boldsymbol{\delta}$	(M)	$\dfrac{1}{N}\boldsymbol{\delta}$	(V)
Modified effective friction tensors	$\tilde{\boldsymbol{\zeta}}_{\nu\mu}$	$\boldsymbol{\zeta}_{\nu\mu} - \{\boldsymbol{\lambda}_\nu^\dagger \cdot \mathbf{Z} \cdot \boldsymbol{\lambda}_\mu\}$	(E)	$(B_{\nu\mu}\zeta_\mu - Zl_\nu l_\mu)\boldsymbol{\delta} \equiv \tilde{\zeta}_{\nu\mu}\boldsymbol{\delta}$	(N)	$\left(\delta_{\nu\mu} - \dfrac{1}{N}\right)\zeta\boldsymbol{\delta}$	(W)
Coupling tensors	$\mathbf{M}_s$	$\sum_\nu \sum_\mu \dfrac{1}{\sqrt{m_\nu}}\{\boldsymbol{R}_\mu \boldsymbol{b}_{\nu s} \cdot \tilde{\boldsymbol{\zeta}}_{\nu\mu}\}$	(F)	$\sum_\nu \sum_\mu \dfrac{\tilde{\zeta}_{\nu\mu}}{\sqrt{m_\nu}}\boldsymbol{R}_\mu \boldsymbol{b}_{\nu s}$	(O)	$\dfrac{\zeta}{\sqrt{m}}\sum_\nu \boldsymbol{R}_\nu \boldsymbol{b}_{\nu s}$	(X)
Modified covariant metric matrix components	$\tilde{g}_{st}$	$\sum_\nu \sum_\mu \dfrac{1}{\sqrt{m_\nu m_\mu}}(\boldsymbol{b}_{\nu s} \cdot \tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot \boldsymbol{b}_{\mu t})$	(G)	$\sum_\nu \sum_\mu \dfrac{\tilde{\zeta}_{\nu\mu}}{\sqrt{m_\nu m_\mu}}(\boldsymbol{b}_{\nu s} \cdot \boldsymbol{b}_{\mu t})$	(P)	$\dfrac{\zeta}{m}g_{st}$	(Y)
Modified contravarant metric matrix components	$\tilde{G}_{st}$	Definition given implicitly above		Definition given implicitly above		$\dfrac{m}{\zeta}G_{st}$	(Z)
Modified reciprocal base vectors	$\boldsymbol{a}_{\nu s}$	$\sum_t \sum_\mu \dfrac{1}{\sqrt{m_\nu m_\mu}}\tilde{G}_{st}[\tilde{\boldsymbol{\zeta}}_{\nu\mu} \cdot \boldsymbol{b}_{\mu t}]$	(H)	$\sum_t \sum_\mu \dfrac{1}{\sqrt{m_\nu m_\mu}}\tilde{G}_{st}\zeta_{\nu\mu}\boldsymbol{b}_{\mu t}$	(Q)	$\sum_t G_{st}\boldsymbol{b}_{\nu t}$	(AA)

Then the base vectors are obtained from Eq. B of Table 16.1-1 as

$$\boldsymbol{b}_{vs} = \sqrt{m}\frac{\partial}{\partial Q_s}(\tfrac{1}{2}av\boldsymbol{u}) = \tfrac{1}{2}\sqrt{m}\,av\boldsymbol{c}_s \tag{16.1-20}$$

in which the c_s are vectors defined in Table E.5-1. Next the matrices (g_{st}) and (G_{st}) are obtained from Eqs. C and D of Table 16.1-1

$$\begin{aligned}(g_{st}) &= \tfrac{1}{4}ma^2\left(\sum_{-(N-1)}^{+(N-1)} v^2\right)\begin{pmatrix}1 & 0\\ 0 & \sin^2\theta\end{pmatrix}\\ &= \tfrac{1}{12}ma^2N(N^2-1)\begin{pmatrix}1 & 0\\ 0 & \sin^2\theta\end{pmatrix}\end{aligned} \tag{16.1-21}$$

$$(G_{st}) = \frac{12}{ma^2N(N^2-1)}\begin{pmatrix}1 & 0\\ 0 & 1/\sin^2\theta\end{pmatrix} \tag{16.1-22}$$

Finally from Eq. E

$$g = \det(g_{st}) = (\tfrac{1}{12}ma^2N(N^2-1)\sin\theta)^2 \tag{16.1-23}$$

For the rigid dumbbell, $N = 2$, and $g = \frac{1}{4}m^2a^4\sin^2\theta$.

EXAMPLE 16.1-2 Calculation of Configurational Quantities for the Three-Bead-Two-Rod Model

Find the various configurational quantites for the short Kramers chain depicted in Fig. 16.1-1.

SOLUTION This model consists of three beads of equal masses and equal friction coefficients connected by two rigid rods of length a, freely jointed at the middle bead. To specify the location of the beads we introduce a set of orthogonal unit vectors $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$ with origin at the center of mass (Fig. 16.1-1). The vectors are oriented such that the plane of the three beads coincides with that given by $\check{\boldsymbol{\delta}}_2$ and $\check{\boldsymbol{\delta}}_3$ and such that $\check{\boldsymbol{\delta}}_3$ bisects the angle between the two links. As generalized coordinates for the description of the orientation and relative internal configuration of the model we use the three Euler angles $Q_1 \equiv \alpha$, $Q_2 \equiv \beta$, $Q_3 \equiv \gamma$ specifying the orientation of triad $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$ with respect to a space-fixed coordinate system, and the coordinate $Q_4 \equiv \chi$, the angle between the two links. The ranges of these coordinates are

$$\begin{aligned}0 \le \alpha < 2\pi \qquad & 0 \le \beta \le \pi\\ 0 \le \gamma < 2\pi \qquad & 0 \le \chi \le \pi\end{aligned}$$

The position vectors of the three beads may now be expressed by

$$\boldsymbol{R}_1 = a(\tfrac{1}{3}\mathrm{K}\check{\boldsymbol{\delta}}_3 - \Sigma\check{\boldsymbol{\delta}}_2) \tag{16.1-24}$$

$$\boldsymbol{R}_2 = -\tfrac{2}{3}a\mathrm{K}\check{\boldsymbol{\delta}}_3 \tag{16.1-25}$$

$$\boldsymbol{R}_3 = a(\tfrac{1}{3}\mathrm{K}\check{\boldsymbol{\delta}}_3 + \Sigma\check{\boldsymbol{\delta}}_2) \tag{16.1-26}$$

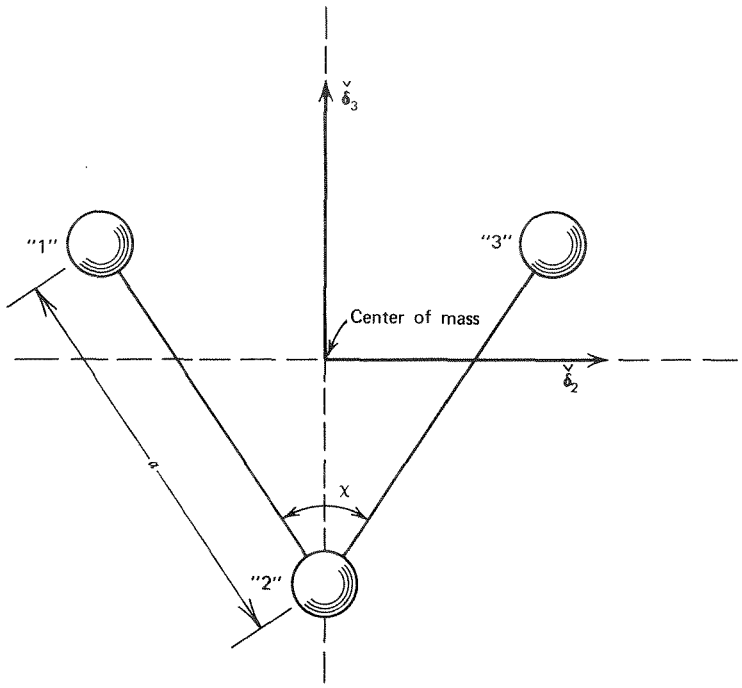


FIGURE 16.1-1. The unit vectors $\check{\delta}_2$ and $\check{\delta}_3$ embedded in the model of three beads and two rigid links. The center of mass is at the origin, and the plane given by $\check{\delta}_2$ and $\check{\delta}_3$ coincides with that determined by the three beads; $\check{\delta}_1$ is not shown, but is oriented such that $\check{\delta}_1, \check{\delta}_2, \check{\delta}_3$ form a right-handed set of orthonormal vectors.

where $\mathrm{K} = \cos(\chi/2)$ and $\Sigma = \sin(\chi/2)$. Hence the matrix with components R_{vm} is

$$(R_{vm}) = a\begin{pmatrix} 0 & -\Sigma & \frac{1}{3}\mathrm{K} \\ 0 & 0 & -\frac{2}{3}\mathrm{K} \\ 0 & \Sigma & \frac{1}{3}\mathrm{K} \end{pmatrix} \tag{16.1-27}$$

The R_{vm} are defined in Eq. F of Table 16.1-1.

Furthermore from Eq. H of Table 16.1-1 we find that

$$\begin{aligned} -3b^{112} = 3b^{121} = \tfrac{3}{2}b^{212} = -\tfrac{3}{2}b^{221} = -3b^{312} = 3b^{321} \\ = 2b^{342} = -2b^{142} = \sqrt{m}a\mathrm{K} \end{aligned} \tag{16.1-28}$$

$$\begin{aligned} -b^{113} = b^{131} = b^{313} = -b^{331} = -6b^{143} = -6b^{343} \\ = 3b^{243} = \sqrt{m}a\Sigma \end{aligned} \tag{16.1-29}$$

The 21 other b^{vtm} are zero. It then follows from the definition of Γ_{uv} in Eq. J of Table 16.1-1 that

$$(\Gamma_{uv}) = ma^2\begin{pmatrix} \frac{2}{3}\mathrm{K}^2 + 2\Sigma^2 & 0 & 0 & 0 \\ 0 & \frac{2}{3}\mathrm{K}^2 & 0 & 0 \\ 0 & 0 & 2\Sigma^2 & 0 \\ 0 & 0 & 0 & \frac{1}{2}\mathrm{K}^2 + \frac{1}{6}\Sigma^2 \end{pmatrix} \tag{16.1-30}$$

The metric matrix components g_{tu} may then be found from Eq. I. From Eq. L it is found that the determinant is

$$g = \det(g_{tu})$$
$$= \tfrac{4}{27}m^4a^8(\sin^2\chi)(1 - \tfrac{1}{4}\cos^2\chi)\sin^2\beta \tag{16.1-31}$$

Since in this example the generalized moment of inertia tensor in Eq. J is diagonal, it may easily be inverted. One then finds from Eq. K that the elements of the inverse metric matrix are

$$ma^2G_{11} = \frac{3}{2}\frac{K^2 + 3\Sigma^2\$^2}{K^2S^2(1 + 2\Sigma^2)} \tag{16.1-32}$$

$$ma^2G_{22} = \frac{3}{2}\frac{K^2 + 3\Sigma^2\not{\phi}^2}{K^2(1 + 2\Sigma^2)} \tag{16.1-33}$$

$$ma^2G_{33} = \frac{3}{2}\frac{C^2}{S^2}\frac{K^2 + 3\Sigma^2\$^2}{K^2(1 + 2\Sigma^2)} + \frac{1}{2\Sigma^2} \tag{16.1-34}$$

$$ma^2G_{44} = \frac{6}{1 + 2K^2} \tag{16.1-35}$$

$$ma^2G_{12} = \frac{9}{2}\frac{\Sigma^2\$\not{\phi}}{K^2S(1 + 2\Sigma^2)} \tag{16.1-36}$$

$$G_{23} = -CG_{12} \tag{16.1-37}$$

$$G_{13} = -CG_{11} \tag{16.1-38}$$

$$G_{14} = G_{24} = G_{34} = 0 \tag{16.1-39}$$

The expressions developed in this example should be compared with those obtained in Example 12.1-1, in which the same molecular model is considered using a different set of configuration coordinates. In particular one may compare the determinants of the metric matrices, g, as given by Eqs. 12.1-17 and 16.1-31. The ratio of the square roots of these two expressions is the Jacobian of the transformation from one set of coordinates to the other set (see Eq. 12.3-4b).

c. Types of Forces

In §13.1 four kinds of forces acting on the beads were described, and in Eq. 13.2-1 these forces were combined in a "force balance." Explicit expressions for these forces were then given in Eqs. 13.2-2 to 4. No particular problems were encountered in writing the force balance or the expressions for the forces inasmuch as the system under consideration (the elastic-dumbbell model) contained no constraints.

In §14.2, on the other hand, we dealt with a system containing a constraint (the rigid-dumbbell model). There we had to be careful to "project out" the θ- and ϕ-components in writing the force balance.

In Chapters 17–19 in the formal kinetic theory for arbitrary models with constraints it is convenient and natural to work with *generalized forces* $\mathscr{F}_s^{(\ )}$, one associated with each

TABLE 16.1-3

Notation for Forces used in Chapters 16–19

	Forces in the Force Balance				
	(1) Hydrodynamic Forces	(2) Brownian Forces	(3) Intramolecular Forces	(4) External Forces	Sum of Forces in (1)–(4)
Generalized forces associated with degree of freedom s	$\mathscr{F}_s^{(h)}$	$\mathscr{F}_s^{(b)}$	$\mathscr{F}_s^{(\phi)}$	$\mathscr{F}_s^{(e)}$	0
Effective forces[a] associated with bead v	$\mathscr{F}_v^{(h)}$	$\mathscr{F}_v^{(b)}$	$\mathscr{F}_v^{(\phi)}$	$\mathscr{F}_v^{(e)}$	$\mathbf{0}$
Effective total forces[b] exerted on bead v	$\boldsymbol{F}_v^{(h)}$	$\boldsymbol{F}_v^{(b)}$	$\boldsymbol{F}_v^{(\phi)}$	$\boldsymbol{F}_v^{(e)}$	$\mathbf{0}$, if there are no constraints
True forces[c] on entire molecule	$\boldsymbol{F}^{(h)}$	$\boldsymbol{F}^{(b)}$	$\mathbf{0}$	$\boldsymbol{F}^{(e)}$	$\mathbf{0}$, for dilute solutions

[a] The effective forces, the effective total forces, and the generalized forces are related by

$$\begin{cases} \mathscr{F}_v^{(\ )} = \sqrt{m_v} \sum_s \sum_t \mathscr{F}_s^{(\ )} G_{st} \boldsymbol{b}_{vt} \\ \mathscr{F}_s^{(\ )} = \sum_v \dfrac{1}{\sqrt{m_v}} (\boldsymbol{b}_{vs} \cdot \boldsymbol{F}_v^{(\ )}) \end{cases} \tag{A}$$

[b] The effective total forces and the effective forces are related by

$$\boldsymbol{F}_v^{(h)} = \mathscr{F}_v^{(h)} + (m_v/m_p)\boldsymbol{F}^{(h)} \quad \text{(for dilute solutions of models with } \textit{no constraints} \text{ only; see Eq. 18.1-16 with } \bar{N} = 1) \tag{B}$$

$$\boldsymbol{F}_v^{(b)} = \mathscr{F}_v^{(b)} + (m_v/m_p)\boldsymbol{F}^{(b)} \quad \text{(cf. Eq. 18.3-13)} \tag{C}$$

$$\boldsymbol{F}_v^{(\phi)} = \mathscr{F}_v^{(\phi)} \quad \text{(because the total intramolecular force is zero)} \tag{D}$$

$$\boldsymbol{F}_v^{(e)} = \mathscr{F}_v^{(e)} + (m_v/m_p)\boldsymbol{F}^{(e)} \quad \text{(cf. Eq. 18.4-12)} \tag{E}$$

For models with no constraints the effective forces and the effective total forces, $\mathscr{F}_v^{(\phi)}$, $\mathscr{F}_v^{(e)}$, $\boldsymbol{F}_v^{(\phi)}$, $\boldsymbol{F}_v^{(e)}$ are true forces derivable from potentials (see Example 17.2-1), and the Brownian forces $\mathscr{F}_v^{(b)}$, $\boldsymbol{F}_v^{(b)}$ are derivable in an analogous sense from $\ln \Psi$.

[c] Note that $\boldsymbol{F}^{(\ )} = \sum_v \boldsymbol{F}_v^{(\ )}$, and that $\boldsymbol{F}^{(\phi)} \equiv \mathbf{0}$. Three of these relations follow immediately from Eqs. C, D, and E above; for the $\boldsymbol{F}_v^{(h)}$ relation see Eq. 18.1-9, which is true without the restrictions stated above for Eq. B.

internal degree of freedom, s, of the molecular model, where ( ) can stand for (h), (b), (ϕ), or (e), the forces associated with hydrodynamic drag, Brownian motion, intramolecular potentials, or external force fields. Closely associated with these generalized forces are the *effective forces* $\mathscr{F}_v^{(\ )}$, and the *effective total forces* $\boldsymbol{F}_v^{(\ )}$, one associated with each bead v.

In Table 16.1-3 we summarize the notation and give some of the most important relations connecting the various forces. In Chapters 17 and 18 precise definitions are given, and the notation for generalized and effective forces enables us to write many kinetic theory relations in compact forms that bring out the physical meanings of the equations. A few of these symbols are used in §§16.2 and 16.3.

§16.2 THE "DIFFUSION EQUATION" FOR THE CONFIGURATIONAL DISTRIBUTION FUNCTION

We recall from chapters 13, 14, and 15 that there are two main parts to the kinetic theory of macromolecular solutions: the establishment and solution of a partial differential equation for ψ, and the development of an expression for the stress tensor involving average values that are integrals containing ψ. For complex macromolecules the same two problems are confronted; in this section we deal with the diffusion equation for ψ, and in the following section we focus our attention on the stress-tensor expression.

In the foregoing chapters we made use of an *equation of continuity* in the configuration space: Eq. 13.2-12 for elastic dumbbells; Eq. 14.2-7 for rigid dumbbells; Eq. 15.1-6 for Rouse chains. All of these are special cases of a more general equation, derived in Chapter 17, and given there as Eq. 17.5-14. If the external forces depend only on the configuration coordinates Q_s^α (that is, they are independent of the center of mass coordinates $\boldsymbol{r}_c^\alpha$), then this equation becomes

$$\frac{\partial}{\partial t}\psi_\alpha = -\sum_s \frac{\partial}{\partial Q_s^\alpha}([\![\dot{Q}_s]\!]^\alpha \psi_\alpha) \tag{16.2-1}$$

The index α indicates that the quantity pertains to solute species α in a multicomponent solution; the solute may be either a mixture of different chemical species or a polydisperse mixture of a single chemical species.

Next we need an expression for $[\![\dot{Q}_s]\!]^\alpha$, the momentum-space-averaged generalized velocity. It is shown later (see Eq. 18.2-42) that[1]

$$[\![\dot{Q}_s]\!]^\alpha = -\sum_t \tilde{G}_{st}^\alpha(\mathscr{F}_t^{(h)\alpha} - \mathbf{M}_t^\alpha : \boldsymbol{\kappa}) \tag{16.2-2}$$

in which $\tilde{G}_{st}^\alpha$ and $\mathbf{M}_t^\alpha$ are quantities given in Table 16.1-2 and $\mathscr{F}_t^{(h)\alpha}$ is a "generalized hydrodynamic force" associated with the tth degree of freedom of the macromolecular model. Equation 16.2-2 is valid for any model, with or without constraints, and with or without hydrodynamic interaction. This equation can be regarded as a "turned-wrong-side-out" version of the general Stokes-law expression in Eq. 16.3-3. As discussed in §18.2 it is convenient to introduce the generalized hydrodynamic forces $\mathscr{F}_s^{(h)\alpha}$ in the solution of the Stokes-law equations, since the number of these generalized forces is the same as the

[1] Equation 16.2-1 is the generalization of the continuity equation in Eq. 13.2-12 for elastic dumbbells and Eq. 14.2-7 for rigid dumbbells. Equation 16.2-2 is the generalization of the components of

$$[\![\dot{\boldsymbol{Q}}]\!] = -\frac{1}{\zeta}(\boldsymbol{F}_2^{(h)} - \boldsymbol{F}_1^{(h)}) + [\boldsymbol{\kappa}\cdot\boldsymbol{Q}] \tag{16.2-2a}$$

which is obtained from the two equations in Eq. 13.2-2 for elastic dumbbells without hydrodynamic interaction. The analogous equation for rigid dumbbells is

$$[\![\dot{\boldsymbol{u}}]\!] = \left(-\frac{1}{\zeta L}(\boldsymbol{F}_1^{(h)} - \boldsymbol{F}_{-1}^{(h)}) + [\boldsymbol{\kappa}\cdot\boldsymbol{u}]\right)\cdot(\boldsymbol{\delta} - \boldsymbol{uu}) \tag{16.2-2b}$$

which is obtained by projecting out the θ and ϕ components from the difference of the two Stokes-law equations given in Eq. 14.2-4. By starting with Eq. 14.6-10 the hydrodynamic-interaction analog of Eq. 16.2-2b is obtained.

number of generalized velocities $[\![\dot{Q}_s]\!]$, whereas the number of effective total forces $F_v^{(h)}$ is larger.

Next the generalized hydrodynamic force $\mathscr{F}_t^{(h)\alpha}$ can be eliminated by using a *force-balance equation* (or equation of motion), which is (see Eq. 17.5-15)

$$\mathscr{F}_t^{(h)\alpha} + \mathscr{F}_t^{(\phi)\alpha} + \mathscr{F}_t^{(b)\alpha} + \mathscr{F}_t^{(e)\alpha} = 0 \tag{16.2-3}$$

in which

$$\mathscr{F}_t^{(\phi)\alpha} = -\frac{\partial}{\partial Q_t^\alpha}\phi^\alpha \tag{16.2-4}$$

is the generalized spring force associated with the intramolecular potential ϕ^α, and $\mathscr{F}_t^{(b)\alpha}$ and $\mathscr{F}_t^{(e)\alpha}$ are the generalized Brownian and external forces respectively; when equilibration in momentum space is assumed the generalized Brownian force is

$$\mathscr{F}_t^{(b)\alpha} = -kT\frac{\partial}{\partial Q_t^\alpha}\ln\left(\frac{\psi_\alpha}{\sqrt{g_\alpha}}\right) \tag{16.2-5}$$

When $\mathscr{F}_t^{(h)\alpha}$ from the above equation is inserted into Eq. 16.2-2, and $[\![\dot{Q}_s]\!]^\alpha$ from that equation is substituted into Eq. 16.2-1, we get

$$\frac{\partial}{\partial t}\psi_\alpha = -\sum_s\sum_t \frac{\partial}{\partial Q_s^\alpha}\left\{\tilde{G}_{st}^\alpha\left[(\mathbf{M}_t^\alpha : \boldsymbol{\kappa})\psi_\alpha - kT\sqrt{g_\alpha}\frac{\partial}{\partial Q_t^\alpha}\left(\frac{\psi_\alpha}{\sqrt{g_\alpha}}\right) - \left(\frac{\partial\phi^\alpha}{\partial Q_t^\alpha}\right)\psi_\alpha + \mathscr{F}_t^{(e)\alpha}\psi_\alpha\right]\right\}$$

Hydrodynamic — Brownian — Intramolecular — External

(16.2-6)

This is the *diffusion equation* for the configurational distribution function ψ_α for solute species α in a multicomponent solution. It includes the effects of hydrodynamic interaction (complete or equilibrium averaged), external forces that do not depend on the center-of-mass location, and beads with differing masses and friction coefficients; it contains Eqs. 13.2-13, 14.6-13, and 15.1-7 as special cases. Let us now list the assumptions inherent in Eq. 16.2-6: (i) dilute solution, (ii) equilibration in momentum space, (iii) homogeneous macroscopic flow field, (iv) mass-times-acceleration terms omitted in the equation of motion for the beads (i.e., no inertial effects), and (v) structureless beads.

If the effective friction tensors, $\zeta_{\nu\mu}$, are diagonal and constant, as in the approximation of equilibrium-averaged hydrodynamic interaction, or if hydrodynamic interaction is neglected, then (see Table 16.1-2, Eq. F)

$$\mathbf{M}_s + \mathbf{M}_s^\dagger = \frac{\partial}{\partial Q_s}\mathbf{K} \tag{16.2-7}$$

where $\mathbf{K}$ is the *structure tensor*

$$\mathbf{K} = \sum_\nu\sum_\mu \tilde{\zeta}_{\nu\mu}\boldsymbol{R}_\mu\boldsymbol{R}_\nu \tag{16.2-8}$$

Thus for potential flows, that is flows described by a symmetric $\boldsymbol{\kappa}$,

$$(\boldsymbol{\kappa}:\mathbf{M}_s) = \frac{1}{2}\left(\boldsymbol{\kappa}:\frac{\partial}{\partial Q_s}\mathbf{K}\right) = \frac{1}{2}\frac{\partial}{\partial Q_s}(\boldsymbol{\kappa}:\mathbf{K}) \tag{16.2-9}$$

From this it follows that for *steady state, homogeneous, potential flows, and equilibrium-averaged (or no) hydrodynamic interaction* the solution to Eq. 16.2-6 is

$$\boxed{\psi_\alpha = \frac{1}{J_\alpha}\sqrt{g_\alpha}\exp[\tfrac{1}{2}(\boldsymbol{\kappa}:\mathbf{K}^\alpha) - \phi^\alpha - \phi^{(e)\alpha}]/kT} \tag{16.2-10}$$

where J_α is the normalization constant; it is assumed here that the generalized external force $\mathscr{F}_t^{(e)\alpha}$ is derivable from a potential: $\mathscr{F}_t^{(e)\alpha} = -\partial\phi^{(e)\alpha}/\partial Q_t^\alpha$. Equation 16.2-10 may be verified by introducing this ψ_α into Eq. 16.2-5; then the generalized force-balance equation gives

$$\mathscr{F}_s^{(h)\alpha} = (\mathbf{M}_s^\alpha:\boldsymbol{\kappa}) \tag{16.2-11}$$

and hence, from Eq. 16.2-2, $[\![\dot{Q}_s]\!] = 0$.

EXAMPLE 16.2-1 The Diffusion Equation for the Orientational Distribution Function for the Multibead-Rod Model

Develop the explicit form of the diffusion equation, Eq. 16.2-6, for the multibead-rod model described in §14.1, including complete hydrodynamic interaction using the Rotne-Prager-Yamakawa interaction tensors.

SOLUTION For the multibead-rod model the Rotne-Prager-Yamakawa hydrodynamic interaction tensors[2] may be written in the form

$$\boldsymbol{\Omega}_{\nu\mu} = \Omega_{\nu\mu}^{(1)}(\boldsymbol{\delta} - \boldsymbol{uu}) + \Omega_{\nu\mu}^{(2)}\boldsymbol{uu} \tag{16.2-12}$$

$$\Omega_{\nu\mu}^{(1)} = \frac{(1-\delta_{\nu\mu})}{4\pi a\eta_s|\nu-\mu|}\left[1 + \frac{2\xi^2}{3(\nu-\mu)^2}\right] \tag{16.2-13}$$

$$\Omega_{\nu\mu}^{(2)} = \frac{(1-\delta_{\nu\mu})}{2\pi a\eta_s|\nu-\mu|}\left[1 - \frac{2\xi^2}{3(\nu-\mu)^2}\right] \tag{16.2-14}$$

where ξ is the ratio of the diameter of the spheres to the distance between the spheres, a; the parameter ξ goes from 0 (mass points) to 1 (osculating spheres). If $\xi = 0$ the Oseen-Burgers tensors are obtained.

From Table 16.1-2, Eq. A, one finds that the dimensionless diffusion tensors are

$$\boldsymbol{\Upsilon}_{\nu\mu} = \delta_{\nu\mu}\boldsymbol{\delta} + \zeta\Omega_{\nu\mu}^{(1)}(\boldsymbol{\delta} - \boldsymbol{uu}) + \zeta\Omega_{\nu\mu}^{(2)}\boldsymbol{uu} \tag{16.2-15}$$

where ζ is the friction coefficient of a bead. Since the dimensionless mobility tensors $\mathbf{B}_{\nu\mu}$ are functions of the unit vector $\boldsymbol{u}$ only, they must be linear combinations of the unit tensor $\boldsymbol{\delta}$ and the dyad $\boldsymbol{uu}$. Thus we write these tensors in the form

$$\mathbf{B}_{\nu\mu} = B_{\nu\mu}^{(1)}(\boldsymbol{\delta} - \boldsymbol{uu}) + B_{\nu\mu}^{(2)}\boldsymbol{uu} \tag{16.2-16}$$

[2] The expressions given here for $\boldsymbol{\Omega}_{\nu\mu}$ simplify to the tensor $\boldsymbol{\Omega}$ in Eq. 14.6-2 by setting $\nu = -1$ and $\mu = +1$, and replacing a by L

One then finds from the definition of these tensors that

$$\sum_{\eta} B_{\nu\eta}^{(k)}[\delta_{\eta\mu} + \zeta\Omega_{\eta\mu}^{(k)}] = \delta_{\nu\mu} \qquad (k = 1, 2) \tag{16.2-17}$$

These equations may be solved for the coefficients $B_{\nu\mu}^{(k)}$. It turns out, however, that we need evaluate only certain sums of the coefficients (see Eq. 14.6-18), and hence we define

$$B_{\mu}^{(k)} = \tfrac{1}{2}\sum_{\nu} \nu B_{\nu\mu}^{(k)} \qquad (k = 1, 2) \tag{16.2-18}$$

and similarly

$$\mathbf{B}_{\mu} = \tfrac{1}{2}\sum_{\nu} \nu \mathbf{B}_{\nu\mu} = B_{\mu}^{(1)}(\boldsymbol{\delta} - \boldsymbol{uu}) + B_{\mu}^{(2)}\boldsymbol{uu} \tag{16.2-19}$$

The $B_{\mu}^{(k)}$ are then determined by the equations

$$\sum_{\eta} B_{\eta}^{(k)}[\delta_{\eta\mu} + \zeta\Omega_{\eta\mu}^{(k)}] = \tfrac{1}{2}\mu \tag{16.2-20}$$

Explicit solutions of these equations have been developed by Bird and Curtiss[3] for $N \leq 5$, with $\xi \neq 0$, and for $N = 6$ and 7 with $\xi = 0$. In particular one finds that for $N = 2$

$$B_1^{(1)} = \tfrac{1}{2}[1 - h(1 + \tfrac{1}{6}\xi^2)]^{-1} \tag{16.2-21}$$

$$B_1^{(2)} = \tfrac{1}{2}[1 - 2h(1 - \tfrac{1}{6}\xi^2)]^{-1} \tag{16.2-22}$$

with $h = \zeta/8\pi\eta_s a$, and for $N = 3$.

$$B_2^{(1)} = [1 - \tfrac{1}{2}h(1 + \tfrac{1}{24}\xi^2)]^{-1} \tag{16.2-23}$$

$$B_2^{(2)} = [1 - h(1 - \tfrac{1}{24}\xi^2)]^{-1} \tag{16.2-24}$$

It may be shown from the form of the equations that in general

$$B_{-\nu}^{(k)} = -B_{\nu}^{(k)} \qquad (k = 1, 2) \tag{16.2-25}$$

and therefore $B_0^{(k)} = 0$.

It follows directly from Eq. B of Table 16.1-2 that the effective friction tensors are

$$\boldsymbol{\zeta}_{\nu\mu} = \zeta\mathbf{B}_{\nu\mu} \tag{16.2-26}$$

and from Eq. 16.2-17 that $B_{\nu\mu}^{(k)} = B_{\mu\nu}^{(k)}$; and thus from Eq. 16.2-16 it is seen that $\mathbf{B}_{\nu\mu} = \mathbf{B}_{\mu\nu}$. It then follows from Eq. D of Table 16.1-2, the antisymmetry of the $B_{\mu}^{(k)}$, Eq. 16.2-25, and Eq. 16.2-19 that

$$\tfrac{1}{2}\sum_{\nu} \nu\boldsymbol{\lambda}_{\nu} = \zeta\left\{\mathbf{Z}^{-1}\cdot\sum_{\mu}\mathbf{B}_{\mu}\right\} = \mathbf{0} \tag{16.2-27}$$

[3] R. B. Bird and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **14**, 85–101 (1984). The coefficients defined here are related to the ϕ_{ν} of this paper and §14.6 as follows: $B_{\nu}^{(1)} = \phi_{\nu}(h, \xi^2, N)$ and $B_{\nu}^{(2)} = \phi_{\nu}(2h, -\xi^2, N)$.

Next, making use of the last result, one finds from Eq. E that a weighted sum of the modified effective friction tensors is

$$\begin{aligned}\boldsymbol{\zeta} &= \tfrac{1}{4}\sum_{\nu}\sum_{\mu}\nu\mu\tilde{\boldsymbol{\zeta}}_{\nu\mu} \\ &= \tfrac{1}{2}\boldsymbol{\zeta}\sum_{\mu}\mu\mathbf{B}_{\mu} \\ &= \tfrac{1}{4}\boldsymbol{\zeta}\sum_{\nu}\sum_{\mu}\nu\mu\mathbf{B}_{\nu\mu}\end{aligned} \tag{16.2-28}$$

This sum is defined as the effective friction tensor of the molecule, in which the effect of each of the beads is weighted by its distance from the center of mass; the tensor is anisotropic with one part proportional to $\boldsymbol{uu}$ and another part proportional to $(\boldsymbol{\delta} - \boldsymbol{uu})$. Explicit expressions for these tensors for small values of N have also been developed by Bird and Curtiss.[3]

One next finds from Eqs. 16.1-19, 16.1-20, and 16.2-28, and from Table 16.1-2, Eq. F, that the coupling tensors are

$$\mathbf{M}_s = a^2\{\boldsymbol{uc}_s\cdot\boldsymbol{\zeta}\} \tag{16.2-29}$$

and from Eq. G that the elements of the modified metric matrix are

$$\tilde{g}_{st} = a^2\{\boldsymbol{c}_s\cdot\boldsymbol{\zeta}\cdot\boldsymbol{c}_t\} \tag{16.2-30}$$

From these expressions it may be shown that

$$\mathbf{M}_s = a^2\zeta B^{(1)}\boldsymbol{uc}_s \tag{16.2-31}$$

$$\tilde{g}_{st} = a^2\zeta B^{(1)}(\boldsymbol{c}_s\cdot\boldsymbol{c}_t) = a^2\zeta B^{(1)}\begin{pmatrix}1 & 0\\ 0 & \sin^2\theta\end{pmatrix} \tag{16.2-32}$$

with

$$B^{(1)} = \tfrac{1}{2}\sum_{\nu}\nu B_{\nu}^{(1)} \tag{16.2-33}$$

The modified contravariant metric matrix is then

$$\tilde{G}_{st} = \frac{1}{a^2\zeta B^{(1)}}\begin{pmatrix}1 & 0\\ 0 & 1/\sin^2\theta\end{pmatrix} \tag{16.2-34}$$

The diffusion equation for the configurational distribution function is given in general by Eq. 16.2-6. Making use of Eqs. 16.2-31 and 34 we find

$$\begin{aligned}\frac{\partial}{\partial t}\psi = &-\frac{\partial}{\partial\theta}(\boldsymbol{uc}_1:\boldsymbol{\kappa})\psi - \frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi}(\boldsymbol{uc}_2:\boldsymbol{\kappa})\psi \\ &+\frac{1}{6\lambda_N^{(1)}}\left\{\frac{\partial}{\partial\theta}\sin\theta\left[\frac{\partial}{\partial\theta}\left(\frac{\psi}{\sin\theta}\right)\right]+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\psi\right\} \\ &+\frac{1}{6kT\lambda_N^{(1)}}\left\{\frac{\partial}{\partial\theta}\left(\psi\frac{\partial}{\partial\theta}\phi^{(e)}\right)+\frac{1}{\sin^2\theta}\frac{\partial}{\partial\phi}\left(\psi\frac{\partial\phi^{(e)}}{\partial\phi}\right)\right\}\end{aligned} \tag{16.2-35}$$

where

$$\lambda_N^{(1)} = \frac{a^2\zeta}{6kT} B^{(1)} \tag{16.2-36}$$

is the time constant for a rod with N beads. Using the notation of §14.1, we may write this equation in the more concise form

$$\frac{\partial}{\partial t}\left(\frac{\psi}{\sin\theta}\right) = \frac{1}{6\lambda_N^{(1)}}\left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}}\left(\frac{\psi}{\sin\theta}\right)\right) - \left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\left[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu} - \frac{1}{6kT\lambda_N^{(1)}}\left(\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)}\right)\right]\left(\frac{\psi}{\sin\theta}\right)\right) \tag{16.2-37}$$

This is the diffusion equation for the multibead rigid rod model, with complete hydrodynamic interaction. It is identical in form to that for the rigid dumbbell with no hydrodynamic interaction, Eq. 14.2-8, and differs only in the definition of the time constant $\lambda_N^{(1)}$.

It follows from Eq. 16.2-20 that in the "free-draining" approximation (hydrodynamic interaction neglected):

$$B_\nu^{(k)} = \tfrac{1}{2}\nu \qquad k = 1, 2 \tag{16.2-38}$$

and then from Eq. 16.2-18 that

$$B^{(k)} = \tfrac{1}{4}\sum_\nu \nu^2 \qquad k = 1, 2 \tag{16.2-39}$$

The sum here, however, is to be taken over the values associated with the beads as indicated in Eq. 16.1-19. Thus,

$$B^{(k)} = \tfrac{1}{12}N(N^2 - 1) \qquad k = 1,2 \tag{16.2-40}$$

and for the rigid dumbbell ($N = 2$), $B^{(k)} = \frac{1}{2}$. The expression for the time constant, Eq. 16.2-36, then reduces to that of the rigid dumbbell (with $a = L$) without hydrodynamic interaction, $\lambda = \zeta L^2/12kT$.

§16.3 EXPRESSIONS FOR THE STRESS TENSOR

In Chapter 13 it is shown how an expression for the stress tensor can be obtained for a dilute polymer solution, in which the polymer molecules are modeled as elastic dumbbells. The derivation given there is quite simple, and the four major contributions—solvent, spring force, external force, and bead momentum transport—are accounted for by elementary physical arguments. These elementary arguments are, however, difficult to apply for models with constraints, for concentrated systems, and for models with complicating factors such as hydrodynamic interaction, anisotropic friction factors, or reptational Brownian motion.

Therefore in Chapters 17 and 18 a general expression for the stress tensor is derived by starting from the Liouville equation in the complete phase space of the polymeric fluid (polymer solution or undiluted polymer). The macroscopic equation of motion is then derived, and in the process formal expressions are obtained for the various contributions to the stress tensor. After that, special restricted expressions can be obtained by introducing approximations appropriate for various kinds of modeling. In this section we summarize

some of the key results for dilute solutions of a mixture of solute species $\alpha = 1, 2, 3, \ldots$; these various species may also be regarded as the molecules of differing lengths present in a polydisperse solution.

The starting point for this discussion is Eq. 18.1-10, which is valid for mixtures, for models with constraints, for beads with internal structure, for systems with hydrodynamic interaction, and for friction coefficients and Brownian motion that may be anisotropic. The only assumptions that are inherent in Eq. 18.1-10 are those of two-body forces and short-range interactions, assumptions that we believe to be not very restrictive in the understanding of the macroscopic properties of polymeric liquids.

Equation 18.1-10 involves a sum over the species index α, which includes all the chemical species in the polymeric liquid. In the present discussion we separate off the contribution of the solvent molecules and consider only the polymer contribution to the stress tensor $\boldsymbol{\pi}_p$; the sums on α then imply summations over the polymer solute species only. Equation 18.1-10 contains a term $\boldsymbol{\pi}_k$, the contribution of the Brownian motion of the centers of mass of the molecules, for which a formal expression is given by Eq. 17.6-6. If equilibration in momentum space is assumed (this corresponds to the assumption of a Maxwellian velocity distribution in §13.3) then the integrals in $\boldsymbol{\pi}_k$ can be evaluated, and this integration leads to an isotropic contribution to the stress tensor, $(\sum_\alpha n_\alpha)kT\boldsymbol{\delta}$. The polymer contribution to the stress tensor is then (with $\bar{N} = 1$ in Eq. 18.1-10 for dilute solutions)

$$\boxed{\boldsymbol{\pi}_p = -\sum_\alpha n_\alpha \sum_\nu \langle \boldsymbol{R}_\nu^\alpha \boldsymbol{F}_\nu^{(h)\alpha} \rangle + \sum_\alpha n_\alpha kT\boldsymbol{\delta}} \tag{16.3-1}$$

The brackets indicate the phase-space average, which in this case reduces to the simpler configuration-space average

$$\langle \boldsymbol{R}_\nu^\alpha \boldsymbol{F}_\nu^{(h)\alpha} \rangle = \int \boldsymbol{R}_\nu^\alpha \boldsymbol{F}_\nu^{(h)\alpha} \psi_\alpha(Q^\alpha, t)\, dQ^\alpha \tag{16.3-2}$$

The quantity $\boldsymbol{F}_\nu^{(h)\alpha}$ is the hydrodynamic force on bead ν of a molecule of species α arising from interactions with the solvent molecules. The hydrodynamic force is given by a generalized Stokes' law expression that accounts for model constraints and hydrodynamic interaction (see Eq. 18.2-23)

$$\boldsymbol{F}_\nu^{(h)\alpha} = -\sum_\mu \tilde{\boldsymbol{\zeta}}_{\nu\mu}^\alpha \cdot \left\{ \frac{1}{\sqrt{m_\mu^\alpha}} \left(\sum_s [\![\dot{Q}_s]\!]^\alpha \boldsymbol{b}_{\mu s}^\alpha \right) - [\boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu^\alpha] \right\} \tag{16.3-3}$$

We point out in passing that Eq. 16.3-3 is a set of $3N_\alpha$ equations (for each α), and that from this set of equations the set of $d_\alpha \leq 3(N_\alpha - 1)$ equations (for each α) for the $[\![\dot{Q}_s]\!]^\alpha$ ($s = 1, 2, 3, \ldots, d_\alpha$) can be obtained as shown in Eq. 16.2-2. This "turning-wrong-side-out" of the Stokes' law expressions to get the expressions for the $[\![\dot{Q}_s]\!]^\alpha$ is facilitated by the use of the quantities displayed in Table 16.1-2, and the details of this inversion are the subject of §18.2. Finally we note that Eq. 16.3-3 includes as special cases Eq. 13.2-2 (for elastic dumbbells), and Eqs. 14.6-9 and 14.6-10 (for rigid dumbbells with hydrodynamic interaction).

Equation 16.3-1 is a generalization of the *Kramers–Kirkwood expression for the stress tensor*. The only assumptions inherent in this generalization are (i) dilute solutions, (ii) pairwise additivity of forces, (iii) the short-range force assumption, and (iv) equilibration in momentum space. We now show how three other forms for $\boldsymbol{\pi}_p$ can be obtained from Eq.

16.3-1. The first of these is as general as Eq. 16.3-1, but the other two result from introducing two different sets of restrictions.

First we use the expression for the average, $[\![\dot{Q}_s]\!]^\alpha$, given by Eq. 16.2-2 in the expression for the hydrodynamic force, $\boldsymbol{F}_v^{(h)\alpha}$, in Eq. 16.3-3. Then it follows from the definition of the coupling tensor $\mathbf{M}_s^\alpha$ (see Eq. F of Table 16.1-2) and the symmetry of the $\tilde{\zeta}_{\nu\mu}^\alpha$, Eq. 18.2-21, that

$$\sum_v \boldsymbol{R}_v^\alpha \boldsymbol{F}_v^{(h)\alpha} = \sum_{st} \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha (\mathscr{F}_t^{(h)\alpha} - \mathbf{M}_t^\alpha : \boldsymbol{\kappa}) + \sum_{v\mu} \{\boldsymbol{R}_v^\alpha \boldsymbol{R}_\mu^\alpha \cdot \boldsymbol{\kappa}^\dagger \cdot \zeta_{\mu\nu}^\alpha\} \tag{16.3-4}$$

One may then use this result in the expression for the stress tensor, Eq. 16.3-1, along with the force balance on the generalized forces and the approximation of equilibration in momentum space to show that

$$\begin{aligned}
\boldsymbol{\pi}_p = & \sum_\alpha n_\alpha kT \sum_{st} \left\langle \frac{1}{\sqrt{g^\alpha}} \frac{\partial}{\partial Q_t^\alpha} (\sqrt{g^\alpha}\, \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha) \right\rangle \\
& + \sum_\alpha n_\alpha \sum_{st} \langle \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha (\mathscr{F}_t^{(\phi)\alpha} + \mathscr{F}_t^{(e)\alpha}) \rangle \\
& + \sum_\alpha n_\alpha \sum_{st} \langle \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha \mathbf{M}_t^{\alpha\dagger} \rangle : \boldsymbol{\kappa}^\dagger \\
& - \sum_\alpha n_\alpha \sum_{v\mu} \langle \boldsymbol{R}_v^\alpha \tilde{\zeta}_{v\mu}^\alpha \boldsymbol{R}_\mu^\alpha \rangle : \boldsymbol{\kappa}^\dagger \\
& + \sum_\alpha n_\alpha kT \boldsymbol{\delta}
\end{aligned} \tag{16.3-5}$$

This expression can be put into an alternative form by making use of the modified reciprocal base vectors

$$\boldsymbol{a}_{vs}^\alpha = \sum_t \sum_\mu \frac{1}{\sqrt{m_v^\alpha m_\mu^\alpha}} \tilde{G}_{st}^\alpha [\boldsymbol{b}_{\mu t}^\alpha \cdot \tilde{\zeta}_{\mu v}^\alpha] \tag{16.3-6}$$

These vectors satisfy the relations

$$\sum_v \sqrt{m_v^\alpha}\, \boldsymbol{a}_{vs}^\alpha = \mathbf{0} \tag{16.3-7}$$

$$\sum_v (\boldsymbol{a}_{vs}^\alpha \cdot \boldsymbol{b}_{vt}^\alpha) = \delta_{st} \tag{16.3-8}$$

as may be seen by using the definitions in Table 16.1-2. Then

$$\sum_t \tilde{G}_{st}^\alpha \mathbf{M}_t^\alpha = \sum_v \sqrt{m_v^\alpha}\, \boldsymbol{R}_v^\alpha \boldsymbol{a}_{vs} \tag{16.3-9}$$

$$\sum_s \sum_t \tilde{G}_{st}^\alpha \mathbf{M}_s^\alpha \mathbf{M}_t^\alpha = \sum_{tv\mu\eta} \sqrt{\frac{m_v^\alpha}{m_\mu^\alpha}}\, \boldsymbol{R}_v^\alpha \boldsymbol{a}_{vt}^\alpha \tilde{\zeta}_{\eta\mu}^\alpha \cdot \boldsymbol{b}_{\mu t}^\alpha \boldsymbol{R}_\eta^\alpha \tag{16.3-10}$$

The expression for the stress tensor may then be written

$$\boxed{\begin{aligned}\boldsymbol{\pi}_p = &\sum_\alpha n_\alpha kT \sum_{sv} \left\langle \frac{1}{\sqrt{g^\alpha}} \frac{\partial}{\partial Q_s^\alpha} (\sqrt{g^\alpha m_v^\alpha}\, \boldsymbol{R}_v^\alpha \boldsymbol{a}_{vs}^\alpha) \right\rangle \\ &+ \sum_\alpha n_\alpha \sum_{sv} \langle \sqrt{m_v^\alpha}\, \boldsymbol{R}_v^\alpha \boldsymbol{a}_{vs}^\alpha (\mathscr{F}_s^{(\phi)\alpha} + \mathscr{F}_s^{(e)\alpha}) \rangle \\ &+ \sum_\alpha n_\alpha \sum_{v\mu\eta} \sqrt{\frac{m_v^\alpha}{m_\eta^\alpha}} \left\langle \boldsymbol{R}_v^\alpha \left[\left(\sum_s \boldsymbol{a}_{vs}^\alpha \boldsymbol{b}_{\eta s}^\alpha \right) - \delta_{v\eta} \boldsymbol{\delta} \right] \cdot \tilde{\zeta}_{\eta\mu}^\alpha \boldsymbol{R}_\mu^\alpha \right\rangle : \boldsymbol{\kappa}^\dagger \\ &+ \sum_\alpha n_\alpha kT \boldsymbol{\delta} \end{aligned}} \tag{16.3-11}$$

This relation is a generalization of the *modified Kramers expression for the stress tensor* given in Eq. B of Table 14.3-1. Equations 16.3-1 and 16.3-11 are completely equivalent in that they contain the same physical assumptions.

Next we obtain two simplified expressions for $\boldsymbol{\pi}_p$: one for models with no constraints, by simplifying Eq. 16.3-11, and another for models with equilibrium-averaged or no hydrodynamic interaction, by simplifying Eq. 16.3-1.

a. Models with No Constraints

If the molecular model involves no constraints one may use Eq. 12D.3-5 along with Eqs. 16.3-6 and 7 to show that $\boldsymbol{a}_{vs}^\alpha = \sum_t G_{st}^\alpha \boldsymbol{b}_{vt}^\alpha$. With this relation one may show that the third and fourth terms on the right of Eq. 16.3-11 cancel and that the first two terms may be rearranged to give as the expression for the stress tensor

$$\boldsymbol{\pi}_p = \sum_\alpha n_\alpha \sum_v \langle \boldsymbol{R}_v^\alpha (\boldsymbol{F}_v^{(b)\alpha} + \boldsymbol{F}_v^{(\phi)\alpha} + \boldsymbol{F}_v^{(e)\alpha}) \rangle + \sum_\alpha n_\alpha kT \boldsymbol{\delta} \tag{16.3-12}$$

In this expression

$$\boldsymbol{F}_v^{(b)\alpha} = -kT \frac{\partial}{\partial \boldsymbol{r}_v^\alpha} \ln \left(\frac{\Psi_\alpha}{\sqrt{g^\alpha}} \right) \tag{16.3-13}$$

$$\boldsymbol{F}_v^{(\phi)\alpha} = -\frac{\partial}{\partial \boldsymbol{r}_v^\alpha} \phi^\alpha \tag{16.3-14}$$

$$\boldsymbol{F}_v^{(e)\alpha} = -\frac{\partial}{\partial \boldsymbol{r}_v^\alpha} \phi^{(e)\alpha} \tag{16.3-15}$$

are the Brownian, intramolecular, and external forces on a bead. The integral involving the Brownian force may then be evaluated to give an isotropic contribution and one finds that

$$\boxed{\boldsymbol{\pi}_p = \sum_\alpha n_\alpha \sum_v \langle \boldsymbol{R}_v^\alpha (\boldsymbol{F}_v^{(\phi)\alpha} + \boldsymbol{F}_v^{(e)\alpha}) \rangle + \sum_\alpha N_\alpha n_\alpha kT \boldsymbol{\delta}} \tag{16.3-16}$$

This relation is a generalization of the *modified Kramers expression for the stress tensor* given in Table 15.2-1.

b. Models with Equilibrium-Averaged Hydrodynamic Interaction or No Hydrodynamic Interaction

To develop another expression for the stress tensor we return to Eqs. 16.3-1 and 3. By combining these relations, we find that the symmetric part of the stress tensor is

$$\boldsymbol{\pi}_p^{(s)} = -\tfrac{1}{2}\sum_\alpha n_\alpha \sum_{\nu\mu} \{\langle \boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{R}_\mu^\alpha \rangle : \boldsymbol{\kappa}^\dagger + \boldsymbol{\kappa} : \langle \boldsymbol{R}_\mu^\alpha \tilde{\zeta}_{\mu\nu}^\alpha \boldsymbol{R}_\nu^\alpha \rangle\}$$
$$+ \tfrac{1}{2}\sum_\alpha n_\alpha \sum_{\nu\mu s} \frac{1}{\sqrt{m_\mu^\alpha}} \langle [\![\dot{Q}_s^\alpha]\!] \{ \boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \cdot \boldsymbol{b}_{\mu s}^\alpha + \boldsymbol{b}_{\mu s}^\alpha \cdot \tilde{\zeta}_{\mu\nu}^\alpha \boldsymbol{R}_\nu^\alpha \} \rangle$$
$$+ \sum_\alpha n_\alpha kT\boldsymbol{\delta} \tag{16.3-17}$$

It also follows from the equation of continuity, Eq. 16.2-1, that

$$\frac{\partial}{\partial t}\sum_{\nu\mu} \langle \boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{R}_\mu^\alpha \rangle = \sum_{\nu\mu s} \left\langle [\![\dot{Q}_s]\!]^\alpha \frac{\partial}{\partial Q_s^\alpha} (\boldsymbol{R}_\nu^\alpha \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{R}_\mu^\alpha) \right\rangle \tag{16.3-18}$$

If the $\tilde{\zeta}_{\nu\mu}^\alpha$ are diagonal, $\tilde{\zeta}_{\nu\mu}^\alpha = \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{\delta}$, with constant $\tilde{\zeta}_{\nu\mu}^\alpha$, these two equations may be combined to give

$$\boldsymbol{\pi}_p^{(s)} = \tfrac{1}{2}\sum_\alpha n_\alpha \left\{ \frac{\partial}{\partial t} \langle \mathbf{K}^\alpha \rangle - \boldsymbol{\kappa} \cdot \langle \mathbf{K}^\alpha \rangle - \langle \mathbf{K}^\alpha \rangle \cdot \boldsymbol{\kappa}^\dagger \right\} + \sum_\alpha n_\alpha kT\boldsymbol{\delta} \tag{16.3-19}$$

in which $\mathbf{K}^\alpha = \sum_{\nu\mu} \tilde{\zeta}_{\nu\mu}^\alpha \boldsymbol{R}_\nu^\alpha \boldsymbol{R}_\mu^\alpha$ are the tensors defined in Eq. 16.2-8. This expression then applies in the approximation of equilibrium-averaged hydrodynamic interaction or if hydrodynamic interaction is neglected. Hence, we find that in these cases

$$\boxed{\boldsymbol{\pi}_p^{(s)} = \tfrac{1}{2}\sum_\alpha n_\alpha \langle \mathbf{K}^\alpha \rangle_{(1)} + \sum_\alpha n_\alpha kT\boldsymbol{\delta}} \tag{16.3-20}$$

in which the operation of convected differentiation is introduced (see Eq. D.2-4). It may be shown that in the absence of external forces the stress tensor is symmetric, so that Eq. 16.3-20 is a generalization of the *Giesekus expression for the stress tensor*, special examples of which have been encountered in Eq. D of Tables 13.3-1, 14.3-1, and 15.2-1. One important consequence of Eq. 16.3-20 is that *for any bead-rod-spring model with equilibrium-averaged (or no) hydrodynamic interaction, Ψ_2 is identically zero* in a steady shear flow with $v_x = \dot{\gamma}y$, $v_y = 0$, $v_z = 0$, since in such a flow the yy- and zz-components of $\langle \mathbf{K}^\alpha \rangle_{(1)}$ are always zero.

EXAMPLE 16.3-1 The Stress Tensor for the Multibead-Rod Model

Develop an explicit expression for the stress tensor for the multibead-rod model described in §14.1 and further discussed in Examples 16.1-1 and 16.2-1.

SOLUTION We use the coordinates and notation developed in Example 16.2-1 and the general expression for the stress tensor, Eq. 16.3-1. Since there is no intramolecular potential ($\phi = 0$), one finds from Eqs. 16.2-2 to 5 that

$$[\![\dot{Q}_s]\!] = -\sum_t \tilde{G}_{st}\left[kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - (\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(e)}\right] \tag{16.3-21}$$

When this expression is used in Eq. 16.3-3 one finds that

$$\sum_\nu \boldsymbol{R}_\nu \boldsymbol{F}_\nu^{(h)} = \sum_\nu \sum_\mu \boldsymbol{R}_\nu \left\{\tilde{\boldsymbol{\zeta}}_{\nu\mu}\cdot\left(\frac{1}{\sqrt{m_\mu}}\sum_s\sum_t \tilde{G}_{st}\boldsymbol{b}_{\mu s} \times\left[kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - (\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(e)}\right] + [\boldsymbol{\kappa}\cdot\boldsymbol{R}_\mu]\right)\right\} \tag{16.3-22}$$

Then using the results of the previous examples (Eqs. 16.1-20, 16.2-19, 16.2-26, 16.2-28), one finds that

$$\begin{aligned}\sum_\nu \boldsymbol{R}_\nu \boldsymbol{F}_\nu^{(h)} &= a^2\left\{\boldsymbol{u}\boldsymbol{\zeta}\cdot\left(\sum_s\sum_t \tilde{G}_{st}\boldsymbol{c}_s\left[kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - (\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(e)}\right] + [\boldsymbol{\kappa}\cdot\boldsymbol{u}]\right)\right\} \\ &= a^2\zeta B^{(1)}\sum_s\sum_t \tilde{G}_{st}\boldsymbol{u}\boldsymbol{c}_s\left[kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - (\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}_t^{(e)}\right] \\ &\quad + a^2\zeta B^{(1)}\{\boldsymbol{u}\boldsymbol{u}\cdot\boldsymbol{\kappa}^\dagger\} + a^2\zeta(B^{(2)} - B^{(1)})\{\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}:\boldsymbol{\kappa}\}\end{aligned} \tag{16.3-23}$$

where $B^{(1)}$ is the quantity defined in Eq. 16.2-33 and

$$B^{(2)} = \tfrac{1}{2}\sum_\nu \nu B_\nu^{(2)} \tag{16.3-24}$$

On the other hand, it follows from Eqs. 16.2-31 and 34 that

$$\begin{aligned}a^2\zeta B^{(1)}\sum_s\sum_t \tilde{G}_{st}\boldsymbol{u}\boldsymbol{c}_s(\mathbf{M}_t:\boldsymbol{\kappa}) &= a^2\zeta B^{(1)}\left\{\boldsymbol{u}\left[\boldsymbol{c}_1\boldsymbol{c}_1 + \frac{\boldsymbol{c}_2\boldsymbol{c}_2}{\sin^2\theta}\right]\boldsymbol{u}:\boldsymbol{\kappa}^\dagger\right\} \\ &= a^2\zeta B^{(1)}\{\boldsymbol{u}[\boldsymbol{\delta} - \boldsymbol{u}\boldsymbol{u}]\boldsymbol{u}:\boldsymbol{\kappa}^\dagger\}\end{aligned} \tag{16.3-25}$$

Thus, Eq. 16.3-23 can be simplified appreciably

$$\begin{aligned}\sum_\nu \boldsymbol{R}_\nu \boldsymbol{F}_\nu^{(h)} &= a^2\zeta\left\{B^{(2)}\{\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}:\boldsymbol{\kappa}\} + B^{(1)}\sum_s\sum_t \tilde{G}_{st}\boldsymbol{u}\boldsymbol{c}_s\left(kT\frac{\partial}{\partial Q_t}\ln\left(\frac{\psi}{\sqrt{g}}\right) - \mathscr{F}_t^{(e)}\right)\right\} \\ &= a^2\zeta B^{(2)}\{\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}:\boldsymbol{\kappa}\} + kT\boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}\left[\ln\left(\frac{\psi}{\sqrt{g}}\right) + \frac{1}{kT}\phi^{(e)}\right]\end{aligned} \tag{16.3-26}$$

The last result may be used in Eq. 16.3-1 to obtain an expression for the polymer contribution to the stress tensor of a dilute solution of multibead rigid rods, with complete hydrodynamic interaction. For a system involving a single solute the expression becomes

$$\begin{aligned}\boldsymbol{\pi}_p = &-na^2\zeta B^{(2)}\langle\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\boldsymbol{u}\rangle:\boldsymbol{\kappa} \\ &-nkT\int\boldsymbol{u}\left(\frac{\partial}{\partial\boldsymbol{u}}\frac{\psi}{\sin\theta}\right)d\boldsymbol{u} + nkT\boldsymbol{\delta} - n\left\langle\boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}\phi^{(e)}\right\rangle\end{aligned} \tag{16.3-27}$$

where the angular brackets indicate an average weighted with the orientational distribution function, ψ. Then using Eq. E.7-3 one finds that

$$\boldsymbol{\pi}_p = -3nkT\langle \boldsymbol{uu} \rangle - 6nkT\lambda_N^{(2)}\langle \boldsymbol{uuuu} \rangle : \boldsymbol{\kappa} - n\left\langle \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}\phi^{(e)} \right\rangle + 2nkT\boldsymbol{\delta} \tag{16.3-28}$$

where

$$\lambda_N^{(2)} = \frac{a^2\zeta}{6kT}B^{(2)} \tag{16.3-29}$$

is another time constant associated with this model (cf. Eq. 16.2-36 for the definition of $\lambda_N^{(1)}$).

The last expression for the stress tensor is identical in form to that for the rigid dumbbell without hydrodynamic interaction (see Eq. 14.3-3) and differs only in the definition of the time constant, $\lambda_N^{(2)}$. It is noted that with hydrodynamic interaction, two time constants arise: $\lambda_N^{(1)}$ in the diffusion equation, and $\lambda_N^{(2)}$ in the expression for the stress tensor. As discussed in Example 16.2-1, in the "free-draining approximation", $B^{(1)} = B^{(2)}$ and thus the two time constants are identical. For the rigid dumbbell ($N = 2$) without hydrodynamic interaction, $B^{(2)} = \frac{1}{2}$ and $\lambda_N^{(2)}$ in Eq. 16.3-28 reduces to the λ for the rigid dumbbell defined just after Eq. 14.2-6.

§16.4 SECOND-ORDER FLUID CONSTANTS FOR ARBITRARY BEAD-ROD-SPRING MODELS WITH EQUILIBRIUM-AVERAGED HYDRODYNAMIC INTERACTION[1]

In §15.3 we found that for the Rouse bead-spring chain model with no hydrodynamic interaction, we could get the complete constitutive equation without having to solve the diffusion equation for the configurational distribution function. In §15.4 we found the analogous result for equilibrium-averaged hydrodynamic interaction. In Chapter 14 we found that for rigid dumbbells we could, after considerable effort, obtain the first few terms in a memory-integral expansion for arbitrary time-dependent flows.

If, however, we restrict our attention to the first- and second-order fluid constants in the retarded-motion expansion, we discover that formal expressions can be obtained for bead-rod-spring models of arbitrary complexity. We show in this section how to obtain these general expressions.

We start by writing down two expressions that we wish to equate—the first is the retarded motion expansion from continuum mechanics (cf. Eqs. 6.2-1 and D.4-3) and the second is the molecular theory expression (cf. Eq. 16.3-20):

$$\text{Continuum theory:} \quad \boldsymbol{\tau} = -[b_1\boldsymbol{\gamma}_{(1)} + b_2\boldsymbol{\gamma}_{(2)} + b_{11}\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(1)}\} + \cdots] \tag{16.4-1}$$

$$\text{Molecular theory:} \quad \boldsymbol{\tau} = -\eta_s\boldsymbol{\gamma}_{(1)} + \tfrac{1}{2}n\langle \mathbf{K} \rangle_{(1)} \tag{16.4-2}$$

Equation 16.3-20 has been written here for a single polymer solute species. Keep in mind that Eq. 16.4-2 is valid for models with equilibrium-averaged hydrodynamic interaction (or no hydrodynamic interaction) and no external forces. We now want to obtain formal expressions for the constants b_1, b_2, and b_{11} in terms of the constants that describe the

[1] This section is an extension of Section XVI of C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (I. Prigogine and S. A. Rice, eds.) (1976).

mechanical model. The constants b_1 and b_2 are obtainable from linear viscoelastic measurements or from steady-state shear flow experiments

$$\text{Steady-state shear flow:} \quad b_1 = \lim_{\dot{\gamma}\to 0} \eta \qquad b_2 = -\tfrac{1}{2} \lim_{\dot{\gamma}\to 0} \Psi_1 \tag{16.4-3}$$

$$\text{Small-amplitude oscillatory motion:} \quad b_1 = \lim_{\omega\to 0} \eta' \qquad b_2 = -\lim_{\omega\to 0} \frac{\eta''}{\omega} \tag{16.4-4}$$

Furthermore, a dimensionless ratio formed from b_1 and b_2 is related to the "steady-state compliance" J_e^0 used by polymer chemists (cf. Eq. 3.4-15) thus

$$-\frac{nkTb_2}{(b_1-\eta_s)^2} = \frac{J_e^0 \tilde{N} kT}{cM[\eta]_0^2} \tag{16.4-5}$$

which is known experimentally to be in the range of 0.2 to 0.4 for many macromolecular solutions.

First we note that b_{11} is equal to $\Psi_{2,0}$, the second normal-stress coefficient at zero shear rate. But we know that Eq. 16.4-2 gives $\Psi_2 = 0$ for all shear rates, and therefore b_{11} must be zero (see comments after Eq. 16.3-20).

Next we show that b_1 and b_2 may be obtained by considering steady-state, homogeneous, potential flows only. For this special flow category, with $\boldsymbol{v} = \boldsymbol{v}_0 + [\boldsymbol{\kappa}\cdot\boldsymbol{r}]$ and $\boldsymbol{\kappa} = \boldsymbol{\kappa}^\dagger$, we have from Eqs. 16.4-1 and 16.4-2

$$\text{Continuum theory:} \quad \boldsymbol{\tau} = -2b_1\boldsymbol{\kappa} + 4b_2\{\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}\} + \cdots \tag{16.4-6}$$

$$\text{Molecular theory:} \quad \boldsymbol{\tau} = -2\eta_s\boldsymbol{\kappa} - \tfrac{1}{2}n\{\boldsymbol{\kappa}\cdot\langle\mathbf{K}\rangle + \langle\mathbf{K}\rangle\cdot\boldsymbol{\kappa}\} \tag{16.4-7}$$

We now have to evaluate $\langle\mathbf{K}\rangle$ by using the expression for ψ in Eq. 16.2-10; in the latter we expand that portion of the exponential involving $\boldsymbol{\kappa}$ in a Taylor series and retain two terms only

$$\langle\mathbf{K}\rangle \doteq \frac{\int \mathbf{K}\sqrt{g}\, e^{-\phi/kT}[1 + (1/2kT)(\boldsymbol{\kappa}:\mathbf{K})]\, dQ}{\int \sqrt{g}\, e^{-\phi/kT}[1 + (1/2kT)(\boldsymbol{\kappa}:\mathbf{K})]\, dQ} = \frac{\mathbf{I}_{n1} + \mathbf{I}_{n2}}{I_{d1} + I_{d2}} \tag{16.4-8}$$

The scalar I_{d1} is just the normalizing constant for $\psi_{eq}(Q)$:

$$I_{d1} = \int \sqrt{g}\, e^{-\phi/kT}\, dQ \tag{16.4-9}$$

as may be seen from Eq. 12.3-4. To get I_{d2} we consider the integrations over the Euler angles separately and then make use of Eq. E.11-5

$$\begin{aligned} I_{d2} &= \frac{1}{2kT}\boldsymbol{\kappa}:\int\left[\iiint \mathbf{K}\sin\beta\, d\alpha\, d\beta\, d\gamma\right]\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= \frac{1}{2kT}\boldsymbol{\kappa}:\int[8\pi^2(\tfrac{1}{3})(\mathbf{K}:\boldsymbol{\delta})\boldsymbol{\delta}]\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= 0 \end{aligned} \tag{16.4-10}$$

since $(\boldsymbol{\kappa}:\boldsymbol{\delta}) = \text{tr}\,\boldsymbol{\kappa} = 0$ for an incompressible fluid. Here we have used Eq. L of Table 16.1-1 and used the abbreviation $\Gamma = \det(\Gamma_{uv})$; in addition the abbreviation $dQ' = dQ_4 dQ_5 dQ_6 \cdots$ has been used. In a similar way the tensor $\mathbf{I}_{n1}$ is evaluated

$$\begin{aligned} \mathbf{I}_{n1} &= \int \mathbf{K}\sqrt{g}\, e^{-\phi/kT}\, dQ \\ &= \int\left\{\iiint \mathbf{K}\sin\beta\, d\alpha\, d\beta\, d\gamma\right\}\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= \int\{8\pi^2(\tfrac{1}{3})(\text{tr}\,\mathbf{K})\boldsymbol{\delta}\}\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= \tfrac{1}{3}\boldsymbol{\delta}\int(\text{tr}\,\mathbf{K})\sqrt{g}\, e^{-\phi/kT}\, dQ \end{aligned} \tag{16.4-11}$$

To evaluate the tensor $\mathbf{I}_{n2}$ we make use of §E.9, in which the fourth-order isotropic tensors are discussed

$$\begin{aligned} \mathbf{I}_{n2} &= \frac{1}{2kT}\boldsymbol{\kappa}:\int \mathbf{K}\mathbf{K}\sqrt{g}\, e^{-\phi/kT}\, dQ \\ &= \frac{1}{2kT}\sum_{J=0}^{2}(\boldsymbol{\kappa}:\mathbf{I}_J)\int(8\pi^2\,\mathbf{K}\mathbf{K}\vdots\mathbf{I}_J)\sqrt{\Gamma}\, e^{-\phi/kT}\, dQ' \\ &= \frac{1}{2kT}(\boldsymbol{\kappa}:\mathbf{I}_2)\int(\mathbf{K}\mathbf{K}\vdots\mathbf{I}_2)\sqrt{g}\, e^{-\phi/kT}\, dQ \\ &= \frac{1}{2kT}\left(\frac{1}{\sqrt{5}}\boldsymbol{\kappa}\right)\int\frac{1}{\sqrt{5}}((\text{tr}\,\mathbf{K}^2) - \tfrac{1}{3}(\text{tr}\,\mathbf{K})^2)\sqrt{g}\, e^{-\phi/kT}\, dQ \end{aligned} \tag{16.4-12}$$

When the last four results are combined and use is made of the definition of $\langle\ \rangle_{eq}$ in Eq. 12.4-6, we get (through terms linear in velocity gradients)

$$\langle\mathbf{K}\rangle = \tfrac{1}{3}\langle\text{tr}\,\mathbf{K}\rangle_{eq}\,\boldsymbol{\delta} + \frac{1}{10kT}\langle(\text{tr}\,\mathbf{K}^2) - \tfrac{1}{3}(\text{tr}\,\mathbf{K})^2\rangle_{eq}\,\boldsymbol{\kappa} \tag{16.4-13}$$

When this expression for $\langle\mathbf{K}\rangle$ is substituted into Eq. 16.4-7 and the coefficients of $\boldsymbol{\kappa}$ and $\{\boldsymbol{\kappa}\cdot\boldsymbol{\kappa}\}$ compared with those of Eq. 16.4-6 we get for the *second-order-fluid constants* for

arbitrary bead-rod-spring models with or without equilibrium-averaged hydrodynamic interaction

$$b_1 = \eta_s + \frac{n}{6}\langle \text{tr } \mathbf{K} \rangle_{\text{eq}} \tag{16.4-14}$$

$$b_2 = -\frac{n}{40kT}\langle (\text{tr } \mathbf{K}^2) - \tfrac{1}{3}(\text{tr } \mathbf{K})^2 \rangle_{\text{eq}} \tag{16.4-15}$$

The tensor $\mathbf{K}$ is defined in Eq. 16.2-8 and $\langle B \rangle_{\text{eq}}$ is defined by Eq. 12.4-6

$$\langle B \rangle_{\text{eq}} = \frac{\int B \sqrt{g}\, e^{-\phi/kT}\, dQ}{\int \sqrt{g}\, e^{-\phi/kT}\, dQ} = \frac{\int B \sqrt{\Gamma}\, e^{-\phi/kT}\, dQ'}{\int \sqrt{\Gamma}\, e^{-\phi/kT}\, dQ'} \tag{16.4-16}$$

the first form implying integrations over all generalized coordinates Q_s ($s = 1, 2, 3, \ldots, d$), and the second implying that Q_1, Q_2, Q_3 have been taken to be the Euler angles α, β, γ, and that the integrations are to be performed over $Q_4, Q_5, Q_6, \ldots, Q_d$. In obtaining the second form we make use of the invariance of the expressions to be averaged in Eqs. 16.4-14 and 16.4-15 to a pure rotation of the molecular model. For rigid models the only generalized coordinates are the Euler angles, and hence the averaging indicated by $\langle \ldots \rangle$ does not need to be performed.

It is therefore possible to get the second-order-fluid constants b_1, b_2, b_{11} for dilute polymer solutions using any bead-rod-spring models with equilibrium-averaged hydrodynamic interaction (or no hydrodynamic interaction). To get these results it is necessary to know only the *equilibrium* configuration-space distribution function, the latter being obtainable from Eq. 12.3-4. It can be shown that b_2 is negative (or zero) for all molecular models of the type used here (see Problem 16B.1).

In Table 16.4-1 we give some examples of b_1 and b_2 values for a variety of models without hydrodynamic interaction in order to illustrate the connection between structure and rheological properties. A few comments about this table are appropriate:

1. In general b_2 is much more sensitive to structure than b_1; usually the normal stresses are higher for the more flexible structures.
2. Note that a rigid square, a rigid rhombus, a freely jointed rhombus, and an elastic rhombus (all with side length L) have the same viscosity, whereas they have different normal stresses.
3. A rod with three beads and length $2L$ has $b_1 - \eta_s = \frac{1}{3}n\zeta L^2$ whereas the freely jointed system with the same overall length has $b_1 - \eta_s = \frac{2}{9}n\zeta L^2$; this shows the influence of flexibility on viscosity.
4. Note that the rigid tridumbbell has a zero first normal stress coefficient if all three dumbbell lengths are the same; this is characteristic of spherically symmetric systems.
5. The three-bead-two-rod model with a bending potential is interesting because it shows that the viscosity and normal stress coefficient both decrease as one goes from a stiff three-bead rod to a "bendable" rod. A similar decrease occurs

TABLE 16.4-1

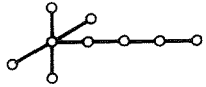
Values of b_1 and b_2 for Several Models with No Hydrodynamic Interaction[a, b]

Model	Meaning of L	$\frac{b_1 - \eta_s}{n\zeta L^2}$	$-\frac{b_2 kT}{n\zeta^2 L^4}$	$-\frac{nkTb_2}{(b_1 - \eta_s)^2}$
Rigid dumbbell[c] with two beads connected by a rod.	Length of rod	$\frac{1}{12}$	$\frac{1}{240}$	0.60
Lopsided rigid dumbbell[d] with two dissimilar beads connected by a rod; $(1/\zeta) = (1/\zeta_1) + (1/\zeta_2)$.	Length of rod	$\frac{1}{12}$	$\frac{1}{240}$	0.60
Hookean dumbbell[c] with two beads connected by a linear spring with spring constant H.	$\sqrt{kT/H}$	$\frac{1}{4}$	$\frac{1}{16}$	1
Kramers freely jointed bead-rod chain[e, f, g] (3, 4, and 5 beads)	Length of each rod	$\frac{2}{9}$ $\frac{5}{12}$ $\frac{2}{3}$	0.02069 0.06554 0.16224	0.419 $N = 3$ 0.378 $N = 4$ 0.365 $N = 5$
Freely jointed bead-spring chain with Fraenkel springs in the limit that the springs are infinitely stiff[f, g] (3, 4, and 5 beads)	Length of infinitely stiff springs	$\frac{2}{9}$ $\frac{5}{12}$ $\frac{2}{3}$	0.02099 0.06667 0.16489	0.425 $N = 3$ 0.384 $N = 4$ 0.371 $N = 5$
Three-bead, two-rod model with bending potential $\phi = \frac{1}{2}K(\chi - \pi)^2$ where χ is the included angle[f, l]	Length of each rod	$\frac{1}{3}\left(1 - \frac{kT}{3K} + \cdots\right)$	$\frac{1}{15}\left(1 - \frac{7}{6}\frac{kT}{K} + \cdots\right)$	$0.60\left(1 - \frac{kT}{2K} + \cdots\right)$
Rouse model of N beads joined linearly by $N - 1$ linear springs each with spring constant H.	$\sqrt{kT/H}$	$\frac{(N^2 - 1)}{12}$	$\frac{(N^2 - 1)(2N^2 + 7)}{720}$	$\frac{(2N^2 + 7)}{5(N^2 - 1)} = 0.4\left(1 + \frac{9}{2N^2} + \cdots\right)$

Bead-spring ring[n] of N beads joined by N linear springs with spring constant H	$\sqrt{kT/H}$	$\frac{(N^2-1)}{24}$	$\frac{(N^2-1)(N^2+11)}{2880}$	$\frac{(N^2+11)}{5(N^2-1)} = 0.2\left(1+\frac{12}{N^2}+\cdots\right)$
Freely jointed bead-spring chain with infinitely stiffened Fraenkel springs[f] of length L_0	L_0	$\frac{(N^2-1)}{36}$	$\frac{(N^2-1)(10N^3-12N^2+35N-12)}{32400N}$	$0.4\left(1-\frac{6}{5N}+\cdots\right)$
Kirkwood–Riseman freely rotating bead-rod chain[h] with $\xi_1 = \xi_2 = \cdots = \arccos\frac{1}{3} = 70.53^\circ$ in Fig. 11.2-1 (3, 4. . . . , 8 beads)	Length of each rod	0.2593 0.5389 0.9272 1.427 2.039 2.764	0.0255 0.1015 0.2963 0.7047 1.453 2.697	0.380 $N=3$ 0.349 $N=4$ 0.345 $N=5$ 0.346 $N=6$ 0.349 $N=7$ 0.353 $N=8$
Two beads joined by a string[i]	Length of string	$\frac{3}{5}$	$\frac{9}{35}$	0.71
Rigid plane polygon[m] of N beads connected by N rods of length b.	Radius of circumscribed circle $L = \frac{b/2}{\sin(\pi/N)}$	$\frac{N}{6}$	$\frac{N^2}{240}$	0.15
Four beads joined with rods to form a rigid plane rhombus[j] with included angle 2σ (cf. Fig. 16.4-2).	Side of rhombus	$\frac{1}{3}$	$\frac{1}{15}(1-\frac{3}{4}\sin^2 2\sigma)$	$0.60(1-\frac{3}{4}\sin^2 2\sigma)$
Four beads joined with rods to form a freely jointed plane rhombus.[j]	Side of rhombus	$\frac{1}{3}$	$\frac{1}{30}$	0.30
Four beads joined with rods to form a freely jointed rhombus[j]; one opposite pair of beads is joined by a Fraenkel spring with spring constant H and equilibrium position $L/\sqrt{2}$.	Side of rhombus	$\frac{1}{3}$	$\frac{1}{60}[1+(24I_5+60\sqrt{2}I_4+96I_3+24\sqrt{2}I_2)(2I_1+\sqrt{2}I_0)^{-1}]$ where $I_n = \int_{-1/\sqrt{2}}^{1-1/\sqrt{2}} u^n e^{-a^2u^2}\,du$ and $a^2 = 2HL^2/kT$	$0.30\left[1-\frac{2\sqrt{2}}{105}a^2+\cdots\right]$

(continued)

TABLE 16.4-1 (*Continued*)

Rigid tridumbbell ("Doppelkreuzhantel")[k], formed by joining three identical rigid dumbbells at their midpoints in a mutually orthogonal configuration.	Length of one dumbbell rod	$\frac{1}{4}$	0	0
	Length of rod between beads	$\frac{7}{3}$	$\frac{16}{15}$	0.20
	Length of rod between beads	$\frac{73}{27}$	$\frac{2116}{1215}$	0.24
	Length of rod between beads	$\frac{103}{27}$	$\frac{5776}{1215}$	0.34

[a] This table is an extension of Table V of C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31-117 (I. Prigogine and S. A. Rice, eds.) (1976).
[b] See §6.2 for a discussion of the retarded motion expansion.
[c] R. B. Bird, H. R. Warner, Jr., and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1-90 (1971).
[d] S. I. Abdel-Khalik and R. B. Bird, *Appl. Sci. Res.*, **30**, 268-270 (1975).
[e] R. S. Rivlin, *Trans. Faraday Soc.*, **45**, 737-748 (1949).
[f] O. Hassager, *J. Chem. Phys.*, **60**, 2111 2124 (1974); see also §16.5.
[g] C. F. Curtiss and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **2**, 392 396 (1977).
[h] X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303-321 (1986).
[i] H. R. Warner, Jr., *Ind. Eng. Chem. Fundamentals*, **11**, 379-387 (1972).
[j] C. F. Curtiss, R. B. Bird and O. Hassager, *loc. cit.*, Table V.
[k] H. Giesekus, *Rheol. Acta*, **2**, 101-112 (1962).
[l] D. B. Roitman and B. H. Zimm, *J. Chem. Phys.*, **81**, 6333-6347 (1984).
[m] E. Paul and R. M. Mazo, *J. Chem. Phys.*, **51**, 1102-1107 (1969); errata in this paper are discussed in C. Y. Mou and R. M. Mazo, *J. Chem. Phys.*, **67**, 5972-5973 (1977).
[n] J. M. Wiest, S. R. Burdette, T. W. Liu, and R. B. Bird, *J. Non-Newtonian Fluid Mech.* (1987).

in going from the Kirkwood–Riseman chain with fixed angles to the Kramers freely jointed chain.

6. The last three models show how the viscosity and normal stress coefficients increase as the structures become more and more lopsided.
7. Values of the dimensionless group $-nkTb_2/(b_1 - \eta_s)^2$ for the models listed vary from 0 to 1. Note that this group does not contain the model parameters ζ and L.
8. It is interesting to compare the results for the Kramers freely jointed bead-rod chain and the freely jointed bead-rod chain obtained by freezing out Fraenkel springs (see Example 12.5-2): the b_1 values are identical, and the b_2 values differ by less than 2% for $N = 3$, 4, and 5.

To illustrate the use of Eqs. 16.4-14 and 16.4-15 we give three examples—the first two for rigid models including equilibrium averaged hydrodynamic interaction, and the third for a flexible model with an internal potential.

EXAMPLE 16.4-1 Second-Order Fluid Constants for the Multibead-Rod Model with Equilibrium Averaged Hydrodynamic Interaction

Obtain the second-order-fluid constants, b_1 and b_2, for the multibead-rod model described in §14.1 and further discussed in Examples 16.1-1, 16.2-1, and 16.3-1. Include the effects of hydrodynamic interaction in the equilibrium-averaged approximation.

SOLUTION The dimensionless diffusion tensors for this model are given by Eq. 16.2-15. Upon equilibrium averaging this expression, that is, averaging over all orientations of the rod with an isotropic distribution, one finds that the $H_{\nu\mu}$ of Eq. I of Table 16.1-2 are

$$H_{\nu\mu} = \delta_{\nu\mu} + \zeta\Omega_{\nu\mu} \tag{16.4-17}$$

where from Eqs. 16.2-13 and 14,

$$\Omega_{\nu\mu} = \tfrac{2}{3}\,\Omega^{(1)}_{\nu\mu} + \tfrac{1}{3}\,\Omega^{(2)}_{\nu\mu} = \frac{(1 - \delta_{\nu\mu})}{3\pi a\eta_s|\nu - \mu|} \tag{16.4-18}$$

It is interesting to note that since the parameter ξ is lost in the equilibrium averaging, in this approximation the Rotne–Prager–Yamakawa interaction tensors and the Oseen–Burgers tensors lead to the same result.

The dimensionless mobility coefficients $B_{\nu\mu}$ are (see Eq. J of Table 16.1-2) now determined by the equations

$$\sum_{\eta} B_{\nu\eta}\,(\delta_{\eta\mu} + \zeta\Omega_{\eta\mu}) = \delta_{\nu\mu} \tag{16.4-19}$$

which are similar to Eqs. 16.2-17 but with the two sets of matrices, $\Omega^{(1)}_{\nu\mu}$ and $\Omega^{(2)}_{\nu\mu}$ replaced by the average, $\Omega_{\nu\mu}$. As in the treatment of complete hydrodynamic interaction, we next define the sums

$$B_\eta = \tfrac{1}{2}\sum_{\nu} \nu B_{\nu\eta} \tag{16.4-20}$$

which are determined by the equations

$$\sum_{\eta} B_\eta\,(\delta_{\eta\mu} + \zeta\Omega_{\eta\mu}) = \tfrac{1}{2}\mu \tag{16.4-21}$$

From these equations it may be shown that

$$B_{\eta} = -B_{\eta} \tag{16.4-22}$$

It is also interesting to note that these equations are similar to the equations for the $B_{\eta}^{(1)}$ and $B_{\eta}^{(2)}$ in Eqs. 16.2-20. The solutions, B_{η}, may be obtained from those of the previous equations by setting $\xi = 0$ and from $B_{\eta}^{(1)}$ by replacing h by $\frac{4}{3}h$ or from $B_{\eta}^{(2)}$ by replacing h by $\frac{2}{3}h$.

From the definition of the tensor, $\mathbf{K}$ (see Eq. 16.2-8), the expression for the $\boldsymbol{R}_{\nu}$ (see Fig. 14.1-2), and the antisymmetry of the B_{η} one finds that

$$\mathbf{K} = a^2\zeta B\boldsymbol{uu} \tag{16.4-23}$$

where

$$B = \tfrac{1}{2}\sum_{\eta}\eta B_{\eta} = \tfrac{1}{4}\sum_{\nu\mu}\nu\mu B_{\nu\mu} \tag{16.4-24}$$

One then finds from Eqs. 16.4-14 and 15 that

$$b_1 = \eta_s + \tfrac{1}{6}na^2\zeta B \tag{16.4-25}$$

$$b_2 = -\frac{n\zeta^2a^4}{60kT}B^2 \tag{16.4-26}$$

One may compare the present results with those obtained without equilibrium averaging, which may be shown from Eqs. 14.6-23 and 24 to be

$$b_1 = \eta_s + \tfrac{1}{30}n\zeta a^2\,(3B^{(1)} + 2B^{(2)}) \tag{16.4-27}$$

$$b_2 = -\frac{n\zeta^2a^4}{60kT}(B^{(1)})^2 \tag{16.4-28}$$

That is, in the approximation of equilibrium averaging the two constants $B^{(1)}$ and $B^{(2)}$ are replaced by a single average constant, B, or equivalently the two time constants of Eqs. 14.6-23 and 14.6-24 are replaced by a single average time constant. In particular one finds that for the rigid dumbbell ($N = 2$), with equilibrium averaging

$$b_1 = \eta_s + \tfrac{1}{12}n\zeta a^2[1 - \tfrac{4}{3}h]^{-1} \tag{16.4-29}$$

$$b_2 = -\frac{n\zeta^2a^4}{240kT}[1 - \tfrac{4}{3}h]^{-2} \tag{16.4-30}$$

as compared to the analogous results with complete hydrodynamic interaction, obtained from Eqs. 14.6-23 and 24

$$b_1 = \eta_s + \frac{\tfrac{1}{12}n\zeta a^2[1 - \tfrac{8}{5}h(1 - \tfrac{1}{12}\xi^2)]}{[1 - h(1 + \tfrac{1}{6}\xi^2)][1 - 2h(1 - \tfrac{1}{6}\xi^2)]} \tag{16.4-31}$$

$$b_2 = -\frac{n\zeta^2a^4}{240kT}[1 - h(1 + \tfrac{1}{6}\xi^2)]^{-2} \tag{16.4-32}$$

For rigid dumbbells we have summarized the results in Table 16.4-2.

TABLE 16.4-2

Effect of Hydrodynamic Interaction on the Second-Order-Fluid Constants for Rigid Dumbbells (all entries for $h = \frac{3}{8}$, its maximum value)

Type of hydrodynamic interaction	$\frac{b_1 - \eta_s(\text{H.I.})}{b_1 - \eta_s(\text{no H.I.})}$	$\frac{b_2(\text{H.I.})}{b_2(\text{no H.I.})}$
Equilibrium averaged hydrodynamic interaction	2	4
Complete hydrodynamic interaction according to Oseen–Burgers	$\frac{64}{25} = 2.56$	$\frac{64}{25} = 2.56$
Complete hydrodynamic interaction according to Rotne–Prager–Yamakawa (with $\xi = 1$)	$\frac{32}{15} = 2.13$	$\frac{256}{81} = 3.16$

EXAMPLE 16.4-2 Second-Order Fluid Constants for the Rigid Tridumbbell with Equilibrium-Averaged Hydrodynamic Interaction

Obtain b_1 and b_2 for the rigid tridumbbell, made up of dumbbells with lengths L_1, L_2, and L_3. Use a set of embedded vectors as shown in Fig. 16.4-1, and number the beads as indicated; all m_v and ζ_v are taken to be equal. Include hydrodynamic interaction in the equilibrium averaged approximation.

SOLUTION The position vectors of the six beads are

$$\boldsymbol{R}_v = \tfrac{1}{2} L_v \check{\boldsymbol{\delta}}_v \tag{16.4-33}$$

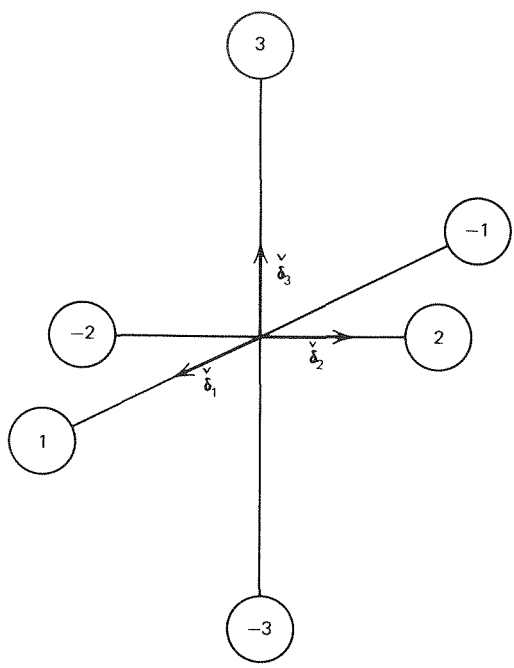


FIGURE 16.4-1. The rigid tridumbbell showing the embedded unit vectors $\check{\boldsymbol{\delta}}_n$.

where for convenience we let $L_{-\nu} = -L_\nu$ and $\check{\boldsymbol{\delta}}_{-\nu} = \check{\boldsymbol{\delta}}_\nu$. The vector between a pair of beads is then

$$\boldsymbol{R}_{\nu\mu} = \boldsymbol{R}_\mu - \boldsymbol{R}_\nu = \tfrac{1}{2}(L_\mu \check{\boldsymbol{\delta}}_\mu - L_\nu \check{\boldsymbol{\delta}}_\nu) \tag{16.4-34}$$

and the magnitude of this vector is

$$R_{\nu\mu} = \tfrac{1}{4}[L_\nu^2 + L_\mu^2 - 2L_\nu L_\mu(\delta_{\nu\mu} + \delta_{\nu,-\mu})] \tag{16.4-35}$$

a constant. The equilibrium average of the Rotne–Prager–Yamakawa interaction tensor (Eq. 14.6-2) is then the same as that of the Oseen–Burgers interaction tensor (Eqs. 13.6-5 and 15.4-3):

$$\Omega_{\nu\mu} = \frac{(1 - \delta_{\nu\mu})}{6\pi\eta_s R_{\nu\mu}} \tag{16.4-36}$$

The dimensionless mobility coefficients, $B_{\nu\eta}$, are determined by

$$\sum_\eta B_{\nu\eta}(\delta_{\eta\mu} + \Omega_{\eta\mu}) = \delta_{\nu\mu} \tag{16.4-37}$$

Next it is convenient to define a set of vectors

$$\boldsymbol{B}_\eta = \tfrac{1}{2}\sum_\nu L_\nu B_{\nu\eta} \check{\boldsymbol{\delta}}_\nu \tag{16.4-38}$$

From Eqs. 16.4-37, it follows that these vectors are determined by the equations

$$\sum_\eta \boldsymbol{B}_\eta(\delta_{\eta\mu} + \Omega_{\eta\mu}) = \tfrac{1}{2}L_\mu \check{\boldsymbol{\delta}}_\mu \tag{16.4-39}$$

From Eqs. 16.4-35 and 16.4-36 it follows that $\Omega_{-\nu,-\mu} = \Omega_{\nu\mu}$ and thus one finds from the last equation that

$$\boldsymbol{B}_{-\eta} = -\boldsymbol{B}_\eta \tag{16.4-40}$$

With this antisymmetry we find that for $\mu > 0$

$$\sum_{\eta>0} \boldsymbol{B}_\eta(\delta_{\eta\mu} + \tilde{\Omega}_{\eta\mu}) = \tfrac{1}{2}L_\mu \check{\boldsymbol{\delta}}_\mu \tag{16.4-41}$$

where for $\eta > 0$ and $\mu > 0$

$$\begin{aligned}\tilde{\Omega}_{\eta\mu} &= \Omega_{\eta\mu} - \Omega_{-\eta\mu} \\ &= -\frac{1}{6\pi\eta_s L_\eta}\delta_{\eta\mu}\end{aligned} \tag{16.4-42}$$

is diagonal. One then finds from Eqs. 16.4-41 and 42, that for $\mu > 0$

$$\boldsymbol{B}_\mu = \tfrac{1}{2}L_\mu(1 - \tfrac{4}{3}h_\mu)^{-1}\check{\boldsymbol{\delta}}_\mu \tag{16.4-43}$$

$$h_\mu = \frac{1}{8\pi\eta_s L_\mu} \tag{16.4-44}$$

From Eq. M of Table 16.1-2, Eq. 16.4-38, and the antisymmetry of the $\boldsymbol{B}_\eta$, Eq. 16.4-40, one finds that

$$\begin{aligned}\sum_\nu l_\nu L_\nu \check{\boldsymbol{\delta}}_\nu &= \frac{\sum_{\nu\mu} B_{\nu\mu} L_\nu \check{\boldsymbol{\delta}}_\nu}{\sum_{\nu\mu} B_{\nu\mu}} \\ &= 2\frac{\sum_\mu \boldsymbol{B}_\mu}{\sum_{\nu\mu} B_{\nu\mu}} \\ &= \mathbf{0}\end{aligned} \tag{16.4-45}$$

One may now show from Eqs. 16.2-8, 16.4-33, and N of Table 16.1-2

$$\begin{aligned}\mathbf{K} &= \tfrac{1}{4}\zeta \sum_\nu \sum_\mu L_\nu L_\mu B_{\nu\mu} \check{\boldsymbol{\delta}}_\nu \check{\boldsymbol{\delta}}_\mu \\ &= \tfrac{1}{2}\zeta \sum_\nu L_\nu \boldsymbol{B}_\nu \check{\boldsymbol{\delta}}_\nu \\ &= \tfrac{1}{2}\zeta \sum_{\nu>0} L_\nu^2 (1 - \tfrac{4}{3}h_\nu)^{-1} \check{\boldsymbol{\delta}}_\nu \check{\boldsymbol{\delta}}_\nu\end{aligned} \tag{16.4-46}$$

From this it follows that

$$b_1 = \eta_s + \frac{n\zeta}{12} \sum_{\nu=1}^{3} L_\nu^2 (1 - \tfrac{4}{3}h_\nu)^{-1} \tag{16.4-47}$$

$$b_2 = -\frac{n\zeta^2}{160kT} \left\{ \sum_{\nu=1}^{3} L_\nu^4 (1 - \tfrac{4}{3}h_\nu)^{-2} - \tfrac{1}{3}\left[\sum_{\nu=1}^{3} L_\nu^2 (1 - \tfrac{4}{3}h_\nu)^{-1} \right]^2 \right\} \tag{16.4-48}$$

In the limit that two of the L_ν become zero this result reduces to that for the rigid dumbbell with equilibrium averaged hydrodynamic interaction given at the end of the last example.

EXAMPLE 16.4-3 Second-Order Fluid Constants for the Elastic Rhombus

Use the results given in Problem 16C.4 to obtain the coefficients b_1 and b_2 for the elastic rhombus model, shown in Fig. 16.4-2. Neglect hydrodynamic interaction.

SOLUTION The position vectors for the beads are given in Eq. 16C.4-1. From these we can compute the elements of the (K_{mn})-matrix:

$$K_{11} = 2\zeta L^2 \cos^2\sigma, \qquad K_{22} = 2\zeta L^2 \sin^2\sigma \tag{16.4-49}$$

Then from the elements of the $(\Gamma_{\mu\nu})$-matrix we can obtain the determinant:

$$\Gamma = 8m^2 L^8 \sin^2 2\sigma \tag{16.4-50}$$

The potential energy of the system is

$$\phi = \tfrac{1}{2}H(2L\cos\sigma - \sqrt{2}L)^2 \tag{16.4-51}$$

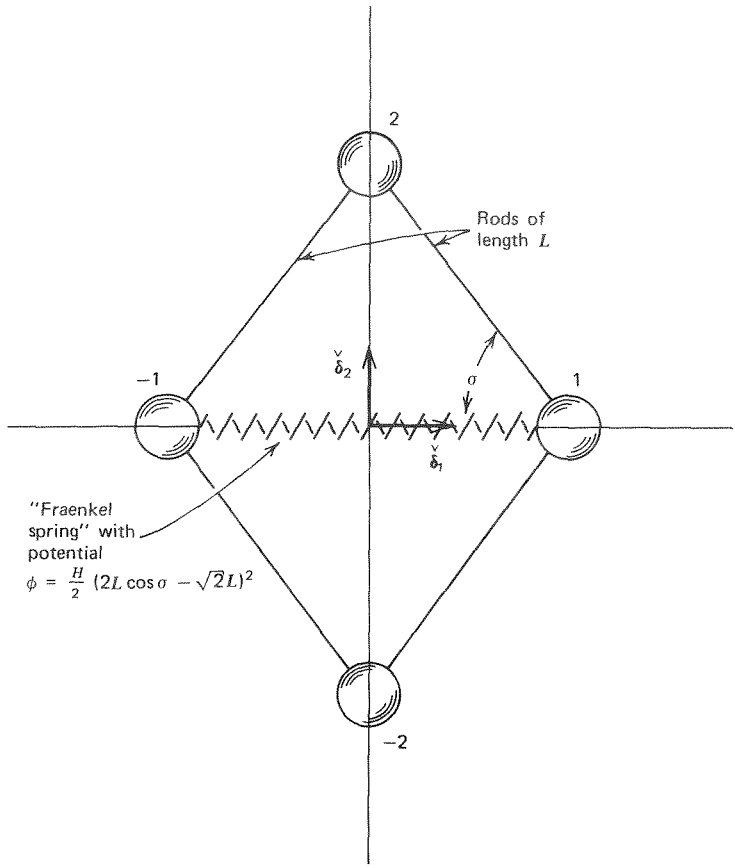


FIGURE 16.4-2. Elastic rhombus model with four identical beads.

Then b_1 is found using the second form of Eq. 16.4-16 for the $\langle\ \rangle_{eq}$ averaging

$$b_1 - \eta_s = \frac{n\zeta}{6}\langle 2L^2\rangle_{eq} = \frac{n\zeta L^2}{3} \tag{16.4-52}$$

which is the same as b_1 for the "limp" (i.e., flexible but with no spring) rhombus or the rigid rhombus. Finally b_2 is calculated thus

$$b_2 = -\frac{n\zeta^2 L^4}{15kT}\frac{\int_0^{\pi/2}(\sin 2\sigma)[\exp - H(2L\cos\sigma - \sqrt{2}L)^2/2kT](1 - \frac{3}{4}\sin^2 2\sigma)d\sigma}{\int_0^{\pi/2}(\sin 2\sigma)[\exp - H(2L\cos\sigma - \sqrt{2}L)^2/2kT]d\sigma}$$

$$= -\frac{n\zeta^2 L^4}{30kT}\left(1 - \frac{4\sqrt{2}}{105}\frac{HL^2}{kT} + \cdots\right) \tag{16.4-53}$$

The factor in front is just b_2 for a limp rhombus, and the quantity in brackets is the "correction factor" for a weak Hookean spring.

§16.5 STEADY FLOWS OF FREE-DRAINING KRAMERS BEAD-ROD CHAINS

In this section we consider the Kramers freely jointed, linear, bead-rod chain model, which is appropriate for linear, flexible polymers. Some of the properties of this model have been discussed in §§11.3, 12.1, and 12.3. To discuss this model further we use a double-index notation to indicate the generalized coordinates, which are taken to be the polar angles $\theta_k = Q_{k1}$ and $\phi_k = Q_{k2}$ specifying the direction of the unit vector, $\boldsymbol{u}_k$, from bead k to bead $k+1$. That is, the first index indicates the number of the rod and the second index specifies the polar angle. Then the vector representing the kth rod is

$$\begin{aligned} a\boldsymbol{u}_k &= \boldsymbol{R}_{k+1} - \boldsymbol{R}_k \\ &= \sum_v \bar{B}_{kv}\boldsymbol{R}_v \end{aligned} \tag{16.5-1}$$

where a is the length of a rod, and the $\bar{B}_{kv}$ are the coefficients defined by Eq. 11.6-5. This relation may be inverted to give (cf. Eq. 12.1-13):

$$\boldsymbol{R}_v = a\sum_k B_{vk}\boldsymbol{u}_k \tag{16.5-2}$$

where the B_{vk} are the coefficients defined by Eq. 11.6-6. In addition, we note that

$$\sum_v \boldsymbol{R}_v\boldsymbol{R}_v = a^2\sum_{ij} C_{ij}\boldsymbol{u}_i\boldsymbol{u}_j \tag{16.5-3}$$

where the C_{ij} are the elements of the Kramers matrix defined by Eq. 11.6-7. This quantity appears in the tensor $\mathbf{K}$ of Eq. 16.2-8; when there is no hydrodynamic interaction $\mathbf{K} = \zeta\sum_v \boldsymbol{R}_v\boldsymbol{R}_v$.

It is shown in §12.1 that for the Kramers chain the base vectors are

$$\boldsymbol{b}_{v,kp} = a\sqrt{m}B_{vk}\boldsymbol{c}_{kp} \tag{16.5-4}$$

where the $\boldsymbol{c}_{kp}$ are the vectors defined in Table E.5-1. From these expressions one finds that the elements of the metric matrix are

$$g_{ip,jq} = ma^2C_{ij}(\boldsymbol{c}_{ip}\cdot\boldsymbol{c}_{jq}) \tag{16.5-5}$$

To discuss the inverse metric matrix we first define the elements of a modified Rouse matrix

$$\hat{A}_{ij} = (\boldsymbol{u}_i\cdot\boldsymbol{u}_j)A_{ij} \tag{16.5-6}$$

where the A_{ij} are the elements of the Rouse matrix defined by Eq. 11.6-8. The elements of the matrix inverse to the modified Rouse matrix are designated by $\hat{C}_{ij}$, so that

$$\sum_j \hat{A}_{ij}\hat{C}_{jk} = \delta_{ik} \tag{16.5-7}$$

It may be shown[1] that the elements of the inverse metric matrix are

$$G_{ip,jq} = \frac{1}{ma^2} \sum_{kl} A_{ik} A_{jl} (\mathbf{K}_{kl} : \boldsymbol{d}_{jq} \boldsymbol{d}_{ip}) \tag{16.5-8}$$

where the $\boldsymbol{d}_{jq}$ are vectors which are also defined in Table E.5-1 and the $\mathbf{K}_{kl}$ are the *Kramers tensors*

$$\mathbf{K}_{ij} = C_{ij}\boldsymbol{\delta} - \hat{C}_{ij}\boldsymbol{u}_i\boldsymbol{u}_j \tag{16.5-9}$$

These expressions are used in the discussion of undiluted polymers in Chapter 19. Up to this point we have been concerned solely with geometric quantities related to the chain model. Keep in mind that the metric matrices occur in the diffusion equation, Eq. 16.2-6, and in the stress-tensor expression of Eq. 16.3-5.

The equilibrium configurational distribution function, ψ_{eq}, of a Kramers chain is discussed in §12.3 and given by Eq. 12.3-5 in terms of the determinant, g, of the metric matrix. A recursive expression for this determinant is given by Eqs. 12.1-18 and 19 and explicit expressions for $N = 3$ are developed in Examples 12.1-1 and 16.1-2. Using these expressions for the equilibrium configurational distribution function and the methods developed in the previous section, one may calculate the second-order fluid constants. The results for $N = 3$ with the constraints (the bead-rod model) are

$$b_1 = \eta_s + \frac{2}{9} n\zeta a^2 \tag{16.5-10}$$

$$b_2 = -\frac{1}{1080}\left(\frac{80\pi + 3\sqrt{3}}{2\pi + 3\sqrt{3}}\right)\frac{n\zeta^2 a^4}{kT} \tag{16.5-11}$$

These values for b_1 and b_2 as well as those for $N = 4$ and 5 are given[2] in Table 16.4-1. In the same table we also list the corresponding results for a bead-spring chain with Fraenkel springs that have been taken to be infinitely stiff. Such chains have the random-walk distribution at equilibrium (Eq. 12.5-14), and for this distribution b_1 and b_2 can be obtained[3] for any N:

$$b_1 = \eta_s + \tfrac{1}{36}(N^2 - 1)n\zeta a^2 \tag{16.5-12}$$

$$b_2 = -\frac{(N^2 - 1)(10N^3 - 12N^2 + 35N - 12)}{32400N}\frac{n\zeta^2 a^4}{kT} \tag{16.5-13}$$

These last two formulas (also listed in Table 16.4-1) can be derived from Eqs. 16.4-14 and 15 by using θ_i and ϕ_i ($i = 1, 2, \ldots, N-1$) as the generalized coordinates. Of course $b_{11} = 0$ for this model since hydrodynamic interaction is neglected.

It turns out that Eq. 16.5-12 for b_1 is also valid for the Kramers chain,[2] but, as can be seen in Table 16.4-1, Eq. 16.5-13 for b_2 gives results different from those of the Kramers chain. For $N = 3$, 4, and 5 the difference is less than 2%.

[1] C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, 2016-2025 (1981).

[2] C. F. Curtiss and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **2**, 392-396 (1977).

[3] R. S. Rivlin, *Trans. Faraday Soc.*, **45**, 739-748 (1949); O. Hassager, *J. Chem. Phys.*, **60**, 2111-2124 (1974). Rivlin did not obtain the b_1 and b_2 of the retarded-motion expansion, which was not known in 1949, but instead got the coefficients in the Reiner-Rivlin equation for potential flows.

EXAMPLE 16.5-1 Elongational Viscosity for the Kramers Bead-Rod Chain[4]

Consider a dilute suspension of Kramers chains in a steady elongational flow field. Develop expressions for the steady-state elongational viscosity asymptotically valid in the limits of large and small elongation rates.

SOLUTION (a) General Expression for the Elongational Viscosity

Since we are dealing with a steady potential flow, the distribution function is given formally by Eq. 16.2-10. Hence we may follow the general procedure used in Example 13.5-1 for a FENE dumbbell. First we write the $\boldsymbol{\kappa}$ tensor for steady elongational flow in the form

$$\boldsymbol{\kappa} = (3\boldsymbol{\delta}_3\boldsymbol{\delta}_3 - \boldsymbol{\delta})\frac{\dot{\varepsilon}}{2} \tag{16.5-14}$$

Here $\boldsymbol{\delta}$ is the second-order unit tensor and $\boldsymbol{\delta}_3$ is the space-fixed unit vector along the axis of elongation. According to the Giesekus expression, Eq. 16.3-20, we may write the stress tensor as follows:

$$\begin{aligned}\boldsymbol{\tau} &= -\eta_s\dot{\boldsymbol{\gamma}} - n\zeta\left\{\boldsymbol{\kappa}\cdot\sum_v\langle \boldsymbol{R}_v\boldsymbol{R}_v\rangle\right\} \\ &= -\eta_s\dot{\boldsymbol{\gamma}} - n\zeta a^2\left\{\boldsymbol{\kappa}\cdot\sum_i\sum_j C_{ij}\langle \boldsymbol{u}_i\boldsymbol{u}_j\rangle\right\}\end{aligned} \tag{16.5-15}$$

Here we have also used Eq. 16.5-3. We now find for the elongational viscosity defined by Eq. D.5-14:

$$\begin{aligned}\bar{\eta} &= \frac{\tau_{22} - \tau_{33}}{\dot{\varepsilon}} \\ &= \frac{((\boldsymbol{\delta}_2\boldsymbol{\delta}_2 - \boldsymbol{\delta}_3\boldsymbol{\delta}_3):\boldsymbol{\tau})}{\dot{\varepsilon}}\end{aligned} \tag{16.5-16}$$

We substitute Eqs. 16.5-14 and 15 into Eq. 16.5-16. After using the expression for $\boldsymbol{u}_i$ in Table E.5-2 we find

$$\bar{\eta} = 3\eta_s + n\zeta a^2\left\langle\sum_i\sum_j C_{ij}(C_iC_j + \tfrac{1}{2}S_iS_js_is_j)\right\rangle \tag{16.5-17}$$

We here use the notation that $C_k = \cos\theta_k$, $S_k = \sin\theta_k$, $c_k = \cos\phi_k$, and $s_k = \sin\phi_k$. We may also show that

$$\left(\boldsymbol{\kappa}:\sum_v \boldsymbol{R}_v\boldsymbol{R}_v\right) = a^2\sum_i\sum_j C_{ij}[C_iC_j - \tfrac{1}{2}S_iS_j(s_is_j + c_ic_j)]\dot{\varepsilon}/2 \tag{16.5-18}$$

Hence it follows from Eq. 16.2-10 and Eqs. 16.5-17 and 18 that

$$\bar{\eta} = 3\eta_s + n\zeta a^2 I_2/I_1 \tag{16.5-19}$$

[4] O. Hassager, *J. Chem. Phys.*, **60**, 2111–2124 (1974).

where

$$I_1 = \tfrac{1}{2}\int_0^{2\pi}\cdots\int_0^{\pi}\exp\left\{X\sum_i\sum_j C_{ij}[C_iC_j - 1 - \tfrac{1}{2}S_iS_j(s_is_j + c_ic_j)]\right\}h_N\prod_k S_k\,d\theta_k\,d\phi_k \quad (16.5\text{-}20)$$

$$I_2 = \tfrac{1}{2}\int_0^{2\pi}\cdots\int_0^{\pi}\sum_k\sum_l C_{kl}(C_kC_l + \tfrac{1}{2}S_kS_ls_ks_l)\exp\left\{X\sum_i\sum_j C_{ij}[C_iC_j - 1 - \tfrac{1}{2}S_iS_j(s_is_j + c_ic_j)]\right\}h_N\prod_k S_k\,d\theta_k\,d\phi_k \quad (16.5\text{-}21)$$

Here $X = \zeta a^2\dot{\varepsilon}/2kT$ is a dimensionless elongation rate, and we have multiplied both numerator and denominator by $\frac{1}{2}\exp(-X\sum_i\sum_j C_{ij})$ for later convenience.

The elongational viscosity for the particular freely jointed chain with $N = 3$ as computed from Eqs. 16.5-19 to 16.5-21 is shown in Fig. 16.5-1. For large values of N, however, a numerical evaluation of the integrals in Eqs. 16.5-20 and 21 is not feasible, and we therefore turn to a discussion of asymptotic expansions.

(b) Asymptotic Expansion for High Elongation Rates

We notice that the exponents in Eqs. 16.5-20 and 21 are negative everywhere except at the points $\theta_i = 0$ $(i = 1, 2, \ldots, (N-1))$ and $\theta_i = \pi$ $(i = 1, 2, \ldots, (N-1))$ where they are zero. As X becomes large, practically all the contribution to the integrals will occur in a small region around these points, and we may consequently restrict the ranges of integration to these regions. After expanding the θ_i part of the integrands in powers of θ_i retaining terms through second order in θ_i we find for I_2

$$I_2 = \int_0^{2\pi}\cdots\int_0^{\varepsilon}\sum_k\sum_l C_{kl}(1 - \tfrac{1}{2}\theta_k^2 - \tfrac{1}{2}\theta_l^2 + \tfrac{1}{2}\theta_k\theta_ls_ks_l)\exp\left\{X\sum_i\sum_j C_{ij}[1 - \tfrac{1}{2}\theta_i^2 - \tfrac{1}{2}\theta_j^2 - \tfrac{1}{2}\theta_i\theta_j(s_is_j + c_ic_j)]\right\}\prod_h \theta_h\,d\theta_h\,d\phi_h \quad (16.5\text{-}22)$$

where ε is a small number chosen so that the integrand is negligible for $\theta_i > \varepsilon$. The expression for I_1 is the same as the expression for I_2 except that the integrand consists of the exponential function alone. We have here used the expansion $h_N = 1 + O(\theta_i^4)$ for the correlation function (see Eqs. 12.1-18, 19). We now introduce a Cartesian coordinate system that locally maps the (θ_i, ϕ_i) system

$$\begin{cases} x_i = \theta_i c_i, \\ y_i = \theta_i s_i, \end{cases} \qquad i = 1, 2, \ldots, (N-1) \quad (16.5\text{-}23)$$

We emphasize that this coordinate transformation is a local transformation for the region of interest, and that there does not exist a global Cartesian coordinate system for the entire configuration space. The Jacobian of the transformation in Eq. 16.5-23 is

$$\det\left\{\frac{\partial(\theta_i, \phi_i)}{\partial(x_i, y_i)}\right\} = \prod_k S_k^{-1} \quad (16.5\text{-}24)$$

We may now rewrite the integrals I_2 and I_1 as follows:

$$I_2 \sim \int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\sum_k\sum_l [C_{kl} - \tfrac{1}{2}D_{kl}(x_kx_l + y_ky_l) + \tfrac{1}{2}C_{kl}(x_kx_l + 2y_ky_l]\exp\left[-\frac{X}{2}\sum_i\sum_j D_{ij}(x_ix_j + y_iy_j)\right]\prod_h dx_h\,dy_h \qquad (X \to \infty) \quad (16.5\text{-}25)$$

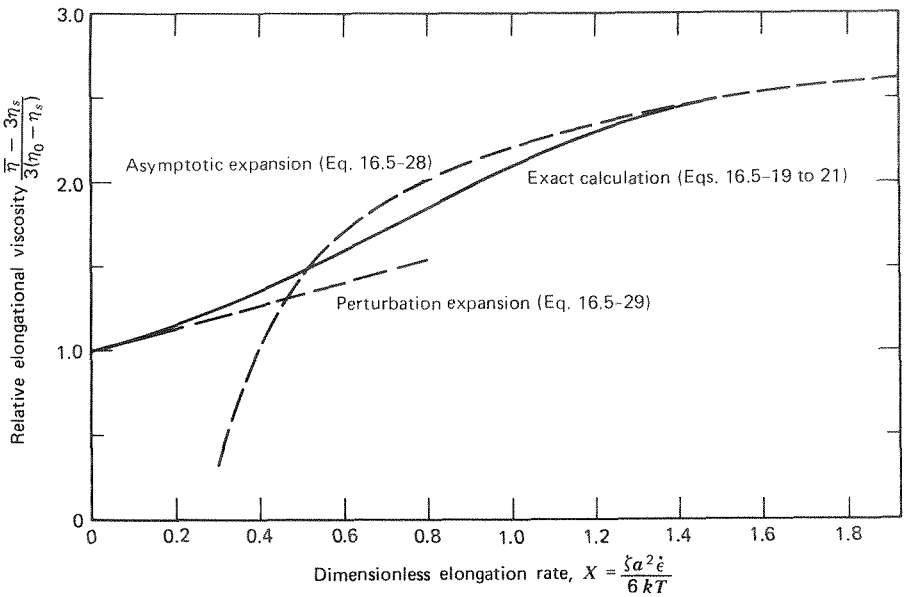


FIGURE 16.5-1. Elongational viscosity of the freely jointed bead-rod model with $N = 3$. The figure compares the asymptotic expansion Eq. 16.5-28 for large elongation rates and the perturbation expansion Eq. 16.5-29 for small elongation rates with the exact calculation from Eqs. 16.5-19 to 16.5-21. Reproduced from O. Hassager, *J. Chem. Phys.*, **60**, 2111–2124 (1974).

Again the expression for I_1 is the same as the expression for I_2 except that the integrand consists of the exponential function alone. We have also introduced the matrix with elements D_{ij} defined by

$$D_{ii} = C_{ii} + 2\sum_k C_{ik} = (N+1)C_{ii} \tag{16.5-26}$$

$$D_{ij} = C_{ij} \qquad i \neq j \tag{16.5-27}$$

It may be shown that the quadratic form $\sum_i \sum_j D_{ij} x_i x_j$ is non-negative for all values of x_i and zero only at the origin. Hence for large values of X the integrands in I_1 and I_2 will be practically zero outside the region of interest around the origin, and the ranges of integration have conveniently been extended to infinity with negligible error. The integrals I_1 and I_2 are now in standard forms and may be performed analytically. After some manipulation we may write the elongational viscosity for the freely jointed chain at large elongational rates in the form

$$\frac{\bar{\eta} - 3\eta_s}{3(\eta_0 - \eta_s)} \sim N - \frac{24[N - 1 - \frac{3}{2}\sum_i \sum_j C_{ij} D_{ji}^{-1}]kT}{(N^2 - 1)\zeta a^2 \dot{\varepsilon}} + \cdots \qquad (\dot{\varepsilon} \to \infty)$$

$$\sim N\left(1 - \frac{24kT}{N^2 \zeta a^2 \dot{\varepsilon}} + \cdots\right) \qquad (N \gg 1) \qquad (\dot{\varepsilon} \to \infty) \tag{16.5-28}$$

where $\eta_0 - \eta_s = (1/36)n\zeta a^2(N^2 - 1)$ is the polymer contribution to the zero-shear-rate viscosity. In the second line we have specialized the expression to chains with a large number of links.[5]

[5] The quantity $\sum_i \sum_j C_{ij} D_{ji}^{-1}$ is tabulated by O. Hassager, *J. Chem. Phys.*, **60**, p. 2121 (1974).

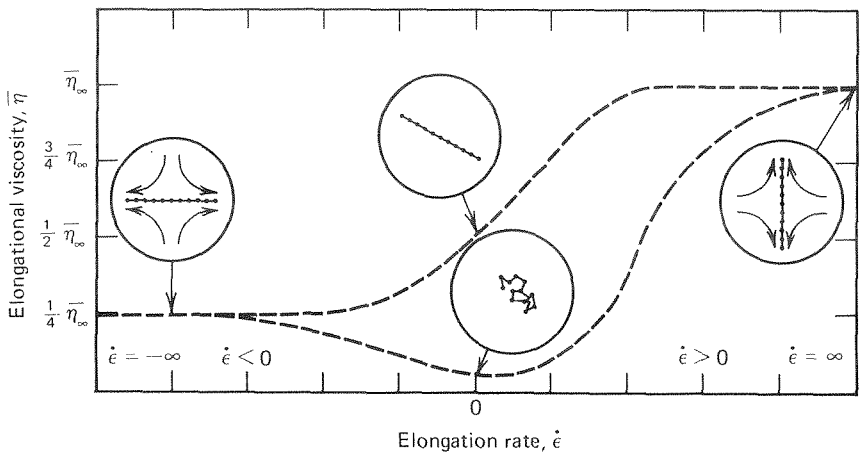


FIGURE 16.5-2. Qualitative plot of elongational viscosity versus elongation rate, illustrating the different behavior of flexible and rigid macromolecules. At large rates of deformation both kinds of molecules are in a linear configuration, and the curves have common asymptotes. At small rates of deformation the flexible molecules coil up, whereas the rigid ones do not. Reproduced from O. Hassager, *J. Chem. Phys.*, **60**, 2111–2124 (1974).

(c) Expansion for Low Elongation Rates

The expansion for low elongation rates may be obtained directly from the second-order-fluid model with the approximate constants given in Eqs. 16.5-12 and 16.5-13. We find then

$$\frac{\bar{\eta} - 3\eta_s}{3(\eta_0 - \eta_s)} \sim 1 + \left(\frac{10N^3 - 12N^2 + 35N - 12}{900N}\right)\frac{\zeta a^2 \dot{\varepsilon}}{kT} + \cdots \qquad (\dot{\varepsilon} \to 0)$$

$$\sim 1 + \frac{N^2 \zeta a^2 \dot{\varepsilon}}{90kT} + \cdots \qquad (N \gg 1) \qquad (\dot{\varepsilon} \to 0) \qquad (16.5\text{-}29)$$

Here again in the second line we have specialized the expression for chains with a large number of links. An appreciation of the extent to which the analytical expansions for small and large elongation rates portray the exact behavior of $\bar{\eta}$ may be obtained for $N = 3$ from a comparison with the exact numerical evaluation of the integrals as shown in Fig. 16.5-1.

It is interesting to note that the elongational viscosity increases by a factor of N from zero elongation rate to large elongation rates. For flexible macromolecules this may be a very large number. The result in Eq. 16.5-28 compares favorably with one set of experimental data.[6]

In conclusion it is fitting to point out the difference in behavior between the freely jointed bead-rod chain (with N beads and $N - 1$ rods of length a) and the multibead rod (with N beads and interbead distance a). In Fig. 16.5-2 we see a qualitative comparison of the elongational viscosity curves as a function of elongation rate and the corresponding molecular-model behavior (cf. Table 14.4-2 for $\bar{\eta}$ vs. $\dot{\varepsilon}$ for rigid dumbbells).

§16.6 STEADY FLOWS FOR FREE-DRAINING KIRKWOOD-RISEMAN BEAD-ROD CHAINS

The Kirkwood–Riseman freely rotating chain model differs from the Kramers chain discussed in the previous section in that the angles between successive rods are fixed. In this discussion we take all of these angles to be the same and equal to ξ as shown in Fig. 11.2-1.

[6] S. T. J. Peng and R. F. Landel, *Rheology*, Vol. 2, Plenum Press, New York (1980), pp. 385–391; the fluids used in their experiments were not dilute and some entanglement effects must have been present. See also fn. 15 of §13.5.

To describe this system we first consider an "embedded" coordinate system in which the z-axis with associated unit vector $\check{\boldsymbol{\delta}}_3$ is in the direction of the unit vector $\boldsymbol{u}_1$. The unit vector $\check{\boldsymbol{\delta}}_1$ is then normal to $\check{\boldsymbol{\delta}}_3$ and in the plane containing the first and second links with $(\check{\boldsymbol{\delta}}_1 \cdot \boldsymbol{u}_2)$ being positive. A third unit vector is chosen so that the vectors $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$ form a right-handed set. The Euler angles describing the orientation of this embedded $\check{\boldsymbol{\delta}}_1$, $\check{\boldsymbol{\delta}}_2$, $\check{\boldsymbol{\delta}}_3$-frame are taken as the first three generalized coordinates, $Q_1 = \alpha$, $Q_2 = \beta$, and $Q_3 = \gamma$; these are the angles labelled ξ_{01}, ξ_1, and ξ_{12} in Fig. 11.6-1. The coordinates ξ_1 and ξ_{01} are also the same as the polar angles θ_1 and ϕ_1, respectively, of the unit vector $\boldsymbol{u}_1$. The remaining $N - 3$ generalized coordinates, Q_4, Q_5, $Q_6, \ldots, Q_N$ are the angles between the planes containing successive pairs of links, the angles $\xi_{23}, \xi_{34}, \ldots, \xi_{N-2,N-1}$ of Fig. 11.6-1; each of these angles goes from 0 to 2π.

The (Ω_{mn})-matrix, defined by Eq. 16.1-1, is an orthogonal matrix, which describes the relation between the space-fixed and body-fixed axes. The matrix elements can be written as the scalar products of the unit vectors associated with the two coordinate systems:

$$\Omega_{mn} = (\check{\boldsymbol{\delta}}_m \cdot \boldsymbol{\delta}_n) \tag{16.6-1}$$

We may also define a tensor $\boldsymbol{\Omega}$, which has components Ω_{mn} in the space-fixed frame:

$$\begin{aligned} \boldsymbol{\Omega} &= \sum_m \sum_n \boldsymbol{\delta}_m \boldsymbol{\delta}_n \Omega_{mn} \\ &= \sum_n \boldsymbol{\delta}_n \check{\boldsymbol{\delta}}_n \end{aligned} \tag{16.6-2}$$

The tensor $\boldsymbol{\Omega}$ converts the space-fixed unit vectors to the body-fixed unit vectors according to $[\boldsymbol{\delta}_n \cdot \boldsymbol{\Omega}] = \check{\boldsymbol{\delta}}_n$.

It is now convenient to introduce a set of orthogonal matrices with elements $\Omega_{mn}^{(k)}$, which are scalar products of unit vectors associated with neighboring links in the chain

$$\Omega_{mn}^{(k)} = (\boldsymbol{\delta}_m^{(k)} \cdot \boldsymbol{\delta}_n^{(k-1)}) \tag{16.6-3}$$

The orthonormal triad of unit vectors $\boldsymbol{\delta}_1^{(k)}$, $\boldsymbol{\delta}_2^{(k)}$, $\boldsymbol{\delta}_3^{(k)}$ is identical to the triad of unit vectors $\boldsymbol{s}_k$, $\boldsymbol{t}_k$, $\boldsymbol{u}_k$ introduced in §11.6; the unit vectors $\boldsymbol{\delta}_n^{(0)}$ are identical to the space-fixed unit vectors $\boldsymbol{\delta}_n$. The $\Omega_{mn}^{(k)}$, with $k > 1$, are given by the matrix of Eq. 16.1-2, but with α, β, γ replaced by $\xi_{k-1,k}$, ξ, 0 respectively; and $\Omega_{mn}^{(1)}$ is given by the same matrix with α, β, γ replaced by ξ_{01}, ξ_1, 0. Next we define a set of tensors $\boldsymbol{\Omega}^{(k)}$, which have components $\Omega_{mn}^{(k)}$ with respect to axes corresponding to the unit vectors $\boldsymbol{\delta}_m^{(k)}$, so that

$$\begin{aligned} \boldsymbol{\Omega}^{(k)} &= \sum_m \sum_n \boldsymbol{\delta}_m^{(k)} \boldsymbol{\delta}_n^{(k)} \Omega_{mn}^{(k)} \\ &= \sum_n \boldsymbol{\delta}_n^{(k-1)} \boldsymbol{\delta}_n^{(k)} \end{aligned} \tag{16.6-4}$$

Note further that $[\boldsymbol{\delta}_n^{(k-1)} \cdot \boldsymbol{\Omega}^{(k)}] = \boldsymbol{\delta}_n^{(k)}$. The parallelism between this paragraph and the foregoing one should be evident.

The vector from the center of mass of the chain to bead v is given by an expression identical to that for the Kramers chain (see Eq. 16.5-2):

$$\boldsymbol{R}_v = a \sum_k B_{vk} \boldsymbol{u}_k \tag{16.6-5}$$

(where $\boldsymbol{u}_k$ is identical to $\boldsymbol{\delta}_3^{(k)}$). As pointed out just after Eq. 16.6-4, $\boldsymbol{u}_k = [\boldsymbol{u}_{k-1} \cdot \boldsymbol{\Omega}^{(k)}]$; when this relation is applied recursively we get

$$\boldsymbol{u}_k = [\boldsymbol{\delta}_3 \cdot \boldsymbol{\Omega}^{(1)} \cdot \boldsymbol{\Omega}^{(2)} \cdot \cdots \cdot \boldsymbol{\Omega}^{(k-1)} \cdot \boldsymbol{\Omega}^{(k)}] \tag{16.6-6}$$

Then using the relation following Eq. 16.6-2, we get

$$\boldsymbol{u}_k = [\check{\boldsymbol{\delta}}_3 \cdot \boldsymbol{\Omega}^{-1} \cdot \boldsymbol{\Omega}^{(1)} \cdot \boldsymbol{\Omega}^{(2)} \cdot \cdots \cdot \boldsymbol{\Omega}^{(k-1)} \cdot \boldsymbol{\Omega}^{(k)})] \tag{16.6-7}$$

Next we define a tensor $\tilde{\boldsymbol{\Omega}}^{(2)}$ closely related to $\boldsymbol{\Omega}^{(2)}$

$$\tilde{\boldsymbol{\Omega}}^{(2)} = \{\boldsymbol{\Omega}^{-1} \cdot \boldsymbol{\Omega}^{(1)} \cdot \boldsymbol{\Omega}^{(2)}\} = \sum_m \check{\boldsymbol{\delta}}_m \boldsymbol{\delta}_m^{(2)} \tag{16.6-8}$$

The components of this tensor in the coordinate system with unit vectors $\boldsymbol{\delta}_n^{(2)}$ are $\tilde{\Omega}_{mn}^{(2)} = (\boldsymbol{\delta}_m^{(2)} \cdot \check{\boldsymbol{\delta}}_n)$, whereas the components of $\boldsymbol{\Omega}^{(2)}$ in the same frame are $\Omega_{mn}^{(2)} = (\boldsymbol{\delta}_m^{(2)} \cdot \boldsymbol{\delta}_n^{(1)})$. Hence the $\Omega_{mn}^{(2)}$ are given by Eq. 16.1-2 with α, β, γ replaced by 0, ξ, 0.

As defined in Eq. 16.1-3, the R_{vn} are the components of $\boldsymbol{R}_v$ in the body-fixed frame. Hence from Eqs. 16.6-5 through 8 we get

$$\begin{aligned} R_{vn} = {} & aB_{v1}\delta_{n3} + aB_{v2}(\check{\boldsymbol{\delta}}_n \check{\boldsymbol{\delta}}_3 : \tilde{\boldsymbol{\Omega}}^{(2)}) \\ & + a \sum_{k=3}^{N-1} B_{vk}(\check{\boldsymbol{\delta}}_n \check{\boldsymbol{\delta}}_3 : \{\tilde{\boldsymbol{\Omega}}^{(2)} \cdot \boldsymbol{\Omega}^{(3)} \cdots \boldsymbol{\Omega}^{(k-1)} \cdot \boldsymbol{\Omega}^{(k)}\}) \end{aligned} \tag{16.6-9}$$

When this expression is written more explicitly using Eqs. 16.6-3, 4, and 8 one finds that

$$R_{vn} = a[B_{v1}\delta_{n3} + B_{v2}\tilde{\Omega}_{3n}^{(2)} + B_{v3}\sum_m \Omega_{3m}^{(3)}\tilde{\Omega}_{mn}^{(2)} + B_{v4}\sum_{mp} \Omega_{3p}^{(4)}\Omega_{pm}^{(3)}\tilde{\Omega}_{mn}^{(2)} + \cdots] \tag{16.6-10}$$

From Eq. 16.1-2 it may be shown that derivative of Ω_{mn} with respect to the first Euler angle is

$$\frac{\partial}{\partial \alpha} \Omega_{mn} = \sum_p \Omega_{mp}\varepsilon_{pn3} \tag{16.6-11}$$

Because the $\Omega_{mn}^{(k)}$ are given by the same matrix as Ω_{mn} in Eq. 16.1-2, but with α, β, γ replaced by $\xi_{k-1,k}$, ξ, 0 (or Q_{k+1}, ξ, 0), it follows at once that ($k \geq 3$)

$$\frac{\partial}{\partial Q_{k+1}} \Omega_{mn}^{(k)} = \sum_p \Omega_{mp}^{(k)}\varepsilon_{pn3} \tag{16.6-12}$$

We have now accumulated enough information to get expressions for the b^{vun} of Eq. 16.1-9 for the Kirkwood–Riseman chain.

From the definition of the b^{vun} we find for $u \geq 4$

$$\begin{aligned} b^{vun} = a\sqrt{m}\Bigg[& B_{v,u-1} \sum_{m,\ldots,r,s} \left(\frac{\partial}{\partial Q_u} \Omega_{3s}^{(u-1)}\right) \Omega_{sr}^{(u-2)} \cdots \tilde{\Omega}_{mn}^{(2)} \\ & + B_{vu} \sum_{m,\ldots,p,r,s} \Omega_{3s}^{(u)} \left(\frac{\partial}{\partial Q_u} \Omega_{sr}^{(u-1)}\right) \Omega_{rp}^{(u-2)} \cdots \tilde{\Omega}_{mn}^{(2)} + \cdots \Bigg] \end{aligned} \tag{16.6-13}$$

Then using the definition for $\tilde{\Omega}_{mn}^{(2)}$ and $\Omega_{mn}^{(k)}$ above we find that, for $u \geq 4$

$$b^{vun} = \sqrt{m}(\boldsymbol{R}_{vu} \cdot \boldsymbol{\Lambda}^{(u)} \cdot \check{\boldsymbol{\delta}}_n) \tag{16.6-14}$$

where

$$\boldsymbol{\Lambda}^{(u)} = \boldsymbol{\delta}_1^{(u-2)}\boldsymbol{\delta}_2^{(u-2)} - \boldsymbol{\delta}_2^{(u-2)}\boldsymbol{\delta}_1^{(u-2)} \tag{16.6-15}$$

$$\boldsymbol{R}_{vu} = a \sum_{v=u-1}^{N-1} B_{vv}\boldsymbol{u}_v \tag{16.6-16}$$

The expression for the b^{vun} for $u \geq 4$ may also be written as

$$b^{vun} = \sqrt{m}([\boldsymbol{v}_u \times \boldsymbol{R}_{vu}] \cdot \check{\boldsymbol{\delta}}_n) \tag{16.6-17}$$

in which $\boldsymbol{v}_u = \boldsymbol{u}_{u-2}$. Equation 16.6-17 can be made valid for $u \leq 3$ by extending the definition of $\boldsymbol{R}_{vu}$

$$\boldsymbol{R}_{vu} = a \sum_{v=1}^{N-1} B_{vv}\boldsymbol{u}_v = \boldsymbol{R}_v \tag{16.6-18}$$

and letting $\boldsymbol{v}_u = -\check{\boldsymbol{\delta}}_u$.

Using Eq. 16.6-17 in the definition of the elements of the generalized moment of inertia matrix, one finds that the elements are

$$\begin{aligned}\Gamma_{uv} &= m \sum_v ([\boldsymbol{v}_u \times \boldsymbol{R}_{vu}] \cdot [\boldsymbol{v}_v \times \boldsymbol{R}_{vv}]) \\ &= m \sum_v [(\boldsymbol{v}_u \cdot \boldsymbol{v}_v)(\boldsymbol{R}_{vu} \cdot \boldsymbol{R}_{vv}) - (\boldsymbol{v}_v \cdot \boldsymbol{R}_{vu})(\boldsymbol{v}_u \cdot \boldsymbol{R}_{vv})]\end{aligned} \tag{16.6-19}$$

Thus one sees that in determining the elements of the generalized moment of inertia matrix, in which at least one index is associated with a generalized coordinate rather than an Euler angle, the vector $\boldsymbol{R}_{vu}$ replaces the vector $\boldsymbol{R}_v$ and the unit vector $\boldsymbol{v}_u$ replaces the unit vector $\check{\boldsymbol{\delta}}_u$ of the body-fixed axes. From the last result it may be shown that the elements of the generalized moment of inertia matrix are for $s, u \leq 3$

$$\Gamma_{su} = ma^2 \sum_{v=1}^{N-1} \sum_{w=1}^{N-1} C_{vw}[\delta_{su}(\boldsymbol{u}_v \cdot \boldsymbol{u}_w) - (\check{\boldsymbol{\delta}}_u \cdot \boldsymbol{u}_v)(\check{\boldsymbol{\delta}}_s \cdot \boldsymbol{u}_w)] \tag{16.6-20}$$

and for $s \leq 3$, $u \geq 4$

$$\Gamma_{su} = -ma^2 \sum_{v=1}^{N-1} \sum_{w=u-1}^{N-1} C_{vw}[(\check{\boldsymbol{\delta}}_s \cdot \boldsymbol{v}_u)(\boldsymbol{u}_v \cdot \boldsymbol{u}_w) - (\boldsymbol{v}_u \cdot \boldsymbol{u}_v)(\check{\boldsymbol{\delta}}_s \cdot \boldsymbol{u}_w)] \tag{16.6-21}$$

and for $s, u \geq 4$

$$\Gamma_{su} = ma^2 \sum_{v=s-1}^{N-1} \sum_{w=u-1}^{N-1} C_{vw}[(\boldsymbol{v}_s \cdot \boldsymbol{v}_u)(\boldsymbol{u}_v \cdot \boldsymbol{u}_w) - (\boldsymbol{v}_u \cdot \boldsymbol{u}_v)(\boldsymbol{v}_s \cdot \boldsymbol{u}_w)] \tag{16.6-22}$$

The elements of the metric matrix, g_{su}, are given in terms of these elements by Eq. 16.1-10.

a. Equilibrium

The equilibrium configurational distribution function is given by Eq. 12.3-4, a consequence of the canonical distribution in phase space. For the freely rotating chain model the intramolecular potential is zero, so that

$$\psi_{eq} = \frac{\sqrt{g}}{\int \sqrt{g}\, dQ} = \frac{\sqrt{\Gamma} \sin \beta}{8\pi^2 \int \sqrt{\Gamma}\, dQ'} \tag{16.6-23}$$

Here $\int \ldots dQ$ indicates integration over all the generalized coordinates (Q_1 to Q_N), and $\int \ldots dQ'$ is the integration over Q_4 to Q_N (i.e., ξ_{23} to $\xi_{N-2,N-1}$); the quantity Γ is the determinant of the generalized moment-of-intertia tensor (see Eq. J of Table 16.1-1).

It is interesting to compare the above expression for ψ_{eq} with that which one obtains by considering a "modified random walk" distribution. In this modified random walk one considers a sequence of N vectors, each of length a. The angle between successive vectors is fixed at ξ, but the point on the circle determined by this fixed angle is taken to be random. Using this modified random walk, Eyring[1] obtained an equilibrium distribution function which in the present notation is

$$\psi_{eq} = \frac{\sin \beta}{8\pi^2 \int_0^{2\pi} \cdots \int_0^{2\pi} d\xi_{23} \cdots d\xi_{N-2,N-1}} = \frac{\sin \beta}{2(2\pi)^{N-1}} \quad \text{(modified random walk)} \tag{16.6-24}$$

This differs from the expression in Eq. 16.6-23 by a factor of $\sqrt{\Gamma}$ (and the concomitant change in the normalization constant). For $N = 3$, that is, three beads and two rods, there are no generalized coordinates other than the Euler angles, and Γ is a constant. Thus for this case the two distributions are identical; but for larger values of N they differ.

For $N = 4$, the four bead-three rod chain, Fan and Liu[2] have developed an explicit expression for Γ and investigated the difference between the distribution functions in Eqs. 16.6-23 and 16.6-24. For $\xi = \arccos(\frac{1}{3})$, the two functions, each divided by $(\sin \beta)/8\pi^2$, are shown in Fig. 16.6-1 as functions of $Q_4 = \xi_{23}$, the angle between the planes containing the first two and the last two rods. The modified random walk value is $1/2\pi$; the distribution function obtained from Eq. 16.6-2 is symmetric about $\xi_{23} = \pi$ with maxima at 0.525π and 1.475π, and local minima at 0 and π. The maxima are 14.5% higher than the random walk value, and the minima are 9.4 and 21.1% lower.

For $N = 5$ ψ_{eq} is a function of two angles, ξ_{23} and ξ_{34}. For the special case of $\xi = \arccos(\frac{1}{3})$ a plot of $8\pi^2\psi_{eq}/\sin \beta$ is given in Fig. 16.6-2. It is clear that there are appreciable deviations from the random walk value.

The equilibrium average of the square of the end-to-end distance of Rouse chains is evaluated in Example 11.4-1. Fan and Liu[2] have evaluated this quantity for freely rotating chains consisting of 8 or fewer beads. Their results are compared with the random walk

[1] H. Eyring, *Phys. Rev.*, **39**, 746–748 (1932); the random-walk distribution has been used for getting the mean square end-to-end distances and other properties by L. R. G. Treloar, *The Physics of Rubber Elasticity*, 2nd ed., Oxford University Press, New York (1958), p. 46; M. Volkenstein, *Configurational Statistics of Polymer Chains*, Interscience, New York (1963); P. J. Flory, *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York (1969), pp. 16–18, 326–333; H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), pp. 35–37. None of these references concern themselves with Eq. 16.6-23, which comes from applying equilibrium statistical mechanics to the Kirkwood–Riseman chain model.

[2] X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303–321 (1986).

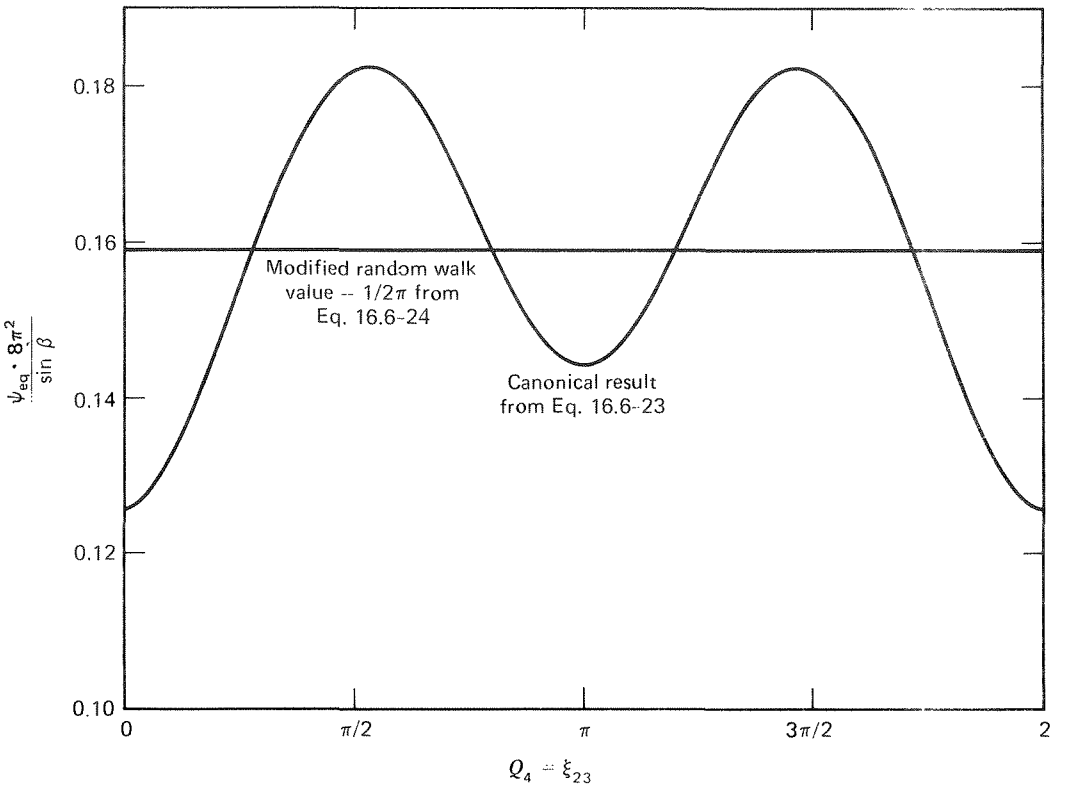


FIGURE 16.6-1. Equilibrium configurational distribution function for the Kirkwood-Riseman chain with four beads and three rods. Reproduced from X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303-321 (1986).

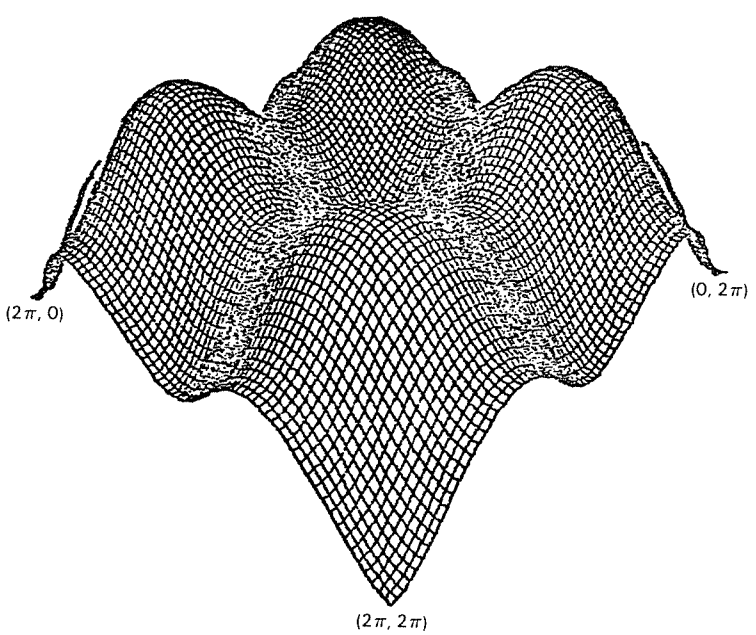


FIGURE 16.6-2. Equilibrium configurational distribution function for the Kirkwood-Riseman chain with five beads and four rods. Reproduced from X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303-321 (1986).

TABLE 16.6-1[a]

Quantities Computed For the Free-Draining Kirkwood-Riseman Chain [with $\xi = \arccos \frac{1}{3}$]

Quantity	Number of Beads, N	Canonical[b]	Random Walk[c]	Ratio
Mean square	3	2.667	2.667	1.000
end-to-end	4	4.601	4.556	0.9901
distance	5	6.621	6.519	0.9846
$\langle r^2 \rangle_{eq}/a^2$	6	8.671	8.506	0.9811
	7	10.727	10.502	0.9790
	8	12.783	12.501	0.9779
Zero-shear-rate	3	0.25926	0.25926	1.0000
viscosity	4	0.53894	0.53704	0.9965
$(\eta_0 - \eta_s)/n\zeta a^2$	5	0.92720	0.92099	0.9933
	6	1.4268	1.4132	0.9905
	7	2.0390	2.0149	0.9882
	8	2.7643	2.7266	0.9863
Zero-shear-rate	3	0.02551	0.02551	1.0000
first-normal-stress	4	0.10150	0.10062	0.9913
coefficient	5	0.29630	0.29284	0.9883
$\Psi_{1,0}kT/2n\zeta^2a^4$	6	0.70472	0.69496	0.9862
	7	1.4525	1.4299	0.9844
	8	2.6967	2.6506	0.9829

[a] X. J. Fan and T. W. Liu, *J. Non-Newtonian Fluid Mech.*, **19**, 303-321 (1986).
[b] From Eq. 16.6-23.
[c] From Eq. 16.6-24.

values in Table 16.6-1. It is interesting to note that the deviation of the ratio of these two numbers from unity increases monotonically with N for $N \leq 8$; the behavior for larger values of N is not known.

b. Second-Order Fluid Constants

It was pointed out in the previous section that one may use the methods developed in §16.4 to evaluate the second order fluid constants b_1 and b_2, once one knows the equilibrium configurational distribution function. Fan and Liu[2] have evaluated b_1 and b_2 for freely rotating chains with 3 and 4 beads analytically and for $N \leq 8$ numerically. For $N = 3$ they find that

$$\frac{(b_1 - \eta_s)}{n\zeta a^2} = \frac{1}{9}(2 + \cos \xi) \tag{16.6-25}$$

$$\frac{-b_2 kT}{n\zeta^2 a^4} = \frac{1}{540}(7 + 16 \cos \xi + 13 \cos^2 \xi) \tag{16.6-26}$$

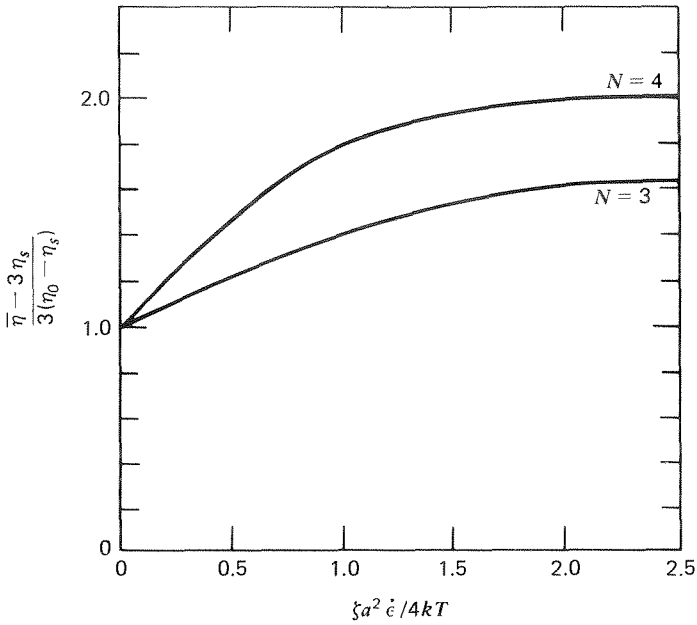


FIGURE 16.6-3. Elongational viscosity for Kirkwood–Riseman chains with three and four beads.

The values which they obtained for chains with $N \leq 8$ and with $\xi = \arccos(\frac{1}{3})$ are compared with the values obtained using the random walk distribution in Table 16.6-1. Again, it is interesting to note that the deviation of the ratio of these values from unity grows with increasing N.

c. Elongational Viscosity

Fan and Liu[2] have also computed the steady state elongational viscosity for freely rotating chains of three and four beads. The values which they obtained are illustrated in Fig. 16.6-3 as plots of the reduced elongational viscosity $(\bar{\eta} - 3\eta_s)/3(\eta_0 - \eta_s)$ as functions of a dimensionless elongation rate $\dot{\epsilon}\zeta a^2/4kT$. For both $N = 3$ and $N = 4$ the reduced elongational viscosity increases monotonically with elongation rate, apparently approaching a limit as $\dot{\epsilon} \to \infty$. Comparison of the curves in Fig. 16.6-3 with the Kramers chain results in Fig. 16.5-1 and in Eq. 16.5-28 suggests that incorporation of "chain stiffness" into the chain model (by fixing the angles between pairs of adjacent rods) lowers the limiting value of $\bar{\eta}$ as $\dot{\epsilon} \to \infty$. Unfortunately there are no experimental data on $\bar{\eta}$ for dilute solutions of polymer chains of varying backbone stiffness.

§16.7 UNSTEADY FLOWS FOR FREE-DRAINING BEAD-ROD MODELS

In this section we present a general framework[1] for obtaining the relaxation modulus of linear viscoelasticity for bead-rod models with identical beads and no internal potentials. The method summarized in Eqs. 16.7-12 to 16.7-15 is in principle applicable to

[1] O. Hassager, *J. Chem. Phys.*, **60**, 4001–4008 (1974).

flexible bead-rod models of arbitrary complexity although it is practical only for models with a small number of degrees of freedom.

Let us introduce a homogeneous periodic potential flow of the form

$$\boldsymbol{\kappa} = \boldsymbol{\kappa}_0 \, \mathscr{R}e\{e^{i\omega t}\} \tag{16.7-1}$$

in which $\boldsymbol{\kappa}_0 = \boldsymbol{\kappa}_0^\dagger$ and $(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{1/2} \ll kT/\zeta L^2$ where L designates any fixed length characteristic of the model. Under the linear conditions considered here, the distribution function ψ will be of the form

$$\psi = \frac{1}{J} g^{1/2}[1 + \mathscr{R}e\{\phi_1 e^{i\omega t}\} + \cdots] \tag{16.7-2}$$

Here J is a normalization constant, and ϕ_1, which is a function of the generalized coordinates and linear in $(\zeta L^2/kT)(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{1/2}$, may be complex, thus allowing for a phase lag. When this expression is introduced in the general diffusion equation for ψ (Eq. 16.2-6), it follows that for potential flow ϕ_1 must be a solution of

$$\left(\frac{kT}{\zeta L^2}\right)\nabla^2\phi_1 - i\omega\phi_1 = (1/2L^2)\nabla^2\left(\boldsymbol{\kappa}_0 : \sum_v \boldsymbol{R}_v\boldsymbol{R}_v\right) \tag{16.7-3}$$

In Eq. 16.7-3 we use the notation ∇^2 for the Laplacian operator in the configuration space defined by

$$\nabla^2\Lambda = mL^2 g^{-1/2} \sum_t \sum_u \frac{\partial}{\partial Q_t}\left(g^{1/2} G_{tu} \frac{\partial}{\partial Q_u}\Lambda\right) \tag{16.7-4}$$

In order to solve Eq. 16.7-3 we consider first the "Helmholtz equation" in the configuration space

$$\nabla^2 f + \nu f = 0 \tag{16.7-5}$$

This equation has nontrivial solutions for a set of real, non-negative eigenvalues $\nu = \nu_p$. The corresponding eigenfunctions $f = f_p$ are orthogonal with respect to the weighting function $g^{1/2}$ and may be normalized such that

$$\int \bar{f}_p f_q g^{1/2}\, dQ = \delta_{pq} \tag{16.7-6}$$

where the bar on f_p indicates a complex conjugate. We now expand ϕ_1 and $(\boldsymbol{\kappa}_0 : \Sigma_v \boldsymbol{R}_v\boldsymbol{R}_v)$ as follows:

$$\phi_1 = \sum_{p=0}^{\infty} A_p f_p \tag{16.7-7}$$

$$\left(\boldsymbol{\kappa}_0 : \sum_v \boldsymbol{R}_v\boldsymbol{R}_v\right) = (\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{1/2} L^2 \sum_{p=0}^{\infty} \alpha_p f_p \tag{16.7-8}$$

where the A_p and the α_p are independent of the generalized coordinates. Using the orthogonality of the eigenfunctions we may solve the latter equation formally for α_p to get

$$\alpha_p = (\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{-1/2} L^{-2} \left(\boldsymbol{\kappa}_0 : \int \sum_{\nu} R_\nu R_\nu \bar{f}_p g^{1/2}\, dQ \right) \tag{16.7-9}$$

When Eqs. 16.7-7 and 8 are introduced in the linearized diffusion equation Eq. 16.7-3, we may solve the resulting equation for the expansion coefficients A_p. The final result is that the distribution function *in the linear range* considered may be formally written

$$\psi = \frac{1}{J_{eq}} g^{1/2} \left[1 + \frac{\zeta}{2} (\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)^{1/2} L^2 \mathscr{R}e \left\{ \sum_{p=0}^{\infty} \frac{\alpha_p \nu_p f_p e^{i\omega t}}{\nu_p kT + i\omega\zeta L^2} \right\} + \cdots \right] \tag{16.7-10}$$

where

$$J_{eq} = \int g^{1/2}\, dQ \tag{16.7-11}$$

The distribution function in Eq. 16.7-10 must now be introduced in the expression for the stress tensor Eq. 16.3-11 to obtain the rheological response of the suspension to the imposed velocity gradient. After a lengthy development the result may be recast in terms of the relaxation modulus $G(s)$ of linear viscoelasticity (or the G_I of the memory-integral expansion in Eq. 9.6-12) as follows:

$$G(s) = 2\eta_s \delta(s) + n\zeta L^2 a \delta(s) + nkT \sum_{p=0}^{\infty} b_p e^{-s/\lambda_p} \tag{16.7-12}$$

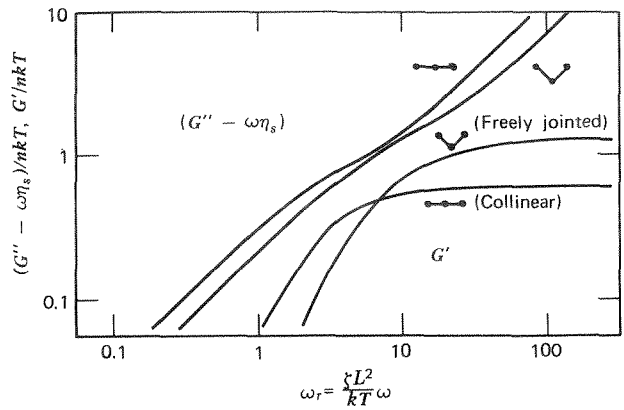
$$a = \frac{1}{J_{eq}} \left[\left(\frac{1}{3L^2} \sum_{\nu} \int (\boldsymbol{R}_\nu \cdot \boldsymbol{R}_\nu) g^{1/2}\, dQ \right) - \frac{1}{4} \sum_{p=0}^{\infty} |\alpha_p|^2 \nu_p \right] \tag{16.7-13}$$

$$b_p = \frac{1}{8J_{eq}} |\alpha_p|^2 \nu_p^2 \tag{16.7-14}$$

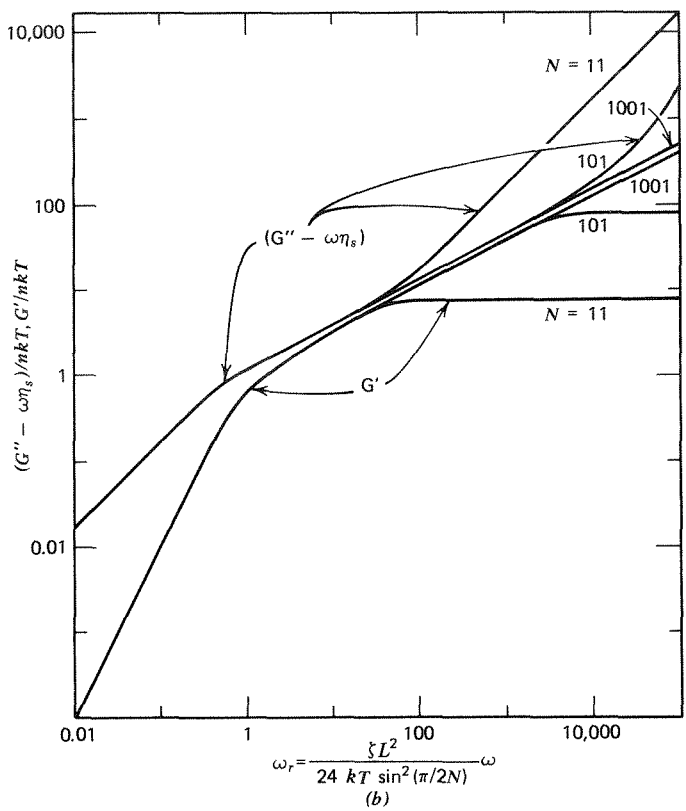
$$\lambda_p = \frac{\zeta L^2}{\nu_p kT} \tag{16.7-15}$$

Thus we see that the relaxation modulus of linear viscoelasticity for arbitrary bead-rod models with no internal potentials may be determined by the following sequence of steps:

- **i.** The metric tensor components g_{tu} and G_{tu} and the determinant g of §16.1 must be calculated in terms of a set of generalized coordinates and a model-fixed reference length L.
- **ii.** The Helmholtz equation given in Eqs. 16.7-4 and 5 must be formulated and solved for the eigenvalues ν_p and eigenfunctions f_p.
- **iii.** The expansion coefficients α_p must be determined from the eigenfunctions f_p by use of Eq. 16.7-8 or 16.7-9 with any arbitrary symmetrical $\boldsymbol{\kappa}_0$. Then the relaxation modulus $G(s)$ is given by Eqs. 16.7-12 to 16.7-15.



(a)



(b)

FIGURE 16.7-1. The dynamic moduli G' and G'' for various chainlike bead-rod models of N identical beads with friction coefficients ζ joined by rigid rods of length a: (*a*) Results of O. Hassager, *J. Chem. Phys.*, **60**, 4001–4008 (1974) for $N = 3$ comparing the freely jointed three-bead model with the three-bead model in which the rods are required to be collinear. (*b*) Results of M. Fixman and J. Kovac, *J. Chem. Phys.*, **61**, 4950–4954 (1974) for freely jointed chains with large values of N.

The fluid response in any arbitrary linear viscoelastic experimcnt may in principle be calculated from the relaxation modulus $G(s)$ as illustrated in Chapter 5. In Fig. 16.7-1a we show the dynamic moduli G' and G'' for a free-draining chainlike bead-rod model with $N = 3$ as calculated by the above procedure. Furthermore Fixman and Kovac[2] have recalculated the dynamic moduli for a chainlike model with three beads by using a method in which the constant bond lengths are incorporated by the use of infinitely stiff springs. The dynamic moduli as calculated by these two methods agree within about 1% over the entire frequency range; these results therefore provide additional evidence in favor of the suggestion in §16.5 that the practical difference between the two different methods of treating constraints is small, at least in the linear range.

The method of Fixman and Kovac is efficient for models with a large number of degrees of freedom. Thus in Fig. 16.7-1b we show the Fixman–Kovac[2] results for the dynamic moduli of free-draining chainlike bead-rod models for various large values of N. We see that the results are in good qualitative agreement with the data in Fig. 13.5-3. In particular we see that $G''(\omega) - \omega\eta_s$ increases linearly with ω at high frequencies or equivalently that the dynamic viscosity $\eta'(\omega) - \eta_s$ approaches a limiting value larger than zero at high frequencies. This important qualitative feature is not predicted by the Rouse–Zimm molecular theories discussed in Chapter 15. As is shown in Problem 16C.5 the nonzero plateau value of $\eta'(\omega) - \eta_s$ at high frequencies is related to the constraints or "stiff" potentials that keep bond lengths and bond angles nearly constant. There may, however, be other factors such as excluded volume effects that could be responsible for the observed nonzero limiting value of the polymer contribution to the dynamic viscosity.

We conclude this section with an example that illustrates the use of the method given here for obtaining the relaxation modulus for bead-rod models.

EXAMPLE 16.7-1 Calculation of the Relaxation Modulus for Arbitrary Rigid Axisymmetrical Bead-Rod Models

Consider a rigid collection of identical beads (each with mass m) with two principal moments of inertia equal. It is desired to find the relaxation modulus of linear viscoelasticity for this model in terms of the principal moments of inertia, $I_1 (= I_2)$ and I_3.

SOLUTION We use the method outlined in the text above.

i. First, we install a triad of unit vectors $\check{\boldsymbol{\delta}}_m$ fixed in the model such that $\check{\boldsymbol{\delta}}_3$ is along the axis of symmetry of the moment of inertia ellipsoid. As generalized coordinates for the model we use the three Euler angles specifying the orientation of the model-fixed unit vectors $\check{\boldsymbol{\delta}}_m$ with respect to a set of space-fixed unit vectors $\boldsymbol{\delta}_m$. The position vector $\boldsymbol{R}_v$ of the vth bead with respect to the center of mass may then be expressed by

$$\boldsymbol{R}_v = \sum_m \check{\boldsymbol{\delta}}_m R_{vm} \tag{16.7-16}$$

The principal moments of inertia, I_1 and I_3, are then

$$I_1 = m \sum_v (R_{v2}^2 + R_{v3}^2) \tag{16.7-17}$$

$$I_3 = 2m \sum_v R_{v1}^2 \tag{16.7-18}$$

[2] M. Fixman and J. Kovac, *J. Chem. Phys.*, **61**, 4950–4954 (1974).

We may now specify the various configurational quantities for the model using the framework given in Table 16.1-1. In particular we need the results that

$$g = I_1^2 I_3 S^2 \tag{16.7-19}$$

and

$$(G_{uv}) = \begin{pmatrix} I_1^{-1}S^{-2} & 0 & -I_1^{-1}S^{-2}C \\ 0 & I_1^{-1} & 0 \\ -I_1^{-1}S^{-2}C & 0 & I_1^{-1}S^{-2}C^2 + I_3^{-1} \end{pmatrix} \tag{16.7-20}$$

where $S = \sin\beta$ and $C = \cos\beta$. Furthermore from Eqs. 16.7-11 and 16.7-19 we find that

$$J_{eq} = 8\pi^2 I_1 I_3^{1/2} \tag{16.7-21}$$

ii. Second, we need to formulate the Helmholtz equation for the configuration space distribution function from the determinant g and the components of the contravariant metric matrix G_{uv}. From Eqs. 16.7-4, 5, 19, and 20 we find after some reduction

$$\frac{mL^2}{I_1}\left\{\frac{\partial^2 f}{\partial\beta^2} + \frac{C}{S}\frac{\partial f}{\partial\beta} + \frac{1}{S^2}\frac{\partial^2 f}{\partial\alpha^2} + \left[\left(\frac{C}{S}\right)^2 + \frac{I_1}{I_3}\right]\frac{\partial^2 f}{\partial\gamma^2} - 2\frac{C}{S^2}\frac{\partial^2 f}{\partial\alpha\partial\gamma}\right\} + vf = 0 \tag{16.7-22}$$

Equation 16.7-22 is identical to the quantum mechanical Schrödinger equation for the rotational wave function of a "symmetric top" molecule. The solutions of the equation which are everywhere finite[3] and also periodic in α and γ may be written in the form

$$f_{JKM} = \sqrt{\frac{2J+1}{8\pi^2 I_1 I_3^{1/2}}}\, D^J(\alpha, \beta, \gamma)_{KM} \tag{16.7-23}$$

The eigenvalues corresponding to these eigenfunctions are

$$v_{JKM} = \frac{mL^2}{I_1} J(J+1) + mL^2\left(\frac{1}{I_3} - \frac{1}{I_1}\right)K^2 \tag{16.7-24}$$

The indices J, K, and M may assume the following values:

$$\begin{aligned} J &= 0, 1, 2, 3, \ldots \\ K &= 0, \pm 1, \pm 2, \ldots, \pm J \\ M &= 0, \pm 1, \pm 2, \ldots, \pm J \end{aligned}$$

The functions $D^J(\alpha, \beta, \gamma)_{KM}$ are known as the representation coefficients of the three-dimensional rotation group, and are generalizations of the spherical harmonics to three angles. These functions are discussed in Appendix E, and the orthogonality relations they satisfy are given in Eq. E.12-4. From Eqs. E.12-4, 16.7-11, and 16.7-19 the normalization constant given in Eq. 16.7-23 can be derived.

[3] The solution given by O. Hassager, *J. Chem Phys.*, **60**, 4001–4008 (1974), was given in terms of the Jacobi polynomials.

iii. Third, we must consider the expansion coefficients α_{JKM} (called α_p in Eq. 16.7-9). For this purpose we consider the integral appearing on the right side of Eq. 16.7-9. It follows from Eq. 16.7-16 that this integral is

$$\sum_{\nu} \iiint \boldsymbol{R}_\nu \boldsymbol{R}_\nu f_{JKM} \sqrt{g}\, dQ_1\, dQ_2\, dQ_3 = \sqrt{\frac{(2J+1)}{8\pi^2}}\, I_1 I_3^{1/2} \sum_{\nu mn} R_{\nu m} R_{\nu n} \times \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \check{\boldsymbol{\delta}}_m \check{\boldsymbol{\delta}}_n D^J(\alpha, \beta, \gamma)_{KM} \sin\beta\, d\alpha\, d\beta\, d\gamma \quad (16.7\text{-}25)$$

The unit vectors $\check{\boldsymbol{\delta}}_m$, embedded in the rigid bead-rod structure, are functions of the Euler angles. These unit vectors are related to the space-fixed unit vectors according to Eq. 16.1-1. Hence the last expression becomes

$$\sqrt{\frac{(2J+1)}{8\pi^2}}\, I_1 I_3^{1/2} \sum_{\nu mnpq} R_{\nu m} R_{\nu n} \boldsymbol{\delta}_p \boldsymbol{\delta}_q \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} \Omega_{mp} \Omega_{nq} D^J(\alpha, \beta, \gamma)_{KM} \sin\beta\, d\alpha\, d\beta\, d\gamma \quad (16.7\text{-}26)$$

The rotation matrix elements Ω_{mn} are, however, closely related to the functions $D^J(\alpha, \beta, \gamma)_{KM}$ with $J = 1$ (they are both irreducible representations of degree 1). Using this relation, which is given by Eqs. E.12-5 and E.12-6, the integral in Eq. 16.7-26 then becomes

$$\sum_{K'K''M'M''} \overline{T}_{K'm} T_{M'p} \overline{T}_{K''n} T_{M''q} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} D^1_{K'M'} D^1_{K''M''} D^J_{KM} \sin\beta\, d\alpha\, d\beta\, d\gamma = 8\pi^2 \sum_{K'K''M'M''} \overline{T}_{K'm} T_{M'p} \overline{T}_{K''n} T_{M''q} \begin{pmatrix} 1 & 1 & J \\ K' & K'' & K \end{pmatrix} \begin{pmatrix} 1 & 1 & J \\ M' & M'' & M \end{pmatrix} \quad (16.7\text{-}27)$$

Here we have written the integrals in terms of quantities known as "3j-symbols" (see Eq. E.12-12). When this result is substituted into Eq. 16.7-25, we find that

$$\sum_{\nu} \iiint \boldsymbol{R}_\nu \boldsymbol{R}_\nu f_{JKM} \sqrt{g}\, dQ_1\, dQ_2\, dQ_3 = \sqrt{\frac{8\pi^2}{2J+1}}\, I_1 I_3^{1/2} \sum_{\nu mn} R_{\nu m} R_{\nu n} \Theta_{JK,mn} \bar{\boldsymbol{\Theta}}_{JM} \quad (16.7\text{-}28)$$

in which the $\boldsymbol{\Theta}_{JM}$ are the tensors defined by Eq. E.12-12 and the $\Theta_{JK,mn}$ are the elements of these tensors defined by Eq. E.12-13. This result is then substituted into Eq. 16.7-9 to obtain an expression for the expansion coefficients α_{JKM}

$$\alpha_{JKM} = \sqrt{\frac{8\pi^2}{2J+1}}\, I_1 I_3^{1/2} \frac{(\boldsymbol{\kappa}_0 : \bar{\boldsymbol{\Theta}}_{JM})}{\sqrt{(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)}} \frac{1}{L^2} \sum_{\nu mn} R_{\nu m} R_{\nu n} \Theta_{JK,mn} \quad (16.7\text{-}29)$$

The tensors $\boldsymbol{\Theta}_{JM}$ are nonzero only for $J = 0, 1, 2$; they are displayed in Table E.12-1. Because $\boldsymbol{\Theta}_{00}$ is a multiple of the unit tensor and because $\boldsymbol{\kappa}_0$ is traceless, we conclude that α_{000} is zero. The three tensors with $J = 1$ are antisymmetric, and since $\boldsymbol{\kappa}_0$ is symmetric, it is evident that the α_{1KM} are also zero. We thus know that the α_{JKM} are nonzero only for $J = 2$. Note that the $\boldsymbol{\Theta}_{2M}$ are all traceless and symmetric. From the explicit expressions for the $\boldsymbol{\Theta}_{2M}$ and Eqs. 16.7-17 and 16.7-18, we find that the sum in Eq. 16.7-29 is zero unless $K = 0$. Thus the only nonzero α_{JKM} are

$$\alpha_{20M} = \sqrt{8\pi^2 \cdot \tfrac{2}{15} \cdot I_1 I_3^{1/2}} \left(\frac{I_1 - I_3}{mL^2}\right) \frac{(\boldsymbol{\kappa}_0 : \bar{\boldsymbol{\Theta}}_{2M})}{\sqrt{(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0)}} \quad (16.7\text{-}30)$$

The corresponding eigenvalues are independent of M and are given by Eq. 16.7-24 as

$$\nu_{20M} = \frac{6mL^2}{I_1} \tag{16.7-31}$$

An arbitrary traceless symmetric tensor involves five independent coefficients and may therefore by written as a linear combination of the five independent tensors $\boldsymbol{\Theta}_{2K}$. This enables us to write $\boldsymbol{\kappa}_0$ as

$$\boldsymbol{\kappa}_0 = \sum_K a_K \boldsymbol{\Theta}_{2K} \tag{16.7-32}$$

where the a_K are the independent constants. It may be shown then, using Eq. E.12-14 that

$$(\boldsymbol{\kappa}_0 : \bar{\boldsymbol{\Theta}}_{2M}) = a_M \tag{16.7-33}$$

$$(\boldsymbol{\kappa}_0 : \boldsymbol{\kappa}_0) = \sum_K |a_K|^2 = 2\kappa_0^2 \tag{16.7-34}$$

in which the scalar κ_0 is the magnitude of the tensor $\boldsymbol{\kappa}_0$. One then finds from Eq. 16.7-30 that

$$\alpha_{20M} = \sqrt{\frac{I_1 I_3^{1/2}}{30}} \frac{4\pi(I_1 - I_3)}{mL^2} \frac{a_M}{\kappa_0} \tag{16.7-35}$$

and therefore

$$\sum_M |\alpha_{20M}|^2 = \frac{16\pi^2}{15}(I_1 - I_3)^2 \frac{I_1 I_3^{1/2}}{m^2 L^4} \tag{16.7-36}$$

This expression is clearly independent of the detailed form of $\boldsymbol{\kappa}_0$, and the eigenvalues given by Eq. 16.7-31 are independent of M. From these results it follows that the relaxation modulus given by Eq. 16.7-12 is independent of the flow field as, of course, the continuum theory requires.

With the results in Eqs. 16.7-16, 17, 18, 21, 31, and 36 we find from Eqs. 16.7-12 to 15 that the relaxation modulus for the general rigid collection of identical beads in which two of the principal moments of inertia are equal is:

$$G(s) = 2\eta_s \delta(s) + n\zeta L^2 a \delta(s) + nkTbe^{-s/\lambda} \tag{16.7-37}$$

in which

$$a = \frac{2I_1 + I_3}{6mL^2} - \frac{(I_1 - I_3)^2}{5mL^2 I_1}, \quad b = \frac{3(I_1 - I_3)^2}{5I_1^2}, \quad \lambda = \frac{\zeta L^2}{\nu kT} = \frac{\zeta I_1}{6mkT} \tag{16.7-38}$$

The principal moments of inertia, I_1 and I_3, must be determined for individual models from Eqs. 16.7-17 and 16.7-18. Values of a, b, and ν for several models are given in Table 16.7-1.

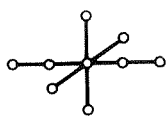
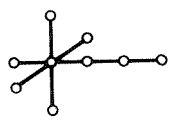
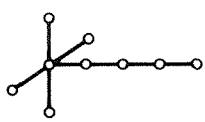
The relaxation modulus in Eq. 16.7-37 may be used to calculate the dynamic moduli of linear viscoelasticity defined in the text that follows Eq. D.5-5:

$$\frac{2G'(\omega)}{ankT\nu} = \frac{2b}{a\nu} \frac{(\lambda\omega)^2}{1 + (\lambda\omega)^2} \tag{16.7-39}$$

$$\frac{2[G''(\omega) - \omega\eta_s]}{ankT\nu} = \lambda\omega\left[1 + \frac{2b}{a\nu} \frac{1}{1 + (\lambda\omega)^2}\right] \tag{16.7-40}$$

TABLE 16.7-1

Values of a, b, and ν of Eq. 16.7-38 and of Fig. 16.7-2 for Several Axisymmetrical Models[a]

Model	Meaning of L	a	b	ν	$\frac{2b}{a\nu}$
Rigid dumbbell with two beads connected by a rod[b]	Length of rod	$\frac{1}{15}$	$\frac{3}{5}$	12	1.5000
Rigid plane polygon[c] of N beads connected by N rods of length b	Radius of circumscribed circle $L = \frac{b/2}{\sin(\pi/N)}$	$\frac{7}{30}N$	$\frac{3}{5}$	$12/N$	0.4286
Rigid tridumbbell (Doppelkreuzhantel[d]), formed by joining three identical rigid dumbbells at their midpoint in a mutually orthogonal configuration	Length of one dumbbell rod	$\frac{1}{2}$	0	6	0.0000
	Length of rod[e] between beads	$\frac{18}{5}$ 3.6000	$\frac{4}{15}$ 0.2666	$\frac{1}{2}$ 0.5000	0.2962
	Length of rod[e] between beads	4253/1080 3.9380	1587/5120 0.3100	27/64 0.4219	0.3732
	Length of rod[e] between beads	31082/6345 4.8987	4332/11045 0.3920	27/94 0.2872	0.5573

[a] Table from O. Hassager, *J. Chem. Phys.*, **60**, 4001–4008 (1974).
[b] R. B. Bird, H. R. Warner, Jr. and D. C. Evans, *Adv. Polym. Sci.*, **8**, 1–90 (1971).
[c] E. Paul and R. M. Mazo, *J. Chem. Phys.*, **51**, 1102–1107 (1969); for errata see C. Y. Mou and R. M. Mazo, *J. Chem. Phys.*, **67**, 5972–5973 (1977).
[d] H. Giesekus, *Rheol. Acta*, **2**, 101–112 (1962).
[e] C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (I. Prigogine and S. A. Rice, eds.) (1976).

These dimensionless moduli are shown in Fig. 16.7-2 for various values of $2b/a\nu$. The ordering parameter $2b/a\nu$ provides a measure of the extent to which the model deviates from a spherically symmetrical structure. The minimum value of $2b/a\nu$ is 0, which is obtained for spherically symmetrical structures such as the symmetric rigid tridumbbell, and the maximum value is $\frac{3}{2}$, which is obtained for long slender bodies such as the rigid dumbbell model or the multibead-rod model.

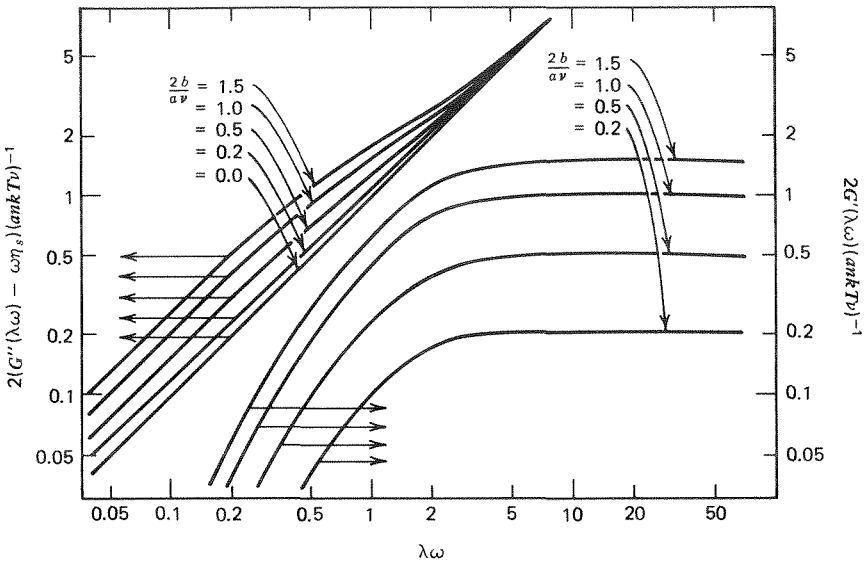


FIGURE 16.7-2. The dimensionless dynamic moduli of Eqs. 16.7-39 and 16.7-40 for axisymmetrical rigid models for various values of the ordering parameter $2b/av$. The parameters a, b, and v are determined from the principal moments of inertia of the molecule by Eq. 16.7-38. Values for sample models are given in Table 16.7-1. Reproduced from O. Hassager, *J. Chem. Phys.*, **60**, 4001–4008 (1974).

PROBLEMS

16B.1 Proof that b_2 in the Second Order Fluid is Negative

Show that Eq. 16.4-15 can be rewritten as

$$b_2 = -\frac{n}{40kT}\left\langle \sum_p \sum_q \left(K_{pq} - \frac{1}{3}\delta_{pq} \sum_r K_{rr} \right)^2 \right\rangle_{eq} \tag{16B.1-1}$$

and that therefore b_2 is negative (or zero) for dilute solutions of polymers modeled by arbitrary bead-rod-spring models with equilibrium-averaged hydrodynamic interaction.

16B.2 Second Normal-Stress Coefficient

Verify the statement after Eq. 16.3-20 that Eq. 16.3-20 predicts that the second normal-stress coefficient is zero in steady shear flow. How is this result used in §16.4? Is the nonzero Ψ_2 in Eq. 14.6-25 in conflict with the above cited statement?

16B.3 Configurational Distribution Function for Steady, Homogeneous, Potential Flow

Show how to go from the general expression in Eq. 16.2-10 to expressions given earlier in Eqs. 13.2-14 and 14.2-9.

16C.1 Effect of Ring Closure on Second-Order-Fluid Constants

Obtain the entries in Table 16.4-1 for the ringlike model made up of N beads joined by N linear springs, each with spring constant H. How do η_0 and $\Psi_{1,0}$ change when N-bead linear chains undergo ring closure to form N-bead rings?

16C.2 Diffusion Equation for the Configurational Distribution Function for Rouse Chains

Show how to obtain Eq. 15.1-7, the diffusion equation for chainlike bead-spring models, by simplification of the general equation in Eq. 16.2-6. Use the generalized coordinates suggested in Example 12.1-2. Show that for the chain with equal masses and friction coefficients we get

$$\frac{\partial \psi}{\partial t} + \sum_n \sum_i \sum_p \sum_j \frac{\partial}{\partial Q_{in}} \left\{ \frac{1}{\zeta} A_{ij} \delta_{np} \left[\psi \zeta \sum_v (\boldsymbol{\kappa} : \boldsymbol{R}_v B_{vj} \boldsymbol{\delta}_p) - kT \frac{\partial \psi}{\partial Q_{jp}} - \psi \frac{\partial}{\partial Q_{jp}} \phi \right] \right\} = 0 \qquad \text{(16C.2-1)}$$

Consider now the hydrodynamic term. When. Eq. 12.1-20 is used, this term becomes

$$\sum_n \sum_i \sum_p \sum_j \sum_v \sum_k \frac{\partial}{\partial Q_{in}} [A_{ij} \delta_{np} \psi (\boldsymbol{\kappa} : B_{vk} \boldsymbol{Q}_k B_{vj} \boldsymbol{\delta}_p)] \qquad \text{(16C.2-2)}$$

The sums on v and j can be performed (in that order) using Eq. 11.6-7 and the fact that the Kramers and Rouse matrices are the inverse of one another. Then the sums on k and p may be carried out using the definition of the Kronecker delta. This leads finally to

$$\sum_n \sum_i \frac{\partial}{\partial Q_{in}} (\psi \boldsymbol{\kappa} : \boldsymbol{Q}_i \boldsymbol{\delta}_n) = \sum_n \sum_i \frac{\partial}{\partial Q_{in}} (\psi [\boldsymbol{\kappa} \cdot \boldsymbol{Q}_i]_n) = \sum_i \left(\frac{\partial}{\partial \boldsymbol{Q}_i} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{Q}_i] \psi \right) \qquad \text{(16C.2-3)}$$

which is just the hydrodynamic term in Eq. 15.1-7. The other terms may be transformed in a similar way.

16C.3 Stress Tensor for the Rouse Model from General Formula

Show how to get Eqs. A and D of Table 15.2-1 from general results in §16.3. To do this assume a monodisperse solution, and use the free-draining bead-spring chain.

16C.4 Calculation of Configurational Quantities for the Elastic Rhombus Model[1]

This model is shown in Fig. 16.4-2; it consists of four identical beads arranged in planar fashion joined by four rods of length L arranged to form a rhombus. The joints at the beads are universal joints and two opposing beads are connected by a Fraenkel spring (Table 11.5-1) whose equilibrium length is $L\sqrt{2}$. Hence, if the rhombus is not acted on by any forces, it assumes the shape of a square. Forces acting on the model will then deform it into a rhombus in which the spring is either compressed or extended.

[1] C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (1976). A sign error in Eq. 17.7 of this reference is corrected in Eq. 16C.5-2.

PART VII

A GENERAL PHASE-SPACE KINETIC THEORY

In Chapters 13 through 16 we set forth the kinetic theory description of polymer solutions and showed how to obtain the nonequilibrium configurational distribution function and some of the rheological properties. The elementary derivations in Chapter 13 were based on rather simple pictorial arguments and some intuitive statements. Also, we did draw on some results that came from Chapters 17 and 18, when simple physical explanations could not be given. In Chapters 14 and 16, where models with constraints were used, we found it necessary to refer ahead to Chapters 17 and 18 for the complete explanation.

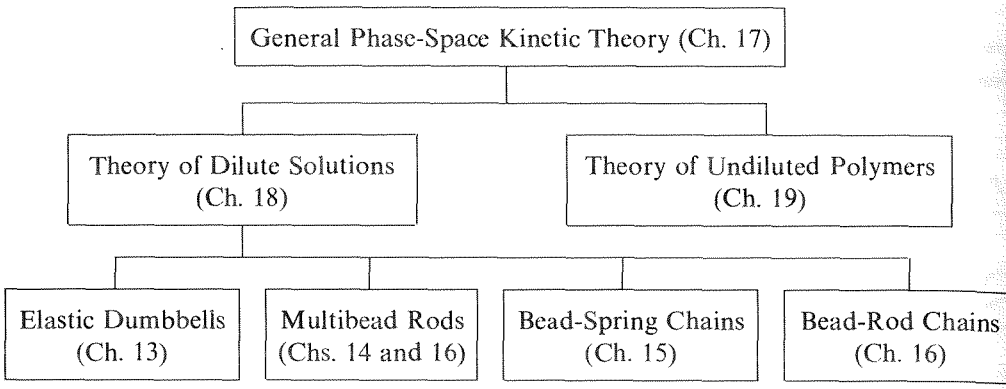
This part of the book contains three closely related chapters. The first of these, Chapter 17, is a rather general phase-space kinetic theory. This chapter makes use of a number of ideas from the phase-space discussion of Chapter 12. In addition Chapter 17 is written for very general mechanical models and also allows for mixtures (or polydisperse systems). The number of assumptions is kept to a minimum in this chapter, so that it can provide a rigorous starting point for a variety of derivations and calculations in the future.

In Chapter 18 the general theory is specialized for dilute solutions, but the mechanical models are kept quite general. All of the results of Chapters 13 through 16 can be obtained as special cases of equations in this chapter. Rather detailed discussions are given of the key approximations that are inherent in most kinetic theories of dilute solutions, such as the introduction of some kind of Stokes' law assumption for the hydrodynamic force and the equilibration in momentum space that leads to the customary expression for the Brownian motion force. In the course of the chapter the stress tensor and the mass-flux vector expressions are obtained, and these then form the starting point for the discussion of the rheological and diffusional behavior of polymers in dilute solution.

In Chapter 19 the general theory of Chapter 17 is applied to concentrated solutions and melts. In such fluids the motion of the polymer chain segments is restricted by the presence of the other molecules in the neighborhood, and it becomes necessary to introduce nonisotropic frictional drag and also to include the notion of "reptation." Although these reptation theories appear to be quite successful, it must be kept in mind that the older "network" theories have also enjoyed a considerable degree of success. These theories, which have an entirely different basis, are discussed in Chapter 20.

It is important to recognize that the material in Chapters 17 through 19 provides the basis for understanding a wide variety of kinetic theories for both dilute solutions and undiluted polymers, for both monodisperse and polydisperse systems, and for models both

with and without constraints. The relation of the topics can be seen from the following chart:



It is clear that from a logical point of view one should begin with Chapter 17 and then develop the various theories for simple models as special cases. However, for most people beginning the study of this subject, we feel that mastery of the physical ideas for simple models should precede the study of the formal theory.

CHAPTER 17

PHASE-SPACE THEORY OF POLYMERIC LIQUIDS[1]

In this chapter we derive from first principles the equation of continuity for the configuration-space distribution function, the equations of internal motion for the constituent molecules, and the expression for the stress tensor. The derivations are sufficiently general that the results are applicable to both polymer solutions and undiluted polymers; the fluids may be mixtures of different polymers, or they may be polydisperse polymers. In the first four sections the only assumptions that are made are the assumption of some kind of mechanical model for the molecules and the assumption of pairwise additivity of forces between "beads." In the final two sections a few additional minor assumptions are made: the variation of the distribution functions over molecular-scale distances is neglected, and the acceleration terms in the equation of motion are omitted. It is felt that these assumptions have little effect on the molecular descriptions of rheological phenomena.

In §17.1 we start with a discussion of the classical mechanics of a polymeric fluid, whose constituent molecules are modeled as bead-spring-rod systems; here we allow the "beads" to be of finite size and arbitrary shape. In §17.2 statistical ideas are introduced and the equations of continuity and motion of classical hydrodynamics are obtained from the "general equation of change." This general equation of change is used at several points in this chapter; its importance in the development of the theory cannot be overemphasized (see Fig. 17.0-1). Then in §17.3 various contracted distribution functions are defined, and notations for average values are introduced; it is here that the configurational distribution functions for single molecules and for pairs of molecules are defined. In §17.4 the various contributions to the stress tensor are obtained as integrals involving the distribution functions; the pictorial presentation in Fig. 17.4-1 should be examined before embarking on this section. The stress tensor expressions obtained in this section are further simplified in §17.6, by making use of the equations of motion for the internal degrees of freedom developed in §17.5.

The chapter is so designed that it can be read superficially by those who just wish to have some idea as to the origins of the key starting equations of Chapters 13 through 16. On the other hand, a careful study of this and the following two chapters can provide a good understanding of the fundamental principles of polymer kinetic theory. Many of the topics in these three chapters have not yet been fully explored or exploited.

[1] This chapter is based on C. F. Curtiss, R. B. Bird, and O. Hassager, *Adv. Chem. Phys.*, **35**, 31–117 (1976); C. F. Curtiss and R. B. Bird, *Physica*, **118A**, 191–204 (1983). The approach used here was inspired by the pioneering work on statistical mechanical theory and transport phenomena by J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 817–829 (1950).

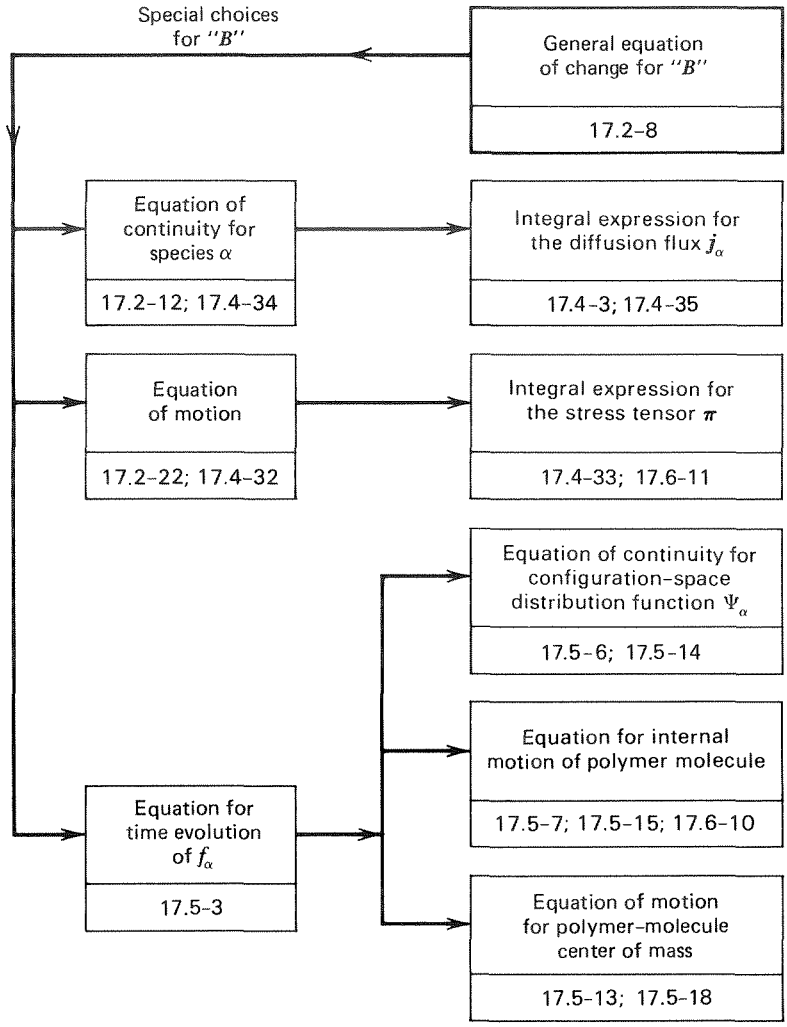


FIGURE 17.0-1. "Flow chart" for Chapter 17, showing how the key results follow from the general equation of change.

§17.1 CLASSICAL DYNAMICS OF A COMPLEX SYSTEM

The discussions of this chapter are based on a very general model of a polymeric solution or undiluted polymer, visualized as a collection of a large number of molecules of various kinds. Each molecule is modeled as a collection of "finite beads" of arbitrary shape. These finite beads are then joined in an arbitrary manner by "springs" or "massless rods." In Fig. 17.1-1 several such molecular models of varying degrees of complexity are illustrated. Note that the "beads" in Chapters 11 through 16 are taken to be point masses (or spheres of finite size in some of the hydrodynamic interaction studies), whereas here the "finite beads" may be "needles" or arbitrary rigid bodies. At certain points in the development we may wish to restrict the model to the point masses considered earlier, in which case we will refer to "structureless beads."

To describe, at any instant, the orientation of the νth finite bead with respect to a fixed coordinate system we introduce a set of generalized coordinates, $q_{\nu\sigma}$. If the bead is a

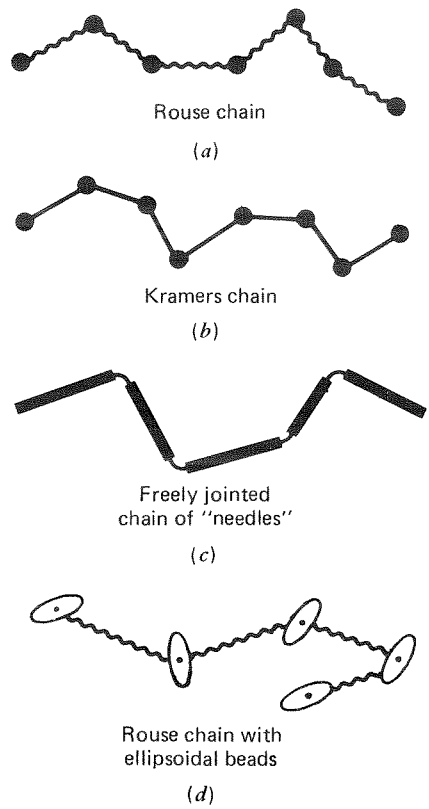


FIGURE 17.1-1. Examples of molecular models for use in kinetic theory.

"needle," then $\sigma = 1, 2$ and two such coordinates (θ_v, ϕ_v) are needed to describe the orientation; if it is an arbitrary rigid body, then $\sigma = 1, 2, 3$ and three Euler angles $(\alpha_v, \beta_v, \gamma_v)$ are required. If the bead is simply a mass point, there are no such coordinates.

The kinetic energy of a finite bead, with respect to a coordinate system translating with its own center of mass, is a quadratic form in the time derivatives, $\dot{q}_{v\sigma}$, of the generalized coordinates

$$\mathscr{K}_v = \tfrac{1}{2} \sum_{\sigma} \sum_{\tau} g_{v,\sigma\tau} \dot{q}_{v\sigma} \dot{q}_{v\tau} \tag{17.1-1}$$

where the $g_{v,\sigma\tau}$ are the elements of the "metric matrix" of the finite bead; these are, in general, functions of the coordinates $q_{v\sigma}$. As an example, if the finite bead is a "needle" of moment of inertia, I, the two coordinates may be taken to be the usual polar angles describing the orientation: $q_{v1} = \theta_v$; $q_{v2} = \phi_v$. The diagonal elements of the metric matrix are then

$$g_{v,11} = I \tag{17.1-2}$$

$$g_{v,22} = I \sin^2 q_{v1} = I \sin^2 \theta_v \tag{17.1-3}$$

and the off-diagonal elements are zero.

The internal kinetic energy, $\mathscr{K}_{\text{int}}$, of the entire molecular model is then the sum of the rotational kinetic energies $\mathscr{K}_v$ and the translational kinetic energies $\frac{1}{2}m_v\dot{\boldsymbol{R}}_v^2$ of the finite beads

$$\mathscr{K}_{\text{int}} = \sum_v \left(\tfrac{1}{2}m_v\dot{\boldsymbol{R}}_v^2 + \mathscr{K}_v\right) \tag{17.1-4}$$

Here m_v is the mass of the vth finite bead, and $\boldsymbol{R}_v$ is the vector from the center of mass of the entire molecular model to the center of mass of the vth finite bead; the vector $\dot{\boldsymbol{R}}_v$ is the bead velocity.

The molecular models being considered here may contain constraints; for example, the connectors between the finite beads may have fixed lengths or may have fixed angles between them. Hence there may be relations among the $\boldsymbol{R}_v$ and $q_{v\sigma}$. It is therefore necessary to introduce a set of generalized coordinates Q_s, which are *independent* and sufficient in number to describe the orientation of the molecular model in space, the relative locations of the finite beads, and the orientations of all the finite beads. The number of required generalized coordinates is fixed by the model, but the detailed choice of the coordinates is arbitrary. Various choices that may be made for chain models are discussed in §11.6

We next introduce the base vectors, $\boldsymbol{b}_{vs}$, defined in Eq. 12.1-6 as well as a set of similar quantities $b_{v\sigma s}$ associated with the finite bead orientations

$$\boldsymbol{b}_{vs} = \sqrt{m_v}\,\frac{\partial}{\partial Q_s}\boldsymbol{R}_v \tag{17.1-5}$$

$$b_{v\sigma s} = \frac{\partial}{\partial Q_s}q_{v\sigma} \tag{17.1-6}$$

so that the time derivatives may be written

$$\dot{\boldsymbol{R}}_v = \frac{1}{\sqrt{m_v}}\sum_s \dot{Q}_s\boldsymbol{b}_{vs} \tag{17.1-7}$$

$$\dot{q}_{v\sigma} = \sum_s \dot{Q}_s b_{v\sigma s} \tag{17.1-8}$$

Using the last two relations, we may rewrite the expression for the kinetic energy of a molecule in a coordinate system moving with its center of mass, Eq. 17.1-4, as a quadratic form in the time derivatives, $\dot{Q}_s$, of the generalized coordinates

$$\mathscr{K}_{\text{int}} = \tfrac{1}{2}\sum_s\sum_t g_{st}\dot{Q}_s\dot{Q}_t \tag{17.1-9}$$

where the coefficients are defined as

$$g_{st} = g_{st}^{(1)} + g_{st}^{(2)} \tag{17.1-10}$$

and

$$g_{st}^{(1)} = \sum_v (\boldsymbol{b}_{vs}\cdot\boldsymbol{b}_{vt}) \tag{17.1-11}$$

$$g_{st}^{(2)} = \sum_v\sum_\sigma\sum_\tau g_{v,\sigma\tau}b_{v\sigma s}b_{v\tau t} \tag{17.1-12}$$

The g_{st} are the elements of the metric matrix of the molecule and are in general functions of the generalized coordinates Q_s. The first term in the expression for the metric matrix $g_{st}^{(1)}$, defined by Eq. 17.1-11, is given by Eq. 12.1-7. In Chapter 12 the polymer molecules were modeled as collections of structureless beads, and for this reason the second term, $g_{st}^{(2)}$, did not arise.

As discussed in §12.1 the momentum conjugate to Q_s is defined as

$$P_s = \frac{\partial}{\partial \dot{Q}_s} \mathscr{K}_{\text{int}} = \sum_t g_{st} \dot{Q}_t \tag{17.1-13}$$

Also as discussed earlier these equations may always be inverted formally to give

$$\dot{Q}_s = \sum_t G_{st} P_t \tag{17.1-14}$$

where the G_{st} are the elements of the matrix which is the inverse of the metric matrix, g_{st}.

The last set of equations may be used to transform the expression for the kinetic energy of a molecule in a center of mass coordinate system as given by Eq. 17.1-9 to the form

$$\mathscr{K}_{\text{int}} = \tfrac{1}{2} \sum_s \sum_t G_{st} P_s P_t \tag{17.1-15}$$

The *Hamiltonian of a single molecule* in the same coordinate system is then a function of the coordinates Q_s and momenta P_s, given by

$$\mathscr{H}_{\text{int}} = \mathscr{K}_{\text{int}} + \phi \tag{17.1-16}$$

where ϕ, the intramolecular potential, is a function of the generalized coordinates Q_s.

The system which we study from the point of view of statistical mechanics is a collection of a large number of molecules—in general, of different types. If we consider a solution, the solvent molecules are modeled simply as mass points without structure although more complex models could be used. Such a system is illustrated in Fig. 17.1-2. In this discussion, we use Greek indices ($\alpha, \beta, \gamma, \ldots$) to indicate the molecular species, followed when necessary by italic indices ($i, j, k, \ldots$) to label the various molecules of the species. For example we use $\boldsymbol{r}^{\alpha i}$ as the vector from a space-fixed origin to the center of mass of molecule i of species α, which may be a polymer or a solvent molecule. The linear momentum of this molecule is then $\boldsymbol{p}^{\alpha i}$. Indices such as α and αi are omitted whenever they appear to be cumbersome and when no confusion can occur.

The *Hamiltonian of the entire system* in Fig. 17.1-2 is the sum of the energies of the separate molecules (each of which in turn is the sum of the kinetic energy of the motion of the center of mass, the internal Hamiltonian, and the potential $\phi^{(e)\alpha i}$ which describes the "external" force on a molecule of species α) and the intermolecular potential, Φ, associated with the forces between the molecules. This Hamiltonian may be written as

$$\mathscr{H}^{(T)} = \sum_\alpha \sum_i \left[\frac{1}{2m^\alpha} (\boldsymbol{p}^{\alpha i})^2 + \mathscr{H}_{\text{int}}^{\alpha i} + \phi^{(e)\alpha i} \right] + \Phi \tag{17.1-17}$$

where m^α is the mass of a molecule of species α.

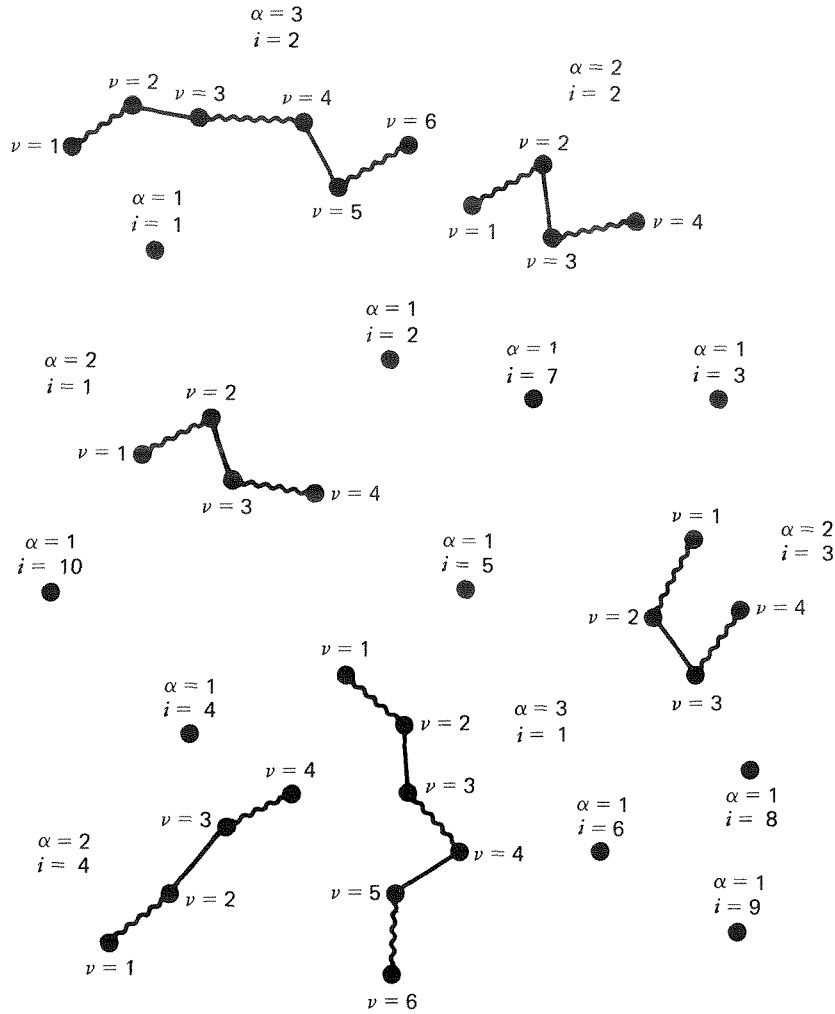


FIGURE 17.1-2. Sketch of a polymer solution containing a solvent ($\alpha = 1$) and two polymer species ($\alpha = 2, \alpha = 3$). Both polymer species have "constraints" (rigid portions indicated by an inflexible rod).

Hamilton's equations of motion, which describe the time derivatives of the coordinates and momenta, are given by Eqs. 12.2-6 and 12.2-7. Before writing these equations, we define several quantities. First, the force on the center of mass of molecule i of species α due to the external force is

$$\boldsymbol{F}^{(e)\alpha i} = -\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} \phi^{(e)\alpha i} \tag{17.1-18}$$

and that due to all the other molecules is

$$\boldsymbol{F}^{\alpha i} = -\frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} \Phi \tag{17.1-19}$$

In a similar manner we define four generalized forces associated with the coordinate Q_s,

$$\mathscr{F}_s^{(k)\alpha i} = -\tfrac{1}{2}\sum_{tu} P_t^{\alpha i} P_u^{\alpha i} \frac{\partial}{\partial Q_s^{\alpha i}} G_{tu}^{\alpha i} \tag{17.1-20}$$

$$\mathscr{F}_s^{(\phi)\alpha i} = -\frac{\partial}{\partial Q_s^{\alpha i}} \phi^{\alpha i} \tag{17.1-21}$$

$$\mathscr{F}_s^{(e)\alpha i} = -\frac{\partial}{\partial Q_s^{\alpha i}} \phi^{(e)\alpha i} \tag{17.1-22}$$

$$\mathscr{F}_s^{(d)\alpha i} = -\frac{\partial}{\partial Q_s^{\alpha i}} \Phi \tag{17.1-23}$$

The first of these is associated with generalized forces arising from the use of non-Cartesian coordinates; the remaining three are associated with intramolecular, external, and intermolecular forces. In addition it is convenient to define

$$\mathscr{F}_s^{\alpha i} = \mathscr{F}_s^{(k)\alpha i} + \mathscr{F}_s^{(\phi)\alpha i} + \mathscr{F}_s^{(e)\alpha i} + \mathscr{F}_s^{(d)\alpha i} \tag{17.1-24}$$

as the sum of all four contributions.

In terms of the real forces and generalized forces, *Hamilton's equations of motion* are (cf. Eqs. 12.2-6 and 12.2-7)

$$\dot{\boldsymbol{r}}^{\alpha i} = \frac{\partial \mathscr{H}^{(T)}}{\partial \boldsymbol{p}^{\alpha i}} = \frac{1}{m^\alpha}\boldsymbol{p}^{\alpha i} \tag{17.1-25}$$

$$\dot{Q}_s^{\alpha i} = \frac{\partial \mathscr{H}^{(T)}}{\partial P_s^{\alpha i}} = \sum_t G_{st}^{\alpha i} P_t^{\alpha i} \tag{17.1-26}$$

$$\dot{\boldsymbol{p}}^{\alpha i} = -\frac{\partial \mathscr{H}^{(T)}}{\partial \boldsymbol{r}^{\alpha i}} = \boldsymbol{F}^{(e)\alpha i} + \boldsymbol{F}^{\alpha i} \tag{17.1-27}$$

$$\dot{P}_s^{\alpha i} = -\frac{\partial \mathscr{H}^{(T)}}{\partial Q_s^{\alpha i}} = \mathscr{F}_s^{\alpha i} \tag{17.1-28}$$

These equations describe the time evolution of the dynamical state of an entire system.

The concept of a phase space is discussed in §12.3. This is a multidimensional space, the coordinates of which are the configuration and momentum coordinates of a system. In this case, it is convenient to consider a phase space described by the coordinates of all of the molecules making up the macroscopic system of interest—the polymer solution or melt. As time evolves, the coordinates of the system change and trace out a "trajectory" in this space. The derivatives of these coordinates along such a trajectory are described by the last set of equations. From Eqs. 17.1-7 and 17.1-14, it follows that the time derivative, along such a trajectory, of the vector $\boldsymbol{R}_v^{\alpha i}$ is

$$\dot{\boldsymbol{R}}_v^{\alpha i} = \frac{1}{\sqrt{m_v^\alpha}} \sum_{st} G_{st}^{\alpha i} P_t^{\alpha i} \boldsymbol{b}_{vs}^{\alpha i} \tag{17.1-29}$$

A "dynamical variable" is any function of the coordinates and momenta of a system, that is, a function "in the phase space," which in general varies along a particular trajectory. The right side of the last equation may be considered to be such a dynamical variable, and we note that the derivatives with respect to the phase space variables of this function are

$$\frac{\partial}{\partial Q_s^{\alpha i}} \dot{R}_v^{\alpha i} = \frac{1}{\sqrt{m_v^\alpha}} \sum_{tu} P_u^{\alpha i} \left[\frac{\partial}{\partial Q_s^{\alpha i}} (G_{tu}^{\alpha i} b_{vt}^{\alpha i}) \right] \tag{17.1-30}$$

$$\frac{\partial}{\partial P_s^{\alpha i}} \dot{R}_v^{\alpha i} = \frac{1}{\sqrt{m_v^\alpha}} \sum_{t} G_{st}^{\alpha i} b_{vt}^{\alpha i} \tag{17.1-31}$$

These results are used in the next section in developing the equation of motion.

EXAMPLE 17.1-1 The Two-Needle Model

Obtain the elements of the metric matrices, g_{st} and G_{st}, and the determinant, g, for the molecular model consisting of two needles joined as illustrated in Fig. 17.1-3.

SOLUTION Let θ_v and ϕ_v be the angles describing the directions of the unit vectors, $\boldsymbol{u}_v$, in the directions of the two needles. The length of each needle is l, and the center of mass of the needle is located a distance ωl from the end at which the needles just touch (with $\omega \neq 0$). Thus,

$$\boldsymbol{R}_2 - \boldsymbol{R}_1 = \omega l(\boldsymbol{u}_1 + \boldsymbol{u}_2) \tag{17.1-32}$$

and

$$\begin{aligned} \boldsymbol{R}_1 &= -\tfrac{1}{2}\omega l(\boldsymbol{u}_1 + \boldsymbol{u}_2) \\ \boldsymbol{R}_2 &= \tfrac{1}{2}\omega l(\boldsymbol{u}_1 + \boldsymbol{u}_2) \end{aligned} \tag{17.1-33}$$

These relations among the $\boldsymbol{R}_v$ and $q_{v\sigma}$ are the constraints associated with the condition that the ends of the needles just touch.

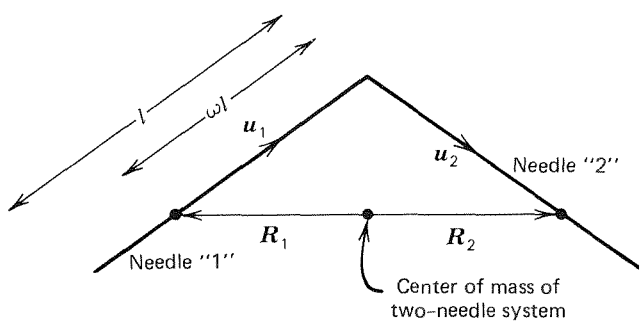


FIGURE 17.1-3. The two-needle model. The needles are joined head to tail, and the center of mass of a needle is a distance ωl from the joint.

The coordinates Q_s, with $s = 1, 2, 3, 4$, are now taken to be θ_1, ϕ_1, θ_2, and ϕ_2, respectively. One then finds from the definitions of the $\boldsymbol{b}_{vs}$, Eq. 17.1-5, and the last equations that

$$\begin{aligned}
\boldsymbol{b}_{11} &= -\tfrac{1}{2}\sqrt{m\omega l}\boldsymbol{s}_1 \\
\boldsymbol{b}_{12} &= -\tfrac{1}{2}\sqrt{m\omega l}\boldsymbol{t}_1 \sin\theta_1 \\
\boldsymbol{b}_{13} &= -\tfrac{1}{2}\sqrt{m\omega l}\boldsymbol{s}_2 \\
\boldsymbol{b}_{14} &= -\tfrac{1}{2}\sqrt{m\omega l}\boldsymbol{t}_2 \sin\theta_2 \\
\boldsymbol{b}_{2s} &= -\boldsymbol{b}_{1s}
\end{aligned} \tag{17.1-34}$$

where $\boldsymbol{s}_v$ and $\boldsymbol{t}_v$ are unit vectors normal to $\boldsymbol{u}_v$ described in Table E.5-1. Since the Q_s are the $q_{v\sigma}$ renumbered, it follows from the definition of the $b_{v\sigma s}$, Eq. 17.1-6, that

$$\begin{aligned}
b_{111} &= 1 \\
b_{122} &= 1 \\
b_{213} &= 1 \\
b_{224} &= 1
\end{aligned} \tag{17.1-35}$$

and the other $b_{v\sigma s}$ are zero.

Next, one finds from the definition of $g_{st}^{(1)}$, Eq. 17.1-11, that

$$(\tfrac{1}{2}ml^2\omega^2)^{-1} g_{st}^{(1)} = \begin{pmatrix} 1 & 0 & (\boldsymbol{s}_2\cdot\boldsymbol{s}_1) & (\boldsymbol{t}_2\cdot\boldsymbol{s}_1)S_2 \\ 0 & S_1^2 & (\boldsymbol{s}_2\cdot\boldsymbol{t}_1)S_1 & (\boldsymbol{t}_2\cdot\boldsymbol{t}_1)S_2S_1 \\ (\boldsymbol{s}_1\cdot\boldsymbol{s}_2) & (\boldsymbol{t}_1\cdot\boldsymbol{s}_2)S_1 & 1 & 0 \\ (\boldsymbol{s}_1\cdot\boldsymbol{s}_2)S_2 & (\boldsymbol{t}_1\cdot\boldsymbol{t}_2)S_1S_2 & 0 & S_2^2 \end{pmatrix} \tag{17.1-36}$$

where $S_1 = \sin\theta_1$, $S_2 = \sin\theta_2$ and from Eqs. 17.1-2, 3, and 12 that

$$\frac{1}{I} g_{st}^{(2)} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & S_1^2 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & S_2^2 \end{pmatrix} \tag{17.1-37}$$

The metric matrix, g_{st}, is given by Eq. 17.1-10 as the sum of these two matrices. This matrix may be written as

$$(\tfrac{1}{2}ml^2\omega^2)^{-1} g_{st} = \begin{pmatrix} A & 0 & (\boldsymbol{s}_1\cdot\boldsymbol{s}_2) & (\boldsymbol{s}_1\cdot\boldsymbol{t}_2)S_2 \\ 0 & AS_1^2 & (\boldsymbol{t}_1\cdot\boldsymbol{s}_2)S_1 & (\boldsymbol{t}_1\cdot\boldsymbol{t}_2)S_1S_2 \\ (\boldsymbol{s}_1\cdot\boldsymbol{s}_2) & (\boldsymbol{t}_1\cdot\boldsymbol{s}_2)S_1 & A & 0 \\ (\boldsymbol{s}_1\cdot\boldsymbol{t}_2)S_2 & (\boldsymbol{t}_1\cdot\boldsymbol{t}_2)S_1S_2 & 0 & AS_2^2 \end{pmatrix} \tag{17.1-38}$$

where

$$A = 1 + \frac{2I}{ml^2\omega^2} \tag{17.1-39}$$

The square root of the determinant of the matrix is

$$g^{1/2} = (\tfrac{1}{2}ml^2\omega^2)^2 A(A^2 - 1)^{1/2} S_1 S_2 h^{1/2} \tag{17.1-40}$$

where

$$h = 1 - \frac{(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)^2}{A^2} \tag{17.1-41}$$

As discussed in §12.3, the equilibrium distribution in configuration space, of molecular models with no intramolecular potential is $g^{1/2}$. Thus the factor $h^{1/2}$ describes the deviation of the equilibrium distribution for this model from that arising from a "random" distribution of angles.

A needle with a fraction $(1 - \omega)$ of its mass at the "head" end and a fraction ω of its mass at the "tail" end would have a moment of inertia of

$$I = \omega(1 - \omega)ml^2 \tag{17.1-42}$$

It is interesting to note that if $\omega = \frac{2}{3}$ this model is similar to the "three-bead, two-rod" model discussed in Example 16.1-2, and since $A = 2$ the equilibrium distribution of angles is the same. On comparing Eq. 17.1-39 with Eq. 12.1-16 one finds that indeed the two models lead to identical metric matrices, if $l = (\frac{3}{2})^{1/2}a$.

The inversion of the metric matrix leads to the values

$$\begin{aligned}
QG_{11} &= AS_1^2S_2^2[A^2 - 1 + (\boldsymbol{t}_1 \cdot \boldsymbol{u}_2)^2] \\
QG_{12} &= -AS_1S_2^2(\boldsymbol{s}_1 \cdot \boldsymbol{u}_2)(\boldsymbol{t}_1 \cdot \boldsymbol{u}_2) \\
QG_{13} &= -S_1^2S_2^2[A^2(\boldsymbol{s}_1 \cdot \boldsymbol{s}_2) + (\boldsymbol{t}_1 \cdot \boldsymbol{t}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)] \\
QG_{14} &= -S_1^2S_2[A^2(\boldsymbol{s}_1 \cdot \boldsymbol{t}_2) - (\boldsymbol{t}_1 \cdot \boldsymbol{s}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)] \\
QG_{22} &= AS_2^2[A^2 - 1 + (\boldsymbol{s}_1 \cdot \boldsymbol{u}_2)^2] \\
QG_{23} &= -S_1S_2^2[A^2(\boldsymbol{t}_1 \cdot \boldsymbol{s}_2) - (\boldsymbol{s}_1 \cdot \boldsymbol{t}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)] \\
QG_{24} &= -S_1S_2[A^2(\boldsymbol{t}_1 \cdot \boldsymbol{s}_2) + (\boldsymbol{s}_1 \cdot \boldsymbol{s}_2)(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)] \\
QG_{33} &= AS_1^2S_2^2[A^2 - 1 + (\boldsymbol{t}_2 \cdot \boldsymbol{u}_1)^2] \\
QG_{34} &= -AS_1^2S_2(\boldsymbol{s}_2 \cdot \boldsymbol{u}_1)(\boldsymbol{t}_2 \cdot \boldsymbol{u}_1) \\
QG_{44} &= AS_1^2[A^2 - 1 + (\boldsymbol{s}_2 \cdot \boldsymbol{u}_1)^2]
\end{aligned} \tag{17.1-43}$$

where

$$Q = \tfrac{1}{2}ml^2\omega^2A^2(A^2 - 1)hS_1^2S_2^2 \tag{17.1-44}$$

From these expressions one may obtain the elements of the metric matrix, G_{st}, for the three-bead two-rod model by setting $\omega = \frac{2}{3}$, $A = 2$, and $l = (\frac{3}{2})^{1/2}a$.

§17.2 ENSEMBLE AVERAGES AND EQUATIONS OF CHANGE

In the foregoing section, it is pointed out that the dynamical state of a single macroscopic system consisting of many solvent and polymer molecules may be described by a "system point" in the associated phase space. In general, the dynamical state changes with time and the point traces out a trajectory in the phase space. For convenience in the next

few paragraphs, we use the single symbol x to describe a point in the phase space, that is, the full set of coordinates that describe the space. A trajectory is then described by the time evolution of the point $x(t)$.

In the statistical treatment, it is shown that the actual or "probable" behavior of a physical system is described by the average behavior of a large number, or "ensemble," of identical systems. The dynamical state of such an ensemble is described by a distribution of system points in the phase space, $f(x, t)$, and the average behavior is described by the time evolution of such a distribution. In the present discussion, the distribution function, $f(x, t)$, is normalized so that the integral over all of the phase space is unity

$$\int f(x, t)dx = 1 \tag{17.2-1}$$

Thus $f(x, t)dx$ is the fraction of system points that lies in the multidimensional hypercube dx in the phase space. Note that the distribution function introduced here is a generalization of that used in Eq. 12.3-1.

The development of the equation for the time evolution of the phase-space distribution function $f(x, t)$ is similar to that given in §13.2 for the "equation of continuity" of the configuration-space distribution function for a single dumbbell. The essential point in the development is that no system points are lost or created: as time evolves they simply move through the phase space describing the time evolution of the dynamical state of each system in the ensemble. Thus, by analogy with Eq. 13.2-10 we have

$$\frac{\partial f}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}(\dot{x}_i f) \tag{17.2-2}$$

where the x_i are the generalized coordinates and conjugate momenta.

Next we continue the analogy with the derivation of the "diffusion equation" in §13.2 and introduce the expressions for the time derivatives of the phase-space coordinates given by Hamilton's equations of motion, Eqs. 17.1-25 to 28. When these are substituted into Eq. 17.2-2 we obtain the *Liouville equation*[1]

$$\boxed{\frac{\partial f}{\partial t} = -\mathscr{L} f} \tag{17.2-3}$$

in which $\mathscr{L}$ is the Liouville operator

$$\mathscr{L} = \sum_\alpha \sum_i \left(\frac{1}{m^\alpha} \boldsymbol{p}^{\alpha i} \cdot \frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} + \sum_s \sum_t G_{st}^{\alpha i} P_t^{\alpha i} \frac{\partial}{\partial Q_s^{\alpha i}} + [\boldsymbol{F}^{(e)\alpha i} + \boldsymbol{F}^{\alpha i}] \cdot \frac{\partial}{\partial \boldsymbol{p}^{\alpha i}} + \sum_s \mathscr{F}_s^{\alpha i} \frac{\partial}{\partial P_s^{\alpha i}} \right) \tag{17.2-4}$$

In obtaining this last equation many of the terms cancelled since mixed second derivatives of the full Hamiltonian of the system with respect to a coordinate and a momentum do not depend on the order of differentiation.

The physical properties of a macroscopic system are ensemble averages of certain dynamical variables or functions in the phase space. Let us denote an arbitrary dynamical

[1] J. Liouville, *Journ. de Math. Pures et Appliquées*, 1. Sér., **3**, 342–349 (1838).

variable by $B(x)$, an arbitrary function in the phase space that does not depend explicitly on the time. The average over the ensemble is then denoted by the angular brackets:

$$\langle B \rangle = \int B(x) f(x, t) dx \tag{17.2-5}$$

by analogy with the use of angular brackets in §12.4.

An equation for the time evolution of the average value of an arbitrary dynamical variable B may be obtained by using the continuity equation in Eq. 17.2-2 in the following way:

$$\begin{aligned} \frac{\partial}{\partial t} \langle B \rangle &= \int B(x) \frac{\partial}{\partial t} f(x, t) dx \\ &= -\sum_i \int B(x) \frac{\partial}{\partial x_i} (\dot{x}_i f) dx \\ &= \sum_i \int \dot{x}_i f \frac{\partial}{\partial x_i} B(x) dx \end{aligned} \tag{17.2-6}$$

In the last step an integration by parts was performed, and use was made of the fact that for dynamical variables $B(x)$ of physical interest, $B(x)\dot{x}f$ evaluated at the limits of the variables is zero or, for periodic coordinates, the terms at the two ends cancel. If, now, use is made of Hamilton's equations of motion of the previous section, then we obtain

$$\frac{\partial}{\partial t} \langle B \rangle = \int f(x, t)[\mathscr{L} B(x)] dx \tag{17.2-7}$$

or

$$\boxed{\frac{\partial}{\partial t} \langle B \rangle = \langle \mathscr{L} B \rangle} \tag{17.2-8}$$

This is called the *general equation of change* for an arbitrary dynamical variable $B(x)$. We shall now use this result to obtain the equations of continuity and motion for the polymer solution, and in §17.5 it will be used again to obtain equations for the time evolution of lower-order distribution functions.

a. The Equations of Continuity

As particularly simple examples of the general equation of change, we consider the equations of continuity of each species. For this purpose we take as the dynamical variable

$$B = \sum_i \sum_\nu m_\nu^\alpha \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_\nu^{\alpha i} - \boldsymbol{r}) \tag{17.2-9}$$

This dynamical variable is a function in the phase space, which depends only on a subset of the phase space variables (the configuration coordinates of all the molecules of species α) and depends parametrically on the vector $\boldsymbol{r}$. A particular term in the sum is zero unless the

center of mass of bead v of molecule i of this species is at position $\boldsymbol{r}$. Our statistical treatment begins with interpretation of the average of this dynamical variable

$$\rho_\alpha(\boldsymbol{r}, t) = \left\langle \sum_i \sum_v m_v^\alpha \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_v^{\alpha i} - \boldsymbol{r}) \right\rangle \tag{17.2-10}$$

as the mass concentration at $\boldsymbol{r}$ of species α. It is to be pointed out that in making this identification, we note, explicitly, that the mass of a polymer molecule is distributed in space and is not simply located at the center of mass of the molecule, as is usually assumed, implicitly, in the statistical treatment of systems of small molecules. On the other hand, we have assumed implicitly, that all of the mass of a finite bead is located at the center of mass of the bead.

The mass concentration ρ_α, as defined by Eq. 17.2-10, is a function of $\boldsymbol{r}$ because the dynamical variable B depends parametrically on $\boldsymbol{r}$ and a function of time because in general the distribution function used to obtain the average varies with time. To make use of the general equation of change, Eq. 17.2-8, we next consider the operation of the Liouville operator given by Eq. 17.2-4 on one term in the expression for the dynamical variable B defined by Eq. 17.2-9. Thus we find that

$$\begin{aligned}
\mathscr{L}\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_v^{\alpha i} - \boldsymbol{r}) &= \left(\frac{1}{m^\alpha} \boldsymbol{p}^{\alpha i} \cdot \frac{\partial}{\partial \boldsymbol{r}^{\alpha i}} + \sum_s \sum_t G_{st}^{\alpha i} P_t^{\alpha i} \frac{\partial}{\partial Q_s^{\alpha i}} \right) \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_v^{\alpha i} - \boldsymbol{r}) \\
&= -\left(\frac{1}{m^\alpha} \boldsymbol{p}^{\alpha i} + \frac{1}{\sqrt{m_v^\alpha}} \sum_s \sum_t G_{st}^{\alpha i} P_t^{\alpha i} \boldsymbol{b}_{vs}^{\alpha i} \right) \cdot \nabla \, \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_v^{\alpha i} - \boldsymbol{r}) \\
&= -\nabla \cdot \left(\frac{1}{m^\alpha} \boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_v^{\alpha i} \right) \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_v^{\alpha i} - \boldsymbol{r})
\end{aligned} \tag{17.2-11}$$

The general equation of change then becomes the *equation of continuity for species* α,

$$\boxed{\frac{\partial}{\partial t} \rho_\alpha = -(\nabla \cdot \rho_\alpha \boldsymbol{v}_\alpha)} \tag{17.2-12}$$

where

$$\boldsymbol{v}_\alpha(\boldsymbol{r}, t) = \frac{1}{\rho_\alpha} \left\langle \sum_i \sum_v m_v^\alpha \left(\frac{1}{m^\alpha} \boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_v^{\alpha i} \right) \delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_v^{\alpha i} - \boldsymbol{r}) \right\rangle \tag{17.2-13}$$

is the mass average velocity of molecules of species α. The product $\rho_\alpha \boldsymbol{v}_\alpha$ is the density of linear momentum associated with these molecules. This expression is analogous to that for the mass density, Eq. 17.2-10. In the expression for the momentum density the extension in space is again recognized (the $\boldsymbol{R}_v^{\alpha i}$ term); and the momentum of the beads relative to the motion of the center of mass of the molecule is also acknowledged (the $\dot{\boldsymbol{R}}_v^{\alpha i}$ term). On the other hand, in this expression the spatial extent of the finite beads is once again neglected.

The total density is the sum

$$\rho = \sum_\alpha \rho_\alpha \tag{17.2-14}$$

and the total momentum density is the sum

$$\rho v = \sum_{\alpha} \rho_\alpha v_\alpha \tag{17.2-15}$$

With these definitions, it readily follows from Eqs. 17.2-13 that

$$\boxed{\frac{\partial}{\partial t}\rho = -(\nabla \cdot \rho v)} \tag{17.2-16}$$

This is the overall *equation of continuity* (Eq. D.6-2 or Eq. 1.1-4); for an incompressible fluid it simplifies to

$$(\nabla \cdot v) = 0 \tag{17.2-17}$$

The *mass flux of species* α relative to the stream velocity[2] is

$$j_\alpha = \rho_\alpha(v_\alpha - v) \tag{17.2-18}$$

A kinetic theory expression for this flux leads to expressions for the (translational) diffusivities in polymeric liquids (see Eqs. 18.4-29 and 19.4-28).

b. The Equation of Motion

Next we proceed with an analogous development that leads to the equation of motion. In this development certain terms are ultimately identified as making up the stress tensor and in this way we obtain an expression for the stress tensor in terms of integrals over the distribution functions.

For this development, we take as the dynamical variable

$$B = \sum_{\alpha i v} m_v^\alpha \left(\frac{1}{m^\alpha} p^{\alpha i} + \dot{R}_v^{\alpha i}\right)\delta(r^{\alpha i} + R_v^{\alpha i} - r) \tag{17.2-19}$$

It follows directly from this definition and Eqs. 17.2-13 and 15 that the average of this dynamical variable is ρv so that in this case the left side of the general equation of change, Eq. 17.2-8, is $\partial \rho v/\partial t$.

In contrast with the previous development, in which we derived equations of continuity for each species, here we develop a single equation describing the conservation of linear momentum of the mixture. The reason for this difference lies in the basic dynamics of the system. Since we are considering a nonreacting mixture, collisions among the molecules do not alter the chemical constitution. On the other hand collisions do affect the amount of linear momentum associated with each species, but not the total amount of linear momentum. For this reason, it is only when the total momentum is considered that one is lead to a "conservation" equation with no source terms—other than those associated with external forces.

[2] See Eq. D.6-1 for the equation of continuity in terms of j_α. For further information on various definitions of diffusion fluxes see R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960), §16.1.

The Liouville operator, $\mathscr{L}$, is a linear, first order, differential operator and hence the operation of $\mathscr{L}$ on $\boldsymbol{B}$ leads to terms analogous to those obtained in the development of the equation of continuity and additional terms arising from the differentiation of the additional factor $[(1/m^{\alpha})\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_{v}^{\alpha i}]$. The result is

$$\begin{aligned}\mathscr{L}\boldsymbol{B} = &-\nabla\cdot\sum_{\alpha i v} m_{v}^{\alpha}\left(\frac{1}{m^{\alpha}}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_{v}^{\alpha i}\right)\left(\frac{1}{m^{\alpha}}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_{v}^{\alpha i}\right)\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_{v}^{\alpha i} - \boldsymbol{r}) \\ &+ \sum_{\alpha i v} m_{v}^{\alpha}\left[\frac{1}{m^{\alpha}}[\boldsymbol{F}^{(e)\alpha i} + \boldsymbol{F}^{\alpha i}] + \sum_{st} G_{st}^{\alpha i} P_{t}^{\alpha i}\left(\frac{\partial}{\partial Q_{s}^{\alpha i}}\dot{\boldsymbol{R}}_{v}^{\alpha i}\right)\right. \\ &\left. + \sum_{s} \mathscr{F}_{s}^{\alpha i}\left(\frac{\partial}{\partial P_{s}^{\alpha i}}\dot{\boldsymbol{R}}_{v}^{\alpha i}\right)\right]\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_{v}^{\alpha i} - \boldsymbol{r})\end{aligned} \tag{17.2-20}$$

The derivatives of $\dot{\boldsymbol{R}}_{v}^{\alpha i}$ with respect to the phase space variables are given by Eqs. 17.1-30 and 31. When we use these we find that it is convenient to define an "effective force" on bead v as

$$\mathscr{F}_{v} = \frac{m_{v}}{m_{p}}[\boldsymbol{F}^{(e)} + \boldsymbol{F}] + \sqrt{m_{v}}\sum_{s}\sum_{t}\left[\mathscr{F}_{s} G_{st}\boldsymbol{b}_{vt} + \sum_{u}\sum_{v} G_{uv} P_{v} P_{s}\left(\frac{\partial}{\partial Q_{u}} G_{st}\boldsymbol{b}_{vt}\right)\right] \tag{17.2-21}$$

It is to be noted that in this expression and in a number of those that follow, we omit for convenience the superscripts α and i specifying the species and identifying a particular molecule of that species. When this is done we use m_p to indicate the total mass of a molecule (polymer or solvent) rather than the more explicit m^{α}.

With the results developed above the general equation of change, Eq. 17.2-8 may be written in the form of the *equation of motion*

$$\boxed{\frac{\partial}{\partial t}\rho\boldsymbol{v} = -[\nabla\cdot\rho\boldsymbol{v}\boldsymbol{v}] - [\nabla\cdot\boldsymbol{\pi}^{(k)}] + \boldsymbol{S}} \tag{17.2-22}$$

in which

$$\boldsymbol{\pi}^{(k)} = \left\langle \sum_{\alpha i v} m_{v}^{\alpha}\left(\frac{1}{m^{\alpha}}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_{v}^{\alpha i} - \boldsymbol{v}\right)\left(\frac{1}{m^{\alpha}}\boldsymbol{p}^{\alpha i} + \dot{\boldsymbol{R}}_{v}^{\alpha i} - \boldsymbol{v}\right)\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_{v}^{\alpha i} - \boldsymbol{r})\right\rangle \tag{17.2-23}$$

$$\boldsymbol{S} = \left\langle \sum_{\alpha i v} \mathscr{F}_{v}^{\alpha i}\delta(\boldsymbol{r}^{\alpha i} + \boldsymbol{R}_{v}^{\alpha i} - \boldsymbol{r})\right\rangle \tag{17.2-24}$$

Equation 17.2-22 is similar in form to the equation of motion as given by Eq. D.6-3 or Eq. 1.1-8. The first two terms on the right arise from the first term in the expression for $\mathscr{L}\boldsymbol{B}$, Eq. 17.2-20. This first term in $\mathscr{L}\boldsymbol{B}$ has been separated to give the term containing $\rho\boldsymbol{v}\boldsymbol{v}$, the convective term associated with the bulk flow of the fluid relative to the fixed frame, and another term, containing $\boldsymbol{\pi}^{(k)}$, which is usually referred to as the "kinetic contribution" to the stress tensor and describes the momentum transport due to the "Brownian" motion of the beads relative to a coordinate system moving with fluid velocity $\boldsymbol{v}$. The source term $\boldsymbol{S}$ describes the momentum transport associated with the effective force $\mathscr{F}_{v}^{\alpha i}$, defined by Eq. 17.2-21. It will be shown that except for the term in $\mathscr{F}_{v}^{\alpha i}$ containing the external force $\boldsymbol{F}^{(e)}$, the quantity $\boldsymbol{S}$ may also be written as the divergence of a tensor; this procedure will

then lead to additional contributions to the stress tensor associated with the various real and effective forces (compare Eqs. 17.2-22 and 17.4-32).

As examples, we may consider the explicit form of the effective force that appears in the source term of the equation of motion for several specific models. In particular, if one considers the elastic dumbbell model which is discussed in Chapter 13, one finds that the expressions for the effective forces given by Eq. 17.2-21 become for beads "1" and "2"

$$\mathscr{F}_1 = \tfrac{1}{2}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) + \frac{\partial \phi}{\partial Q}\boldsymbol{u} \tag{17.2-25}$$

$$\mathscr{F}_2 = \tfrac{1}{2}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) - \frac{\partial \phi}{\partial Q}\boldsymbol{u} \tag{17.2-26}$$

where $\boldsymbol{F}^{(e)}$ and $\boldsymbol{F}$ are the forces on the center of mass of the dumbbell due to the external and intermolecular potentials, respectively. In each expression the last term is the force on the bead due to the intramolecular potential which is in the direction of the spring ($\boldsymbol{u}$ is the unit vector $\boldsymbol{Q}/Q$). The analogous expressions for the specific case of the rigid dumbbell discussed in Chapter 14 are

$$\mathscr{F}_{-1} = \tfrac{1}{2}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) + \frac{2}{L}\mathscr{K}_{\text{int}}\boldsymbol{u} \tag{17.2-27}$$

$$\mathscr{F}_1 = \tfrac{1}{2}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) - \frac{2}{L}\mathscr{K}_{\text{int}}\boldsymbol{u} \tag{17.2-28}$$

where $\mathscr{K}_{\text{int}}$ is the rotational kinetic energy of the dumbbell defined by the general expression, Eq. 17.1-15, and $\boldsymbol{F}^{(e)}$ and $\boldsymbol{F}$ are defined as in Eqs. 17.2-25 and 17.2-26. In these equations the last terms are effective forces arising from the constraints; these terms are obtained from the last G_{st}-term in Eq. 17.2-21 with the help of Example 16.1-1.

EXAMPLE 17.2-1 The Effective Force for Models with No Constraints

Simplify Eq. 17.2-21 for the effective force $\mathscr{F}_v$, for models with no constraints and with beads that are mass points.

SOLUTION For any model with mass points (structureless beads) joined together with springs in any kind of connectivity, one can specify the location of the beads relative to the center of mass of the molecule by a set of vectors $\boldsymbol{Q}_k$. For a linear chain the $\boldsymbol{Q}_k$ would be the "connector vectors," but for a model with branching or closed loops the $\boldsymbol{Q}_k$ may be selected arbitrarily. In either case, if the generalized coordinates Q_s are taken to be the Cartesian components of $\boldsymbol{Q}_k$, we know that the g_{st} and G_{st} matrices do not depend on the generalized coordinates (cf. Eqs. 12.1-23 and 12.1-24). If this choice is made, then in Eq. 17.2-21 the term containing the double sum on u and v vanishes.

The force $\mathscr{F}_s$ in Eq. 17.2-21 can be obtained from Eqs. 17.1-20 to 24 as

$$\begin{aligned}\mathscr{F}_s &= -\frac{\partial}{\partial Q_s}(\phi + \phi^{(e)} + \Phi) \\ &= -\sum_{\mu}\frac{1}{\sqrt{m_\mu}}\left(\boldsymbol{b}_{\mu s}\cdot\frac{\partial}{\partial \boldsymbol{r}_\mu}(\phi + \phi^{(e)} + \Phi)\right)\end{aligned} \tag{17.2-29}$$

the second line being obtained by using the chain rule of partial differentiation (see §E.1). When this expression for $\mathscr{F}_s$ is inserted into Eq. 17.2-21, then use of 12D.3-5, a relation valid for systems with no constraints, gives

$$\mathscr{F}_v = \frac{m_v}{m_p}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) - \sqrt{m_v}\sum_\mu \frac{1}{\sqrt{m_\mu}}\left(\delta_{v\mu} - \frac{\sqrt{m_v m_\mu}}{m_p}\right)\frac{\partial}{\partial \boldsymbol{r}_\mu}(\phi + \phi^{(e)} + \Phi)$$

$$= \frac{m_v}{m_p}(\boldsymbol{F}^{(e)} + \boldsymbol{F}) - \frac{\partial}{\partial \boldsymbol{r}_v}(\phi + \phi^{(e)} + \Phi) + \frac{m_v}{m_p}\sum_\mu \frac{\partial}{\partial \boldsymbol{r}_\mu}(\phi + \phi^{(e)} + \Phi) \qquad (17.2\text{-}30)$$

Since the sum of the intramolecular forces on the beads of one molecule is zero, it follows that $-\sum_\mu (\partial/\partial \boldsymbol{r}_\mu)\phi$ is zero. In addition $-\sum_\mu (\partial/\partial \boldsymbol{r}_\mu)\phi^{(e)}$ is just the total external force on the molecule, $\boldsymbol{F}^{(e)}$, and $-\sum_\mu(\partial/\partial \boldsymbol{r}_\mu)\Phi$ is the total force $\boldsymbol{F}$ on the molecule due to all the other molecules. Therefore, some cancellation occurs and

$$\mathscr{F}_v = -\frac{\partial}{\partial \boldsymbol{r}_v}(\phi + \phi^{(e)} + \Phi) \qquad (17.2\text{-}31)$$

Thus, we see that if the molecular model involves no constraints the effective force $\mathscr{F}_v$, is simply the sum of the true forces arising from the various potentials. This general result is clearly consistent with the explicit expression for the elastic dumbbell model given by Eqs. 17.2-25 and 26; but for the rigid dumbbell model, which involves a constraint, the expressions for $\mathscr{F}_v$ have a different form (Eqs. 17.2-27 and 28).

§17.3 CONTRACTED DISTRIBUTION FUNCTIONS

In the foregoing sections a distribution function $f(x, t)$ in the full phase space of the system was introduced. Then the physical quantities of interest ρ, $\rho \boldsymbol{v}$, $\boldsymbol{\pi}^{(k)}$, and $\boldsymbol{S}$ were written as ensemble averages involving this distribution function. It will, however, be more convenient to express these averages in terms of certain "contracted distribution functions:"

The singlet phase-space distribution functions.
The pair phase-space distribution functions.
The singlet configuration-space distribution functions.
The pair configuration-space distribution functions.

In this section we define these contracted distribution functions, and then in the next section we obtain expressions for the stress tensor and other physical quantities in terms of these functions.

The singlet phase-space distribution function is the nonequilibrium generalization of the phase-space distribution function f_{eq} discussed in §12.3. Here we define the function for species α as

$$f_\alpha(\boldsymbol{r}, Q, \boldsymbol{p}, P, t) = \left\langle \sum_i \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r})\delta(Q^{\alpha i} - Q)\delta(\boldsymbol{p}^{\alpha i} - \boldsymbol{p})\delta(P^{\alpha i} - P) \right\rangle \qquad (17.3\text{-}1)$$

The argument Q is symbolic for the full set of generalized coordinates and $\delta(Q^{\alpha i} - Q)$ is symbolic for the corresponding product of δ-functions. Similar comments apply to P and

$\delta(P^{\alpha i} - P)$. The function $f_\alpha(r, Q, p, P, t)$ is the probable number density of molecules of species α in the phase-space; that is

$$f_\alpha(r, Q, p, P, t)dr\, dQ\, dp\, dP \tag{17.3-2}$$

is the probable number of molecules of this species with center of mass in the region dr about r and with momentum p, internal coordinates Q, and conjugate momenta P in the ranges dp, dQ, and dP about p, Q, and P.

The second set of contracted distribution functions is defined in an analogous manner

$$f_{\alpha\beta}(r', Q', r'', Q'', p', P', p'', P'', t) = \left\langle \sum_i \sum_j \delta(r^{\alpha i} - r')\delta(Q^{\alpha i} - Q')\delta(r^{\beta j} - r'')\delta(Q^{\beta j} - Q'') \times \delta(p^{\alpha i} - p')\delta(P^{\alpha i} - P')\delta(p^{\beta j} - p'')\delta(P^{\beta j} - P'') \right\rangle \tag{17.3-3}$$

These are functions in the two-molecule phase spaces. They are the joint probable number densities of molecules of the species indicated. If the two species are alike ($\alpha = \beta$), the terms in the double sum in which $i = j$ are to be omitted. These functions vary rapidly with the separation distance between the centers of mass of the molecules at separation distances of the order of molecular dimensions, but vary slowly with the position of the center of mass of the pair. For this reason it is convenient to change variables and define a related set of functions

$$\tilde{f}_{\alpha\beta}(r, R, Q', Q'', p', P', p'', P'', t) = f_{\alpha\beta}(r', Q', r'', Q'', p', P', p'', P'', t) \tag{17.3-4}$$

where

$$r = \frac{m'_p r' + m''_p r''}{m'_p + m''_p} \tag{17.3-5}$$

$$R = r'' - r' \tag{17.3-6}$$

In the new set of functions the variables r' and r'' are replaced by r, the vector to the center of mass of the pair, and R, the vector from the center of mass of the "first" molecule to that of the "second."

Next we define the configuration-space distribution functions by integrating the various phase space distribution functions over the momentum coordinates. As in the development of §12.3, the integration of the singlet function leads to the single-molecule configuration-space distribution function:

$$\Psi_\alpha(r, Q, t) = \iint f_\alpha(r, Q, p, P, t)dp\, dP \tag{17.3-7}$$

The integral of this function over the internal coordinates

$$\int \Psi_\alpha(r, Q, t)dQ = n_\alpha(r, t) \tag{17.3-8}$$

is the number density of molecules of species α (cf. Eq. 12.3-2).

In a similar manner the distribution functions in the configuration spaces of pairs are defined by integrating the $f_{\alpha\beta}$ over the momenta

$$\Psi_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', t) = \iiiint f_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', \boldsymbol{p}', P', \boldsymbol{p}'', P'', t)d\boldsymbol{p}'\, dP'\, d\boldsymbol{p}''\, dP'' \tag{17.3-9}$$

The functions, $\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q', Q'', t)$, are defined in a similar manner by integrating the corresponding phase-space functions over the momenta. If the two molecules are sufficiently far apart that they are statistically independent, that is, uncorrelated, the joint probability becomes a product of the separate probabilities, that is

$$\lim_{|\boldsymbol{r}''-\boldsymbol{r}'|\to\infty} \Psi_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', t) = \Psi_\alpha(\boldsymbol{r}', Q', t)\Psi_\beta(\boldsymbol{r}'', Q'', t) \tag{17.3-10}$$

Use is made of this later.

In the development of the next section, we make use of the symmetry of the pair distribution functions in configuration space. From the definitions, Eqs. 17.3-3 and 9, it follows that

$$\Psi_{\beta\alpha}(\boldsymbol{r}'', Q'', \boldsymbol{r}', Q', t) = \Psi_{\alpha\beta}(\boldsymbol{r}', Q', \boldsymbol{r}'', Q'', t) \tag{17.3-11}$$

and thus

$$\tilde{\Psi}_{\beta\alpha}(\boldsymbol{r}, \boldsymbol{R}, Q'', Q', t) = \tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, -\boldsymbol{R}, Q', Q'', t) \tag{17.3-12}$$

We conclude this section with the introduction of a convenient notation for an average over the momentum space. For any function, B, defined in the phase space of the system, we define the average

$$[\![B]\!]^\alpha = \frac{1}{\Psi_\alpha(\boldsymbol{r}, Q, t)} \iint \left\langle B \sum_i \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r})\delta(Q^{\alpha i} - Q)\delta(\boldsymbol{p}^{\alpha i} - \boldsymbol{p})\delta(P^{\alpha i} - P) \right\rangle d\boldsymbol{p}\, dP$$

$$= \frac{1}{\Psi_\alpha(\boldsymbol{r}, Q, t)} \left\langle B \sum_i \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r})\delta(Q^{\alpha i} - Q) \right\rangle \tag{17.3-13}$$

This average is a function in the configuration space of a single molecule of species α, and involves taking the ensemble average over all the momentum coordinates and over all configuration coordinates except those of a single molecule of species α. From the definition of the singlet phase space distribution function, Eq. 17.3-1, it follows that if B is a function, $b(\boldsymbol{r}, Q, \boldsymbol{p}, P)$, in the phase space of a single molecule of species α, this average reduces to

$$[\![b]\!]^\alpha = \frac{1}{\Psi_\alpha(\boldsymbol{r}, Q, t)} \iint b(\boldsymbol{r}, Q, \boldsymbol{p}, P)f_\alpha(\boldsymbol{r}, Q, \boldsymbol{p}, P, t)d\boldsymbol{p}\, dP \tag{17.3-14}$$

and becomes identical to the average in §12.4. In the applications of this chapter, the function B will, in general, depend on the momentum coordinates of a single molecule of species α only, but will depend on the configuration coordinates of several molecules.

§17.4 THE STRESS TENSOR IN TERMS OF THE CONFIGURATION SPACE DISTRIBUTION FUNCTIONS

We now return to the expressions for the various macroscopic properties and express them in terms of the singlet and pair distribution functions. From the expression, Eq. 17.2-10, for the *mass concentration* associated with molecules of species α and the definitions of the previous section, one finds that

$$\rho_\alpha(\boldsymbol{r}, t) = \sum_\nu m_\nu^\alpha \iiint f_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, \boldsymbol{p}, P, t) dQ\, d\boldsymbol{p}\, dP$$

$$= \sum_\nu m_\nu^\alpha \int \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t) dQ \tag{17.4-1}$$

The displaced position argument in the distribution function in the integrand arises from the finite extension of the polymer molecules in space.

In a similar manner one finds from Eq. 17.2-13, that the *momentum density* associated with molecules of a particular species α is

$$\rho_\alpha \boldsymbol{v}_\alpha = \sum_\nu m_\nu^\alpha \iiint \left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu\right) f_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, \boldsymbol{p}, P, t) dQ\, d\boldsymbol{p}\, dP$$

$$= \sum_\nu m_\nu^\alpha \int \left[\!\left[\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu\right]\!\right]^\alpha \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t) dQ \tag{17.4-2}$$

The *mass flux* of α is then

$$\boldsymbol{j}_\alpha = \sum_\nu m_\nu \int \left[\!\left[\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right]\!\right]^\alpha \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t) dQ \tag{17.4-3}$$

Next we turn to the *kinetic contribution to the stress tensor* as given by Eq. 17.2-23. This may be written as the sum of integrals involving the singlet distribution functions:

$$\boldsymbol{\pi}^{(k)} = \sum_{\alpha\nu} m_\nu^\alpha \int \left[\!\left[\left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right)\left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right)\right]\!\right]^\alpha \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_\nu, Q, t) dQ \tag{17.4-4}$$

Most of the remainder of this section will be concerned with the *source term* $\boldsymbol{S}$ in the equation of motion (Eq. 17.2-24). Before embarking on this discussion we introduce some additional notation for the effective forces.

Let us return to the expression for the effective force, $\mathscr{F}_v$, as given by Eq. 17.2-21, and separate the expression into terms involving the external forces, intramolecular effects, and intermolecular effects. Thus we first define

$$\mathscr{F}_v^{(e)} = \sqrt{m_v} \sum_{st} \mathscr{F}_s^{(e)} G_{st} \boldsymbol{b}_{vt} \tag{17.4-5}$$

$$\mathscr{F}_v^{(S)} = \sqrt{m_v} \sum_{st} \left[(\mathscr{F}_s^{(k)} + \mathscr{F}_s^{(\phi)}) G_{st} \boldsymbol{b}_{vt} + \sum_{uv} G_{uv} P_v P_s \left(\frac{\partial}{\partial Q_u} G_{st} \boldsymbol{b}_{vt} \right) \right] \tag{17.4-6}$$

$$\mathscr{F}_v^{(D)} = \frac{m_v}{m_p} \boldsymbol{F} + \sqrt{m_v} \sum_{st} \mathscr{F}_s^{(d)} G_{st} \boldsymbol{b}_{vt} \tag{17.4-7}$$

so that

$$\mathscr{F}_v = \left[\frac{m_v}{m_p} \boldsymbol{F}^{(e)} + \mathscr{F}_v^{(e)} \right] + \mathscr{F}_v^{(S)} + \mathscr{F}_v^{(D)} \tag{17.4-8}$$

The superscripts (S) and (D) stand for "single" and "double." The relation between these vector effective forces and the scalar forces introduced in §17.1 is summarized in Table 17.4-1.

The source term in the equation of motion as defined by Eq. 17.2-24 may be separated in an analogous manner and written as

$$\boldsymbol{S} = \boldsymbol{S}^{(e)} + \boldsymbol{S}^{(S)} + \boldsymbol{S}^{(D)} \tag{17.4-9}$$

Since $(m_v/m_p)\boldsymbol{F}^{(e)} + \mathscr{F}_v^{(e)}$ and $\mathscr{F}_v^{(S)}$ are functions of the phase-space coordinates of a single molecule only, the corresponding contributions to the source term are obtained by performing integrations over all momenta and the configuration coordinates of all other molecules. This leads directly to

$$\boldsymbol{S}^{(e)} = \sum_{\alpha v} \int \left(\frac{m_v^\alpha}{m^\alpha} \boldsymbol{F}^{(e)\alpha} + \mathscr{F}_v^{(e)\alpha} \right) \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_v, Q, t) dQ \tag{17.4-10}$$

$$\boldsymbol{S}^{(S)} = \sum_{\alpha v} \int [\![\mathscr{F}_v^{(S)\alpha}]\!]^\alpha \Psi_\alpha(\boldsymbol{r} - \boldsymbol{R}_v, Q, t) dQ \tag{17.4-11}$$

In the treatment of $\boldsymbol{S}^{(D)}$, the contribution of the intermolecular effects, we assume that the intermolecular potential is the sum of contributions associated with pairs of molecules

$$\Phi = \tfrac{1}{2} \sum_{\alpha i \beta j} \Phi^{\alpha i, \beta j} \tag{17.4-12}$$

where $\Phi^{\alpha i, \beta j}$ depends only on the configuration coordinates of the pair of molecules αi and βj, and the terms with both $\alpha = \beta$ *and* $i = j$ are zero. With the above assumption the source term, $\boldsymbol{S}^{(D)}$, may be written in terms of integrals involving only the pair distribution functions.

TABLE 17.4-1

Generalized and Effective Forces

Generalized Forces			Effective Forces			
Symbol	Defining Equation	Expression	Symbol	Defining Equation	Expression	$\sum_v \mathscr{F}_v^{(\ldots)}$
$\mathscr{F}_s^{(k)}$	17.1-20	—	$\mathscr{F}_v^{(S)}$	17.4-6		$\mathbf{0}$
$\mathscr{F}_s^{(\phi)}$	17.1-21	$-\dfrac{\partial}{\partial Q_s}\phi$				
$\mathscr{F}_s^{(e)}$	17.1-22	$-\dfrac{\partial}{\partial Q_s}\phi^{(e)}$	$\mathscr{F}_v^{(e)}$	17.4-5	$\sqrt{m_v}\sum_{st} G_{st}\mathscr{F}_s^{(e)}\boldsymbol{b}_{vt}$	$\mathbf{0}$
$\mathscr{F}_s^{(d)}$	17.1-23	$-\dfrac{\partial}{\partial Q_s}\Phi$	$\mathscr{F}_v^{(D)}$	17.4-7	$\dfrac{m_v}{m_p}\boldsymbol{F} + \sqrt{m_v}\sum_{st} G_{st}\mathscr{F}_s^{(d)}\boldsymbol{b}_{vt}$	$\boldsymbol{F}$
$\mathscr{F}_s$	17.1-24	$\sum \mathscr{F}_s^{(\ldots)}$	$\mathscr{F}_v$	17.2-21	$\left[\dfrac{m_v}{m_p}\boldsymbol{F}^{(e)} + \mathscr{F}_v^{(e)}\right] + \mathscr{F}_v^{(S)} + \mathscr{F}_v^{(D)}$	$\boldsymbol{F} + \boldsymbol{F}^{(e)}$

With the assumption of "two-molecule" forces (Eq. 17.4-12) it follows from the definition of $\mathscr{F}_\nu^{(D)}$ in Eq. 17.4-7, and Eq. 17.1-23 that

$$\mathscr{F}_\nu^{(D)\alpha i} = \sum_{\beta j} \mathscr{F}_\nu^{\alpha i, \beta j} \tag{17.4-13}$$

That is, the effective intermolecular force on a bead of molecule i of species α is the sum of contributions from all of the other molecules of the same or different species. If we abbreviate αi by α and βj by β, a typical term in the sum is given by

$$\mathscr{F}_\nu^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta) = \frac{m_\nu^\alpha}{m^\alpha} \boldsymbol{F}^{\alpha\beta} + \sqrt{m_\nu^\alpha} \sum_{st} \mathscr{F}_s^{\alpha\beta} G_{st}^\alpha \boldsymbol{b}_{\nu t}^\alpha \tag{17.4-14}$$

where $\boldsymbol{R}_{\alpha\beta} = \boldsymbol{r}_\beta - \boldsymbol{r}_\alpha$ and

$$\boldsymbol{F}^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta) = -\frac{\partial}{\partial \boldsymbol{r}^\alpha} \Phi^{\alpha\beta} \tag{17.4-15}$$

$$\mathscr{F}_s^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta) = -\frac{\partial}{\partial Q_s^\alpha} \Phi^{\alpha\beta} \tag{17.4-16}$$

The contribution of the intermolecular effects to the source term is given by

$$\boldsymbol{S}^{(D)} = \sum_{\alpha\beta\nu} \iiint \mathscr{F}_\nu^{\alpha\beta} \Psi_{\alpha\beta}(\boldsymbol{r} - \boldsymbol{R}_\nu^\alpha, Q_\alpha, \boldsymbol{r}_\beta, Q_\beta, t) dQ_\alpha \, d\boldsymbol{r}_\beta \, dQ_\beta \tag{17.4-17}$$

where $\mathscr{F}_\nu^{\alpha\beta}$ may be interpreted as the effective force on bead ν of a molecule of species α with the center of mass at $\boldsymbol{r} - \boldsymbol{R}_\nu$ due to a molecule of species β with center of mass at $\boldsymbol{r}_\beta$. The right side may be written using the alternate form of the pair distribution function as

$$\sum_{\alpha\beta\nu} \iiint \mathscr{F}_\nu^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}) \Psi_{\alpha\beta}\left(\boldsymbol{r} - \boldsymbol{R}_\nu^\alpha + \frac{m^\beta}{m^\alpha + m^\beta} \boldsymbol{R}_{\alpha\beta}, \boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta, t\right) dQ_\alpha \, dQ_\beta \, d\boldsymbol{R}_{\alpha\beta} \tag{17.4-18}$$

where the effective force is now that associated with a pair of molecules with the center of mass of the pair at the position indicated by the first argument of the distribution function and with the vector from α to β being $\boldsymbol{R}_{\alpha\beta}$.

Next, we develop an alternate form of the last result. To do this we first interchange the summation labels to obtain

$$\sum_{\alpha\beta\nu} \iiint \mathscr{F}_\nu^{\beta\alpha}(\boldsymbol{R}_{\beta\alpha}) \Psi_{\beta\alpha}\left(\boldsymbol{r} - \boldsymbol{R}_\nu^\beta + \frac{m^\alpha}{m^\alpha + m^\beta} \boldsymbol{R}_{\beta\alpha}, \boldsymbol{R}_{\beta\alpha}, Q_\beta, Q_\alpha, t\right) dQ_\alpha \, dQ_\beta \, d\boldsymbol{R}_{\beta\alpha} \tag{17.4-19}$$

and second make use of the symmetry of the pair distribution functions. We change the integration variable, implying integration from $-\infty$ to $+\infty$ in both expressions:

$$\sum_{\alpha\beta\nu} \iiint \mathscr{F}_\nu^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta}) \Psi_{\alpha\beta}\left(\boldsymbol{r} - \boldsymbol{R}_\nu^\beta - \frac{m^\alpha}{m^\alpha + m^\beta} \boldsymbol{R}_{\alpha\beta}, \boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta, t\right) dQ_\alpha \, dQ_\beta \, d\boldsymbol{R}_{\alpha\beta} \tag{17.4-20}$$

Finally, $\boldsymbol{S}^{(D)}$ may be written as one-half the sum of the expressions given by Eqs. 17.4-18 and 20,

$$\frac{1}{2}\sum_{\alpha\beta\nu}\iiint \mathscr{F}_{\nu}^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta})\,\tilde{\Psi}_{\alpha\beta}\left(\boldsymbol{r}-\boldsymbol{R}_{\nu}^{\alpha}+\frac{m^{\beta}}{m^{\alpha}+m^{\beta}}\boldsymbol{R}_{\alpha\beta},\boldsymbol{R}_{\alpha\beta},\boldsymbol{Q}_{\alpha},\boldsymbol{Q}_{\beta},t\right)d\boldsymbol{Q}_{\alpha}\,d\boldsymbol{Q}_{\beta}\,d\boldsymbol{R}_{\alpha\beta}$$

$$+\frac{1}{2}\sum_{\alpha\beta\nu}\iiint \mathscr{F}_{\nu}^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta})\,\tilde{\Psi}_{\alpha\beta}\left(\boldsymbol{r}-\boldsymbol{R}_{\nu}^{\beta}-\frac{m^{\alpha}}{m^{\alpha}+m^{\beta}}\boldsymbol{R}_{\alpha\beta},\boldsymbol{R}_{\alpha\beta},\boldsymbol{Q}_{\alpha},\boldsymbol{Q}_{\beta},t\right)d\boldsymbol{Q}_{\alpha}\,d\boldsymbol{Q}_{\beta}\,d\boldsymbol{R}_{\alpha\beta} \quad (17.4\text{-}21)$$

We have now completed the task of rewriting a number of macroscopic quantities (ρ_{α}, $\rho_{\alpha}\boldsymbol{v}_{\alpha}$, $\boldsymbol{j}_{\alpha}$, $\boldsymbol{\pi}^{(k)}$, and the three contributions to $\boldsymbol{S}$) in terms of the lower-order distribution functions Ψ_{α} and $\tilde{\Psi}_{\alpha\beta}$.

One final job remains, namely that of writing $\boldsymbol{S}^{(S)}$, $\boldsymbol{S}^{(D)}$, and part of $\boldsymbol{S}^{(e)}$ as divergences of tensors, so that the equation of motion (Eq. 17.2-22) can be put into the standard form given in Eq. D.6-3. This is accomplished by expanding Ψ_{α} and $\tilde{\Psi}_{\alpha\beta}$ about the position coordinate $\boldsymbol{r}$, which appears in the first independent variable of the distribution functions; to do this we use a generalized Taylor expansion given in §E.2. It turns out that the first term in the Taylor expansion is exactly zero for $\boldsymbol{S}^{(S)}$ and $\boldsymbol{S}^{(D)}$ as may be easily seen from the following arguments. If in Eq. 17.4-11 we replace $\Psi_{\alpha}(\boldsymbol{r}-\boldsymbol{R}_{\nu}, Q, t)$ by $\Psi_{\alpha}(\boldsymbol{r}, Q, t)$, then the summation on ν can be performed to give

$$\sum_{\nu}\mathscr{F}_{\nu}^{(S)\alpha}=\boldsymbol{0} \quad (17.4\text{-}22)$$

where we have made use of Eq. 17.4-6 and the fact that $\sum_{\nu}\sqrt{m_{\nu}}\boldsymbol{b}_{\nu t}=\boldsymbol{0}$; consequently with this replacement $\boldsymbol{S}^{(S)}=\boldsymbol{0}$. Similarly when in Eq. 17.4-21 we replace the distribution functions by $\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_{\alpha}, Q_{\beta}, t)$, then the summations on ν give

$$\sum_{\nu}\left[\mathscr{F}_{\nu}^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta})+\mathscr{F}_{\nu}^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta})\right]=\boldsymbol{F}^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta})+\boldsymbol{F}^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta}) \quad (17.4\text{-}23)$$

where Eq. 17.4-14 has been used. Since $\boldsymbol{F}^{\alpha\beta}$ is the total force on a molecule of α exerted by a molecule of β, it is evident that

$$\boldsymbol{F}^{\beta\alpha}(-\boldsymbol{R}_{\alpha\beta})=-\boldsymbol{F}^{\alpha\beta}(\boldsymbol{R}_{\alpha\beta}) \quad (17.4\text{-}24)$$

As a result in this approximation the two terms in Eq. 17.4-21 cancel one another and $\boldsymbol{S}^{(D)}=\boldsymbol{0}$.

Now we transform the expressions for $\boldsymbol{S}^{(e)}$, $\boldsymbol{S}^{(S)}$, and $\boldsymbol{S}^{(D)}$ by applying the generalized Taylor theorem of Eq. E.2-2 to Ψ_{α} and $\tilde{\Psi}_{\alpha\beta}$ as functions of their first variable. When this theorem is applied to $\boldsymbol{S}^{(e)}$ in Eq. 17.4-10 we find that

$$\boldsymbol{S}^{(e)}=n\bar{\boldsymbol{F}}^{(e)}-[\nabla\cdot\boldsymbol{\pi}^{(e)}] \quad (17.4\text{-}25)$$

where

$$\bar{\boldsymbol{F}}^{(e)}=\frac{1}{n}\sum_{\alpha}\int \boldsymbol{F}^{(e)\alpha}\,\Psi_{\alpha}(\boldsymbol{r}, Q, t)dQ \quad (17.4\text{-}26)$$

$$\boldsymbol{\pi}^{(e)}=\sum_{\alpha}\sum_{\nu}\iint_{0}^{1}\boldsymbol{R}_{\nu}\left(\frac{m_{\nu}^{\alpha}}{m_{\alpha}}\boldsymbol{F}^{(e)\alpha}+\mathscr{F}_{\nu}^{(e)\alpha}\right)\Psi_{\alpha}(\boldsymbol{r}-\xi\boldsymbol{R}_{\nu}, Q, t)d\xi\,dQ \quad (17.4\text{-}27)$$

In the expansion of $S^{(e)}$ the first term does not vanish, and this term $n\bar{F}^{(e)}$, corresponds to the external force term in the equation of motion ($\sum_i \rho_i \mathbf{g}_i$ in Eq. D.6-3).

In a similar manner one finds from Eq. 17.4-11, the expression for the contribution of the intramolecular effects, $S^{(S)}$, that

$$S^{(S)} = -[\nabla \cdot \pi^{(S)}] \tag{17.4-28}$$

where

$$\pi^{(S)} = \sum_{\alpha} \sum_{\nu} \int\int_0^1 \boldsymbol{R}_\nu [\![\mathscr{F}_\nu^{(S)\alpha}]\!]^\alpha \Psi_\alpha (\boldsymbol{r} - \xi \boldsymbol{R}_\nu, Q, t)\, d\xi\, dQ \tag{17.4-29}$$

In this case, the term analogous to $\bar{F}^{(e)}$ is zero because of Eq. 17.4-22 as just discussed.

The theorem is next applied to the "two-molecule" contribution, $S^{(D)}$, as given by Eq. 17.4-21. Again for the reasons discussed above the first term is zero and

$$S^{(D)} = -[\nabla \cdot \pi^{(D)}] \tag{17.4-30}$$

Before writing the expression for $\pi^{(D)}$, however, it is convenient to use the symmetry argument as discussed above to write the expression in the somewhat simpler unsymmetrized form

$$\pi^{(D)} = \sum_{\alpha\beta\nu} \int\int\int\int_0^1 \left(\boldsymbol{R}_\nu^\alpha - \frac{m^\beta}{m^\alpha + m^\beta} \boldsymbol{R}_{\alpha\beta} \right) \mathscr{F}_\nu^{\alpha\beta} \times \tilde{\Psi}_{\alpha\beta} \left(\boldsymbol{r} - \xi \boldsymbol{R}_\nu^\alpha + \frac{m^\beta}{m^\alpha + m^\beta} \xi \boldsymbol{R}_{\alpha\beta}, \boldsymbol{R}_{\alpha\beta}, Q_\alpha, Q_\beta, t \right) d\xi\, dQ_\alpha\, dQ_\beta\, d\boldsymbol{R}_{\alpha\beta} \tag{17.4-31}$$

We see finally that the *equation of motion*, Eq. 17.2-22 now can be written in the form of Eq. D.6-3 or Eq. 1.1-8,

$$\boxed{\frac{\partial}{\partial t} \rho \boldsymbol{v} = -[\nabla \cdot \rho \boldsymbol{v}\boldsymbol{v}] - [\nabla \cdot \pi] + n\bar{\boldsymbol{F}}^{(e)}} \tag{17.4-32}$$

where π is the *stress tensor*, which may be written as

$$\boxed{\pi = \pi^{(k)} + \pi^{(e)} + \pi^{(S)} + \pi^{(D)}} \tag{17.4-33}$$

The four contributions to the stress tensor are those associated with the molecular motion, external forces, intramolecular potentials, and intermolecular potentials (see Fig. 17.4-1).

Finally let us write down the analogous results for the *equation of continuity for species* α (cf. Eq. 17.2-12)

$$\boxed{\frac{\partial}{\partial t} \rho_\alpha = -(\nabla \cdot \rho_\alpha \boldsymbol{v}) - (\nabla \cdot \boldsymbol{j}_\alpha)} \tag{17.4-34}$$

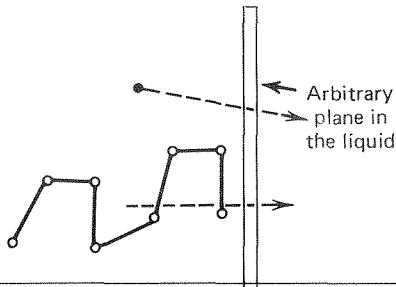
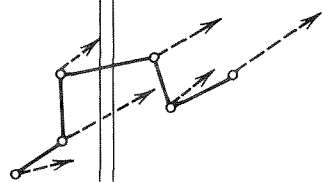
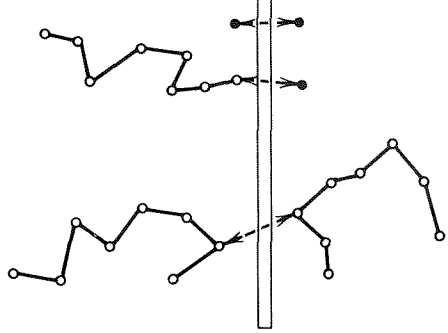
ntribution	Formal Expression	Pictorial Representation	Mechanism Involved
$\pi^{(k)}$	17.4-4		Momentum transport across plane by motion of solvent and polymer species (the "kinetic" contribution).
$\pi^{(e)}$	17.4-27		Force transmitted across plane because of the exertion of external forces on the solvent and polymer species (the "external force" contribution).
$\pi^{(S)}$	17.4-29		Force transmitted across plane by *intra*molecular forces in a polymer molecule straddling the plane (the "singlet" contribution).
$\pi^{(D)}$	17.4-31		Force transmitted across plane because of *inter*molecular forces between molecules of the same or different species (the "doublet" distribution).

FIGURE 17.4-1. Contributions to the stress tensor π in Eq. 17.4-33, pictured here for a liquid containing one solvent species and one polymer species.

in which the mass flux $\boldsymbol{j}_\alpha$ is

$$\boldsymbol{j}_\alpha = m_p \int \left[\!\!\left[\frac{1}{m_p}\boldsymbol{p} - \boldsymbol{v} \right]\!\!\right]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t) dQ$$
$$- \nabla \cdot \sum_\nu m_\nu \int\!\!\int_0^1 \boldsymbol{R}_\nu \left[\!\!\left[\frac{1}{m_p}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v} \right]\!\!\right]^\alpha \Psi_\alpha(\boldsymbol{r} - \xi \boldsymbol{R}_\nu, Q, t) d\xi\, dQ \qquad (17.4\text{-}35)$$

This result is obtained by applying the generalized Taylor theorem to Eq. 17.4-3. The first term in this expression may be interpreted as the product of the mass of a molecule and the

difference between the average velocity of the center of mass and the stream velocity of the fluid. This is the principal term. The second term is a correction which arises from the finite extent of the molecules.

This completes the formal development of the equations of change for momentum and mass and the derivation of integral expressions for the fluxes π and j_α in terms of the contracted distribution functions.

§17.5 EQUATIONS OF CONTINUITY FOR CONFIGURATIONAL DISTRIBUTION FUNCTIONS

In the foregoing section, we developed integral expressions for the various contributions to the stress tensor that involve the low-order distribution functions. The next step is the development of methods for evaluating or approximating these functions. For this purpose we return to the general equation of change, Eq. 17.2-8, and take as the dynamical variable of interest,

$$B = \sum_i B_i \tag{17.5-1}$$

$$B_i = \delta(\boldsymbol{r}^{\alpha i} - \boldsymbol{r})\delta(Q^{\alpha i} - Q)\delta(\boldsymbol{p}^{\alpha i} - \boldsymbol{p})\delta(P^{\alpha i} - P) \tag{17.5-2}$$

From the definition in Eq. 17.3-1, it is seen that the average of this dynamical variable is a singlet phase-space distribution function. Making use of the expression for the Liouville operator, Eq. 17.2-4, we then find that the general equation of change, Eq. 17.2-8 becomes for this special choice of the dynamical variable

$$\boxed{\frac{\partial}{\partial t} f_\alpha + \left(\frac{1}{m^\alpha}\boldsymbol{p}\cdot\nabla f_\alpha\right) + \sum_{st} P_s \frac{\partial}{\partial Q_t}(G_{st} f_\alpha) + \left(\boldsymbol{F}^{(e)}\cdot\frac{\partial}{\partial \boldsymbol{p}} f_\alpha\right) + \left(\frac{\partial}{\partial \boldsymbol{p}}\cdot\left\langle \sum_i \boldsymbol{F}^{\alpha i} B_i \right\rangle\right) + \sum_s \frac{\partial}{\partial P_s}\left\langle \sum_i \mathscr{F}_s^{\alpha i} B_i \right\rangle = 0} \tag{17.5-3}$$

This is the *equation for the time evolution of* f_α. The first four terms on the left of this equation along with the portion of the last term arising from the external and intramolecular potentials would occur in the "one-molecule Liouville equation." Setting the sum of these terms equal to zero gives an equation that would describe the time evolution of the singlet distribution for molecules moving independently and not interacting with any other molecules. The remaining terms describe the effect of interactions with the other molecules of the system. If we assume that the intermolecular potential energy Φ is the sum of two-molecule terms as given by Eq. 17.4-12, then these interaction terms may be written in terms of the pair distribution functions. First, we find that the fifth term involves

$$\left\langle \sum_i \boldsymbol{F}^{\alpha i} B_i \right\rangle = \sum_\beta \int \boldsymbol{F}^{\alpha\beta} f_{\alpha\beta}(\boldsymbol{r}, Q, \boldsymbol{r}_\beta, Q_\beta, \boldsymbol{p}, P, \boldsymbol{p}_\beta, P_\beta, t) d\boldsymbol{r}_\beta\, dQ_\beta\, d\boldsymbol{p}_\beta\, dP_\beta \tag{17.5-4}$$

where $\boldsymbol{F}^{\alpha\beta}$, as defined by Eq. 17.4-15, is the net force on a molecule of species α due to a molecule of species β.

In treating the last term in Eq. 17.5-3, we again, in a manner similar to the treatment of the source term in the equation of motion (see Eqs. 17.4-5 to 8), partition $\mathscr{F}_s^{\alpha i}$ into contributions due to the effects of external, intramolecular, and intermolecular forces. Thus we find from Eq. 17.1-24 that

$$\left\langle \sum_i \mathscr{F}_s^{\alpha i} B_i \right\rangle = (\mathscr{F}_s^{(e)} + \mathscr{F}_s^{(k)} + \mathscr{F}_s^{(\phi)}) f_\alpha + \sum_\beta \int \mathscr{F}_s^{\alpha\beta} f_{\alpha\beta}(\boldsymbol{r}, Q, \boldsymbol{r}_\beta, Q_\beta, \boldsymbol{p}, P, \boldsymbol{p}_\beta, P_\beta, t) d\boldsymbol{r}_\beta \, dQ_\beta \, d\boldsymbol{p}_\beta \, dP_\beta \qquad (17.5\text{-}5)$$

where $\mathscr{F}_s^{\alpha\beta}$ is the generalized force defined by Eq. 17.4-16. These terms describe the effects of the various forces on the orientation and other internal coordinates of a molecule.

If the expressions given by Eqs. 17.5-4 and 5 are used in Eq. 17.5-3, we obtain an equation for the time evolution of the singlet distribution function. This equation, however, involves the pair distribution functions and hence cannot be solved without a knowledge of these functions. This type of problem is typical of statistical treatments of non-equilibrium systems, and a "truncation" scheme is usually resorted to in order to obtain a "closed" set of equations. In the present treatment three major approximations are introduced to accomplish this truncation. One of these is the "short range force" approximation which we use to reduce the problem to one in the phase space of a single molecule (see §18.1 and Eq. 18.1-4); the second is an approximation, resembling Stokes' law for the average force on a bead (see §18.2, Eq. 18.2-1, and §19.2, Eq. 19.1-4); and the third is an approximation concerning the momentum dependence of the singlet distribution function which leads to an expression for the "Brownian" forces and further reduces the problem to one in the configuration space of a single molecule (see §§18.3 and 19.2).

When the differential equation, Eq. 17.5-3, for the singlet phase-space distribution function is integrated over all of the momentum coordinates, we obtain the *equation of continuity for the configuration-space distribution function*

$$\frac{\partial}{\partial t} \Psi_\alpha + \frac{1}{m^\alpha} \nabla \cdot ([\![\boldsymbol{p}]\!]^\alpha \Psi_\alpha) + \sum_s \sum_t \frac{\partial}{\partial Q_s} (G_{st} [\![P_t]\!]^\alpha \Psi_\alpha) = 0 \qquad (17.5\text{-}6)$$

In doing the integration the terms involving the pair distribution function drop out.

Another set of equations may be obtained from Eq. 17.5-3 by first multiplying by P_s and then integrating over all the momenta. This procedure gives the *equations of motion for the internal coordinates of a polymer molecule*

$$\frac{\partial}{\partial t} ([\![P_s]\!]^\alpha \Psi_\alpha) + \frac{1}{m^\alpha} \nabla \cdot ([\![\boldsymbol{p} P_s]\!]^\alpha \Psi_\alpha) = (\mathscr{F}_s^{(e)\alpha} + \mathscr{F}_s^{(\phi)\alpha} + \mathscr{F}_s^{(b)\alpha} + \mathscr{F}_s^{(h)\alpha}) \Psi_\alpha \qquad (17.5\text{-}7)$$

where

$$\mathscr{F}_s^{(b)\alpha} = [\![\mathscr{F}_s^{(k)}]\!]^\alpha - \frac{1}{\Psi_\alpha} \sum_t \frac{\partial}{\partial Q_t} ([\![\dot{Q}_t P_s]\!]^\alpha \Psi_\alpha) \qquad (17.5\text{-}8)$$

$$\mathscr{F}_s^{(h)\alpha} = \frac{1}{\Psi_\alpha} \sum_\beta \iint \mathscr{F}_s^{\alpha\beta} \Psi_{\alpha\beta}(\boldsymbol{r}, Q, \boldsymbol{r}_\beta, Q_\beta, t) \, d\boldsymbol{r}_\beta \, dQ_\beta \qquad (17.5\text{-}9)$$

TABLE 17.5-1

Generalized Forces

Symbol	Defining Equation	Expression	Symbol	Defining Equation	Expression
$\mathscr{F}_s^{(k)}$	17.1-20	—	$\mathscr{F}_s^{(b)}$	17.5-8	$[\![\mathscr{F}_s^{(k)}]\!]^\alpha + \cdots$
$\mathscr{F}_s^{(\phi)}$	17.1-21	$-\dfrac{\partial}{\partial Q_s}\phi$	$\mathscr{F}_s^{(\phi)}$	17.1-21	$-\dfrac{\partial}{\partial Q_s}\phi$
$\mathscr{F}_s^{(e)}$	17.1-22	$-\dfrac{\partial}{\partial Q_s}\phi^{(e)}$	$\mathscr{F}_s^{(e)}$	17.1-22	$-\dfrac{\partial}{\partial Q_s}\phi^{(e)}$
$\mathscr{F}_s^{(d)}$	17.1-23	$-\dfrac{\partial}{\partial Q_s}\Phi$	$\mathscr{F}_s^{(h)}$	17.5-9	$\dfrac{1}{\Psi_\alpha}\sum_\beta \iint \mathscr{F}_s^{\alpha\beta}\Psi_{\alpha\beta}\,d\boldsymbol{r}_\beta\,dQ_\beta$

The quantity $\mathscr{F}_s^{(b)\alpha}$ is a generalized force associated with Brownian forces, and $\mathscr{F}_s^{(h)\alpha}$ is related to the hydrodynamic forces. The generalized forces appearing in Eq. 17.5-7 are summarized in Table 17.5-1.

A similar set of equations associated with the motion of the center of mass of a molecule may be obtained by first multiplying Eq. 17.5-3 by $\boldsymbol{p}$ and integrating over the momenta. Before writing this equation, however, we define a force $\boldsymbol{F}^{(h)\alpha}$, which may be interpreted as the total hydrodynamic force on a molecule of species α, as

$$\boldsymbol{F}^{(h)\alpha} = \frac{1}{\bar{N}\Psi_\alpha}\sum_\beta \iint \boldsymbol{F}^{\alpha\beta}\Psi_{\alpha\beta}(\boldsymbol{r}, Q, \boldsymbol{r}_\beta, Q_\beta, t)d\boldsymbol{r}_\beta\,dQ_\beta \tag{17.5-10}$$

where

$$\bar{N} = \sum_\alpha x_\alpha N_\alpha \tag{17.5-11}$$

$$x_\alpha = \frac{n_\alpha}{\sum_\beta n_\beta} \tag{17.5-12}$$

In this definition we have introduced[1] the average number, $\bar{N}$, of beads per molecule (*including* the solvent, if any) in terms of the number of beads, N_α, making up a molecule of species α, and the mole fraction, x_α, of this species. With these definitions we find from Eq. 17.5-3 that the *equation of motion for the centers of mass of molecules of species* α is

$$\frac{\partial}{\partial t}([\![\boldsymbol{p}]\!]^\alpha\Psi_\alpha) + \frac{1}{m_p}\nabla\cdot([\![\boldsymbol{pp}]\!]^\alpha\Psi_\alpha) + \sum_{st}\frac{\partial}{\partial Q_t}(G_{st}[\![P_s\boldsymbol{p}]\!]^\alpha\Psi_\alpha) = (\boldsymbol{F}^{(e)\alpha} + \bar{N}\boldsymbol{F}^{(h)\alpha})\Psi_\alpha \tag{17.5-13}$$

[1] In later developments we approximate $\boldsymbol{F}^{(h)\alpha}$ by a Stokes' law type of expression involving a friction coefficient. It should be emphasized that the introduction of $\bar{N}$ at this point along with the physical interpretation of the friction coefficient leads directly to $D_{\text{tr}} \propto M^{-1/2}$ for the diffusion of a solute in a dilute solution with hydrodynamic interaction, $D_{\text{tr}} \propto M^{-1}$ for solutions with no hydrodynamic interaction, and $D_{\text{tr}} \propto M^{-2}$ for self diffusion in an undiluted polymer (see §§18.4 and 19.4). Note also that $\bar{N}$ is introduced in an analogous fashion in Eq. 18.1-8 for the hydrodynamic force $\boldsymbol{F}_v^{(h)\alpha}$ on a single bead v, and this plays a crucial role in the description of the molecular-weight dependence of the rheological properties of polymer melts (see Example 19.6-1).

The equation of motion discussed in §17.2 results from integrating this equation over the configuration coordinates Q_s and summing the equations over the species index α.

Equations 17.5-6 (equation of continuity for Ψ_α), 17.5-7 (equation of internal motion), and 17.5-13 (equation of center-of-mass motion) are key equations in the kinetic theory. Up to this point these equations are free from assumptions, but somewhat too general for most purposes. We now show that the introduction of a small number of minor assumptions simplifies the equations considerably. It is these slightly less rigorous equations that we use in subsequent chapters; in addition they are written in forms reminiscent of the equations given in Chapters 13-16.

It is to be expected that the distribution function, f_α, varies slowly with the position variable, $\boldsymbol{r}$, and that this variation over distances of the order of molecular dimensions may be neglected. This approximation allows us to neglect the second term in the equation of continuity, Eq. 17.5-6, and write the *equation of continuity for* Ψ_α as

$$\boxed{\begin{aligned}\frac{\partial}{\partial t}\Psi_\alpha &= -\sum_{st}\frac{\partial}{\partial Q_s}\left(G_{st}[\![P_t]\!]^\alpha\Psi_\alpha\right)\\ &= -\sum_{s}\frac{\partial}{\partial Q_s}\left([\![\dot{Q}_s]\!]^\alpha\Psi_\alpha\right)\end{aligned}} \tag{17.5-14}$$

Once an expression is introduced for the momentum space averages, $[\![P_t]\!]^\alpha$ or $[\![\dot{Q}_s]\!]^\alpha$, this equation becomes the "diffusion" equation for the distribution function.

The terms on the left of the equation of motion, Eq. 17.5-7 may be interpreted as "acceleration terms" and those on the right as force terms. If we neglect the acceleration terms, as we have done in Chapters 13-16, then the equation of motion becomes a simple *generalized force balance*

$$\boxed{\mathscr{F}_s^{(e)\alpha} + \mathscr{F}_s^{(\phi)\alpha} + \mathscr{F}_s^{(b)\alpha} + \mathscr{F}_s^{(h)\alpha} = 0} \tag{17.5-15}$$

The first two terms are related to the external and intramolecular or "connector" forces and, as previously mentioned, $\mathscr{F}_s^{(b)\alpha}$ and $\mathscr{F}_s^{(h)\alpha}$ are related to the Brownian and hydrodynamic forces. The manner in which these generalized forces are related to those introduced in §17.1 in the discussion of the Liouville equation is summarized in Table 17.5-1.

Equation 17.5-13 may be written in a form analogous to Eq. 17.5-7,

$$m^\alpha\left[\frac{\partial}{\partial t}(\boldsymbol{v}\Psi_\alpha) + \nabla\cdot(\boldsymbol{v}\boldsymbol{v}\Psi_\alpha)\right] + \frac{\partial}{\partial t}([\![\boldsymbol{p} - m^\alpha\boldsymbol{v}]\!]^\alpha\Psi_\alpha) + \nabla\cdot(\boldsymbol{v}[\![\boldsymbol{p} - m^\alpha\boldsymbol{v}]\!]^\alpha\Psi_\alpha)$$
$$+ \nabla\cdot([\![\boldsymbol{p} - m^\alpha\boldsymbol{v}]\!]^\alpha\boldsymbol{v}\Psi_\alpha) = (\bar{N}\boldsymbol{F}^{(h)\alpha} + \boldsymbol{F}^{(b)\alpha} + \boldsymbol{F}^{(e)\alpha})\Psi_\alpha \tag{17.5-16}$$

where

$$\boldsymbol{F}^{(b)\alpha} = -\frac{1}{m^\alpha\Psi_\alpha}\nabla\cdot([\![(\boldsymbol{p} - m^\alpha\boldsymbol{v})(\boldsymbol{p} - m^\alpha\boldsymbol{v})]\!]^\alpha\Psi_\alpha) - \frac{1}{\Psi_\alpha}\sum_{st}\frac{\partial}{\partial Q_s}(G_{st}[\![P_t\boldsymbol{p}]\!]^\alpha\Psi_\alpha) \tag{17.5-17}$$

is interpreted as the total Brownian force on a molecule. The first term on the left of Eq. 17.5-16 is an acceleration term which we neglect; if, in addition, we neglect those terms

which contain the momentum-space average of the linear expression $(\boldsymbol{p} - m^\alpha \boldsymbol{v})$, then this equation also reduces to a *force balance*,

$$\boxed{\bar{N}\boldsymbol{F}^{(h)\alpha} + \boldsymbol{F}^{(b)\alpha} + \boldsymbol{F}^{(e)\alpha} = \boldsymbol{0}} \tag{17.5-18}$$

involving the total forces on a molecule: the hydrodynamic force $\boldsymbol{F}^{(h)\alpha}$ (Eq. 17.5-10), the Brownian force $\boldsymbol{F}^{(b)\alpha}$ (17.5-17) and the external force $\boldsymbol{F}^{(e)\alpha}$ (Eq. 17.1-18). The neglect of the terms containing $[\![\boldsymbol{p} - m^\alpha \boldsymbol{v}]\!]^{(\alpha)}$ is possible if f_α is an even function of $\boldsymbol{p} - m^\alpha \boldsymbol{v}$, as is indeed true at equilibrium; the validity of this assumption away from equilibrium needs further investigation.

§17.6 SIMPLIFIED EXPRESSIONS FOR THE STRESS TENSOR AND THE MASS FLUX

Now that we have simplified the equations of continuity and motion, the next task is to introduce some minor simplifications in the expressions for the contributions to the stress tensor: $\boldsymbol{\pi}^{(k)}$, $\boldsymbol{\pi}^{(e)}$, $\boldsymbol{\pi}^{(S)}$, and $\boldsymbol{\pi}^{(D)}$. In the arguments of the distribution functions we make the following simplifications:

In Eq. 17.4-4:	replace $\boldsymbol{r} - \boldsymbol{R}_\nu$ by $\boldsymbol{r}$
In Eq. 17.4-27 and 29:	replace $\boldsymbol{r} - \xi\boldsymbol{R}_\nu$ by $\boldsymbol{r}$
In Eq. 17.4-31:	replace $\boldsymbol{r} - \xi\boldsymbol{R}_\nu + [m^\beta/(m^\alpha + m^\beta)]\xi\boldsymbol{R}$ by $\boldsymbol{r}$

These approximations correspond to expanding the distribution functions about $\boldsymbol{r}$, using the generalized Taylor theorem in Eq. E.2-2, and neglecting all higher order terms, which would contain spatial gradients. From a molecular point of view this corresponds to neglecting the variation of Ψ_α and $\tilde{\Psi}_{\alpha\beta}$ over distances comparable to molecular dimensions.

When one makes the above assumptions, the stress tensor contributions can be simplified as follows:

$$\boldsymbol{\pi}^{(k)} = \sum_{\alpha\nu} m_\nu^\alpha \int \left[\!\!\left[\left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right)\left(\frac{1}{m^\alpha}\boldsymbol{p} + \dot{\boldsymbol{R}}_\nu - \boldsymbol{v}\right) \right]\!\!\right]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t)dQ \tag{17.6-1}$$

$$\boldsymbol{\pi}^{(e)} = \sum_{\alpha\nu} \int \boldsymbol{R}_\nu \mathscr{F}_\nu^{(e)\alpha} \Psi_\alpha(\boldsymbol{r}, Q, t)dQ \tag{17.6-2}$$

$$\boldsymbol{\pi}^{(S)} = \sum_{\alpha\nu} \int \boldsymbol{R}_\nu [\![\mathscr{F}_\nu^{(S)\alpha}]\!]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t)\, dQ \tag{17.6-3}$$

$$\begin{aligned}\boldsymbol{\pi}^{(D)} = &-\tfrac{1}{2}\sum_{\alpha\beta} \iiint \boldsymbol{R}\boldsymbol{F}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t)dQ_\alpha\, dQ_\beta\, d\boldsymbol{R} \\ &+ \sum_{\alpha\beta\nu st} \sqrt{m_\nu^\alpha} \iiint \mathscr{F}_s^{\alpha\beta} G_{st}^\alpha \boldsymbol{R}_\nu^\alpha \boldsymbol{b}_{\nu t}^\alpha \tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t)dQ_\alpha\, dQ_\beta\, d\boldsymbol{R}\end{aligned} \tag{17.6-4}$$

In the first term of the expression for $\boldsymbol{\pi}^{(D)}$, we have made use of the symmetry of the pair distribution function in a manner similar to that used in the discussion of $\boldsymbol{\pi}^{(D)}$ in §17.4 to replace the factor $m^\beta/(m^\alpha + m^\beta)$ by simply $\frac{1}{2}$.

We now show how the above contributions can be combined with the result that some cancellations occur, and then a remarkably simple expression for the stress tensor emerges. In the development it is convenient to introduce the effective forces defined on the right side of Table 17.6-1; since the effective forces $\mathscr{F}_v^{(\cdots)}$ are all related to the generalized forces $\mathscr{F}_s^{(\cdots)}$ in the same way, their use should cause no confusion. We start by rewriting the kinetic contribution, Eq. 17.6-1, as the sum of two terms:

$$\boldsymbol{\pi}^{(k)} = \boldsymbol{\pi}_k + \sum_{\alpha v} m_v^\alpha \int [\![\dot{\boldsymbol{R}}_v \dot{\boldsymbol{R}}_v]\!]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \tag{17.6-5}$$

$$\boldsymbol{\pi}_k = \sum_\alpha m^\alpha \int \left[\!\!\left[\left(\frac{1}{m^\alpha} \boldsymbol{p} - \boldsymbol{v} \right) \left(\frac{1}{m^\alpha} \boldsymbol{p} - \boldsymbol{v} \right) \right]\!\!\right]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \tag{17.6-6}$$

The first term on the right side of Eq. 17.6-5 describes the effect of the Brownian motion of the centers of mass of the molecules and the second that due to the motion of the beads relative to center of mass of the molecule.

Next let us consider the term in the expression for $\boldsymbol{\pi}^{(S)}$, as given by Eq. 17.6-3, resulting from the last term in the expression for $\mathscr{F}_v^{(S)}$, Eq. 17.4-6. This term may be written by performing an integration by parts:

$$\begin{aligned}
&\sum_{\alpha vstu} \sqrt{m_v^\alpha} \int [\![\dot{Q}_u P_s]\!]^\alpha \boldsymbol{R}_v \left(\frac{\partial}{\partial Q_u} G_{st}^\alpha \boldsymbol{b}_{vt}^\alpha \right) \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \\
&\quad = -\sum_{\alpha vstu} \sqrt{m_v^\alpha} \int \left\{ \frac{\partial}{\partial Q_u} \boldsymbol{R}_v [\![\dot{Q}_u P_s]\!]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t) \right\} G_{st}^\alpha \boldsymbol{b}_{vt}^\alpha \, dQ \\
&\quad = -\sum_{\alpha vstu} \int \boldsymbol{b}_{vu}^\alpha [\![\dot{Q}_u P_s]\!]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t) G_{st}^\alpha \boldsymbol{b}_{vt}^\alpha \, dQ \\
&\qquad - \sum_{\alpha vstu} \sqrt{m_v^\alpha} \int \boldsymbol{R}_v \left\{ \frac{\partial}{\partial Q_u} [\![\dot{Q}_u P_s]\!]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t) \right\} G_{st}^\alpha \boldsymbol{b}_{vt}^\alpha \, dQ
\end{aligned} \tag{17.6-7}$$

The term in the next to last line of the last equation differs from the second term in the expression for $\boldsymbol{\pi}^{(k)}$, Eq. 17.6-5, only in the sign and hence cancels this term. It is then convenient to combine the last term in Eq. 17.6-7 with $\boldsymbol{\pi}^{(S)}$ (as given by Eq. 17.6-3). This then gives for the sum of the two contributions to the stress tensor:

$$\boldsymbol{\pi}^{(k)} + \boldsymbol{\pi}^{(S)} = \boldsymbol{\pi}_k + \sum_{\alpha v} \int \boldsymbol{R}_v (\mathscr{F}_v^{(\phi)\alpha} + \mathscr{F}_v^{(b)\alpha}) \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \tag{17.6-8}$$

Next, one returns to Eq. 17.5-9, which defines $\mathscr{F}_s^{(h)\alpha}$, rewrites the integral in terms of $\tilde{\Psi}_{\alpha\beta}$ and approximates $\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r} + \frac{1}{2}\boldsymbol{R}, \boldsymbol{R}, t)$ by $\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, t)$. Then, in the second term in $\boldsymbol{\pi}^{(D)}$, as given in Eq. 17.6-4, $\tilde{\Psi}_{\alpha\beta}$ can be eliminated in favor of Ψ_α by means of Eq. 17.5-9; in the process $\mathscr{F}_s^{(h)\alpha}$

TABLE 17.6-1

Generalized and Effective Forces

Symbol	Defining Equation	Expression	Symbol	Defining Equation
$\mathscr{F}_s^{(b)}$	17.5-8	—	$\mathscr{F}_v^{(b)}$	$\sqrt{m_v}\sum_{st}\mathscr{F}_s^{(b)}G_{st}\boldsymbol{b}_{vt}$
$\mathscr{F}_s^{(\phi)}$	17.1-21	$-\dfrac{\partial}{\partial Q_s}\phi$	$\mathscr{F}_v^{(\phi)}$	$\sqrt{m_v}\sum_{st}\mathscr{F}_s^{(\phi)}G_{st}\boldsymbol{b}_{vt}$
$\mathscr{F}_s^{(e)}$	17.1-22	$-\dfrac{\partial}{\partial Q_s}\phi^{(e)}$	$\mathscr{F}_v^{(e)}$	$\sqrt{m_v}\sum_{st}\mathscr{F}_s^{(e)}G_{st}\boldsymbol{b}_{vt}$
$\mathscr{F}_s^{(h)}$	17.5-9	$\dfrac{1}{\Psi_\alpha}\sum_\beta\iint\mathscr{F}_s^{\alpha\beta}\Psi_{\alpha\beta}\,d\boldsymbol{r}_\beta\,dQ_\beta$	$\mathscr{F}_v^{(h)}$	$\sqrt{m_v}\sum_{st}\mathscr{F}_s^{(h)}G_{st}\boldsymbol{b}_{vt}$

appears, and this scalar force can be expressed in terms of the vector force $\mathscr{F}_v^{(h)\alpha}$ according to Table 17.6-1. These substitutions then enable us to rewrite the second term in $\pi^{(D)}$ as

$$\sum_{\alpha v}\int \boldsymbol{R}_v\mathscr{F}_v^{(h)\alpha}\Psi_\alpha(\boldsymbol{r}, Q, t)dQ \tag{17.6-9}$$

This has the same form as the integrals in Eq. 17.6-2 and 8.

Finally we note that the generalized force balance in Eq. 17.5-15 can be written, using Table 17.6-1, as an effective force balance

$$\boxed{\mathscr{F}_v^{(e)\alpha}+\mathscr{F}_v^{(\phi)\alpha}+\mathscr{F}_v^{(b)\alpha}+\mathscr{F}_v^{(h)\alpha}=\boldsymbol{0}} \tag{17.6-10}$$

When we now add together the various contributions to the stress tensor (Eqs. 17.6-8, 17.6-2, 17.6-9, and the first term in Eq. 17.6-4) and use the force balance, we obtain the following extraordinarily simple expression for the stress tensor of a polymeric liquid:[1]

$$\boxed{\boldsymbol{\pi}=\boldsymbol{\pi}_k-\tfrac{1}{2}\sum_{\alpha\beta}\iiint\boldsymbol{R}\boldsymbol{F}^{\alpha\beta}\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t)dQ_\alpha\,dQ_\beta\,d\boldsymbol{R}} \tag{17.6-11}$$

The first term, which is given by Eq. 17.6-6, is the kinetic contribution (i.e., the effect of the Brownian motion of the centers of mass of the molecules). The second term describes the effects of the net intermolecular forces between the centers of mass of the molecules. The evaluation of this term requires a knowledge of the pair distribution functions $\tilde{\Psi}_{\alpha\beta}$.

[1] This equation seems to be a generalization of Eq. 5.15 of J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.*, **18**, 817–829 (1950); see also M. Fixman, *J. Chem. Phys.*, **42**, 3831–3837 (1965).

We conclude by pointing out that the mass flux j_α can be simplified in a manner analogous to the treatment of the contributions to π in Eqs. 17.6-1 to 4. From Eq. 17.4-35 we obtain

$$\boxed{j_\alpha = m_p \int \left[\!\left[\frac{1}{m_p} \boldsymbol{p} - \boldsymbol{v} \right]\!\right]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t) dQ - \nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu [\![\dot{\boldsymbol{R}}_\nu]\!]^\alpha \Psi_\alpha(\boldsymbol{r}, Q, t) dQ} \tag{17.6-12}$$

It is shown in the next two chapters that the first term is the principal contribution, linear in the concentration gradient and the external force.

PROBLEMS

17B.1 Effective Forces in Models with No Constraints

Show that for a molecular model with no constraints each of the effective forces listed in Table 17.4-1 is the negative of the derivative of a potential (that is, a *true* force).

17B.2 Metric Matrix of a Special Two-Needle Model

Show that the metric matrix, g_{st}, of the "two-needle" molecular model described in Example 17.1-1 with $\omega = \frac{2}{3}$ is identical to the metric matrix of the three-bead, two-rod model described in Example 12.1-1, if the needles are idealized as mass points separated by massless rods.

17C.1 Three-Bead Models

Develop explicit expressions for each of the forces listed in Table 17.4-1 for the two related molecular models: (a) the three-bead, two-spring model (see Example 12.1-2) and (b) the three-bead, two-rod model (see Example 12.1-1).

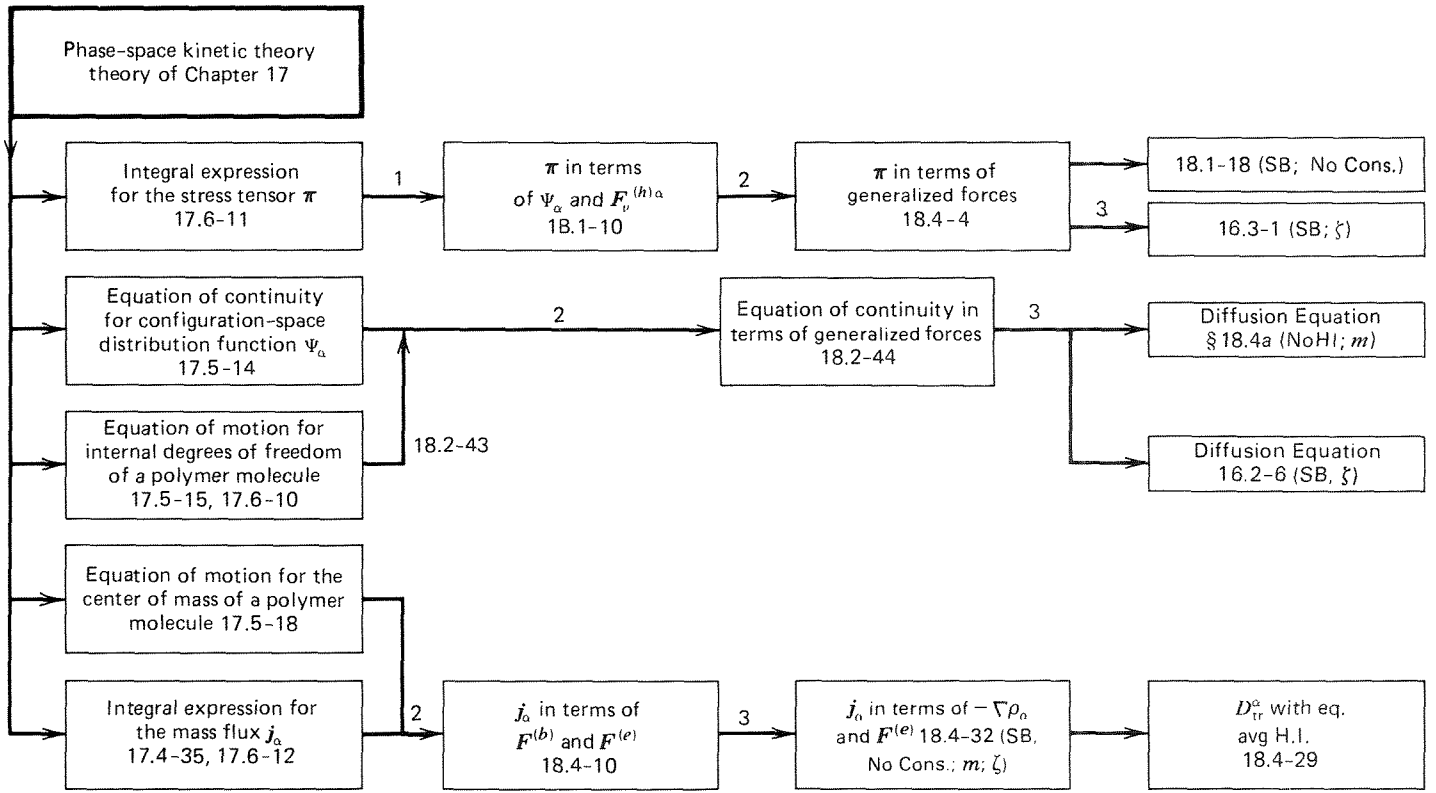
CHAPTER 18

PHASE-SPACE THEORY FOR DILUTE SOLUTIONS

In the foregoing chapter we obtained the five major results listed at the left of Fig. 18.0-1. These key equations, which are all obtained from a common source (the general equation of change), contain only the minor assumptions listed in the opening paragraph of Chapter 17. However, in order to evaluate various quantities appearing in these general results we would have to know not only the configurational distribution function Ψ_α for a single molecule, but also the pair distribution function $\Psi_{\alpha\beta}$ and the single-molecule phase-space distribution function f_α (needed for the calculation of the $[\![\ ]\!]$-averages). If we can avoid the necessity of obtaining $\Psi_{\alpha\beta}$ and f_α, considerable simplification ensues, and the theoretical results are more easily applied. This chapter is devoted primarily to the introduction of three major approximations, which we believe to be appropriate for dilute polymer solutions, that do indeed eliminate $\Psi_{\alpha\beta}$ and f_α from further consideration. These approximations are:

1. The *short-range force approximation*, which states that the only non-negligible contributions from the *inter*molecular forces are those occuring when "beads" belonging to two different molecules are in very close proximity. We feel that this approximation is quite reasonable.
2. The *Stokes' law empiricism* for the hydrodynamic drag on a bead (or some modification of this linear relation between the drag force and the bead velocity); this assumption may be less defensible but, as we have seen in Chapters 13–16, it has been used in all of the theories discussed so far. The version of Stokes' law introduced here includes the possibility of a tensor friction coefficient.
3. The *equilibration-in-momentum-space approximation*, which has also been used in the earlier developments and which leads to the standard results for the terms ascribed to Brownian motion; very little has been done to explore deviations from the Maxwellian velocity distribution.

These three major approximations are discussed in the above order in §§18.1, 2, and 3 respectively; their roles in the theoretical developments are made clear in Fig. 18.0-1. In the treatment of undiluted polymers discussed in Chapter 19 the short-range force approximation as discussed in this chapter is used, but a different form of the Stokes' law empiricism is introduced (see §19.1) and the assumption of equilibration-in-momentum-space is replaced by an approximation describing "reptation" (see §19.2).


Phase-space kinetic theory theory of Chapter 17
Integral expression for the stress tensor π 17.6-11
1
π in terms of Ψ_α and $F_v^{(h)\alpha}$ 18.1-10
2
π in terms of generalized forces 18.4-4
3
18.1-18 (SB; No Cons.)
16.3-1 (SB; ζ)
Equation of continuity for configuration-space distribution function Ψ_α 17.5-14
2
Equation of continuity in terms of generalized forces 18.2-44
3
Diffusion Equation §18.4a (NoHI; m)
Equation of motion for internal degrees of freedom of a polymer molecule 17.5-15, 17.6-10
18.2-43
Diffusion Equation 16.2-6 (SB, ζ)
Equation of motion for the center of mass of a polymer molecule 17.5-18
Integral expression for the mass flux j_α 17.4-35, 17.6-12
2
j_α in terms of $F^{(b)}$ and $F^{(e)}$ 18.4-10
3
j_α in terms of $-\nabla\rho_\alpha$ and $F^{(e)}$ 18.4-32 (SB, No Cons.; m; ζ)
D_{tr}^{α} with eq. avg H.I. 18.4-29

The first three sections of this chapter are written in such a way that a variety of physical ideas are included:

Hydrodynamic interaction.
Finite beads.
Constraints.
External forces.
Non-isotropic friction tensors in the Stokes' law relation.
Beads with different masses and friction tensors.

This means that the results given in §§18.1-3 can provide the description of a variety of different "models" of polymeric fluids. We have in these equations the starting point for studying the effects of hydrodynamic interaction or anisotropic Brownian motion; bead-spring models with no constraints or bead-rod models with constraints; models with structureless beads or models with finite beads; models with all beads alike or with beads that may have different masses and friction coefficients. Many of the models that can be generated have yet to be explored.

In the last section of this chapter, §18.4, we summarize certain key results for the kinetic theory of dilute solutions: the diffusion equation for Ψ_α; the stress tensor π; and the mass flux j_α and the translational diffusivity D_{tr}^{α}. We also point out connections with Chapter 16 and other earlier chapters.

§18.1 THE SHORT-RANGE FORCE APPROXIMATION

The first major approximation of the development is made as a first step towards eliminating the need for the pair distribution function and thereby reduces the problem to one in the phase space of a single molecule. For this purpose we first assume that the potential energy of a pair of molecules is the sum of the potential energies associated with pairs of beads on different molecules

$$\Phi^{\alpha\beta} = \sum_{\nu} \sum_{\mu} \Phi_{\nu\mu}^{\alpha\beta} \tag{18.1-1}$$

Then the force between the centers of mass, introduced in Eq. 17.4-15, is a similar sum

$$\boldsymbol{F}^{\alpha\beta} = \sum_{\nu} \sum_{\mu} \boldsymbol{F}_{\nu\mu}^{\alpha\beta} \tag{18.1-2}$$

FIGURE 18.0-1. "Flow chart" for Chapter 18 showing how the key results are obtained from Chapter 17.

MAJOR APPROXIMATIONS	SIMPLIFICATION OF MODEL
1. Short-range force approximation	NoHI – no hydrodynamic interaction
	No Cons. – no constraints
2. Modified Stokes' law empiricism	SB – structureless beads
	ζ – scalar friction coefficient
3. Equilibration in momentum space approximation	m – all beads have same mass

where

$$\boldsymbol{F}_{\nu\mu}^{\alpha\beta} = -\frac{\partial}{\partial \boldsymbol{r}^{\alpha}} \Phi_{\nu\mu}^{\alpha\beta} \tag{18.1-3}$$

is the contribution to the force on the center of mass of a molecule of species α due to the force on bead ν arising from bead μ on a molecule of species β. This force depends on the vector between the centers of mass of the two beads $\alpha\nu$ and $\beta\mu$ as well as any additional coordinates that may be required to specify the orientation of the finite beads.

According to the *short-range force approximation* the force $\boldsymbol{F}_{\nu\mu}^{\alpha\beta}$ is small unless the beads ν (of molecule α) and μ (of molecule β) are very close to one another (see Fig. 18.1-1). Thus, as an approximation in the integral of the second term of the expression for the stress tensor $\boldsymbol{\pi}$ (Eq. 17.6-11), we can say that $\boldsymbol{F}_{\nu\mu}^{\alpha\beta}$ is zero unless

$$\boldsymbol{R} = \boldsymbol{R}_{\nu}^{\alpha} - \boldsymbol{R}_{\mu}^{\beta} \tag{18.1-4}$$

so that

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k - \tfrac{1}{2} \sum_{\alpha\beta\nu\mu} \iiint (\boldsymbol{R}_{\nu}^{\alpha} - \boldsymbol{R}_{\mu}^{\beta}) \boldsymbol{F}_{\nu\mu}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, \boldsymbol{R}, Q_{\alpha}, Q_{\beta}, t) dQ_{\alpha}\, dQ_{\beta}\, d\boldsymbol{R} \tag{18.1-5}$$

It then follows from the symmetry of the pair distribution function (§17.3) that

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k - \sum_{\alpha\beta\nu} \iiint \boldsymbol{R}_{\nu}^{\alpha} \boldsymbol{F}_{\nu}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, \boldsymbol{R}, Q_{\alpha}, Q_{\beta}, t) dQ_{\alpha}\, dQ_{\beta}\, d\boldsymbol{R} \tag{18.1-6}$$

where

$$\boldsymbol{F}_{\nu}^{\alpha\beta} = \sum_{\mu} \boldsymbol{F}_{\nu\mu}^{\alpha\beta} \tag{18.1-7}$$

is the force on the center of mass of a molecule of species α due to forces on bead ν arising from interactions with a molecule of species, β.

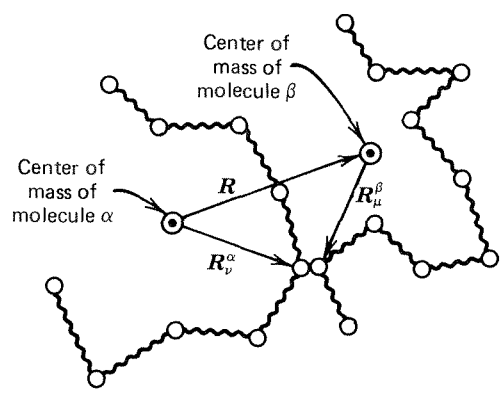


FIGURE 18.1-1. Bead ν of molecule α and bead μ of molecule β are located at the same point in space, so that $\boldsymbol{R} = \boldsymbol{R}_{\nu}^{\alpha} - \boldsymbol{R}_{\mu}^{\beta}$.

Next, by analogy with the definition of $\boldsymbol{F}^{(h)\alpha}$ given in Eq. 17.5-10 we define the hydrodynamic force on bead ν of molecule α by

$$\boldsymbol{F}_{\nu}^{(h)\alpha} = \frac{1}{\bar{N}\Psi_{\alpha}} \sum_{\beta} \iint \boldsymbol{F}_{\nu}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(r, R, Q_{\alpha}, Q_{\beta}, t) dQ_{\beta}\, dR \tag{18.1-8}$$

in which $\bar{N} = \sum x_{\alpha} N_{\alpha}$ is the average number of beads per molecule in the mixture with mole fractions x_{α} (Eq. 17.5-11). From this definition and Eqs. 18.1-2 and 7, it follows that the total hydrodynamic force on a molecule is:

$$\boldsymbol{F}^{(h)\alpha} = \sum_{\nu} \boldsymbol{F}_{\nu}^{(h)\alpha} \tag{18.1-9}$$

The definitions of hydrodynamic forces are summarized in Table 18.1-1.

With the definition of $\boldsymbol{F}_{\nu}^{(h)\alpha}$ above we can rewrite the expression for the stress tensor, Eq. 18.1-6, as:

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k - \bar{N} \sum_{\alpha\nu} \int \boldsymbol{R}_{\nu}^{\alpha} \boldsymbol{F}_{\nu}^{(h)\alpha} \Psi_{\alpha}(r, Q, t) dQ \tag{18.1-10}$$

where $\boldsymbol{\pi}_k$ is given by Eq. 17.6-6. In this form the single-molecule distribution function Ψ_{α} appears explicitly. Of course, the pair distribution function $\tilde{\Psi}_{\alpha\beta}$ is contained in the definition of $\boldsymbol{F}_{\nu}^{(h)\alpha}$; however, in the next section, after we introduce an empirical expression for $\boldsymbol{F}_{\nu}^{(h)\alpha}$, the pair distribution function no longer appears in any of the working equations. In addition we point out that Eq. 18.1-10 is a generalization of Eqs. 13.3-16 (elastic dumbbells) and 15.2-2 (bead-spring chains).

TABLE 18.1-1

Hydrodynamic Forces

Symbol	Defining Equation	Expression	Symbol	Defining Equation	Expression
$\mathscr{F}_{s}^{\alpha\beta}$	17.4-16	$-\frac{\partial}{\partial Q_s^{\alpha}} \Phi^{\alpha\beta}$	$\mathscr{F}_{s}^{(h)\alpha}$	17.5-9	$\frac{1}{\Psi_{\alpha}} \sum_{\beta} \iint \mathscr{F}_{s}^{\alpha\beta} \Psi_{\alpha\beta}\, d\boldsymbol{r}_{\beta}\, d$
$\mathscr{F}_{\nu}^{\alpha\beta} - \frac{m_{\nu}^{\alpha}}{m^{\alpha}} \boldsymbol{F}^{\alpha\beta}$	17.4-14	$\sqrt{m_{\nu}^{\alpha}} \sum_{s} \sum_{t} \mathscr{F}_{s}^{\alpha\beta} G_{st}^{\alpha} \boldsymbol{b}_{\nu t}^{\alpha}$	$\mathscr{F}_{\nu}^{(h)\alpha}$	See Table 17.6-1	$\sqrt{m_{\nu}^{\alpha}} \sum_{s} \sum_{t} \mathscr{F}_{s}^{(h)\alpha} G_{st}^{\alpha} \boldsymbol{b}_{\nu}^{\alpha}$
$\boldsymbol{F}_{\nu}^{\alpha\beta}$	18.1-3 18.1-7	$\sum_{\mu} \left(-\frac{\partial}{\partial \boldsymbol{r}^{\alpha}} \Phi_{\nu\mu}^{\alpha\beta} \right) = \sum_{\mu} \boldsymbol{F}_{\nu\mu}^{\alpha\beta}$	$\boldsymbol{F}_{\nu}^{(h)\alpha}$	18.1-8	$\frac{1}{\bar{N}\Psi_{\alpha}} \sum_{\beta} \iint \boldsymbol{F}_{\nu}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}\, dQ_{\beta}$
$\boldsymbol{F}^{\alpha\beta}$	17.4-15	$-\frac{\partial}{\partial \boldsymbol{r}^{\alpha}} \Phi^{\alpha\beta} = \sum_{\nu} \boldsymbol{F}_{\nu}^{\alpha\beta}$	$\boldsymbol{F}^{(h)\alpha}$	17.5-10	$\sum_{\nu} \boldsymbol{F}_{\nu}^{(h)\alpha}$

We conclude this section by developing formulas for the generalized and effective forces that are needed in subsequent developments. The hydrodynamic force $\boldsymbol{F}_{\nu}^{(h)\alpha}$ can be related to the generalized hydrodynamic force $\mathscr{F}_{s}^{(h)\alpha}$ of Eq. 17.5-9. To show this, we return to the definition of $\mathscr{F}_{s}^{\alpha\beta}$ in Eq. 17.4-16 and introduce the restriction to pairwise additive forces between beads, Eq. 18.1-1. We then find that

$$\mathscr{F}_{s}^{\alpha\beta} = -\sum_{\nu}\sum_{\mu}\frac{\partial}{\partial Q_{s}^{\alpha}}\Phi_{\nu\mu}^{\alpha\beta}$$

$$= \sum_{\nu}\sum_{\mu}\frac{1}{\sqrt{m_{\nu}^{\alpha}}}(\boldsymbol{b}_{\nu s}^{\alpha}\cdot\boldsymbol{F}_{\nu\mu}^{\alpha\beta}) + \sum_{\nu\mu\sigma} b_{\nu\sigma s}T_{\nu\mu,\sigma}^{\alpha\beta} \tag{18.1-11}$$

where

$$T_{\nu\mu,\sigma}^{\alpha\beta} = -\frac{\partial}{\partial q_{\nu\sigma}^{\alpha}}\Phi_{\nu\mu}^{\alpha\beta} \tag{18.1-12}$$

The second term is associated with the effects of the orientation coordinates of a finite bead. If this expression is used in the definition of the generalized hydrodynamic force, Eq. 17.5-9, one finds that

$$\mathscr{F}_{s}^{(h)} = \bar{N}\sum_{\nu}\frac{1}{\sqrt{m_{\nu}}}(\boldsymbol{b}_{\nu s}\cdot\boldsymbol{F}_{\nu}^{(h)}) + \bar{N}\sum_{\nu\sigma} b_{\nu\sigma s}T_{\nu\sigma}^{(h)} \tag{18.1-13}$$

where

$$T_{\nu\sigma}^{(h)\alpha} = \frac{1}{\bar{N}\Psi_{\alpha}}\sum_{\beta\mu}\iint T_{\nu\mu,\sigma}^{\alpha\beta}\tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_{\alpha}, Q_{\beta}, t)dQ_{\beta}\,d\boldsymbol{R} \tag{18.1-14}$$

One then finds from Table 17.6-1 that the effective hydrodynamic force is

$$\mathscr{F}_{\nu}^{(h)} = \bar{N}\sqrt{m_{\nu}}\sum_{st\mu} G_{st}\boldsymbol{b}_{\nu t}\left[\frac{1}{\sqrt{m_{\mu}}}(\boldsymbol{b}_{\mu s}\cdot\boldsymbol{F}_{\mu}^{(h)}) + \sum_{\sigma} b_{\mu\sigma s}T_{\mu\sigma}^{(h)}\right] \tag{18.1-15}$$

Only in special situations however, is it possible—even in principle—to solve this set of equations and express the $\boldsymbol{F}_{\mu}^{(h)}$ in terms of the $\mathscr{F}_{\nu}^{(h)}$; the following example illustrates this point. Note that Eqs. 18.1-13 and 15, simplified for structureless beads, appear in Eq. A of Table 16.1-3.

EXAMPLE 18.1-1 The Stress Tensor for Models with Structureless Beads and No Constraints

If the molecular model is made up of beads which are mass points, and if there are no constraints in the model, Eq. 18.1-15 may be solved for the hydrodynamic forces, $\boldsymbol{F}_{\mu}^{(h)}$. Obtain this solution and use it to obtain an alternative expression for the stress tensor applicable to this restricted molecular model.

SOLUTION For structureless beads $T^{(h)}_{\mu\sigma} = 0$, and for models with no constraints Eq. 12D.3-5 applies. This enables us to simplify Eq. 18.1-15 to

$$\boldsymbol{F}^{(h)}_{v} = \frac{m_v}{m_p}\boldsymbol{F}^{(h)} + \frac{1}{N}\boldsymbol{\mathscr{F}}^{(h)}_{v} \tag{18.1-16}$$

One then finds from Eq. 18.1-10 that

$$\pi = \pi_k - \sum_{\alpha v}\int \boldsymbol{R}_v \boldsymbol{\mathscr{F}}^{(h)\alpha}_{v}\Psi_\alpha(r, Q, t)dQ \tag{18.1-17}$$

It then follows from the force balance, Eq. 17.6-10, that

$$\begin{aligned}\pi &= \pi_k + \sum_{\alpha v}\int \boldsymbol{R}_v(\boldsymbol{\mathscr{F}}^{(e)\alpha}_{v} + \boldsymbol{\mathscr{F}}^{(\phi)\alpha}_{v} + \boldsymbol{\mathscr{F}}^{(b)\alpha}_{v})\Psi_\alpha(r, Q, t)dQ \\ &= \pi_k + \sum_{\alpha v}\int \boldsymbol{R}_v(\boldsymbol{F}^{(e)\alpha}_{v} + \boldsymbol{F}^{(\phi)\alpha}_{v} + \boldsymbol{F}^{(b)\alpha}_{v})\Psi_\alpha(r, Q, t)dQ\end{aligned} \tag{18.1-18}$$

This result should be compared with Eqs. 16.3-16, 15.2-1, and 13.3-14. In §18.4 we obtain a generalization of this result for less restricted models (see Eq. 18.4-4).

§18.2 MODIFIED STOKES' LAW EMPIRICISMS FOR THE HYDRODYNAMIC FORCES

We begin this section with the introduction of the second major approximation in the development—an approximation which resembles Stokes' law for the force on a sphere moving through a fluid (see Example 1.4-1). We follow the tradition of the older kinetic theories and assume that the hydrodynamic force $\boldsymbol{F}^{(h)\alpha}_{v}$ on bead v depends linearly on the difference between the statistically averaged velocity of the bead, $[\![\dot{\boldsymbol{r}}^\alpha_v]\!]^\alpha$, and the local velocity of the continuum background at the position of the bead, $\boldsymbol{v}(\boldsymbol{r}^\alpha_v) + \boldsymbol{v}'(\boldsymbol{r}^\alpha_v)$; here $\boldsymbol{v}$ is the mass-averaged velocity imposed on the fluid mixture by external forces and bounding surfaces, and $\boldsymbol{v}'$ is the perturbation of this velocity field by hydrodynamic interaction (if it is desired to include this effect in dilute solution modeling). In writing this linear relation we allow the coefficient of proportionality to be a tensor, $\boldsymbol{\zeta}^\alpha_v$, which we call the *friction tensor*, and it may be different for different beads; a non-isotropic tensor coefficient is particularly appropriate when finite, nonspherical beads are used in the modeling. Hence we write:

$$\boxed{\boldsymbol{F}^{(h)\alpha}_{v} = -\boldsymbol{\zeta}^\alpha_v \cdot [[\![\dot{\boldsymbol{r}}^\alpha_v]\!]^\alpha - \boldsymbol{v}(\boldsymbol{r}^\alpha_v) - \boldsymbol{v}'(\boldsymbol{r}^\alpha_v)]} \tag{18.2-1}$$

Whereas Stokes' law in classical fluid-dynamics is derived from the creeping flow equations of motion for a sphere moving at constant velocity through a quiescent Newtonian fluid, Eq. 18.2-1 is set forth as an empirical conjecture to describe the resistance encountered by a portion of a macromolecule as it moves about in an irregular way among the various solvent and solute molecules in the liquid. Note that Eq. 18.2-1 is the same as Eq. 13.2-2.

In dilute solutions it is customary to account for hydrodynamic interactions as we have done earlier (see §§13.6, 14.6, 15.4, and 16.1) by writing

$$\boldsymbol{v}'(\boldsymbol{r}^\alpha_v) = -\sum_{\mu}[\boldsymbol{\Omega}^\alpha_{v\mu} \cdot \boldsymbol{F}^{(h)\alpha}_{\mu}] \tag{18.2-2}$$

in terms of the matrix of *hydrodynamic interaction tensors* $\boldsymbol{\Omega}^{\alpha}_{\nu\mu}$; the quantity $\boldsymbol{v}'(\boldsymbol{r}^{\alpha}_{\nu})$ describes the perturbation of the velocity field due to the motion of the other beads of the same molecule. In dilute solutions hydrodynamic interaction involving beads on other molecules is neglected. We do not specify, here, the form of $\boldsymbol{\Omega}^{\alpha}_{\nu\mu}$, but point out that the Oseen-Burgers and Rotne–Prager–Yamakawa expressions have been used in earlier chapters (see §§13.6, 14.6, 15.4).

The velocity $\boldsymbol{v}(\boldsymbol{r}^{\alpha}_{\nu})$ appearing in Eq. 18.2-1 may be expanded in a Taylor series about the center of mass. If we keep only the first two terms we get:

$$\boldsymbol{v}(\boldsymbol{r}^{\alpha}_{\nu}) = \boldsymbol{v}(\boldsymbol{r}^{\alpha}) + [\boldsymbol{\kappa} \cdot \boldsymbol{R}^{\alpha}_{\nu}] \tag{18.2-3}$$

where $\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^{\dagger}$ is the transpose of the velocity gradient evaluated at the center of mass of the molecule of species α. The use of Eq. 18.2-3 is the same as the restriction to *homogeneous flow*, which was used throughout Chapters 13–16.

The main task of this section is to use Eq. 18.2-1 to obtain an expression for $[\![\dot{Q}^{\alpha}_{s}]\!]$ (Eq. 18.2-43) that can be substituted into Eq. 17.5-14 to obtain the diffusion equation, Eq. 18.2-44. The derivation is rather long and tedious, because we wish to retain the capability of including hydrodynamic interaction (using Eq. 18.2-2), and/or a tensorial friction coefficient ($\boldsymbol{\zeta}^{\alpha}_{\nu}$ in Eq. 18.2-1), and/or different friction coefficients for each bead. Before embarking on the derivation, it is useful to define some additional tensors, closely related to those used in §15.4 and §16.1.

As in §15.4 we use the matrix of tensors $\boldsymbol{\Upsilon}_{\nu\mu}$, which we call the *dimensionless diffusion tensors*[1]

$$\boldsymbol{\Upsilon}_{\nu\mu} = \delta_{\nu\mu}\boldsymbol{\delta} + \{\boldsymbol{\zeta}_{\nu} \cdot \boldsymbol{\Omega}_{\nu\mu}\} \tag{18.2-4}$$

Next, we define[2] the matrix of *dimensionless mobility tensors* $\mathbf{B}_{\nu\mu}$ by

$$\sum_{\mu} \{\mathbf{B}_{\nu\mu} \cdot \boldsymbol{\Upsilon}_{\mu\eta}\} = \delta_{\nu\eta}\boldsymbol{\delta} \tag{18.2-5}$$

and the matrix of *effective friction tensors* $\boldsymbol{\zeta}_{\nu\mu}$ by

$$\boldsymbol{\zeta}_{\nu\mu} = \{\mathbf{B}_{\nu\mu} \cdot \boldsymbol{\zeta}_{\mu}\} \tag{18.2-6}$$

Finally we define a set of *weight tensors* $\boldsymbol{\lambda}_{\nu}$ (a generalization of the l_{ν} of §15.4) by

$$\boldsymbol{\lambda}_{\nu} = \{\mathbf{Z}^{-1} \cdot \sum_{\mu} \boldsymbol{\zeta}_{\mu\nu}\} \tag{18.2-7}$$

where $\mathbf{Z}^{-1}$ is the tensor inverse to the *total effective friction tensor*

$$\mathbf{Z} = \sum_{\nu}\sum_{\mu} \boldsymbol{\zeta}_{\mu\nu} \tag{18.2-8}$$

The definition of the $\boldsymbol{\lambda}_{\nu}$ insures that $\sum_{\nu} \boldsymbol{\lambda}_{\nu} = \boldsymbol{\delta}$. These tensors are encountered again in the discussion of translational diffusion in §18.4.

[1] These tensors are closely related to the *diffusion tensors* used by J. G. Kirkwood [*Rec. Trav. Chim.*, **68**, 649–660 (1949), Eq. 14]; see also J. J. Erpenbeck and J. G. Kirkwood, *J. Chem. Phys.*, **38**, 1023–1024 (1963).

[2] See Problem 18B.1 for a proof that this may be done.

It is convenient to require that the friction tensors be symmetric

$$\zeta_\nu^\dagger = \zeta_\nu \tag{18.2-9}$$

and to take the hydrodynamic interaction tensors to have the related property that

$$\Omega_{\nu\mu}^\dagger = \Omega_{\mu\nu} \tag{18.2-10}$$

The Oseen-Burgers tensors (Eq. 15.4-3) and the Rotne-Prager-Yamakawa tensors (Eq. 14.6-2) both have this property. With these restrictions it may be shown that

$$\zeta_{\nu\mu}^\dagger = \zeta_{\mu\nu} \tag{18.2-11}$$

It may further be shown from Eqs. 18.2-7 and 8 that

$$\mathbf{Z}^\dagger = \mathbf{Z} \tag{18.2-12}$$

$$\lambda_\nu^\dagger = \left(\sum_\mu \zeta_{\nu\mu}\right) \cdot \mathbf{Z}^{-1} \tag{18.2-13}$$

These relations, which follow from the assumed symmetry of ζ_ν, lead to considerable simplification of a number of the relations developed in this section.

When the expressions for $\boldsymbol{v}$ and $\boldsymbol{v}'$ (Eqs. 18.2-2 and 3) are inserted into Eq. 18.2-1, and when the hydrodynamic force terms are all collected together on the left side, this equation becomes

$$\sum_\mu \{\Upsilon_{\nu\mu} \cdot \boldsymbol{F}_\mu^{(h)}\} = -\zeta_\nu \cdot [[\![\dot{\boldsymbol{r}}_c]\!] - \boldsymbol{v}(\boldsymbol{r}_c) + [\![\dot{\boldsymbol{R}}_\nu]\!] - \boldsymbol{\kappa} \cdot \boldsymbol{R}_\nu] \tag{18.2-14}$$

Then with the definitions of the dimensionless mobility tensors and the effective friction tensors, Eq. 18.2-14 can be solved for the hydrodynamic force on bead ν:

$$\boldsymbol{F}_\nu^{(h)} = -\sum_\mu \zeta_{\nu\mu} \cdot [[\![\dot{\boldsymbol{r}}_c]\!] - \boldsymbol{v}(\boldsymbol{r}_c) + [\![\dot{\boldsymbol{R}}_\mu]\!] - \boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu] \tag{18.2-15}$$

Therefore the total hydrodynamic force on a molecule, $\boldsymbol{F}^{(h)} = \sum_\nu \boldsymbol{F}_\nu^{(h)}$, is

$$\boldsymbol{F}^{(h)} = -\mathbf{Z} \cdot [[\![\dot{\boldsymbol{r}}_c]\!] - \boldsymbol{v}(\boldsymbol{r}_c) + \sum_\nu \lambda_\nu \cdot [[\![\dot{\boldsymbol{R}}_\nu]\!] - \boldsymbol{\kappa} \cdot \boldsymbol{R}_\nu]] \tag{18.2-16}$$

We can now use the force balance in Eq. 17.5-18 and solve for the "drift velocity" $[\![\dot{\boldsymbol{r}}_c]\!] - \boldsymbol{v}(\boldsymbol{r}_c)$ to get

$$[\![\dot{\boldsymbol{r}}_c]\!] - \boldsymbol{v}(\boldsymbol{r}_c) = \frac{1}{\bar{N}} [\mathbf{Z}^{-1} \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})] - \sum_\nu [\lambda_\nu \cdot ([\![\dot{\boldsymbol{R}}_\nu]\!] - [\boldsymbol{\kappa} \cdot \boldsymbol{R}_\nu])] \tag{18.2-17}$$

where $\boldsymbol{F}^{(b)}$ is the total Brownian force on a molecule, given by Eq. 17.5-17. This equation may be rearranged into the form

$$\sum_\nu [\lambda_\nu \cdot [\![\dot{\boldsymbol{r}}_\nu]\!]] - \boldsymbol{v}(\boldsymbol{r}_c) + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_c] - \sum_\nu [\lambda_\nu \cdot \boldsymbol{\kappa} \cdot \boldsymbol{r}_\nu] = \frac{1}{\bar{N}} [\mathbf{Z}^{-1} \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})] \tag{18.2-18}$$

In this form the equation may be compared with Eq. 15.4-16. If there are no concentration gradients, so that the total Brownian force $\boldsymbol{F}^{(b)}$ is zero, and if the total external force $\boldsymbol{F}^{(e)}$ is zero, then the right side of Eq. 18.2-18 is zero. If, in addition, the ζ_ν are isotropic, and if the hydrodynamic interaction tensors $\boldsymbol{\Omega}_{\nu\mu}$ are equilibrium averaged (and hence isotropic), then the $\boldsymbol{\lambda}_\nu$ are isotropic, and it follows that the quantity $\sum_\nu [\boldsymbol{\lambda}_\nu \cdot \boldsymbol{r}_\nu]$ is convected with the fluid; that is, in the notation of Eq. 15.4-16, we have $\sum_\nu [\boldsymbol{\lambda}_\nu \cdot [\![\dot{\boldsymbol{r}}_\nu]\!]] = \boldsymbol{v}_0 + \boldsymbol{\kappa} \cdot \sum_\nu [\boldsymbol{\lambda}_\nu \cdot \boldsymbol{r}_\nu]$. Thus we see that, with the restrictions just cited, the quantity $\sum_\nu [\boldsymbol{\lambda}_\nu \cdot \boldsymbol{r}_\nu]$ is the hydrodynamic center of resistance $\boldsymbol{r}_h = \sum_\nu l_\nu \boldsymbol{r}_\nu$, and the weight tensors $\boldsymbol{\lambda}_\nu$ are generalizations of the l_ν.

Making use of Eq. 18.2-17, we may rewrite the expression for the hydrodynamic force, Eq. 18.2-15, in the form

$$\boldsymbol{F}_\nu^{(h)} = -\sum_\mu \tilde{\zeta}_{\nu\mu} \cdot [[\![\dot{\boldsymbol{R}}_\mu]\!] - \boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu] - \frac{1}{\bar{N}} [\boldsymbol{\lambda}_\nu^\dagger \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})] \tag{18.2-19}$$

where the $\tilde{\zeta}_{\nu\mu}$ are the modified effective friction tensors

$$\tilde{\zeta}_{\nu\mu} = \zeta_{\nu\mu} - \left\{\left(\sum_\eta \zeta_{\nu\eta}\right) \cdot \boldsymbol{\lambda}_\mu\right\} = \zeta_{\nu\mu} - \{\boldsymbol{\lambda}_\nu^\dagger \cdot \mathbf{Z} \cdot \boldsymbol{\lambda}_\mu\} \tag{18.2-20}$$

In going to the second form of the last expression, we have made use of Eq. 18.2-13. It is to be noted from the last relation that

$$\tilde{\zeta}_{\nu\mu}^\dagger = \tilde{\zeta}_{\mu\nu} \tag{18.2-21}$$

$$\sum_\nu \tilde{\zeta}_{\nu\mu} = \mathbf{0} \tag{18.2-22}$$

Then making use of Eq. 18.2-13 again, along with the definition of the base vectors $\boldsymbol{b}_{\nu s}$, we find that

$$\boldsymbol{F}_\nu^{(h)} = -\sum_{\mu s} \frac{1}{\sqrt{m_\mu}} [\![\dot{Q}_s]\!][\tilde{\zeta}_{\nu\mu} \cdot \boldsymbol{b}_{\mu s}] + \sum_\mu [\tilde{\zeta}_{\nu\mu} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu]] - \frac{1}{\bar{N}} [\boldsymbol{\lambda}_\nu^\dagger \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})] \tag{18.2-23}$$

This is the expression for $\boldsymbol{F}_\nu^{(h)}$ in terms of the $[\![\dot{Q}_s]\!]$. Next we obtain the effective hydrodynamic force $\mathscr{F}_s^{(h)}$ in terms of the $[\![\dot{Q}_s]\!]$ and then solve for the latter. For this purpose, we return to the expression for $\mathscr{F}_s^{(h)}$, as given by Eq. 18.1-13, and consider the term on the right involving the force $\boldsymbol{F}_\nu^{(h)}$. From Eq. 18.2-23, we find that

$$\bar{N} \sum_\nu \frac{1}{\sqrt{m_\nu}} (\boldsymbol{b}_{\nu s} \cdot \boldsymbol{F}_\nu^{(h)}) = -\sum_t \tilde{g}_{st}^{(1)} [\![\dot{Q}_t]\!] + (\mathbf{M}_s^{(1)} : \boldsymbol{\kappa}) - \mathscr{F}_s^{(b,e)} \tag{18.2-24}$$

where

$$\tilde{g}_{st}^{(1)} = \bar{N} \sum_{\nu\mu} \frac{1}{\sqrt{m_\nu m_\mu}} (\boldsymbol{b}_{\nu s} \cdot \tilde{\zeta}_{\nu\mu} \cdot \boldsymbol{b}_{\mu t}) \tag{18.2-25}$$

$$\mathbf{M}_s^{(1)} = \bar{N} \sum_{\nu\mu} \frac{1}{\sqrt{m_\nu}} \{\boldsymbol{R}_\mu \boldsymbol{b}_{\nu s} \cdot \tilde{\zeta}_{\nu\mu}\} \tag{18.2-26}$$

$$\mathscr{F}_s^{(b,e)} = \sum_\nu \frac{1}{\sqrt{m_\nu}} (\boldsymbol{\lambda}_\nu : \boldsymbol{b}_{\nu s} (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})) \tag{18.2-27}$$

The Brownian force $\boldsymbol{F}^{(b)}$ was defined in Eq. 17.5-17; in the absence of hydrodynamic interaction $\mathscr{F}_s^{(b,e)}$ is zero.

The second term in the expression for the hydrodynamic force $\mathscr{F}_s^{(h)}$, as given by Eq. 18.1-13, depends on the model used for the *finite* beads. As an example of a finite bead we consider a cylindrically symmetric body. The potential field acting on such a body does not involve the angle associated with rotation about the symmetry axis and one may use as two of the coordinates, $q_{v\sigma}$, the polar angles $q_{v1} = \theta_v$ and $q_{v2} = \phi_v$ describing the unit vector, $\boldsymbol{u}_v$, along the symmetry axis. The averages, $T_{v\sigma}^{(h)\alpha}$, defined by Eqs. 18.1-12 and 14, may then be written

$$T_{v\sigma}^{(h)\alpha} = -\frac{\partial}{\partial q_{v\sigma}^{\alpha}} \Phi_v^{(h)\alpha} \tag{18.2-28}$$

where

$$\Phi_v^{(h)\alpha} = \frac{1}{\bar{N}\Psi_\alpha} \sum_{\beta\mu} \iint \Phi_{v\mu}^{\alpha\beta} \tilde{\Psi}_{\alpha\beta}(\boldsymbol{r}, \boldsymbol{R}, Q_\alpha, Q_\beta, t) dQ_\beta \, d\boldsymbol{R} \tag{18.2-29}$$

is an average potential due to interactions with the surrounding molecules. These derivatives are closely related to the torque on the bead.

The torque on a cylindrical bead oriented in the direction $\boldsymbol{u}$ in an external potential Φ is given by

$$\boldsymbol{T} = -\left[\boldsymbol{u} \times \frac{\partial}{\partial \boldsymbol{u}} \Phi\right] \tag{18.2-30}$$

Thus, one finds from Eq. 18.2-28 that if the finite bead is modeled as a cylindrical body,

$$T_{v1}^{(h)} = (\boldsymbol{t}_v \cdot \boldsymbol{T}_v^{(h)}), \qquad T_{v2}^{(h)} = -\sin\theta_v \, (\boldsymbol{s}_v \cdot \boldsymbol{T}_v^{(h)}) \tag{18.2-31}$$

where $\boldsymbol{T}_v^{(h)}$ is an average torque on the bead due to the surrounding molecules.

Brenner[3] has shown that the hydrodynamic torque on a cylindrically symmetric body with "fore-aft" symmetry is

$$\boldsymbol{T}_v^{(h)} = -\boldsymbol{\xi}_v \cdot ([\boldsymbol{u}_v \times [\![\dot{\boldsymbol{u}}_v]\!]] - \tfrac{1}{2}[\boldsymbol{\nabla} \times \boldsymbol{v}]) + \tilde{\xi}_v [\boldsymbol{u}_v \times [\boldsymbol{u}_v \cdot \dot{\boldsymbol{\gamma}}]] \tag{18.2-32}$$

where

$$\boldsymbol{\xi}_v = \xi_{v\parallel} \boldsymbol{u}_v \boldsymbol{u}_v + \xi_{v\perp}(\boldsymbol{\delta} - \boldsymbol{u}_v \boldsymbol{u}_v) \tag{18.2-33}$$

and $\xi_{v\parallel}$, $\xi_{v\perp}$, $\tilde{\xi}_v$ are three scalar constants, the rotational friction coefficients. By combining this expression with Eq. 18.2-31, one finds that the second term in the expression for $\mathscr{F}_s^{(h)}$ as given by Eq. 18.1-13 becomes

$$\begin{aligned} \bar{N} \sum_{v\sigma} b_{v\sigma s} T_{v\sigma}^{(h)} = &-\bar{N} \sum_v \xi_{v\perp} (b_{v1s} [\![\dot{\theta}_v]\!] + b_{v2s} (\sin\theta_v)^2 [\![\dot{\phi}_v]\!]) \\ &+ \tfrac{1}{2}\bar{N} \sum_v \sum_\sigma b_{v\sigma s} \boldsymbol{c}_{v\sigma} \boldsymbol{u}_v : \{\xi_{v\perp} \boldsymbol{\omega} + \tilde{\xi}_v \dot{\boldsymbol{\gamma}}\} \end{aligned} \tag{18.2-34}$$

[3] H. Brenner, *Int. J. Multiphase Flow*, **1**, 195 341 (1974).

Then using Eq. 17.1-8 for the $\dot{q}_{\nu\sigma}$, one finds that this equation may be written in a form similar to Eq. 18.2-24

$$\bar{N}\sum_{\nu}\sum_{\sigma} b_{\nu\sigma s}T^{(h)}_{\nu\sigma} = -\sum_{t}\tilde{g}^{(2)}_{st}[\![\dot{Q}_t]\!] + (\mathbf{M}^{(2)}_s:\boldsymbol{\kappa}) \tag{18.2-35}$$

where

$$\tilde{g}^{(2)}_{st} = \bar{N}\sum_{\nu}\xi_{\nu\perp}[b_{\nu 1s}b_{\nu 1t} + (\sin\theta_\nu)^2 b_{\nu 2s}b_{\nu 2t}] \tag{18.2-36}$$

$$\mathbf{M}^{(2)}_s = \tfrac{1}{2}\bar{N}\sum_{\nu}\sum_{\sigma}\xi_{\nu\perp}b_{\nu\sigma s}(\boldsymbol{u}_\nu\boldsymbol{c}_{\nu\sigma} - \boldsymbol{c}_{\nu\sigma}\boldsymbol{u}_\nu) + \tfrac{1}{2}\bar{N}\sum_{\nu}\sum_{\sigma}\tilde{\xi}_\nu b_{\nu\sigma s}(\boldsymbol{u}_\nu\boldsymbol{c}_{\nu\sigma} + \boldsymbol{c}_{\nu\sigma}\boldsymbol{u}_\nu) \tag{18.2-37}$$

We will assume that even if the *finite* beads are modeled as more general rigid bodies the expression may be written in the form of Eq. 18.2-35, with more general expressions for $\tilde{g}^{(2)}_{st}$ and $\mathbf{M}^{(2)}_s$.

When Eqs. 18.2-24 and 35 are used in Eq. 18.1-13 one finds that

$$\mathscr{F}^{(h)}_s = -\sum_{t}\tilde{g}_{st}[\![\dot{Q}_t]\!] + (\mathbf{M}_s:\boldsymbol{\kappa}) - \mathscr{F}^{(b,e)}_s \tag{18.2-38}$$

where

$$\tilde{g}_{st} = \tilde{g}^{(1)}_{st} + \tilde{g}^{(2)}_{st} \tag{18.2-39}$$

$$\mathbf{M}_s = \mathbf{M}^{(1)}_s + \mathbf{M}^{(2)}_s \tag{18.2-40}$$

To solve these equations for the $[\![\dot{Q}_s]\!]$, we introduce a matrix with elements, $\tilde{G}_{st}$, which is the inverse of the $\tilde{g}_{st}$ matrix

$$\sum_{t}\tilde{G}_{st}\tilde{g}_{tu} = \delta_{su} \tag{18.2-41}$$

In terms of this matrix,

$$[\![\dot{Q}_s]\!] = \sum_{t}\tilde{G}_{st}((\mathbf{M}_t:\boldsymbol{\kappa}) - \mathscr{F}^{(h)}_t + \mathscr{F}^{(b,e)}_t) \tag{18.2-42}$$

The effective force balance, Eq. 17.5-15, may then be used to rewrite this as

$$[\![\dot{Q}_s]\!] = \sum_{t}\tilde{G}_{st}(\mathscr{F}^{(e)}_t + \mathscr{F}^{(\phi)}_t + \mathscr{F}^{(b)}_t + \mathscr{F}^{(b,e)}_t + (\mathbf{M}_t:\boldsymbol{\kappa})) \tag{18.2-43}$$

Thus, we see that the generalized velocities are given by expressions involving sums of five generalized forces.

The last result may be used in the equation of continuity, Eq. 17.5-14, to give

$$\boxed{\frac{\partial\Psi_\alpha}{\partial t} + \sum_{st}\frac{\partial}{\partial Q_s}[\tilde{G}_{st}(\mathscr{F}^{(e)}_t + \mathscr{F}^{(\phi)}_t + \mathscr{F}^{(b)}_t + \mathscr{F}^{(b,e)}_t + (\mathbf{M}_t:\boldsymbol{\kappa}))\Psi_\alpha] = 0} \tag{18.2-44}$$

After the expression for the generalized Brownian force $\mathscr{F}_t^{(b)}$ has been inserted into this equation, we have the second-order partial differential equation for Ψ_α known as the *diffusion equation.*

§18.3 POSSIBLE APPROXIMATIONS FOR THE BROWNIAN FORCES

The third major approximation in the development reduces the problem from one in the phase space of a single molecule to one in the configuration space only. This is an approximation for the momentum dependence of the distribution function, which enters into the evaluation of the generalized Brownian forces. The expression for the generalized Brownian force given by Eq. 17.5-8 may be rearranged to give

$$\mathscr{F}_s^{(b)} = -\frac{1}{\Psi_\alpha}\sum_{tu}\frac{\partial}{\partial Q_u}(G_{tu}[\![P_tP_s]\!]\Psi_\alpha) - \tfrac{1}{2}\sum_{tu}[\![P_tP_u]\!]\left(\frac{\partial}{\partial Q_s}G_{tu}\right) \tag{18.3-1}$$

The total Brownian force on a molecule is given by Eq. 17.5-17.

We consider three different assumptions for evaluating the $[\![\ ]\!]$ quantities in the Brownian force expression:

a. The *assumption of equilibration in momentum space*; this can be written down at once for any kind of model. It is this assumption that has heretofore been used universally for dilute solutions in all of the publications by Kirkwood, Zimm, Rouse, and others.

b. *The assumption that f_α is an even function of $\dot{r}_v - v$ and independent of r_c.* This assumption is used only for models with structureless beads and no constraints. It has been used to get the expression given in Eq. 13.2-3, which, in turn, has been used in studies on nonisotropic Brownian motion[1] (see §13.7) and studies on velocity distributions that are Maxwellian about the bead velocities rather than about the center of mass velocity of the bead-spring model.[2]

c. The *assumption of reptational motion*, which is used in the kinetic theory of concentrated polymer solutions and undiluted polymers; the discussion of this assumption is postponed until §19.2.

In this section we discuss the consequences of assumptions (a) and (b).

a. Equilibration in Momentum Space

If one assumes that the momentum dependence of the distribution function is that characteristic of equilibrium, then

$$[\![P_tP_s]\!] = kT\,g_{st} \tag{18.3-2}$$

$$[\![(\boldsymbol{p}_c - m_p\boldsymbol{v})(\boldsymbol{p}_c - m_p\boldsymbol{v})]\!] = m_pkT\,\boldsymbol{\delta} \tag{18.3-3}$$

$$[\![P_s\boldsymbol{p}_c]\!] = \boldsymbol{0} \tag{18.3-4}$$

[1] R. B. Bird and J. R. DeAguiar, *J. Non-Newtonian Fluid Mech.*, **13**, 149–160 (1983); R. B. Bird and J. M. Wiest, *J. Rheol.*, **29**, 519–532 (1985).

[2] R. B. Bird, X. J. Fan, and C. F. Curtiss, *J. Non-Newtonian Fluid Mech.*, **15**, 85–92 (1984); *errata*: in Eq. 4.7, change 6 to 12, and in Eq. 4.9 change $\frac{2}{9}$ to $\frac{1}{9}$.

In connection with Eq. 18.3-2, see Example 12.4-1. If one uses these relations, one finds[3] from Eq. 18.3-1 that the generalized Brownian force associated with the s-degree of freedom is

$$\boxed{\mathscr{F}_s^{(b)} = -kT \frac{\partial}{\partial Q_s} \ln \frac{\Psi_\alpha}{\sqrt{g}}} \tag{18.3-5}$$

and from Eq. 17.5-17, that the total Brownian force on the entire polymer molecule is

$$\boldsymbol{F}^{(b)} = -kT \nabla \ln \Psi_\alpha \tag{18.3-6}$$

It is these expressions that have traditionally been used in polymer kinetic theory. That is, we ignore the influence of the flow field on the velocity distribution.

b. Special Results for Structureless Beads and No Internal Constraints

Equation 18.3-1 for the generalized Brownian force may be written as follows:

$$\begin{aligned}\mathscr{F}_s^{(b)} = &- \frac{1}{\Psi_\alpha} \sum_{vt} \sqrt{m_v}\, \boldsymbol{b}_{vs} \cdot \frac{\partial}{\partial Q_t} ([\![\dot{\boldsymbol{R}}_v \dot{Q}_t]\!]\Psi_\alpha) \\ &- \frac{1}{\Psi_\alpha} \sum_{vt\sigma\tau} b_{v\sigma s} \frac{\partial}{\partial Q_t} (g_{v,\sigma\tau} [\![\dot{q}_{v\tau} \dot{Q}_t]\!]\Psi_\alpha) \\ &+ \tfrac{1}{2} \sum_{v\sigma\tau} \left(\frac{\partial}{\partial Q_s} g_{v,\sigma\tau} \right) [\![\dot{q}_{v\tau} \dot{q}_{v\sigma}]\!]\end{aligned} \tag{18.3-7}$$

In this form, approximations other than the equilibration approximation may be introduced for the momentum averages of the products of the time derivatives. It should be noted, however, that any approximation which does not reduce at equilibrium, that is, in the absence of a flow field, to the results just given in §18.3a, cannot be correct in this limit.

We now restrict the discussion to models with structureless beads, so that the last two terms in Eq. 18.3-7 can be discarded. Then using the defining equation for $\mathscr{F}_v^{(b)}$ in Table 17.6-1 we obtain

$$\mathscr{F}_v^{(b)} = -\frac{1}{\Psi_\alpha} \sum_{\mu stu} \sqrt{m_v m_\mu}\, G_{st} \boldsymbol{b}_{vt} \boldsymbol{b}_{\mu s} \cdot \frac{\partial}{\partial Q_u} ([\![\dot{Q}_u \dot{\boldsymbol{R}}_\mu]\!]\Psi_\alpha) \tag{18.3-8}$$

For models with no constraints Eq. 12D.3-5 allows us to simplify this result to

$$\mathscr{F}_v^{(b)} = -\frac{m_v}{\Psi_\alpha} \sum_s \frac{\partial}{\partial Q_s} ([\![\dot{Q}_s \dot{\boldsymbol{R}}_v]\!]\Psi_\alpha) \tag{18.3-9}$$

[3] In obtaining this result we use the standard result that, since the matrices (g_{uv}) and (G_{uv}) are inverse to one another

$$\sum_u \sum_v g_{uv} \frac{\partial}{\partial Q_t} G_{vu} = -\frac{\partial}{\partial Q_t} \ln g \tag{18.3-4a}$$

where g is the determinant of the g_{uv}.

For such a system the set of r_v may be used as the independent variables rather than the coordinates Q_s and the vector to the center of mass r_c. Making such a transformation, we find from the last equation that

$$\mathscr{F}_v^{(b)} = -\frac{m_v}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial r_\mu}\cdot([\![\dot{R}_\mu \dot{R}_v]\!]\Psi_\alpha) \tag{18.3-10}$$

This force has been defined in such a manner that the sum on the index v gives zero.

The total Brownian force on a molecule is given by Eq. 17.5-17. As long as f_α does not depend on r_c the first term on the right is zero and

$$F^{(b)} = -\frac{1}{\Psi_\alpha}\sum_s \frac{\partial}{\partial Q_s}([\![\dot{Q}_s p_c]\!]\Psi_\alpha) \tag{18.3-11}$$

For models with structureless beads and no internal constraints this expression may be transformed in a similar manner to give

$$F^{(b)} = -\frac{1}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial r_\mu}\cdot([\![\dot{R}_\mu p_c]\!]\Psi_\alpha) \tag{18.3-12}$$

By combining this result with Eq. 18.3-10 one finds that

$$F_v^{(b)} = \frac{m_v}{m_p}F^{(b)} + \mathscr{F}_v^{(b)} = -\frac{m_v}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial r_\mu}\cdot([\![\dot{R}_\mu \dot{r}_v]\!]\Psi_\alpha) \tag{18.3-13}$$

This may be interpreted as the total Brownian force on a bead.

Next, we note that for models with structureless beads and no internal constraints and with f_α independent of r_c:

$$-\frac{m_v}{\Psi_\alpha}\frac{\partial}{\partial r_c}\cdot\left(\left[\!\left[\left(\frac{1}{m_p}p_c - v\right)\dot{r}_v\right]\!\right]\Psi_\alpha\right) = -\frac{m_v}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial r_\mu}\cdot\left(\left[\!\left[\left(\frac{1}{m_p}p_c - v\right)\dot{r}_v\right]\!\right]\Psi_\alpha\right) = 0 \tag{18.3-14}$$

Then, adding the second form of this expression to the right of Eq. 18.3-13, one finds that

$$F_v^{(b)} = -\frac{m_v}{\Psi_\alpha}\sum_\mu \frac{\partial}{\partial r_\mu}\cdot([\![(\dot{r}_\mu - v)\dot{r}_v]\!]\Psi_\alpha) \tag{18.3-15}$$

It is however reasonable to assume that the momentum dependence of the distribution function is an even function of the difference $(\dot{r}_\mu - v)$. With this restriction the last expression reduces to

$$\boxed{F_v^{(b)} = -\frac{m_v}{\Psi_\alpha}\frac{\partial}{\partial r_v}\cdot[[\![(\dot{r}_v - v)(\dot{r}_v - v)]\!]\Psi_\alpha]} \tag{18.3-16}$$

as the expression for the total Brownian force on a mass point. It is this form for the Brownian force that was used in Eqs. 13.2-3 and 13.7-2. Note that $F_v^{(b)}$ is the negative of the divergence of the momentum flux associated with the vth bead; it is exactly this expression that appears as $[\![\dot{R}_v \dot{R}_v]\!]^*\Psi_\alpha$ in the kinetic contribution to the stress tensor (Eq. 17.6-5).

§18.4 THE DIFFUSION EQUATION, THE STRESS TENSOR, AND THE MASS FLUX

The principal results of §§18.1, 18.2, and 18.3(a) are valid for quite general models including tensorial friction coefficients, internal constraints, and hydrodynamic interaction. In parts (a) and (b) of this section, we summarize these main results for the diffusion equation and the expression for the stress tensor. In part (c) we first consider translational diffusion for quite general models and then for models made up of structureless beads, involving no constraints, but with the effects of hydrodynamic interaction included.

a. The Diffusion Equation for Ψ_α

The diffusion equation as given by Eq. 18.2-44 involves the modified metric matrix elements, $\tilde{G}_{st}$, and the coupling tensors, $\mathbf{M}_t$. The modified metric matrix elements are those of the matrix inverse to that with elements $\tilde{g}_{st}$ given by Eq. 18.2-39 as the sum of two terms. The first term, $\tilde{g}^{(1)}_{st}$, is that associated with the structure of the molecule as a whole, and the second, $\tilde{g}^{(2)}_{st}$, is that associated with the structure of the finite beads.

The matrix elements $\tilde{g}^{(1)}_{st}$ are defined by Eq. 18.2-25. If one neglects hydrodynamic interaction and takes the masses of beads to be equal then this expression reduces to (m is the mass of a bead),

$$\tilde{g}^{(1)}_{st} = \frac{\bar{N}}{m}\sum_\nu \zeta_\nu : \boldsymbol{b}_{\nu s}\boldsymbol{b}_{\nu t} - \frac{\bar{N}}{m}\left(\sum_\nu \boldsymbol{b}_{\nu s}\cdot\zeta_\nu\right)\cdot\mathbf{Z}^{-1}\cdot\left(\sum_\mu \zeta_\mu\cdot\boldsymbol{b}_{\mu t}\right) \tag{18.4-1}$$

where $\mathbf{Z} = \sum_\nu \zeta_\nu$. For the example discussed in §18.2, in which the finite beads are taken to have cylindrical symmetry, the modified matrix elements, $\tilde{g}^{(2)}_{st}$, are given by Eq. 18.2-36. We now further restrict the model and take the beads to be "needles," that is, cylindrically symmetric bodies with zero moment of inertia about the symmetry axis. Then on comparing Eq. 18.2-36 with Eq. 17.1-12 one finds that

$$\tilde{g}^{(2)}_{st} = \frac{\bar{N}\xi_\perp}{I} g^{(2)}_{st} \tag{18.4-2}$$

Then $\tilde{g}_{st}$ is obtained by combining Eqs. 18.4-1 and 2.

In a similar manner the coupling tensor $\mathbf{M}_s$ is given by Eq. 18.2-40 as the sum of two terms. An expression for the first term, $\mathbf{M}^{(1)}_s$, which is also associated with the structure of the molecule as a whole is given by Eq. 18.2-26. If one again neglects hydrodynamic interaction and takes the masses of the beads to be equal, this expression reduces to

$$\mathbf{M}^{(1)}_s = \frac{\bar{N}}{\sqrt{m}}\left(\sum_\nu \boldsymbol{R}_\nu \boldsymbol{b}_{\nu s}\cdot\zeta_\nu\right) - \frac{\bar{N}}{\sqrt{m}}\sum_{\nu\mu}\boldsymbol{R}_\mu(\boldsymbol{b}_{\nu s}\cdot\zeta_\nu\cdot\mathbf{Z}^{-1}\cdot\zeta_\mu) \tag{18.4-3}$$

An expression for the second contribution, $\mathbf{M}^{(2)}_s$, to the coupling tensor is given by Eq. 18.2-37.

The diffusion equation is given by Eq. 18.2-44 in terms of these quantities and $\mathscr{F}^{(b,e)}_t$. This latter quantity is defined by Eq. 18.2-27 in terms of the total Brownian and external forces, $\boldsymbol{F}^{(b)}$ and $\boldsymbol{F}^{(e)}$, on a molecule. If these forces are taken to be zero, then $\mathscr{F}^{(b,e)}_t$ is zero. An expression for the generalized intramolecular force, $\mathscr{F}^{(\phi)}_t$, is given by Eq. 17.1-21, and if one

assumes equilibration in momentum space, the generalized Brownian force, $\mathscr{F}_t^{(b)}$, is given by 18.3-5. When these and the results of this subsection are used in Eq. 18.2-44 we have the *diffusion equation* for Ψ_α for models with identical beads (with structure), when hydrodynamic interaction is neglected. The development of this diffusion equation for a specific model is illustrated in Example 18.4-1.

In §16.2 we give the diffusion equation (Eq. 16.2-6) for models with structureless beads and scalar friction coefficients. For those models we retain the full hydrodynamic interaction and allow the beads to have different masses and friction coefficients. Equation 16.2-6 includes as special cases the diffusion equations used in Chapters 13–15.

b. The Stress Tensor

Let us now return to the general expression for the stress tensor given in Eq. 18.1-10 in terms of the hydrodynamic force $\boldsymbol{F}_\nu^{(h)}$. Although Eq. 18.1-10 is both very general and simple in form, it is not particularly useful until one inserts a specific expression for the $\boldsymbol{F}_\nu^{(h)}$. We use Eq. 18.2-19, a modified Stokes' law expression for $\boldsymbol{F}_\nu^{(h)}$, which includes hydrodynamic interaction and beads with structure (including anisotropic friction tensors). Insertion of $\boldsymbol{F}_\nu^{(h)}$ from Eq. 18.2-19 into Eq. 18.1-10 then gives

$$\boxed{\begin{aligned}\boldsymbol{\pi} = \boldsymbol{\pi}_k + \bar{N} \sum_{\alpha\nu\mu} \int \boldsymbol{R}_\nu([\![\dot{\boldsymbol{R}}_\mu]\!] - \boldsymbol{\kappa}\cdot\boldsymbol{R}_\mu)\cdot\tilde{\boldsymbol{\zeta}}_{\mu\nu}\Psi_\alpha(\boldsymbol{r}, Q, t)dQ \\ + \sum_\alpha \sum_\nu \int \boldsymbol{R}_\nu(\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)})\cdot\boldsymbol{\lambda}_\nu\Psi_\alpha(\boldsymbol{r}, Q, t)dQ\end{aligned}} \tag{18.4-4}$$

To utilize this stress tensor formula we need an expression for $[\![\dot{\boldsymbol{R}}_\nu]\!]$; this is obtained by combining Eqs. 17.1-7 and 18.2-43 to get

$$[\![\dot{\boldsymbol{R}}_\nu]\!] = \frac{1}{\sqrt{m_\nu}} \sum_s \sum_t \tilde{G}_{st}\boldsymbol{b}_{\nu s}\left(\mathscr{F}_t^{(e)} + \mathscr{F}_t^{(\phi)} + \mathscr{F}_t^{(b)} + \mathscr{F}_t^{(b,e)} + (\mathbf{M}_t{:}\boldsymbol{\kappa})\right) \tag{18.4-5}$$

Insertion of this expression for $[\![\dot{\boldsymbol{R}}_\nu]\!]$ into Eq. 18.4-4 then gives the stress tensor $\boldsymbol{\pi}$ in terms of the generalized forces $\mathscr{F}_t^{(\ )}$ and the quantity $(\mathbf{M}_t{:}\boldsymbol{\kappa})$; this is then the generalization of the rather simple special result given in Eq. 18.1-18 (see Problem 18C.1). The use of Eqs. 18.4-4 and 5 is illustrated in Example 18.4-1 for a molecular model containing beads with structure.

In §16.3 several formulas for the stress tensor are given, which are less general than Eqs. 18.4-4 and 5. Equations 16.3-1, 11, 16, and 20 include, as special cases, the stress-tensor expressions used in Chapters 13–15.

c. The Mass Flux and the Translational Diffusivity

The mass flux of species α is given by Eq. 17.6-12. The first term on the right side of this equation is an average of the "drift velocity" of a molecule of species α, which in turn is related to the hydrodynamic force on the molecule. We may thus use the force balance equations for species α to express the drift velocity in terms of the Brownian and external forces, and to obtain an expression for the mass-flux vector in terms of the concentration

gradient and the average external force. The second term on the right side of Eq. 17.6-12 results from the finite extension of the polymer molecules in space, and its role in various diffusional phenomena has not yet been explored.

We begin by working with very general molecular models and include the full effects of hydrodynamic interaction. We first form the dot product of $(m_\nu/m_p)\zeta_\nu^{-1}$ with Eq. 18.2-14 to get the drift velocity for the molecule

$$[\![\dot{\boldsymbol{r}}_c]\!] - \boldsymbol{v}(\boldsymbol{r}_c) = -\sum_\nu \sum_\mu \frac{m_\nu}{m_p} [\zeta_\nu^{-1} \cdot \Upsilon_{\nu\mu} \cdot \boldsymbol{F}_\mu^{(h)}] \tag{18.4-6}$$

Insertion of this into Eq. 17.6-12 then gives

$$\begin{aligned} \boldsymbol{j}_\alpha = &-\sum_\nu \sum_\mu m_\nu \int [\zeta_\nu^{-1} \cdot \Upsilon_{\nu\mu} \cdot \boldsymbol{F}_\mu^{(h)}] \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \\ &-\nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu [\![\dot{\boldsymbol{R}}_\nu]\!] \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \end{aligned} \tag{18.4-7}$$

Next we substitute for $\boldsymbol{F}_\mu^{(h)}$ the expression given in Eq. 18.2-19. The result may be simplified by using two identities (see Problem 18D.1)

$$\left\{\zeta_\nu^{-1} \cdot \sum_\mu \Upsilon_{\nu\mu} \cdot \boldsymbol{\lambda}_\mu^\dagger\right\} = \mathbf{Z}^{-1} \tag{18.4-8}$$

$$\left\{\zeta_\nu^{-1} \cdot \sum_\mu \Upsilon_{\nu\mu} \cdot \tilde{\zeta}_{\mu\eta}\right\} = \delta_{\nu\eta}\boldsymbol{\delta} - \boldsymbol{\lambda}_\eta \tag{18.4-9}$$

The mass flux of species α then becomes

$$\begin{aligned} \boldsymbol{j}_\alpha = &\frac{m_p}{\bar{N}} \int \mathbf{Z}^{-1} \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)}) \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \\ &-m_p \sum_\nu \int \boldsymbol{\lambda}_\nu \cdot ([\![\dot{\boldsymbol{R}}_\nu]\!] - [\boldsymbol{\kappa} \cdot \boldsymbol{R}_\nu]) \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \\ &-\nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu [\![\dot{\boldsymbol{R}}_\nu]\!] \Psi_\alpha(\boldsymbol{r}, Q, t) dQ \end{aligned} \tag{18.4-10}$$

To make use of this result, the expression for $[\![\dot{\boldsymbol{R}}_\nu]\!]$ in Eq. 18.4-5 has to be inserted. For further interpretation of this equation, see Problem 18B.2.

Having discussed the mass flux for a quite general model, we now turn to the much simpler models with structureless beads and no constraints. We start with Eq. 18.4-7 for $\boldsymbol{j}_\alpha$ and insert the appropriate expression for the hydrodynamic force $\boldsymbol{F}_\mu^{(h)}$ obtained from Eq. 18.1-16 and the force balances in Eqs. 17.5-18 and 17.6-10

$$\boldsymbol{F}_\mu^{(h)} = -\frac{1}{\bar{N}} (\boldsymbol{F}_\mu^{(b)} + \boldsymbol{F}_\mu^{(e)} + \boldsymbol{F}_\mu^{(\phi)}) \tag{18.4-11}$$

where $\boldsymbol{F}_\mu^{(b)}$ is the total Brownian force on a bead defined by Eq. 18.3-13; $\boldsymbol{F}_\mu^{(e)}$ is the total external force defined in an analogous manner

$$\boldsymbol{F}_\mu^{(e)} = \frac{m_\mu}{m_p}\boldsymbol{F}^{(e)} + \mathscr{F}_\mu^{(e)} \tag{18.4-12}$$

and $\bar{N}$ is the average number of beads per molecule defined by Eq. 17.5-11. Using Eq. 18.4-11 in Eq. 18.4-7, we find that

$$j_\alpha = \frac{1}{\bar{N}}\sum_\nu\sum_\mu m_\nu \int \zeta_\nu^{-1}\cdot\Upsilon_{\nu\mu}\cdot(\boldsymbol{F}_\mu^{(e)} + \boldsymbol{F}_\mu^{(b)} + \boldsymbol{F}_\mu^{(\phi)})\Psi_\alpha\, dQ$$

$$-\nabla\cdot\sum_\nu m_\nu \int \boldsymbol{R}_\nu[\![\dot{\boldsymbol{R}}_\nu]\!]\Psi_\alpha\, dQ \qquad \text{(structureless beads, no constraints)} \tag{18.4-13}$$

Equation 18.4-10 for general models and Eq. 18.4-13 for models with structureless beads and no constraints are the integral expressions for the mass fluxes involving the configurational distribution function Ψ_α.

We now make a specific assumption for the function Ψ_α in order to get mass flux expressions in terms of the translational diffusion tensors. Specifically we assume that the diffusion process is sufficiently slow that Ψ_α can be approximated by the equilibrium distribution function in the absence of external forces (§12.3):

$$\Psi_\alpha = \frac{n_\alpha}{J}\sqrt{g}\, e^{-\phi/kT} \tag{18.4-14}$$

where n_α is the number density of molecules of species α, and J is the normalization constant. Using this expression for the configurational distribution function in the expressions for the Brownian forces, Eqs. 18.3-5 and 6, and the definition of $\mathscr{F}_\mu^{(\phi)}$ in Table 17.6-1 one finds that

$$\mathscr{F}_s^{(b)} = -\mathscr{F}_s^{(\phi)} \tag{18.4-15}$$

$$\boldsymbol{F}_\mu^{(b)} = \frac{m_\mu}{m_p}\boldsymbol{F}^{(b)} - \mathscr{F}_\mu^{(\phi)} \tag{18.4-16}$$

$$\boldsymbol{F}^{(b)} = -kT\nabla \ln n_\alpha \tag{18.4-17}$$

These relations are valid for any choice of molecular model.

Next we consider the very general model used to derive $\boldsymbol{j}_\alpha$ in Eq. 18.4-10. To do this we return to Eq. 18.4-5 and the relations in Table 17.6-1 to obtain the expression for $[\![\dot{\boldsymbol{R}}_\nu]\!]$

$$[\![\dot{\boldsymbol{R}}_\nu]\!] = \frac{1}{\sqrt{m_\nu}}\sum_{st\mu}\frac{1}{\sqrt{m_\mu}}\tilde{G}_{st}\boldsymbol{b}_{\nu s}\boldsymbol{b}_{\mu t}\cdot\boldsymbol{\lambda}_\mu^\dagger\cdot(-kT\nabla \ln n_\alpha + \boldsymbol{F}^{(e)})$$

$$+\frac{1}{\sqrt{m_\nu}}\sum_{st}\tilde{G}_{st}\boldsymbol{b}_{\nu s}(\mathscr{F}_t^{(e)} + \mathbf{M}_t:\boldsymbol{\kappa}) \tag{18.4-18}$$

One then finds from Eq. 18.4-10 that

$$\begin{aligned} \boldsymbol{j}_\alpha = & -\bar{\boldsymbol{\Delta}}^\alpha \cdot \left(\nabla \rho_\alpha - \frac{\rho_\alpha}{kT} \bar{\boldsymbol{F}}^{(e)\alpha} \right) \\ & + m^\alpha \sum_\nu \int \boldsymbol{\lambda}_\nu \cdot \left[\boldsymbol{\kappa} \cdot \boldsymbol{R}_\nu - \sum_s \sum_t \tilde{G}_{st} \boldsymbol{b}_{\nu s} (\mathscr{F}_t^{(e)} + \mathbf{M}_t : \boldsymbol{\kappa}) \right] \Psi_\alpha \, dQ \\ & - \nabla \cdot \sum_\nu m_\nu \int \boldsymbol{R}_\nu [\![\dot{\boldsymbol{R}}_\nu]\!] \Psi_\alpha \, dQ \end{aligned} \tag{18.4-19}$$

Here $\bar{\boldsymbol{F}}^{(e)\alpha}$ is an average total external force on the molecule defined as

$$\bar{\boldsymbol{F}}^{(e)\alpha} = (\bar{\boldsymbol{\Delta}}^\alpha)^{-1} \cdot \langle \boldsymbol{\Delta}^\alpha \cdot \boldsymbol{F}^{(e)\alpha} \rangle_{\text{eq}} \tag{18.4-20}$$

in which $\bar{\boldsymbol{\Delta}}^\alpha$ is an average translational diffusion tensor

$$\bar{\boldsymbol{\Delta}}^\alpha = \langle \boldsymbol{\Delta}^\alpha \rangle_{\text{eq}} \tag{18.4-21}$$

where

$$\boldsymbol{\Delta}^\alpha = \frac{kT}{\bar{N}} \mathbf{Z}_\alpha^{-1} - kT \sum_{\nu\mu st} \frac{1}{\sqrt{m_\nu m_\mu}} \tilde{G}_{st} \{ \boldsymbol{\lambda}_\nu \cdot \boldsymbol{b}_{\nu s} \boldsymbol{b}_{\mu t} \cdot \boldsymbol{\lambda}_\mu^\dagger \} \tag{18.4-22}$$

It is interesting to note that the $\bar{\boldsymbol{F}}^{(e)\alpha}$ in Eq. 18.4-20 is a different average from that which appeared in the definition of $\bar{\boldsymbol{F}}^{(e)\alpha}$ in Eq. 17.4-26 in connection with the equation of motion.

Having obtained the general expression for the average translational diffusion tensor $\bar{\boldsymbol{\Delta}}^\alpha$, we now turn once again to the simple models with structureless beads and no constraints. For such models we find that the mass flux $\boldsymbol{j}_\alpha$ is given by an expression similar to Eq. 18.4-19, but with the second term on the right side missing and with different expressions for the average external force $\bar{\boldsymbol{F}}^{(e)\alpha}$ and the average translational diffusion tensor $\bar{\boldsymbol{\Delta}}^\alpha = \langle \boldsymbol{\Delta}^\alpha \rangle_{\text{eq}}$

$$\bar{\boldsymbol{F}}^{(e)\alpha} = (\bar{\boldsymbol{\Delta}}^\alpha)^{-1} \cdot \left\langle \sum_\mu \boldsymbol{\Delta}_\mu^\alpha \boldsymbol{F}_\mu^{(e)\alpha} \right\rangle_{\text{eq}} \qquad \text{(structureless beads, no constraints)} \tag{18.4-23}$$

$$\boldsymbol{\Delta}^\alpha = \sum_\mu \frac{m_\mu^\alpha}{m^\alpha} \boldsymbol{\Delta}_\mu^\alpha \qquad \text{(structureless beads, no constraints)} \tag{18.4-24}$$

where

$$\boldsymbol{\Delta}_\mu^\alpha = \frac{kT}{\bar{N}} \sum_\nu \frac{m_\nu^\alpha}{m^\alpha} \{ \boldsymbol{\zeta}_\nu^{-1} \cdot \boldsymbol{\Upsilon}_{\nu\mu} \} \tag{18.4-25}$$

This is as far as we go without making further simplifications of the model.

In order to conclude the section with some simple and well-known formulas, we now specialize to a dilute solution of one polymer species (α) in a solvent (a species with $N = 1$,

so that $\bar{N} = 1$); furthermore we take all the beads to be alike, each one with an isotropic friction tensor $\zeta\boldsymbol{\delta}$. Then the diffusion tensor $\boldsymbol{\Delta}^\alpha$, given by Eqs. 18.4-24 and 25, is

$$\boldsymbol{\Delta}^\alpha = \frac{kT}{N_\alpha^2 \zeta} \sum_\nu \sum_\mu \boldsymbol{\Upsilon}^\alpha_{\nu\mu} \tag{18.4-26}$$

Then, if we use the equilibrium configurational distribution function, Eq. 18.4-14, to evaluate the average of this expression for $\boldsymbol{\Delta}^\alpha$ we find that

$$\bar{\boldsymbol{\Delta}}^\alpha = D^\alpha_{\text{tr}} \boldsymbol{\delta} \tag{18.4-27}$$

in which D^α_{tr} is given by *Kirkwood's formula*[1]

$$D^\alpha_{\text{tr}} = \frac{kT}{3N_\alpha^2 \zeta} \sum_\nu \sum_\mu \langle \boldsymbol{\delta} : \boldsymbol{\Upsilon}^\alpha_{\nu\mu} \rangle_{\text{eq}} \tag{18.4-28}$$

Using the definition of the dimensionless diffusion tensors, Eq. 18.2-4, we then find that the *translational diffusivity* of a polymer in which the molecular model involves only structureless beads with no constraints is

$$\boxed{D^\alpha_{\text{tr}} = \frac{kT}{N_\alpha^2 \zeta} \sum_\nu \sum_\mu H^\alpha_{\nu\mu}} \tag{18.4-29}$$

where

$$H^\alpha_{\nu\mu} = \delta_{\nu\mu} + \tfrac{1}{3}\zeta \langle \boldsymbol{\delta} : \boldsymbol{\Omega}^\alpha_{\nu\mu} \rangle_{\text{eq}} \tag{18.4-30}$$

In obtaining this expression we have used the equilibrium distribution function, Eq. 18.4-14, to obtain the expression for the Brownian force, Eq. 18.4-15, and to carry out the average over the configuration space in Eq. 18.4-28. This result may be compared with that given by Eq. 15.4-40; in Problem 15D.2 it is further shown that the Zimm bead-spring model leads to $D^\alpha_{\text{tr}} \propto M_\alpha^{-1/2}$. When hydrodynamic interaction is neglected, Eq. 18.4-29 reduces to

$$D^\alpha_{\text{tr}} = \frac{kT}{N_\alpha \zeta} \tag{18.4-31}$$

as the expression for the diffusivity. When $\bar{\boldsymbol{\Delta}}^\alpha$ of Eq. 18.4-27 is used in Eq. 18.4-19, and when the last term in Eq. 18.4-19 is omitted (this is consistent with the use of the equilibrium distribution function), we find that

$$\boxed{\boldsymbol{j}_\alpha = D^\alpha_{\text{tr}} \left(\nabla \rho_\alpha - \frac{\rho_\alpha}{kT} \bar{\boldsymbol{F}}^{(e)\alpha} \right)} \tag{18.4-32}$$

If the external forces on the beads are alike and independent of the internal coordinates, $\bar{\boldsymbol{F}}^{(e)\alpha}$ is the total force on a molecule. This result shows that the effects of a concentration

[1] J. G. Kirkwood, *J. Polymer Sci.*, **12**, 1–14 (1954), see Eq. 9. See also J. G. Kirkwood, *Macromolecules*, Gordon and Breach, New York (1967), pp. 13, 25, 41, 76, 101; H. Yamakawa, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971), p. 280.

gradient and an external force in producing a mass flux are both described[2] by the diffusivity D_{tr}^{α}. This relation is consistent with the prediction of irreversible thermodynamics in the linear approximation[3] and also with the Nernst–Einstein relation.

EXAMPLE 18.4-1 The Diffusion Equation for the Multirod-Rod Model

Develop the diffusion equation, Eq. 18.2-44, for a molecular model similar to the multibead-rod, but with the beads replaced by rods or "needles" of length $a = L/N$. Neglect hydrodynamic interaction, and consider dilute solutions so that $\bar{N} = 1$.

SOLUTION In this example we take as the molecular model a set of N "needles" aligned along a rod[4] (note that $N \geq 2$). As in the treatment of the multibead-rod in §14.1 (see Fig. 14.1-2) we take the centers of mass of the needles to be at the points

$$\boldsymbol{R}_v = \tfrac{1}{2} av\boldsymbol{u} \qquad v = -(N-1), -(N-3), \ldots, +(N-1) \tag{18.4-33}$$

where a is the length of one needle. The model is such that the needles just touch, and hence the overall length of the rod is $L = Na$. The orientation of the rod (and all of the needles) is described by the unit vector $\boldsymbol{u}$ or the polar angles $\theta = Q_1$ and $\phi = Q_2$. One then finds from the definitions in Eqs. 17.1-5 and 6 that

$$\boldsymbol{b}_{vs} = \tfrac{1}{2} va\sqrt{m}\, \boldsymbol{c}_s, \qquad b_{v\alpha s} = \delta_{\alpha s} \tag{18.4-34,35}$$

where m is the mass of one needle and the $\boldsymbol{c}_s$ are the vectors defined in §E.5.

We take the friction tensors of the needles to be alike and given by

$$\zeta_v = \zeta = \zeta_{\parallel} \boldsymbol{uu} + \zeta_{\perp}(\boldsymbol{\delta} - \boldsymbol{uu}) \tag{18.4-36}$$

where $\zeta_{\parallel}$ and $\zeta_{\perp}$ are the parallel and perpendicular components. We then find from Eq. 18.4-1 that

$$\tilde{g}_{st}^{(1)} = \tfrac{1}{4} a^2 \left(\sum_v v^2 \right) (\zeta : \boldsymbol{c}_s \boldsymbol{c}_t) = \tfrac{1}{12} N(N^2 - 1) a^2 \zeta_{\perp} (\boldsymbol{c}_s \cdot \boldsymbol{c}_t) \tag{18.4-37}$$

and from Eqs. 17.1-2, 3, and 12 and 18.4-2 that

$$\tilde{g}_{st}^{(2)} = N\xi_{\perp}(\boldsymbol{c}_s \cdot \boldsymbol{c}_t) \tag{18.4-38}$$

where $\xi_{\perp}$ is a "rotational friction coefficient" of a needle. Thus, the modified metric matrix is

$$\tilde{g}_{st} = X_{\perp}(\boldsymbol{c}_s \cdot \boldsymbol{c}_t), \qquad X_{\perp} = N[\xi_{\perp} + \tfrac{1}{12}(N^2 - 1) a^2 \zeta_{\perp}] \tag{18.4-39,40}$$

The determinant of this matrix is

$$\tilde{g} = X_{\perp}^2 \sin^2 \theta \tag{18.4-41}$$

[2] It may be pointed out that the diffusivity D_{tr}^{α} is a property of the polymer–solvent mixture. In particular, the value of the friction coefficient ζ depends on the properties of both species.

[3] See J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1954, 1964), Section 11.2; and R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, Wiley, New York (1960), Eq. 18.4-15. Starting with the latter equation, one neglects the thermal- and pressure-diffusion terms and assumes a dilute (and ideal) solution of species α in the solvent, to obtain exactly Eq. 18.4-32 of the present text.

[4] The special case in which $N = 2$ has been treated by A. R. Altenberger and J. S. Dahler, *Macromolecules*, **18**, 1700–1710 (1985).

and the elements of the inverse matrix are

$$\tilde{G}_{st} = \frac{1}{X_\perp}(\boldsymbol{d}_s \cdot \boldsymbol{d}_t) \tag{18.4-42}$$

Next, one finds from Eqs. 18.4-3 and 18.2-37 that the two contributions to the coupling tensor are

$$\mathbf{M}_s^{(1)} = \tfrac{1}{2} N(N^2 - 1)a^2\zeta_\perp \boldsymbol{u}\boldsymbol{c}_s \tag{18.4-43a}$$

$$\mathbf{M}_s^{(2)} = \tfrac{1}{2} N\xi_\perp(\boldsymbol{u}_s\boldsymbol{c}_s - \boldsymbol{c}_s\boldsymbol{u}_s) + \tfrac{1}{2} N\tilde{\xi}(\boldsymbol{u}\boldsymbol{c}_s + \boldsymbol{c}_s\boldsymbol{u}) \tag{18.4-43b}$$

The coupling tensors are thus,

$$\mathbf{M}_s = \tfrac{1}{2}\tilde{X}(\boldsymbol{u}_s\boldsymbol{c}_s + \boldsymbol{c}_s\boldsymbol{u}_s) + \tfrac{1}{2} X_\perp(\boldsymbol{u}\boldsymbol{c}_s - \boldsymbol{c}_s\boldsymbol{u}) \tag{18.4-44}$$

where

$$\tilde{X} = N[\tilde{\xi} + \tfrac{1}{12}(N^2 - 1)a^2\zeta_\perp] \tag{18.4-45}$$

The effective Brownian force is given by Eq. 18.3-5. For this model this expression becomes

$$\mathscr{F}_s^{(b)} = -kT\frac{\partial}{\partial Q_s}\ln\frac{\Psi}{\sin\theta} \tag{18.4-46}$$

Thus one finds that the diffusion equation, Eq. 18.2-44, for this model is

$$\begin{aligned}\frac{\partial}{\partial t}\Psi = {} & \frac{1}{6\lambda}\left\{\frac{\partial}{\partial\theta}\sin\theta\left[\frac{\partial}{\partial\theta}\left(\frac{\Psi}{\sin\theta}\right)\right] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Psi\right\} \\ & - \frac{1}{2X_\perp}\frac{\partial}{\partial\theta}(\boldsymbol{u}\boldsymbol{c}_1 : (\tilde{X}\dot{\boldsymbol{\gamma}} - X_\perp\boldsymbol{\omega})\Psi) - \frac{1}{2X_\perp}\frac{\partial}{\partial\phi}(\boldsymbol{u}\boldsymbol{c}_2 : (\tilde{X}\dot{\boldsymbol{\gamma}} - X_\perp\boldsymbol{\omega})\Psi)\end{aligned} \tag{18.4-47}$$

where

$$\lambda = \frac{X_\perp}{6kT} \tag{18.4-48}$$

is the time constant. This result may also be written in the form

$$\frac{\partial}{\partial t}f = \frac{1}{6\lambda}\left(\frac{\partial}{\partial\boldsymbol{u}}\cdot\frac{\partial}{\partial\boldsymbol{u}}f\right) - \frac{\tilde{X}}{X_\perp}\left(\frac{\partial}{\partial\boldsymbol{u}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{u}\boldsymbol{u}\boldsymbol{u}]f\right) + \frac{(X_\perp - \tilde{X})}{2X_\perp}\left(\boldsymbol{\omega} : \boldsymbol{u}\frac{\partial}{\partial\boldsymbol{u}}f\right) \tag{18.4-49}$$

where

$$f = \frac{\Psi}{n\sin\theta} \tag{18.4-50}$$

This equation is the principal result of this example; it may be compared with that for the multibead-rod with hydrodynamic interaction, Eq. 16.2-37. The two equations differ primarily in the term

involving ω. In addition, the time constants in the two equations are defined differently. It may be shown from the diffusion equation, Eq. 18.4-47, that

$$\frac{\partial}{\partial t}\langle \boldsymbol{uu}\rangle = \frac{1}{3\lambda}\boldsymbol{\delta} - \frac{1}{\lambda}\langle \boldsymbol{uu}\rangle - \frac{\tilde{X}}{X_\perp}\langle \boldsymbol{uuuu}\rangle : \dot{\boldsymbol{\gamma}} + \frac{\tilde{X}}{2X_\perp}\{\langle \boldsymbol{uu}\rangle \cdot \dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}} \cdot \langle \boldsymbol{uu}\rangle\} + \tfrac{1}{2}\{\langle \boldsymbol{uu}\rangle \cdot \boldsymbol{\omega} - \boldsymbol{\omega} \cdot \langle \boldsymbol{uu}\rangle\} \tag{18.4-51}$$

or

$$\lambda\langle \boldsymbol{uu}\rangle_{(1)} = \tfrac{1}{3}\boldsymbol{\delta} - \langle \boldsymbol{uu}\rangle - \lambda\frac{\tilde{X}}{X_\perp}\langle \boldsymbol{uuuu}\rangle : \dot{\boldsymbol{\gamma}} + \frac{\lambda}{2}\left(\frac{\tilde{X}}{X_\perp} - 1\right)\{\langle \boldsymbol{uu}\rangle \cdot \dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}} \cdot \langle \boldsymbol{uu}\rangle\} \tag{18.4-52}$$

where the subscript (1) on $\langle \boldsymbol{uu}\rangle$ indicates the convected derivative. It may also be shown by direct substitution that for steady flows the solution of the diffusion equation, Eq. 18.4-49, is given to first order in κ by

$$f = \frac{1}{4\pi}\left[1 + \frac{3\tilde{X}\lambda}{2X_\perp}(\dot{\boldsymbol{\gamma}} : \boldsymbol{uu}) + \cdots\right] \tag{18.4-53}$$

From this it follows that

$$\langle \boldsymbol{uu}\rangle = \tfrac{1}{3}\boldsymbol{\delta} + \frac{\tilde{X}}{5X_\perp}\lambda\dot{\boldsymbol{\gamma}} + \cdots \tag{18.4-54}$$

$$\langle \boldsymbol{uu}\rangle_{(1)} = -\tfrac{1}{3}\dot{\boldsymbol{\gamma}} + \frac{\lambda\tilde{X}}{10X_\perp}\{\boldsymbol{\omega} \cdot \dot{\boldsymbol{\gamma}} - \dot{\boldsymbol{\gamma}} \cdot \omega\} - \frac{\lambda\tilde{X}}{5X_\perp}\{\dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}}\} + \cdots \tag{18.4-55}$$

$$\langle \boldsymbol{uuuu}\rangle : \dot{\boldsymbol{\gamma}} = \tfrac{2}{15}\dot{\boldsymbol{\gamma}} + \frac{4\lambda\tilde{X}}{35X_\perp}[\{\dot{\boldsymbol{\gamma}} \cdot \dot{\boldsymbol{\gamma}}\} + \tfrac{1}{4}(\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})\boldsymbol{\delta}] + \cdots \tag{18.4-56}$$

These results, which follow directly from Eq. 18.4-49, are used in the next example in the development of the expression for the stress tensor.

EXAMPLE 18.4-2 The Stress Tensor for the Multirod-Rod Model

Use Eq. 18.4-4 to develop an explicit expression for the polymer contribution, $\boldsymbol{\pi}_p$, to the stress tensor of a dilute solution using the multirod-rod model of Example 18.4-1.

SOLUTION The stress tensor of the solution is given by Eq. 18.4-4, in which the sum on the index α includes all solvent and solute species. Here we are dealing with only one solute species and find from Eqs. 18.4-1 and 18.4-4 that the contribution of this polymer species to the total stress tensor is:

$$\boldsymbol{\pi}_p = \boldsymbol{\pi}_k + \frac{X}{X_\perp}\sum_s \int \boldsymbol{u}\boldsymbol{d}_s(\mathscr{F}_s^{(b)} + (\mathbf{M}_s : \boldsymbol{\kappa}))\Psi\, d\theta\, d\phi - \tfrac{1}{12}N(N^2-1)a^2\int \boldsymbol{u}[\boldsymbol{\zeta} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}]\Psi\, d\theta\, d\phi \tag{18.4-57}$$

where

$$X = \tfrac{1}{12} N(N^2 - 1)a^2\zeta_\perp \tag{18.4-58}$$

From this one finds that

$$\boldsymbol{\pi}_p = nkT\,\boldsymbol{\delta} + nkT\frac{X}{X_\perp}\left\{\boldsymbol{\delta} - 3\langle\boldsymbol{uu}\rangle - 3\lambda\left(\frac{\tilde{X}}{X_\perp} + \frac{\zeta_\parallel}{\zeta_\perp} - 1\right)\langle\boldsymbol{uuuu}\rangle : \dot{\boldsymbol{\gamma}} + 3\lambda\left(\frac{\tilde{X}}{X_\perp} - 1\right)\langle\boldsymbol{uu}\rangle\cdot\dot{\boldsymbol{\gamma}}\right\} \tag{18.4-59}$$

In the limiting case that the friction tensor is isotropic ($\zeta_\parallel = \zeta_\perp$) and the rotational friction coefficients are zero, this expression reduces to the Kramers expression for the stress tensor of a multibead rod as given by Eq. A, Table 14.3-1, with the time constant given by Eq. 14.3-1.

When one uses the relation developed from the diffusion equation and given by Eq. 18.4-52 one finds that the symmetric part of the stress tensor is

$$\boldsymbol{\pi}_p^{(s)} = nkT\,\boldsymbol{\delta} + 3nkT\lambda\frac{X}{X_\perp}\left\{\langle\boldsymbol{uu}\rangle_{(1)} + \left(1 - \frac{\zeta_\parallel}{\zeta_\perp}\right)\langle\boldsymbol{uuuu}\rangle : \dot{\boldsymbol{\gamma}}\right\} \tag{18.4-60}$$

and the antisymmetric part is

$$\boldsymbol{\pi}_p^{(a)} = nkT\left(\frac{3X\lambda}{2X_\perp}\right)\left(\frac{\tilde{X}}{X_\perp} - 1\right)\{\langle\boldsymbol{uu}\rangle\cdot\dot{\boldsymbol{\gamma}} - \dot{\boldsymbol{\gamma}}\cdot\langle\boldsymbol{uu}\rangle\} \tag{18.4-61}$$

The first of these relations is a generalization of the Giesekus expression given as Eq. D in Table 14.3-1.

When one uses the results developed from a perturbation solution of the diffusion equation, as given by Eqs. 18.4-54 to 56, in the expression for the full stress tensor one finds that to second order in $\boldsymbol{\kappa}$

$$\boldsymbol{\pi}_p = nkT\boldsymbol{\delta} - b_1\dot{\boldsymbol{\gamma}} + \tfrac{1}{2}b_2\{\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\omega} - \boldsymbol{\omega}\cdot\dot{\boldsymbol{\gamma}}\} + (b_2 - b_{11})\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\} - \tfrac{1}{4}b_{11}(\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}})\boldsymbol{\delta} + \cdots \tag{18.4-62}$$

where

$$b_1 = \frac{nkT\lambda X}{5X_\perp\zeta_\perp}(3\zeta_\perp + 2\zeta_\parallel) \tag{18.4-63}$$

$$b_2 = -\frac{3\,nkT\lambda^2 X\tilde{X}}{5X_\perp{}^2} \tag{18.4-64}$$

$$b_{11} = \frac{12nkT\lambda^2 X\tilde{X}}{35X_\perp{}^2\zeta_\perp}(\zeta_\parallel - \zeta_\perp) \tag{18.4-65}$$

are the second-order fluid constants. Note that, to this order, the stress tensor is symmetric. The antisymmetric contribution does, however, enter at third order; to lowest order,

$$\boldsymbol{\pi}^{(a)} = -\frac{3nkT\lambda^3 X\tilde{X}}{20X_\perp{}^4}(\tilde{X} - X_\perp)^2\{\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\omega} - 2\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{\omega}\cdot\dot{\boldsymbol{\gamma}} + \boldsymbol{\omega}\cdot\dot{\boldsymbol{\gamma}}\cdot\dot{\boldsymbol{\gamma}}\} = \frac{3nkT\lambda^3 X\tilde{X}}{10X_\perp{}^4}(\tilde{X} - X_\perp)^2\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(2)} - \boldsymbol{\gamma}_{(2)}\cdot\boldsymbol{\gamma}_{(1)}\} \tag{18.4-66}$$

where $\boldsymbol{\gamma}_{(1)} \equiv \dot{\boldsymbol{\gamma}}$ and $\boldsymbol{\gamma}_{(2)} = (\boldsymbol{\gamma}_{(1)})_{(1)}$ (see §D.3); note that $\tilde{X} - X_\perp$ is the same as $N(\tilde{\xi} - \xi_\perp)$.

It is interesting that this model leads to a stress tensor that is *not* symmetric. The antisymmetric contribution comes from the inclusion of the hydrodynamic torque terms in Eq. 18.1-13 associated with the finite structure of the beads. The antisymmetric behavior does not arise until the third order since $\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(2)} - \boldsymbol{\gamma}_{(2)}\cdot\boldsymbol{\gamma}_{(1)}\}$ is the lowest order antisymmetric combination of the $\boldsymbol{\gamma}_{(n)}$ tensors.

In order to obtain numerical evaluations of the quantities in Eqs. 18.4-63 to 66, it is necessary to have explicit expressions for the various friction coefficients. Brenner[5] has developed such expressions from "slender body" theory. From hydrodynamic considerations he finds that if a long slender body is modeled as a cylinder of length a and diameter b, then for $a \gg b$

$$\zeta_\perp = \frac{4\pi a\eta_s}{\ln(a/b)}, \qquad \zeta_\parallel = \tfrac{1}{2}\zeta_\perp \tag{18.4-67}$$

$$\xi_\perp = \frac{\pi a^3\eta_s}{3\ln(a/b)}, \qquad \tilde{\xi} = \tfrac{1}{2}\xi_\perp \tag{18.4-68}$$

With these values one finds from Eqs. 18.4-40, 45, and 58 that

$$X_\perp = \frac{N^3\pi a^3\eta_s}{3\ln(a/b)} \tag{18.4-69}$$

$$\tilde{X} = \frac{N(2N^2-1)\pi a^2\eta_s}{6\ln(a/b)} \tag{18.4-70}$$

$$X = \frac{N(N^2-1)\pi a^3\eta_s}{3\ln(a/b)} \tag{18.4-71}$$

and that the second-order fluid constants are

$$b_1 = \tfrac{4}{5}nkT\lambda\left(\frac{N^2-1}{N^2}\right) \tag{18.4-72}$$

$$b_2 = -\tfrac{3}{10}nkT\lambda^2\left[\frac{(N^2-1)(2N^2-1)}{N^4}\right] \tag{18.4-73}$$

$$b_{11} = \tfrac{2}{7}b_2 \tag{18.4-74}$$

From this last relation it follows that $\Psi_{2,0}/\Psi_{1,0} = -\frac{1}{7}$. In addition the third-order contribution to the antisymmetric part of the stress tensor is

$$\boldsymbol{\pi}^{(a)} = \frac{3nkT\lambda^3}{80\,N^8}(N^2-1)(2N^2-1)\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(2)} - \boldsymbol{\gamma}_{(2)}\cdot\boldsymbol{\gamma}_{(1)}\} \tag{18.4-75}$$

In Eqs. 18.4-72 through 18.4-75

$$\lambda = \frac{N^3\pi a^3\eta_s}{6kT\ln(a/b)} \tag{18.4-76}$$

is the time constant.

[5] H. Brenner, *Int. J. Multiphase Flow*, **1**, 195–341 (1974).

PROBLEMS

18B.1 Dimensionless Mobility Tensors

Show that the dimensionless mobility tensors, $\mathbf{B}_{\nu\mu}$, defined by Eq. 18.2-5 may be written in the series form,

$$\mathbf{B}_{\nu\mu} = \delta_{\nu\mu}\boldsymbol{\delta} - \{\boldsymbol{\zeta}_{\nu} \cdot \boldsymbol{\Omega}_{\nu\mu}\} + \sum_{\eta} \{\boldsymbol{\zeta}_{\nu} \cdot \boldsymbol{\Omega}_{\nu\eta} \cdot \boldsymbol{\zeta}_{\eta} \cdot \boldsymbol{\Omega}_{\eta\mu}\} + \cdots \tag{18B.1-1}$$

If it can be shown that this series converges then this result illustrates that the set of tensors $\mathbf{B}_{\nu\mu}$ exists.

18B.2 Drift of the Center of Resistance

Make use of Eq. 18.4-10 and the discussion following Eq. 18.2-18 to show that in the approximation of equilibrium-averaged hydrodynamic interaction

$$\frac{m_p}{\bar{N}} \int \mathbf{Z}^{-1} \cdot (\boldsymbol{F}^{(b)} + \boldsymbol{F}^{(e)}) \Psi_{\alpha}(\boldsymbol{r}, Q, t) dQ = m_p \int (\llbracket \dot{\boldsymbol{r}}_h \rrbracket - \boldsymbol{v}(\boldsymbol{r}_h)) \Psi_{\alpha}(\boldsymbol{r}, Q, t) dQ \tag{18B.2-1}$$

where $\boldsymbol{r}_h$ is the hydrodynamic center of resistance.

18B.3 Translational Diffusion Coefficient for the Elastic Dumbbell Model

Show that, for a dilute solution of polymer molecules modeled as elastic dumbbells with Hookean springs, the expression for the diffusion coefficient given by Eq. 18.4-29 reduces to that given by Eq. 13.6-20.

18C.1 Simplification of the General Expression for the Stress Tensor for a Special Case

Prove directly from Eq. 18.4-4 that, if the model consists of structureless beads with no constraints, the stress tensor is given by Eq. 18.1-18. For this purpose, first note from Eq. 18.4-5 that

$$\sum_{\mu} \llbracket \dot{\boldsymbol{R}}_{\mu} \rrbracket \cdot \tilde{\boldsymbol{\zeta}}_{\mu\nu} = \sqrt{m_{\nu}} \sum_{s} \boldsymbol{a}_{\nu s} (\mathscr{F}_s^{(e)} + \mathscr{F}_s^{(\phi)} + \mathscr{F}_s^{(b)} + \mathscr{F}_s^{(b,e)} + \mathbf{M}_s : \boldsymbol{\kappa}) \tag{18C.1-1}$$

where the $\boldsymbol{a}_{\nu s}$ are the modified reciprocal base vectors defined by Eq. 16.3-6. Next, from the definition of the coupling tensors, $\boldsymbol{M}_s^{(1)}$, Eq. 18.2-26, show that

$$\sum_{\nu} \sqrt{m_{\nu}}\, \boldsymbol{R}_{\nu} \boldsymbol{a}_{\nu s} \mathbf{M}_s^{(1)} = \bar{N} \sum_{\nu\mu\eta} \sqrt{\frac{m_{\nu}}{m_{\eta}}}\, \boldsymbol{R}_{\nu} \boldsymbol{a}_{\nu s} \boldsymbol{R}_{\mu} \boldsymbol{b}_{\eta s} \cdot \tilde{\boldsymbol{\zeta}}_{\eta\mu} \tag{18C.1-2}$$

and therefore that

$$\sum_{\nu\mu} \boldsymbol{R}_{\nu} (\llbracket \dot{\boldsymbol{R}}_{\mu} \rrbracket - \boldsymbol{\kappa} \cdot \boldsymbol{R}_{\mu}) \cdot \tilde{\boldsymbol{\zeta}}_{\mu\nu} = \sum_{\nu s} \sqrt{m_{\nu}}\, \boldsymbol{R}_{\nu} \boldsymbol{a}_{\nu s} (\mathscr{F}_s^{(e)} + \mathscr{F}_s^{(\phi)} + \mathscr{F}_s^{(b)} + \mathscr{F}_s^{(b,e)} + \mathbf{M}_s^{(2)} : \boldsymbol{\kappa})$$
$$+ \sum_{\nu\mu\eta} \sqrt{\frac{m_{\nu}}{m_{\eta}}}\, \boldsymbol{R}_{\nu} \left(\bar{N} \sum_{s} \boldsymbol{a}_{\nu s} \boldsymbol{b}_{\eta s} - \delta_{\nu\eta} \boldsymbol{\delta} \right) \cdot \tilde{\boldsymbol{\zeta}}_{\eta\mu} \boldsymbol{R}_{\mu} : \boldsymbol{\kappa}^{\dagger} \tag{18C.1-3}$$

Next show from the definition of the $\boldsymbol{a}_{vs}$, Eq. 16.3-6, and the definition of the elements of the metric matrix $\tilde{g}^{(1)}_{st}$, Eq. 18.2-25, that

$$\sum_{v} \boldsymbol{a}_{vs} \cdot \boldsymbol{b}_{vt} = \frac{1}{\bar{N}} \left(\delta_{st} - \sum_{u} \tilde{G}_{su} \tilde{g}^{(2)}_{ut} \right) \tag{18C.1-4}$$

$$\sum_{vtu} \boldsymbol{a}_{vs} \cdot \boldsymbol{b}_{vt} \boldsymbol{b}_{\mu u} G_{tu} = \frac{1}{\bar{N}} \sum_{u} G_{su} \boldsymbol{b}_{\mu u} - \frac{1}{\bar{N}} \sum_{tuv} \tilde{G}_{su} \tilde{g}^{(2)}_{ut} G_{tv} \boldsymbol{b}_{\mu v} \tag{18C.1-5}$$

If the beads are structureless and there are no constraints in the model, show from Eqs. 12D.3-5 and 16.3-7 that

$$\boldsymbol{a}_{vs} = \frac{1}{\bar{N}} \sum_{t} G_{st} \boldsymbol{b}_{vt} \tag{18C.1-6}$$

Now use Eq. 12D.3-5 again to verify that

$$\sum_{s} \boldsymbol{a}_{vs} \boldsymbol{b}_{\mu s} = \frac{1}{\bar{N}} \left[\delta_{v\mu} - \frac{\sqrt{m_v m_\mu}}{m} \right] \boldsymbol{\delta} \tag{18C.1-7}$$

Then find from Eq. 18C.1-3 that for structureless beads and no constraints

$$\sum_{v\mu} \boldsymbol{R}_v \left([\![\dot{\boldsymbol{R}}_\mu]\!] - \boldsymbol{\kappa} \cdot \boldsymbol{R}_\mu \right) \cdot \boldsymbol{\zeta}_{\mu v} = \frac{1}{\bar{N}} \sum_{v} \boldsymbol{R}_v \left(\boldsymbol{\mathcal{F}}^{(e)}_v + \boldsymbol{\mathcal{F}}^{(\phi)}_v + \boldsymbol{\mathcal{F}}^{(b)}_v + \boldsymbol{\mathcal{F}}^{(b,e)}_v \right) \tag{18C.1-8}$$

$$\boldsymbol{\mathcal{F}}^{(b,e)}_v = \sqrt{m_v} \sum_{st} G_{st} \boldsymbol{b}_{vs} \boldsymbol{\mathcal{F}}^{(b,e)}_t \tag{18C.1-9}$$

Verify that when this result is used in the expression for the stress tensor, Eq. 18.4-4, the latter reduces to that given by Eq. 18.1-18.

18C.2 Translational Diffusion Coefficient for the Multibead-Rod Model

a. Use the results developed in Examples 16.1-1 and 16.2-1 to show that for a dilute solution of molecules modeled as multibead rods Eq. 18.4-22 reduces to

$$\boldsymbol{\Lambda} = kT \mathbf{Z}^{-1} \tag{18C.2-1}$$

b. From this develop an expression for the translational diffusion coefficient of the system, and show that the result is identical to that given by Eq. 14.6-45.

18D.1 Proof of Tensor Identities Needed in Discussion of Mass Flux

Making use of Eqs. 18.2-6, 7, 11, and 12, prove that

$$\boldsymbol{\lambda}^{\dagger}_{v} = \sum_{\mu} \mathbf{B}_{v\mu} \cdot \boldsymbol{\zeta}_{\mu} \cdot \mathbf{Z}^{-1} \tag{18D.1-1}$$

Then make use of Eq. 18.2-5 to prove Eq. 18.4-8, and Eqs. 18.2-6, 20, and 21 to prove Eq. 18.4-9.

CHAPTER 19

PHASE-SPACE THEORY FOR CONCENTRATED SOLUTIONS AND MELTS

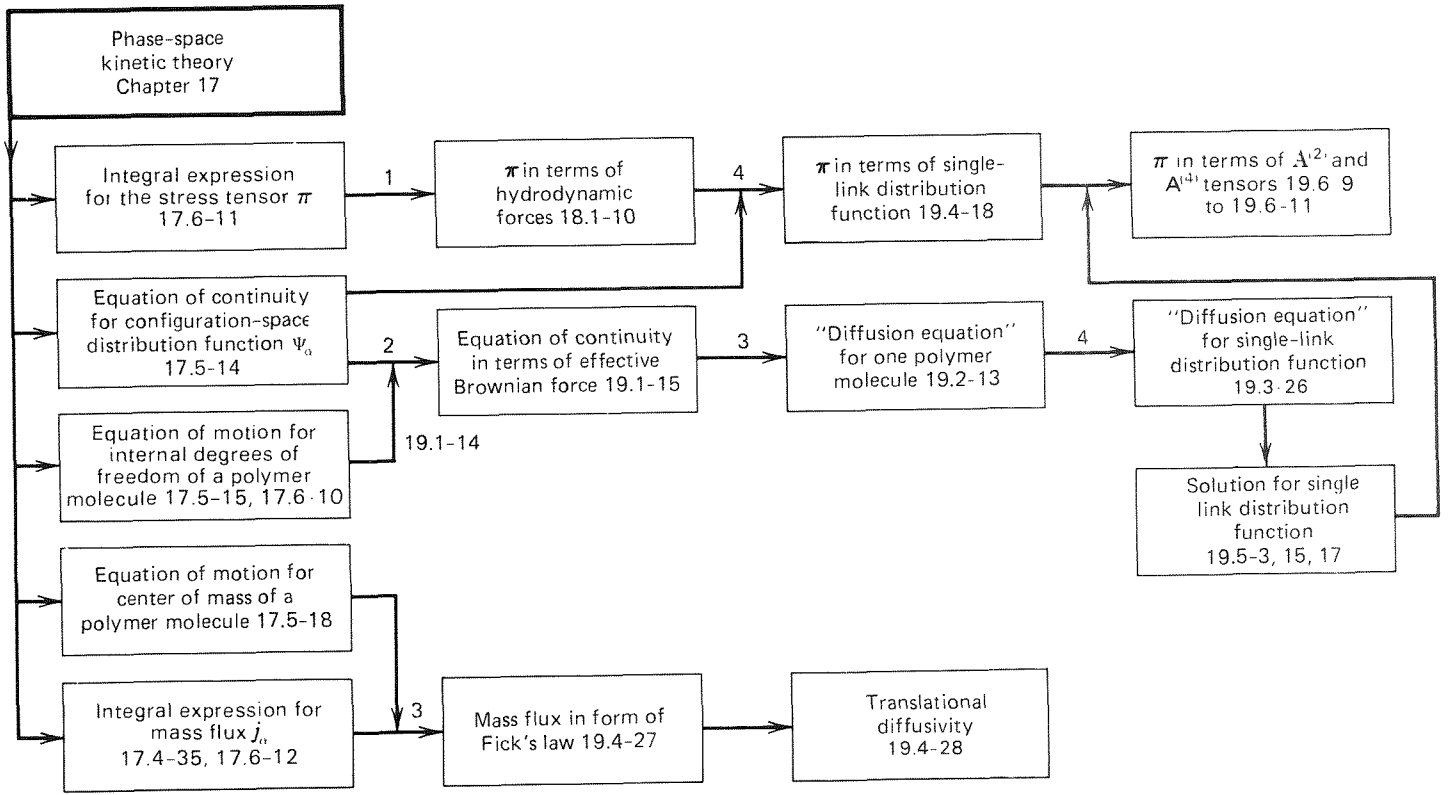
In the foregoing chapter it was shown how the main kinetic theory results of Chapter 17 can be used to develop theories for the rheological responses of dilute polymer solutions. In this chapter we show how to use the same results of Chapter 17 to develop a theory for the rheological behavior of undiluted polymers ("polymer melts"). A comparison of the block diagram in Fig. 19.0-1 with the analogous diagram in Fig. 18.0-1 emphasizes the formal similarity between the two kinetic theory developments.

Dilute polymer solutions and undiluted polymers do have some important differences at the molecular level as can be recognized if we consider the motion of one polymer molecule in the fluid. In Figure 19.0-2 we show the configurations of a polymer chain at time t and time $t + \Delta t$ in a fluid undergoing stress relaxation after cessation of flow. In a *dilute solution* each bead of the polymer chain is bombarded from all sides by the solvent molecules and as the beads go through the solvent, an isotropic Stokes' law appears to be a reasonable assumption for describing the hydrodynamic drag. After a time interval Δt the chain may have wandered off into quite a different configuration. In a *concentrated solution or melt*, however, the polymer chain finds it very difficult to move sideways and its principal motion is more or less in the direction of the chain backbone; that is, we expect the hydrodynamic drag and the Brownian motion to be highly anisotropic. As a consequence the major difference between the dilute solution kinetic theory and the theory for concentrated fluids is in the form of the mathematical expressions used for the hydrodynamic drag (§19.1) and the Brownian motion (§19.2). Two new parameters make their appearance here: ε, which specifies the anisotropy of the hydrodynamic drag force, and ε', which accounts for the anisotropy of the Brownian motion (these parameters correspond roughly to the parameters σ and β in §13.7).

Some polymer physicists[1,2] have chosen to describe the constraints on a polymer chain in a concentrated system by saying that the chain moves in a "tube." The "tube" concept seems to have been very useful for qualitative discussions and for interrelating a wide range of phenomena. Doi and Edwards[2] used the idea of "tube" constraints in setting up the first comprehensive kinetic theory for polymer melts based on the consideration of the motion of a typical polymer chain in a concentrated solution. In our presentation in this

[1] See, for example, S. F. Edwards, *Proc. Phys. Soc.*, **92**, 9–16 (1967); P.-G. de Gennes, and L. Léger, *Ann. Rev. Phys. Chem.*, **33**, 49–61 (1982); P.-G. de Gennes, *Physics Today*, **36**, 33–39 (1983).

[2] M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. II*, **74**, 1789–1832 (1978); **75**, 38–54 (1979). See also M. Doi and S. F. Edwards, *Theory of Polymer Dynamics*, Oxford University Press (1986), Chapter 7.


Phase-space kinetic theory Chapter 17
Integral expression for the stress tensor π 17.6-11
1
π in terms of hydrodynamic forces 18.1-10
4
π in terms of single-link distribution function 19.4-18
π in terms of $A^{(2)}$ and $A^{(4)}$ tensors 19.6 9 to 19.6-11
Equation of continuity for configuration-space distribution function Ψ_α 17.5-14
2
Equation of continuity in terms of effective Brownian force 19.1-15
3
"Diffusion equation" for one polymer molecule 19.2-13
4
"Diffusion equation" for single-link distribution function 19.3-26
Equation of motion for internal degrees of freedom of a polymer molecule 17.5-15, 17.6-10
19.1-14
Solution for single link distribution function 19.5-3, 15, 17
Equation of motion for center of mass of a polymer molecule 17.5-18
Integral expression for mass flux j_α 17.4-35, 17.6-12
3
Mass flux in form of Fick's law 19.4-27
Translational diffusivity 19.4-28

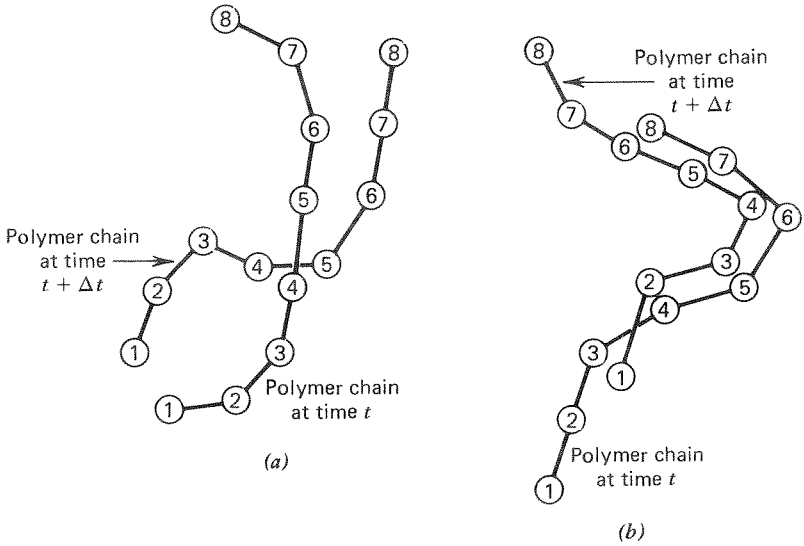


FIGURE 19.0-2. Comparison of the motion of one molecule in (*a*) a dilute polymer solution and in (*b*) a concentrated solution or polymer melt; in the latter the motion of a polymer molecule is severely constrained by the other polymer molecules in the fluid.

chapter we do not follow the Doi–Edwards theory, but rather a more systematic kinetic theory approach[3] that is closely patterned after the dilute solution theories. In spite of the totally different approaches used in these two theories for concentrated systems, many of the key results are closely related; as the story unfolds, we point out the similarities and the salient differences.

This chapter differs in two other respects from Chapter 18. Whereas in the foregoing chapter we worked with arbitrary bead-rod-spring models, the discussion in this chapter is restricted to the Kramers freely jointed bead-rod chain model illustrated in Fig. 11.3-1. In particular, we consider a system consisting of a mixture of molecules of various species α, as shown in Fig. 19.0-3. Each species is modeled as a chain of N_α identical beads, joined by $(N_\alpha - 1)$ links, each of length a, the molecules differing only in length. Some of the properties of the Kramers model have been discussed in §§11.3, 12.1, and 16.5. As pointed out in §16.5 it is convenient in discussing this model to label the generalized coordinates by two indices and take Q_{k1} and Q_{k2} to be the polar angles θ_k and ϕ_k that specify the

[3] C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, 2016–2033 (1982); R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1106 (1982); *J. Chem. Phys.*, **77**, 4747–4757 (1982); H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982); X. J. Fan and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **15**, 341–373 (1984); C. F. Curtiss and R. B. Bird, *Physica*, **118A**, 191–204 (1983); R. B. Bird and C. F. Curtiss, *Phys. Today*, **37**, 36–43 (1984).

FIGURE 19.0-1. Kinetic theory for undiluted polymers (polymer melts).

MAJOR APPROXIMATIONS	MODEL
1. Short-range force approximation 18.1-5	
2. Modified Stokes law empiricism 19.1-1	
3. Approximations for momentum-space averages 19.2-4, 9, 10	Interacting Kramers
4. Mild-curvature approximation 19.3-4, 19.4-12	bead-rod chains

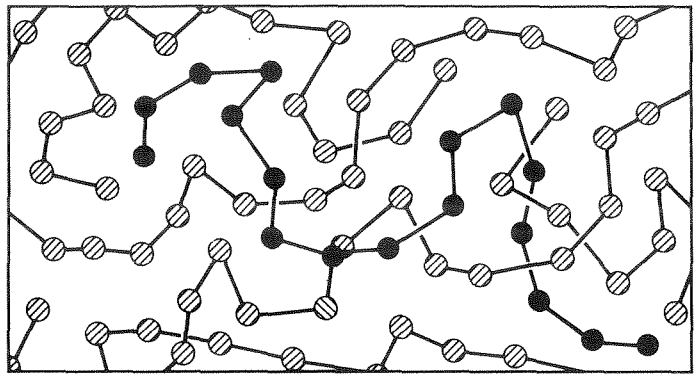


FIGURE 19.0-3. In the model of an undiluted polymer considered in this chapter, the fluid is modeled as a collection of interacting bead-rod chains. Polydispersity is accounted for by allowing a distribution of chain lengths corresponding to a distribution of molecular weights. A polymer molecule of molecular weight M_α is represented by N_α beads joined together with massless rods of length a. The number N_α is equal to M_α/M_0, where M_0 is the "molecular weight" of that segment of the polymer molecule represented by one bead. One chain, corresponding to a species with $N_\alpha = 17$, is shown with solid beads.

orientation of the unit vector, $\boldsymbol{u}_k$, of the link joining beads k and $k+1$. Indices $i, j, k, \ldots$ (ranging from 1 to $N-1$) are used to label the rods; $\nu, \mu, \ldots$ (ranging from 1 to N) are labels for beads; and $p, q, \ldots$ are 1 or 2 corresponding to θ and ϕ.

In this chapter we introduce an additional important approximation—the "mild-curvature approximation." This approximation permits us to follow Doi and Edwards and reduce the problem to one involving only the single-link distribution function $f(\boldsymbol{u}, \sigma, t)$, which gives the probability that a link located a fractional distance σ along the chain has the orientation given by the unit vector $\boldsymbol{u}$ at the time t. The mild curvature assumption is used in §19.3 to get the differential equation for the time evolution of $f(\boldsymbol{u}, \sigma, t)$ and in §19.4 to get an expression for the stress tensor in terms of $f(\boldsymbol{u}, \sigma, t)$. To summarize, then, in addition to the restriction to a specific model, four main approximations are inherent in the theory presented here:

1. The *short-range-force approximation* already discussed in §18.1.
2. The *anisotropic Stokes' law approximation*, discussed in §19.1, which replaces the approximation used in §18.2 for dilute solutions.
3. The *anisotropic Brownian motion* (or "*reptation*") *approximation*, given in §19.2, which replaces the approximations used in §18.3 for dilute solutions.
4. The *mild-curvature approximation*, introduced in §§19.3 and 19.4, which was not used in dilute solution theories.

Thus, aside from the fourth approximation used here, the form of the theory for undiluted polymers is quite similar to that for dilute solutions. This emphasizes the advantage of a unified approach to the kinetic theory of polymeric liquids.

Once the differential equation for $f(\boldsymbol{u}, \sigma, t)$ has been solved (§19.5), then a constitutive equation for the melt may be obtained (§19.6). Finally, in §§19.7 and 19.8, we compare the theoretical material functions with experimental data.

§19.1 THE HYDRODYNAMIC FORCES

As discussed in the previous chapter, to reduce the development from one in the phase space of the entire system to one in the phase space of a single molecule, we introduce an approximation for the hydrodynamic force. In Eq. 18.2-1 a nonisotropic modification of Stokes' law was proposed for the hydrodynamic force acting on the vth bead of the bead-spring-rod model. In this chapter a different kind of modification of Stokes' law is used. We propose empiricisms for the *differences* between the hydrodynamic forces on adjacent pairs of beads[1] and for the *sum* of the hydrodynamic forces on all the beads of the Kramers bead-rod chain model. This is done so that tensor friction coefficients can be introduced that depend on the orientations of the rods. Thus we take (for $1 \leq k \leq N-1$)

$$\boxed{\boldsymbol{F}_{k+1}^{(h)} - \boldsymbol{F}_{k}^{(h)} = -\bar{N}^{\beta}\boldsymbol{\zeta}_k \cdot \{[\![\dot{\boldsymbol{R}}_{k+1} - \dot{\boldsymbol{R}}_k]\!] - [\boldsymbol{v}(\boldsymbol{r} + \boldsymbol{R}_{k+1}) - \boldsymbol{v}(\boldsymbol{r} + \boldsymbol{R}_k)]\}} \tag{19.1-1}$$

where the friction tensors $\boldsymbol{\zeta}_k$ are:

$$\boldsymbol{\zeta}_k = \zeta[\boldsymbol{\delta} - (1-\varepsilon)\boldsymbol{u}_k\boldsymbol{u}_k] \tag{19.1-2}$$

and $\bar{N} = \sum x_\alpha N_\alpha$ is the average number of beads per chain in the polydisperse fluid with mole fractions x_α. This expression for the differences of hydrodynamic forces is a generalization of that introduced in the elementary kinetic theory for dumbbells (see Eqs. 13.2-2 and 13.7-12). In this modified Stokes' law expression three empirical constants appear:[2] the scalar *friction coefficient* ζ, the *link tension coefficient* ε, and the *chain constraint exponent* β. The parameter ε, which determines the anisotropy of the friction tensor, is taken here to be a constant, although it could be taken to be a function of $\dot{\gamma} = (\frac{1}{2}\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})^{1/2}$; if $\varepsilon = 1$ the tensor is isotropic and if $\varepsilon = 0$ there is no component of the difference of the forces on two succeeding beads in the direction of the link joining them (i.e., in the direction of the backbone of the chain). From the viscosity and normal stress curves it has been found that ε is in the range from 0.3 to 0.5 for concentrated solutions and undiluted polymers, both monodisperse and polydisperse. For an explanation of the term "link tension coefficient" see Example 19.1-1. The parameter β is introduced because it appears reasonable that the magnitude of the hydrodynamic force should increase slowly with increasing average length in a polydisperse system. It is found from experimental data on the molecular weight dependence of the zero-shear-rate viscosity that β is about 0.3 to 0.5.

If one assumes homogeneous flow (that is $\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^{\dagger}$ is independent of position), one may make use of Eq. 16.5-1 to rewrite Eq. 19.1-1, in the form

$$\boldsymbol{F}_{k+1}^{(h)} - \boldsymbol{F}_{k}^{(h)} = -\bar{N}^{\beta} a \boldsymbol{\zeta}_k \cdot ([\![\dot{\boldsymbol{u}}_k]\!] - [\boldsymbol{\kappa} \cdot \boldsymbol{u}_k]) \tag{19.1-3}$$

[1] Equation 19.1-1 for Kramers chains in monodisperse concentrated solutions or undiluted polymers was first proposed by C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, 2016-2025, 2026-2033 (1981); the polydisperse expression given in Eq. 19.1-1 is new. Equation 19.1-7 is introduced here for the first time in order to discuss translational diffusion.

[2] In the Doi Edwards development there is no explicit introduction of a Stokes' law type of expression. A chain friction coefficient is introduced via the Nernst-Einstein equation for a chain undergoing a one-dimensional Brownian motion. The Doi-Edwards constitutive equation results from taking $\varepsilon = 0$ and $\beta = 0$ in our development.

For the sake of comparing with Eq. 18.2-19, the above can be rewritten to show the hydrodynamic force on the νth bead

$$\boldsymbol{F}_{\nu}^{(h)} = -\sum_{\mu} \tilde{\zeta}_{\nu\mu} \cdot (\llbracket \dot{\boldsymbol{R}}_{\mu} \rrbracket - [\boldsymbol{\kappa} \cdot \boldsymbol{R}_{\mu}]) + \frac{1}{N} \boldsymbol{F}^{(h)} \tag{19.1-4}$$

where

$$\tilde{\zeta}_{\nu\mu} = \bar{N}^{\beta} \sum_{j} B_{\nu j} \zeta_{j} \bar{B}_{j\mu} \tag{19.1-5}$$

and

$$\boldsymbol{F}^{(h)} = \sum_{\nu} \boldsymbol{F}_{\nu}^{(h)} \tag{19.1-6}$$

is the total hydrodynamic force on a molecule. It is to be noted that the tensors $\tilde{\zeta}_{\nu\mu}$ defined here are not the same as those introduced in §18.2 and Table 16.1-2, but it is convenient to use the same symbol because of the resulting similarity of this equation with Eq. 18.2-19.

Since only the hydrodynamic force differences are introduced by Eq. 19.1-1, the total force $\boldsymbol{F}^{(h)}$ is not yet specified. In this development we take the total hydrodynamic force on a molecule of species α to be

$$\boxed{\boldsymbol{F}^{(h)\alpha} = -\zeta^{\alpha}(\llbracket \dot{\boldsymbol{r}}^{\alpha} \rrbracket - \boldsymbol{v}(\boldsymbol{r}^{\alpha}))} \tag{19.1-7}$$

where ζ^{α} is the (scalar) friction coefficient of the molecule as a whole. This expression is used in §19.4 to develop an expression for the translational diffusion coefficient.

The next step in the development is to obtain an expression for the average generalized velocities $\llbracket \dot{Q}_{ip} \rrbracket$, which when introduced into the equation of continuity leads to the diffusion equation for the distribution function. Because of the similarity of Eq. 19.1-4 to Eq. 18.2-19, much of this development follows closely that of §18.2. As in the previous development, we first note that Eq. 17.1-5 (the definition of the base vectors) can be used to rewrite the expression for $\boldsymbol{F}_{\nu}^{(h)}$ in Eq. 19.1-4 as

$$\boldsymbol{F}_{\nu}^{(h)} = \frac{1}{N} \boldsymbol{F}^{(h)} - \sum_{\mu i p} \frac{1}{\sqrt{m}} [\tilde{\zeta}_{\mu\nu} \cdot \boldsymbol{b}_{\mu, ip}] \llbracket \dot{Q}_{ip} \rrbracket + \sum_{\mu} [\tilde{\zeta}_{\nu\mu} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{R}_{\mu}] \tag{19.1-8}$$

From this we obtain a result (similar to Eq. 18.2-24) associated with each of the generalized coordinates Q_{ip}, that is, the polar angles θ_i and ϕ_i specifying the direction, $\boldsymbol{u}_i$, of link i,

$$\bar{N} \sum_{\nu} \frac{1}{\sqrt{m}} (\boldsymbol{b}_{\nu, ip} \cdot \boldsymbol{F}_{\nu}^{(h)}) = -\sum_{j} \sum_{q} \tilde{g}_{ip, jq} \llbracket \dot{Q}_{jq} \rrbracket + (\mathbf{M}_{ip} : \boldsymbol{\kappa}) \tag{19.1-9}$$

where the metric matrix elements are

$$\tilde{g}_{ip, jq} = \frac{\bar{N}}{m} \sum_{\nu} \sum_{\mu} (\boldsymbol{b}_{\nu, ip} \cdot \tilde{\zeta}_{\nu\mu} \cdot \boldsymbol{b}_{\mu, jq}) \tag{19.1-10}$$

and the coupling tensors are

$$\mathbf{M}_{ip} = \frac{\bar{N}}{\sqrt{m}} \sum_{\nu} \sum_{\mu} \{\boldsymbol{R}_{\mu} \boldsymbol{b}_{\nu, ip} \cdot \tilde{\zeta}_{\nu\mu}\} \tag{19.1-11}$$

It follows from the definition of the $\tilde{g}_{ip,jq}$ (Eq. 19.1-10), the expressions for the base vectors (Eq. 16.5-4), and the definition of the $\tilde{\zeta}_{\nu\mu}$ (Eq. 19.1-5) that

$$\tilde{g}_{ip,jq} = \frac{\bar{N}^{1+\beta\zeta}}{m} g_{ip,jq} \tag{19.1-12}$$

The elements of the inverse matrix are then

$$\tilde{G}_{ip,jq} = \frac{m}{\bar{N}^{1+\beta\zeta}} G_{ip,jq} \tag{19.1-13}$$

where the $G_{ip,jq}$ are given by Eq. 16.5-8. Note that the $\tilde{g}_{ip,jq}$ and the $\tilde{G}_{ip,jq}$ introduced here are not the same as the quantities defined in §18.2 and Table 16.1-2 (see the comment regarding $\tilde{\zeta}_{\nu\mu}$ after Eq. 19.1-6). Thus paralleling the development of §18.2, we find

$$[\![\dot{Q}_{ip}]\!] = \frac{m}{\bar{N}^{1+\beta\zeta}} \sum_{j} \sum_{q} G_{ip,jq} (\mathscr{F}_{jq}^{(c)} + \mathscr{F}_{jq}^{(b)} + \mathbf{M}_{jq} : \boldsymbol{\kappa}) \tag{19.1-14}$$

as the analogue of Eq. 18.2-43.

The last result may be used in the equation of continuity (Eq. 17.5-14); if one neglects the external forces one then finds that

$$\boxed{\frac{\partial \Psi_{\alpha}}{\partial t} = -\frac{1}{\bar{N}^{1+\beta\zeta} a^2} \sum_{ijklpq} A_{ik} A_{jl} \frac{\partial}{\partial Q_{ip}} [(\mathbf{K}_{kl} : \boldsymbol{d}_{jq} \boldsymbol{d}_{ip})(\mathscr{F}_{jq}^{(b)} + \mathbf{M}_{jq} : \boldsymbol{\kappa}) \Psi_{\alpha}]} \tag{19.1-15}$$

where the $\mathbf{K}_{kl}$ are the Kramers tensors defined by Eq. 16.5-9. When one introduces into this equation an approximation for the generalized Brownian forces, $\mathscr{F}_{jq}^{(b)}$, as functions in the configurational space, this equation becomes the diffusion equation for the configurational distribution functions Ψ_{α}.

EXAMPLE 19.1-1 The Link Tension Coefficient

Consider a polymer chain in a steady elongational flow $v_z = \dot{\varepsilon} z$, $v_x = -\frac{1}{2}\dot{\varepsilon} x$, $v_y = -\frac{1}{2}\dot{\varepsilon} y$, where $\dot{\varepsilon}$ is the (constant) elongational rate. Obtain an expression for the tension in a link aligned with the axis of stretching (link "A" in Fig. 19.1-1) and in a link perpendicular to it (link "B" in Fig. 19.1-1).

SOLUTION Equations 19.1-2 and 19.1-3 can be combined, and the resulting expression can be dotted into $\boldsymbol{u}_k$ to give

$$((\boldsymbol{F}_{k+1}^{(h)} - \boldsymbol{F}_{k}^{(h)}) \cdot \boldsymbol{u}_k) = \varepsilon \bar{N}^{\beta} a \zeta (\boldsymbol{\kappa} : \boldsymbol{u}_k \boldsymbol{u}_k) \tag{19.1-16}$$

In steady elongational flow $\boldsymbol{\kappa} = [-\frac{1}{2}(\boldsymbol{\delta}_x \boldsymbol{\delta}_x + \boldsymbol{\delta}_y \boldsymbol{\delta}_y) + \boldsymbol{\delta}_z \boldsymbol{\delta}_z]\dot{\varepsilon}$. For a link aligned with the axis of stretching, $\boldsymbol{u}_k = \boldsymbol{\delta}_z$, and

$$((\boldsymbol{F}_{k+1}^{(h)} - \boldsymbol{F}_{k}^{(h)}) \cdot \boldsymbol{u}_k) = \varepsilon \bar{N}^{\beta} a \zeta \dot{\varepsilon} \tag{19.1-17}$$

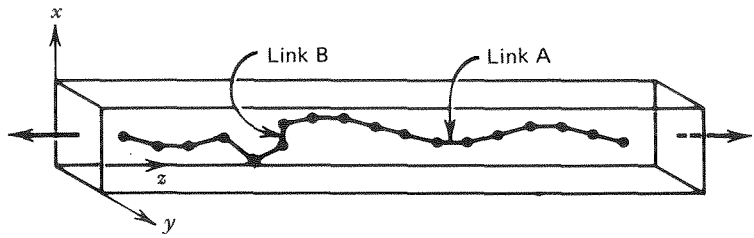


FIGURE 19.1-1. A Kramers chain, representing a macromolecule, in a steady elongational flow. The tension in link A, aligned with the z-axis, is $\varepsilon\bar{N}^{\beta}a\zeta\dot{\varepsilon}$, whereas the tension in link B, aligned with the x-axis, is $-\frac{1}{2}\varepsilon\bar{N}^{\beta}a\zeta\dot{\varepsilon}$. This shows why ε is called the "link tension coefficient."

is the tension in the link. Similarly for a link aligned with, say, the x-axis, the tension is given by

$$((\boldsymbol{F}_{k+1}^{(h)} - \boldsymbol{F}_{k}^{(h)})\cdot\boldsymbol{u}_k) = -\tfrac{1}{2}\varepsilon\bar{N}^{\beta}a\zeta\dot{\varepsilon} \tag{19.1-18}$$

That is, in this case the link feels a compressive force. If one chooses ε to be zero, there is no tension in a link.[3]

§19.2 THE BROWNIAN FORCES

A general expression for the generalized Brownian force is given by Eq. 18.3-7. For the Kramers bead-rod-chain model, in which the beads are taken to be mass points without structure, the second and third terms are zero, and the remaining term can be written as

$$\begin{aligned}\mathscr{F}_{ip}^{(b)} &= -\frac{m}{\Psi_\alpha}\sum_{\nu\mu jq} B_{\nu i}\bar{B}_{j\mu}\boldsymbol{c}_{ip}\cdot\frac{\partial}{\partial Q_{jq}}[\boldsymbol{d}_{jq}\cdot[\![\dot{\boldsymbol{R}}_\mu\dot{\boldsymbol{R}}_\nu]\!]\Psi_\alpha] \\ &= -\frac{ma^2}{\Psi_\alpha}\sum_{jkq} C_{ik}\boldsymbol{c}_{ip}\cdot\frac{\partial}{\partial Q_{jq}}[\boldsymbol{d}_{jq}\cdot[\![\dot{\boldsymbol{u}}_j\dot{\boldsymbol{u}}_k]\!]\Psi_\alpha]\end{aligned} \tag{19.2-1}$$

To eliminate the momentum coordinates from the problem we introduce an approximation for the momentum-space averages, $[\![\dot{\boldsymbol{u}}_j\dot{\boldsymbol{u}}_k]\!]$, arising in the above equation. Then when this expression for $\mathscr{F}_{ip}^{(b)}$ is inserted into Eq. 19.1-14, the latter no longer requires information about the momentum-space distribution function.

a. Equilibration-in-Momentum-Space Approximation

The averages of the products of velocities can be rewritten in terms of products of generalized momenta by using Eqs. 17.1-14 and 16.5-4:

$$\begin{aligned}[\![\dot{\boldsymbol{u}}_i\dot{\boldsymbol{u}}_j]\!] &= \sum_p\sum_q [\![\dot{Q}_{ip}\dot{Q}_{jq}]\!]\boldsymbol{c}_{ip}\boldsymbol{c}_{jq} \\ &= \sum_{pqkrls} G_{ip,kr}G_{jq,ls}[\![P_{kr}P_{ls}]\!]\boldsymbol{c}_{ip}\boldsymbol{c}_{jq}\end{aligned} \tag{19.2-2}$$

[3] This lack of tension for $\varepsilon = 0$ seems to correspond to the assumption of Doi and Edwards, in their theory, that all springs in their "slip-link network" have a uniform tension (F_{eq}) regardless of the flow field.

If we assume equilibration in momentum space (cf. §18.3a), then we find by using Eq. 12.4-10 that

$$[\![\dot{\boldsymbol{u}}_i\dot{\boldsymbol{u}}_j]\!]_{\text{eq}} = kT\sum_p\sum_q G_{ip,jq}\boldsymbol{c}_{ip}\boldsymbol{c}_{jq} \tag{19.2-3}$$

and by using the expression for the metric matrix elements, Eq. 16.5-8, that

$$\begin{aligned}[\![\dot{\boldsymbol{u}}_i\dot{\boldsymbol{u}}_j]\!]_{\text{eq}} &= \frac{kT}{ma^2}\sum_{kl} A_{ik}A_{jl}(\boldsymbol{\delta} - \boldsymbol{u}_i\boldsymbol{u}_i)\cdot\mathbf{K}_{kl}\cdot(\boldsymbol{\delta} - \boldsymbol{u}_j\boldsymbol{u}_j)\\ &= \frac{kT}{ma^2}\sum_{kl} A_{ik}A_{jl}\mathbf{K}_{kl}\end{aligned} \tag{19.2-4}$$

If one uses this expression in Eq. 19.2-1, one obtains an expression for the effective Brownian forces in the approximation of equilibration in momentum space.

b. Reptation Approximation

On the other hand, as a different approximation, we may assume that

$$[\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}(\boldsymbol{r}_c))(\dot{\boldsymbol{r}}_\mu - \boldsymbol{v}(\boldsymbol{r}_c))]\!] = \frac{\alpha}{4}(\boldsymbol{u}_{\nu-1} + \boldsymbol{u}_\nu)(\boldsymbol{u}_{\mu-1} + \boldsymbol{u}_\mu) \tag{19.2-5}$$

where α is a scalar coefficient. The idea behind this approximation is the concept of *reptating*[1] motion, that is, that "on the average" the velocity of a bead relative to the macroscopic velocity, $\dot{\boldsymbol{r}}_\nu - \boldsymbol{v}$, is in the direction of the chain, a direction which is the average of that of the two links associated with the bead. The end beads, of course, must be considered somewhat differently. This idea was introduced earlier in §13.7 in the discussion of encapsulated dumbbells. It should be pointed out, however, that since Eq. 19.2-5 evaluated at equilibrium is inconsistent with Eq. 19.2-4, the reptation approximation cannot be exact at equilibrium. Nevertheless, it appears to be a good approximation away from equilibrium.

To obtain a reasonable estimate of the coefficient α, we note that at equilibrium

$$\begin{aligned}\sum_\nu [\![(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})\cdot(\dot{\boldsymbol{r}}_\nu - \boldsymbol{v})]\!] &= \frac{1}{m}\sum_{\nu ipjq}(\boldsymbol{b}_{\nu,ip}\cdot\boldsymbol{b}_{\nu,jq})[\![\dot{Q}_{ip}\dot{Q}_{jq}]\!]\\ &= \frac{1}{m}\sum_{ipjq} G_{ip,jq}[\![P_{ip}P_{jq}]\!]\\ &= \frac{2(N-1)kT}{m}\end{aligned} \tag{19.2-6}$$

[1] The notion of *reptation* ("snakelike motion") was first proposed by P. -G. de Gennes, *J. Chem. Phys.*, **55**, 572-579 (1971); see also P.-G. de Gennes, *Phys. Today*, **36**, 33-39 (1983). The first use of reptation in polymer kinetic theory and rheology was by M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. II*, **74**, 1789-1832 (1978); **75**, 38-154 (1979).

That is, the total kinetic energy in a coordinate system moving with the stream velocity, $\boldsymbol{v}$, is $(N-1)kT$, which is $\frac{1}{2}kT$ for each degree of freedom. Introducing the approximation Eq. 19.2-5 into this result and neglecting the complications at the ends we find

$$\alpha = \frac{4(N-1)kT/m}{N + \sum_v (\boldsymbol{u}_{v-1} \cdot \boldsymbol{u}_v)} \tag{19.2-7}$$

as the value of quantity α.

Making use of Eq. 16.5-1, we find that Eq. 19.2-5 implies that

$$[\![\dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j]\!]_{\text{rep}} = \frac{\alpha}{a^2} (\delta \boldsymbol{u}_i)(\delta \boldsymbol{u}_j) \tag{19.2-8}$$

where

$$\delta \boldsymbol{u}_i = \tfrac{1}{2}(\boldsymbol{u}_{i+1} - \boldsymbol{u}_{i-1}) \tag{19.2-9}$$

This expression is to be compared with that given by Eq. 19.2-4 which results from assuming equilibration in momentum space.

c. Superposition Approximation

The approximation for the momentum average, $[\![\dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j]\!]$, that we use in the present development is obtained by combining the two approximations just considered:

$$\begin{aligned} [\![\dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j]\!] &= (1-\varepsilon')[\![\dot{\boldsymbol{u}}_i \dot{\boldsymbol{u}}_j]\!]_{\text{rep}} + \varepsilon' [\![\boldsymbol{u}_i \boldsymbol{u}_j]\!]_{\text{eq}} \\ &= \frac{(1-\varepsilon')}{a^2} \alpha (\delta \boldsymbol{u}_i)(\delta \boldsymbol{u}_j) + \frac{\varepsilon' kT}{ma^2} \sum_{kl} A_{ik} A_{jl} \mathbf{K}_{kl} \end{aligned} \tag{19.2-10}$$

where ε' is the *reptation coefficient*. In the Doi–Edwards and Curtiss–Bird theories ε' is taken to be zero, but here we take ε' to be a function of $\dot{\gamma} = (\frac{1}{2}\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})^{1/2}$ such that $\varepsilon' = 1$ when $\dot{\gamma} = 0$ (that is, at equilibrium) and $0 \le \varepsilon' \le 1$ otherwise (that is, away from equilibrium). Except for these conditions the form of ε' is not specified.

When the superposition approximation is introduced into Eq. 19.2-1, we obtain

$$\begin{aligned} \mathscr{F}_{ip}^{(b)} = &- \frac{kT}{\Psi_\alpha} \boldsymbol{c}_{ip} \cdot \sum_{jkq} C_{ik} \frac{\partial}{\partial Q_{jq}} \\ &\times \left[\boldsymbol{d}_{jq} \cdot \left(\frac{m\alpha}{kT} (1-\varepsilon')(\delta \boldsymbol{u}_j)(\delta \boldsymbol{u}_k) + \varepsilon' \sum_{lm} A_{jl} A_{km} \mathbf{K}_{lm} \right) \right] \Psi_a \end{aligned} \tag{19.2-11}$$

as an approximation for the generalized Brownian force.

Next, we introduce the expressions for the generalized Brownian force and the coupling tensor $\mathbf{M}_{ip}$ (from Eq. 19.1-11) into the equation of continuity, Eq. 19.1-15. In doing this, however, we note that

$$\sum_{lq} A_{jl}\{\mathbf{K}_{kl}\cdot\boldsymbol{d}_{jq}\boldsymbol{c}_{jq}\} = \sum_{l} A_{jl}\{\mathbf{K}_{kl}\cdot(\boldsymbol{\delta}-\boldsymbol{u}_j\boldsymbol{u}_j)\}$$
$$= \sum_{l} A_{jl}\mathbf{K}_{kl} \tag{19.2-12}$$

Thus, we obtain

$$\frac{\partial}{\partial t}\Psi_\alpha = \frac{kT}{\bar{N}^{1+\beta}\zeta a^2}\sum_{ijklpq} A_{ik}\frac{\partial}{\partial Q_{ip}}$$
$$\times\left(\boldsymbol{d}_{ip}\cdot\mathbf{K}_{kl}\cdot\left[\frac{\partial}{\partial Q_{jq}}\boldsymbol{d}_{jq}\cdot\left(\frac{m\alpha}{kT}(1-\varepsilon')(\delta\boldsymbol{u}_j)(\delta\boldsymbol{u}_l)\Psi_\alpha+\varepsilon'\sum_{mn}A_{jm}A_{ln}\mathbf{K}_{mn}\Psi_\alpha\right)\right]\right)$$
$$-\frac{1}{\zeta}\sum_{iklp}A_{ik}\frac{\partial}{\partial Q_{ip}}(\boldsymbol{d}_{ip}\cdot\mathbf{K}_{kl}\cdot\boldsymbol{\zeta}_l\cdot\boldsymbol{\kappa}\cdot\boldsymbol{u}_l\Psi_\alpha)$$
$$-\frac{1}{\bar{N}^{1+\beta}\zeta a^2}\sum_{ijklpq}A_{ik}A_{jl}\frac{\partial}{\partial Q_{ip}}(\boldsymbol{d}_{ip}\cdot\mathbf{K}_{kl}\cdot\boldsymbol{d}_{jq}\mathscr{F}_{jq}^{(e)}\Psi_\alpha) \tag{19.2-13}$$

This is the diffusion equation in the configuration space of a single molecule of species α.

§19.3 THE SINGLE-LINK DISTRIBUTION FUNCTION

In the discussion of polymer melts we introduce the "mild-curvature" approximation which was not used in the theory for dilute solutions in Chapter 18. This approximation, which is discussed in more detail later, is the assumption that the configuration-space distribution function, $\Psi_\alpha(Q, t)$, has a significant value only for those configurations in which the chain approximates a curve with continuous derivatives (that is, with no "kinks"). This approximation, which is introduced at two points, reduces the problem to one which involves only the single-link distribution function $f_j^\alpha(\boldsymbol{u}, t)$. This function, which is a contraction of the full configuration-space distribution function, describes the probability that link j in the chain is oriented in the direction $\boldsymbol{u}$.

The single-link distribution function is defined as

$$f_j^\alpha(\boldsymbol{u}, t) = \frac{1}{n_\alpha}\int\delta(\boldsymbol{u}_j-\boldsymbol{u})\Psi_\alpha(Q, t)dQ \tag{19.3-1}$$

From this definition and the definition of Ψ_α, it follows that this function is normalized so that

$$\int f_j^\alpha(\boldsymbol{u}, t)d\boldsymbol{u} = 1 \tag{19.3-2}$$

An equation for the time evolution of the function $f_j^\alpha(\boldsymbol{u}, t)$ is obtained by multiplying the diffusion equation, Eq. 19.2-13, by the appropriate delta function and integrating over the

configuration space. Thus one finds that, in the absence of external forces

$$\frac{\partial}{\partial t} f_j^\alpha = \frac{kT}{n_\alpha \bar{N}^{1+\beta}\zeta a^2} \sum_{iklpq} A_{jk} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} \times \left(\boldsymbol{d}_{jp} \cdot \mathbf{K}_{kl} \cdot \left[\frac{\partial}{\partial Q_{iq}} \boldsymbol{d}_{iq} \cdot \left((1-\varepsilon') \frac{m\alpha}{kT} (\delta \boldsymbol{u}_i)(\delta \boldsymbol{u}_l) \Psi_\alpha + \varepsilon' \sum_{mn} A_{im} A_{ln} \mathbf{K}_{mn} \Psi_\alpha \right) \right] \right) dQ - \frac{1}{n_\alpha \zeta} \sum_{klp} A_{jk} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \mathbf{K}_{kl} \cdot \zeta_l \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_l \Psi_\alpha) dQ \tag{19.3-3}$$

With the mild curvature approximation the right side of this equation may be expressed in terms of the single-link distribution function and thus one obtains an equation describing the time evolution of this function. In the next section the use of the same approximation leads to an expression for the stress tensor which involves only averages with respect to the single-link distribution function.

The integrations on the right side of the last equation are over the entire configuration space of the polymer molecule and thus include all possible configurations of the chain. We will, however, assume that the distribution function, $\Psi_\alpha(Q, t)$, is such that only those configurations in which the chain approximates a curve with continuous derivatives contribute significantly to the integrals. That is, we will assume in these integrals that the orientations of adjacent links do not vary significantly. Thus, since the A_{ij} are zero unless $j = i$ or $j = i \pm 1$, we may use Eq. 16.5-9 and make the approximations that

$$\begin{aligned} \sum_k A_{jk} \mathbf{K}_{kl} &= \delta_{jl} \boldsymbol{\delta} - \sum_k A_{jk} \hat{C}_{kl} \boldsymbol{u}_k \boldsymbol{u}_l \\ &\doteq \delta_{jl} \boldsymbol{\delta} - \sum_k \hat{A}_{jk} \hat{C}_{kl} \boldsymbol{u}_j \boldsymbol{u}_l \\ &= \delta_{jl} (\boldsymbol{\delta} - \boldsymbol{u}_j \boldsymbol{u}_l) \end{aligned} \tag{19.3-4}$$

and from Eq. 19.2-7, that for large N

$$\alpha = \frac{2kT}{m} \tag{19.3-5}$$

With these approximations, the equation for the single-link distribution function, Eq. 19.3-3, becomes

$$\frac{\partial}{\partial t} f_j^\alpha = \frac{2(1-\varepsilon')kT}{n_\alpha \bar{N}^{1+\beta}\zeta a^2} \sum_{pq} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} \left\{ \boldsymbol{d}_{jp} \cdot \frac{\partial}{\partial Q_{jq}} [\boldsymbol{d}_{jq} \cdot (\delta \boldsymbol{u}_j)(\delta \boldsymbol{u}_j) \Psi_\alpha] \right\} dQ + \frac{\varepsilon' kT}{n_\alpha \bar{N}^{1+\beta}\zeta a^2} \sum_{ipq} A_{ji} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} \left[\boldsymbol{d}_{jp} \cdot \frac{\partial}{\partial Q_{iq}} \boldsymbol{d}_{iq} \Psi_\alpha \right] dQ - \frac{1}{n_\alpha} \sum_p \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j \Psi_\alpha) dQ \tag{19.3-6}$$

It is noted in passing that if one introduces the approximation Eq. 19.3-4 into the expression for the generalized Brownian force, Eq. 19.2-11, and sets $\varepsilon' = 1$, (that is, assumes

equilibration in momentum space) one finds that

$$\mathscr{F}_{ip}^{(b)} = -\frac{kT}{\Psi_\alpha}\boldsymbol{c}_{ip}\cdot\sum_q \frac{\partial}{\partial Q_{iq}}\boldsymbol{d}_{iq}\Psi_\alpha$$

$$= -kT\frac{\partial}{\partial Q_{ip}}\ln\left(\frac{\Psi_\alpha}{\sin\theta_i}\right) \tag{19.3-7}$$

This result is identical with that given by Eq. 18.3-5, if in the latter the determinant of the metric tensor, g, is approximated by the value obtained in the random-walk approximation (see §12.3(a)).

With some manipulation the terms on the right of Eq. 19.3-6 may be expressed in terms of the single-link distribution function, and thus one obtains a diffusion equation for this function. We consider, first, the second term on the right. The terms in the sum with $i \neq j$ become zero when the integration over the coordinate Q_{iq} is carried out. Thus, this term becomes

$$\frac{2\varepsilon' kT}{\bar{N}^{1+\beta}\zeta a^2}\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}}f_j^\alpha \tag{19.3-8}$$

The transformation of the first term on the right of Eq. 19.3-6 is somewhat more lengthy. From the definition of the single-link distribution function, Eq. 19.3-1, one finds that for integer k,

$$f_{j+k}^\alpha(\boldsymbol{u}, t) = \frac{1}{n_\alpha}\int \delta(\boldsymbol{u}_j + \boldsymbol{u}_{kj} - \boldsymbol{u})\Psi_\alpha(Q, t)dQ \tag{19.3-9}$$

where

$$\boldsymbol{u}_{kj} = \boldsymbol{u}_{j+k} - \boldsymbol{u}_j \tag{19.3-10}$$

For sufficiently long chains, one may take the index j, appearing as a subscript on $f_j(\boldsymbol{u}, t)$, to be an argument taking on an essentially continuous range of values. Then the left side of Eq. 19.3-9 may be written as a Taylor series,

$$f_j^\alpha(\boldsymbol{u}, t) + k\frac{\partial}{\partial j}f_j^\alpha(\boldsymbol{u}, t) + \tfrac{1}{2}k^2\frac{\partial^2}{\partial j^2}f_j^\alpha(\boldsymbol{u}, t) + \cdots \tag{19.3-11}$$

In a similar manner one replaces the delta function in the integral on the right of Eq. 19.3-9 by a Taylor series in $\boldsymbol{u}_{kj}$ to obtain as an expression for the right side of the equation

$$\frac{1}{n_\alpha}\int \Psi_\alpha(Q, t)\left\{1 + \sum_p(\Delta Q_{jp})\frac{\partial}{\partial Q_{jp}} + \frac{1}{2}\sum_p\sum_q(\Delta Q_{jp})(\Delta Q_{jq})\frac{\partial}{\partial Q_{jq}}\frac{\partial}{\partial Q_{jq}} + \cdots\right\}\delta(\boldsymbol{u}_j - \boldsymbol{u})dQ$$

$$= \frac{1}{n_\alpha}\int \delta(\boldsymbol{u}_j - \boldsymbol{u})\left\{\Psi_\alpha - \sum_p\frac{\partial}{\partial Q_{jp}}[(\Delta Q_{jp})\Psi_\alpha] + \frac{1}{2}\sum_p\sum_q\frac{\partial}{\partial Q_{jp}}\frac{\partial}{\partial Q_{jq}}\right.$$

$$\left.\times[(\Delta Q_{jq})(\Delta Q_{jp})\Psi_\alpha] + \cdots\right\}dQ \tag{19.3-12}$$

where ΔQ_{jp} is the change in the coordinate of $\boldsymbol{u}_j$ associated with the increment $\boldsymbol{u}_{kj}$; that is,

$$\boldsymbol{u}_{kj} = \sum_p \Delta Q_{jp} \cdot \frac{\partial}{\partial Q_{jp}} \boldsymbol{u}_j + \frac{1}{2} \sum_p \sum_q (\Delta Q_{jp})(\Delta Q_{jq}) \frac{\partial}{\partial Q_{jq}} \frac{\partial}{\partial Q_{jp}} \boldsymbol{u}_j + \cdots \tag{19.3-13}$$

The next step is to invert this series and obtain an expression for ΔQ_{jr} as a series in the incremental vector, $\boldsymbol{u}_{kj}$. We first note that the three components of $\boldsymbol{u}_{kj}$ are given as series in ΔQ_{jr} of the form ($r = 1, 2$),

$$(\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) = \Delta Q_{jr} + \frac{1}{2} \sum_p \sum_q (\Delta Q_{jp})(\Delta Q_{jq}) \left(\boldsymbol{d}_{jr} \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{c}_{jp} \right) + \cdots \tag{19.3-14}$$

$$(\boldsymbol{u}_j \cdot \boldsymbol{u}_{kj}) = \frac{1}{2} \sum_p \sum_q (\Delta Q_{jp})(\Delta Q_{jq}) \left(\boldsymbol{u}_j \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{c}_{jp} \right) + \cdots \tag{19.3-15}$$

From the first of these relations one finds that

$$\begin{aligned} \Delta Q_{jr} &= (\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) - \frac{1}{2} \sum_p \sum_q (\boldsymbol{u}_{kj}\boldsymbol{u}_{kj} : \boldsymbol{d}_{jp}\boldsymbol{d}_{jq}) \left(\boldsymbol{d}_{jr} \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{c}_{jp} \right) + \cdots \\ &= (\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) + \frac{1}{2} \sum_p \sum_q (\boldsymbol{u}_{kj}\boldsymbol{u}_{kj} : \boldsymbol{d}_{jq}\boldsymbol{d}_{jp}) \left(\boldsymbol{c}_{jp} \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{d}_{jr} \right) + \cdots \\ &= (\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) + \frac{1}{2} \sum_q \left(\boldsymbol{u}_{kj}\boldsymbol{u}_{kj} : \boldsymbol{d}_{jq}(\boldsymbol{\delta} - \boldsymbol{u}_j\boldsymbol{u}_j) \cdot \frac{\partial}{\partial Q_{jq}} \boldsymbol{d}_{jr} \right) + \cdots \end{aligned} \tag{19.3-16}$$

It follows, however, from Eq. 19.3-15 that the second part of the second term in the last form of this series (the term involving $\boldsymbol{u}_j\boldsymbol{u}_j$) is of higher order in the incremental vector $\boldsymbol{u}_{kj}$, and thus one finds that to second order in $\boldsymbol{u}_{kj}$,

$$\Delta Q_{jr} = (\boldsymbol{d}_{jr} \cdot \boldsymbol{u}_{kj}) + \frac{1}{2} \sum_q \left(\boldsymbol{u}_{kj}\boldsymbol{u}_{kj} : \boldsymbol{d}_{jq} \frac{\partial}{\partial Q_{jq}} \boldsymbol{d}_{jr} \right) + \cdots \tag{19.3-17}$$

When this relation is used in the expression given by Eq. 19.3-13 one finds that the right side of Eq. 19.3-9 is

$$\frac{1}{n_\alpha} \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \left[\Psi_\alpha - \sum_p \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \boldsymbol{u}_{kj} \Psi_\alpha) + \frac{1}{2} \sum_p \sum_q \frac{\partial}{\partial Q_{jp}} \left(\boldsymbol{d}_{jp} \cdot \frac{\partial}{\partial Q_{jq}} (\boldsymbol{d}_{jq} \cdot \boldsymbol{u}_{kj}\boldsymbol{u}_{kj} \Psi_\alpha) \right) \right] dQ \tag{19.3-18}$$

The third term in this expression is similar in form to the first term on the right of Eq. 19.3-6.

If we again assume that the distribution function $\Psi_\alpha(Q, t)$ is such that only those configurations in which the chain approximates a continuous curve contribute significantly to the integral of the last expression, we may for small values of k replace $\boldsymbol{u}_{kj}$, defined by Eq. 19.3-10, by

$$\boldsymbol{u}_{kj} = k\delta\boldsymbol{u}_j \tag{19.3-19}$$

where $\delta \boldsymbol{u}_j$ is defined by Eq. 19.2-9. One may then equate termwise the two sides of Eq. 19.3-9 as given by Eqs. 19.3-11 and 19.3-18 to find that

$$\frac{1}{n_\alpha}\int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \sum_p \sum_q \frac{\partial}{\partial Q_{jp}} \left[\boldsymbol{d}_{jp} \cdot \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \delta \boldsymbol{u}_j \delta \boldsymbol{u}_j \Psi_\alpha) \right] dQ = \frac{\partial^2}{\partial j^2} f_j^\alpha(\boldsymbol{u}, t) \quad (19.3\text{-}20)$$

We have thus expressed the first term on the right of Eq. 19.3-6 in terms of the single-link distribution function.

In the transformation of the third term on the right of Eq. 19.3-6 we use the fact that $\delta(\boldsymbol{u}_j - \boldsymbol{u}) = \delta(\theta_j - \theta)\, \delta(\phi_j - \phi) \sin\theta$.

$$\begin{aligned}
\frac{1}{n_\alpha}\sum_p \int \delta(\boldsymbol{u}_j - \boldsymbol{u}) \frac{\partial}{\partial Q_{jp}} (\boldsymbol{d}_{jp} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j \Psi_\alpha) dQ &= -\frac{1}{n_\alpha}\sum_p \int (\boldsymbol{d}_{jp} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j)\Psi_\alpha \frac{\partial}{\partial Q_{jp}} \delta(\boldsymbol{u}_j - \boldsymbol{u}) dQ \\
&= \frac{1}{n_\alpha}\sum_p \frac{\partial}{\partial Q_p} \int (\boldsymbol{d}_{jp} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j)\Psi_\alpha \delta(\boldsymbol{u}_j - \boldsymbol{u}) dQ \\
&\quad + \frac{1}{n_\alpha} \cot\theta \int (\boldsymbol{d}_{j1} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}_j)\Psi_\alpha \delta(\boldsymbol{u}_j - \boldsymbol{u}) dQ \\
&= \sum_p \left(\boldsymbol{d}_p \cdot \frac{\partial}{\partial Q_p} \boldsymbol{\kappa} \cdot \boldsymbol{u} f_j^\alpha \right) - 2(\boldsymbol{u} \cdot \boldsymbol{\kappa} \cdot \boldsymbol{u}) f_j^\alpha \\
&= \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] f_j^\alpha \right) \quad (19.3\text{-}21)
\end{aligned}$$

One may now combine the results of the previous paragraphs to write Eq. 19.3-6 in the form

$$\frac{\partial}{\partial t} f_j^\alpha = \frac{2(1-\varepsilon')kT}{\bar{N}^{1+\beta}\zeta a^2} \frac{\partial^2}{\partial j^2} f_j^\alpha + \frac{2\varepsilon' kT}{\bar{N}^{1+\beta}\zeta a^2} \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} f_j^\alpha \right) - \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] f_j^\alpha \right) \quad (19.3\text{-}22)$$

It is convenient to rewrite this equation in a somewhat modified form after introducing several definitions. First, we let

$$\sigma = \frac{j}{N_\alpha} \quad (19.3\text{-}23)$$

be the fractional distance along a chain and define

$$f_\alpha(\boldsymbol{u}, \sigma, t) = f_j^\alpha(\boldsymbol{u}, t) \quad (19.3\text{-}24)$$

Then, we let

$$\boxed{\lambda_\alpha = \frac{N_\alpha^2 \bar{N}^{1+\beta}\zeta a^2}{2kT}} \quad (19.3\text{-}25)$$

be a *characteristic time*[1] associated with chains of length N_α. In terms of these quantities the single-link diffusion equation of species α is

$$\boxed{\frac{\partial f_\alpha}{\partial t} = \frac{(1-\varepsilon')}{\lambda_\alpha}\frac{\partial^2}{\partial\sigma^2}f_\alpha + \frac{\varepsilon' N_\alpha^2}{\lambda_\alpha}\left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}}f_\alpha\right) - \left(\frac{\partial}{\partial \boldsymbol{u}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu}]f_\alpha\right)} \tag{19.3-26}$$

If $\varepsilon' = 1$ this equation is identical to the diffusion equation for the distribution function of rigid dumbbells, Eq. 14.2-8, except that the rigid dumbbell time constant λ is replaced by $\lambda_\alpha/6N_\alpha^2$, and if $\varepsilon' = 0$ the equation reduces to the corresponding equation developed by Doi and Edwards[1]. In either case the third term on the right describes the perturbation of the single-link distribution function caused by a velocity gradient. The first two terms on the right describe "diffusion" effects associated with the Brownian motion. If one assumes equilibration in momentum space, $\varepsilon' = 1$, and the diffusion term involves the two dimensional gradient operator, $\partial/\partial\boldsymbol{u}$, that is, changes in orientation of the link. If one takes $\varepsilon' = 0$ the Brownian motion described by the first term is reptating motion. It is interesting to note that the parameter ε, which describes the anisotropy of the friction tensor, does not appear in this equation.

§19.4 THE STRESS TENSOR AND THE MASS FLUX

Most of this section deals with the development of an expression for the stress tensor using the general formula given in §18.1. However, at the end of the section we develop an expression for the mass-flux vector and the translational diffusivity starting with the general formula given in §17.6.

a. The Stress Tensor

To obtain an expression for the stress tensor for a polymeric melt consisting of a mixture of molecules of various lengths we return to the general expression given by Eq. 18.1-10 in terms of the hydrodynamic forces, $\boldsymbol{F}_v^{(h)\alpha}$, and make use of the expression for these forces given by Eq. 19.1-4. Combining these relations and using Eqs. 16.5-2 and 3, we find that

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k + a^2\bar{N}^{1+\beta}\sum_{\alpha jk} C_{jk}\int \boldsymbol{u}_k\zeta_j\cdot(\llbracket\dot{\boldsymbol{u}}_j\rrbracket - [\boldsymbol{\kappa}\cdot\boldsymbol{u}_j])\Psi_\alpha\, dQ \tag{19.4-1}$$

[1] For a *monodisperse* fluid Eq. 19.3-25 becomes $\lambda = N^{3+\beta}\zeta a^2/2kT$. (In their analogous equation M. Doi and S. F. Edwards [*J. Chem. Soc., Faraday Trans. II*, **74**, 1818-1832 (1978)] have $\lambda = \pi^2 T_d$, where $T_d = N^3\zeta a^2/\pi^2 kT$ is the "disengagement time"; that is, there is a difference of a factor of $N^\beta/2$ between the two time constants.) The proportionality $\lambda \propto N^3$ has been obtained by some simple arguments using the "tube model" [see P. G. de Gennes and L. Léger, *Ann. Rev. Phys. Chem.*, **33**, 49-61 (1982) and P. G. De Gennes, *Physics Today*, **36**, 33-39 (1983)]. For *polydisperse* fluids Eq. 19.3-25 contains $\bar{N} = \sum_\alpha x_\alpha N_\alpha$, which is a mole fraction averge of the N_α. Whereas we have $\lambda_\alpha \propto N_\alpha^2\bar{N}^{1+\beta}$, Doi and Edwards recommend $\lambda_\alpha \propto N_\alpha^3$ for species α in a mixture. Example 19.6-1 explores the consequences of this difference in the expression for time constants.

where π_k is the contribution of the Brownian motion of the centers of mass of the polymer molecules defined by Eq. 17.6-6. Use of the explicit expression for the friction tensor, Eq. 19.1-2, in this relation then gives

$$\pi = \pi_k + 2kT\sum_{\alpha jk} \frac{\lambda_\alpha C_{jk}}{N_\alpha^2} \int \{\boldsymbol{u}_k[\![\dot{\boldsymbol{u}}_j]\!] - \boldsymbol{u}_k\boldsymbol{u}_j \cdot \boldsymbol{\kappa}^\dagger + (1-\varepsilon)\boldsymbol{u}_k\boldsymbol{u}_j\boldsymbol{u}_j : \boldsymbol{\kappa}\}\Psi_\alpha \, dQ \quad (19.4\text{-}2)$$

where λ_α is the time constant associated with molecules of species α as defined by Eq. 19.3-25. To eliminate the momentum average $[\![\dot{\boldsymbol{u}}_j]\!]$ from this expression we make use of the general equation of continuity as given by Eq. 17.5-14; multiplication of the latter by $\boldsymbol{u}_j\boldsymbol{u}_k$ and integration over all configurations gives

$$\begin{aligned}
\frac{\partial}{\partial t}\int \boldsymbol{u}_j\boldsymbol{u}_k\Psi_\alpha \, dQ &= -\sum_i \sum_q \int \boldsymbol{u}_j\boldsymbol{u}_k \frac{\partial}{\partial Q_{iq}}([\![\dot{Q}_{iq}]\!]\Psi_\alpha)dQ \\
&= \sum_q \int \Psi_\alpha([\![\dot{Q}_{jq}]\!]\boldsymbol{c}_{jq}\boldsymbol{u}_k + [\![\dot{Q}_{kq}]\!]\boldsymbol{u}_j\boldsymbol{c}_{kq})dQ \\
&= \int \Psi_\alpha([\![\dot{\boldsymbol{u}}_j]\!]\boldsymbol{u}_k + \boldsymbol{u}_j[\![\dot{\boldsymbol{u}}_k]\!])dQ \qquad (19.4\text{-}3)
\end{aligned}$$

From this relation and the expression for the stress tensor given by Eq. 19.4-2, one finds that the symmetric part of the stress tensor is

$$\begin{aligned}
\boldsymbol{\pi}^{(s)} &= \tfrac{1}{2}(\boldsymbol{\pi} + \boldsymbol{\pi}^\dagger) \\
&= \boldsymbol{\pi}_k + kT\sum_{\alpha jk} \frac{\lambda_\alpha}{N_\alpha^2} C_{jk}\Big\{\frac{\partial}{\partial t}\int \boldsymbol{u}_j\boldsymbol{u}_k\Psi_\alpha \, dQ \\
&\quad - \int \boldsymbol{u}_k\boldsymbol{u}_j\Psi_\alpha \, dQ \cdot \boldsymbol{\kappa}^\dagger - \boldsymbol{\kappa} \cdot \int \boldsymbol{u}_j\boldsymbol{u}_k\Psi_\alpha \, dQ \\
&\quad + (1-\varepsilon)\int (\boldsymbol{u}_k\boldsymbol{u}_j + \boldsymbol{u}_j\boldsymbol{u}_k)\boldsymbol{u}_j\boldsymbol{u}_j\Psi_\alpha \, dQ : \boldsymbol{\kappa}\Big\} \qquad (19.4\text{-}4)
\end{aligned}$$

The contribution to the stress tensor of the Brownian motion of the centers of mass of the molecules as given by Eq. 17.6-6 is

$$\boldsymbol{\pi}_k = m\sum_\alpha N_\alpha \int [\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!]^\alpha \Psi_\alpha(Q, t)dQ \qquad (19.4\text{-}5)$$

If one assumes equilibration in momentum space this expression leads to an isotropic term

$$\boldsymbol{\pi}_k = kT\boldsymbol{\delta}\sum_\alpha n_\alpha \qquad (19.4\text{-}6)$$

On the other hand if one uses the reptation approximation one finds from Eq. 19.2-5 that

$$[\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!] = \frac{\alpha}{4N_\alpha^2} \sum_j \sum_k (\boldsymbol{u}_{j-1} + \boldsymbol{u}_j)(\boldsymbol{u}_{k-1} + \boldsymbol{u}_k) \tag{19.4-7}$$

Then introducing the mild curvature approximation, we use Eq. 19.3-5 for α and replace $\boldsymbol{u}_{j-1}$ by $\boldsymbol{u}_j$ to find that

$$[\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!] = \frac{2kT}{N_\alpha^2 m} \sum_j \sum_k \boldsymbol{u}_j \boldsymbol{u}_k \tag{19.4-8}$$

One then finds from Eq. 19.4-5 that in this reptation approximation

$$\boldsymbol{\pi}_k = 2kT \sum_{\alpha jk} \frac{1}{N_\alpha} \int \boldsymbol{u}_j \boldsymbol{u}_k \Psi_\alpha(Q, t) dQ \tag{19.4-9}$$

Next, in analogy with the treatment of the Brownian force in §19.2, we take $\boldsymbol{\pi}_k$ to be a linear combination of this expression and the equilibrium expression given by Eq. 19.4-6,

$$\boldsymbol{\pi}_k = kT \sum_\alpha \left[\varepsilon' n_\alpha \boldsymbol{\delta} + \frac{2(1-\varepsilon')}{N_\alpha} \sum_{jk} \int \boldsymbol{u}_j \boldsymbol{u}_k \Psi_\alpha(Q, t) dQ \right] \tag{19.4-10}$$

determined by the same empirical function, ε', of the invariant $\dot{\gamma}$.

The Kramers matrix C_{jk} is a symmetric matrix with elements given by

$$\begin{aligned} C_{j,j+k} &= \frac{j(N-j)}{N} - \frac{jk}{N} \qquad (0 \le k \le N-j-1) \\ C_{j,j-k} &= \frac{j(N-j)}{N} - \frac{(N-j)k}{N} \qquad (0 \le k \le j-1) \end{aligned} \tag{19.4-11}$$

(See Eqs. 11.6-7 and the following for more information on the Kramers matrix.) Thus, along any row or column a maximum occurs on the diagonal. To obtain an expression for the stress tensor in terms of the single-link distribution function we again make the mild-curvature approximation. We assume the distribution function Ψ_α is such that in the integrals of those terms in the expression for the symmetric part of the stress tensor, Eq. 19.4-4, which are multiplied by C_{jk} we may approximate $\boldsymbol{u}_k$ by $\boldsymbol{u}_j$. Furthermore, it may be shown[1] that the antisymmetric part of the stress tensor is negligible. Then since $\sum_k C_{jk} = \frac{1}{2}j(N-j)$ we find that

$$\begin{aligned} \boldsymbol{\pi} = \boldsymbol{\pi}_k + \frac{1}{2} kT \sum_{\alpha j} n_\alpha \lambda_\alpha \frac{j(N_\alpha - j)}{N_\alpha^2} \Big\{ & \frac{\partial}{\partial t} \langle \boldsymbol{uu} \rangle_j \\ & - \langle \boldsymbol{uu} \rangle_j \cdot \boldsymbol{\kappa}^\dagger - \boldsymbol{\kappa} \cdot \langle \boldsymbol{uu} \rangle_j + 2(1-\varepsilon) \langle \boldsymbol{uuuu} \rangle_j : \boldsymbol{\kappa} \Big\} \end{aligned} \tag{19.4-12}$$

[1] C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, 2016-2033 (1981); see page 2021.

where the angular brackets indicate an average with respect to the single-link distribution function, that is,

$$\langle \boldsymbol{uu} \rangle_j = \int \boldsymbol{uu} f_j(\boldsymbol{u}, t) d\boldsymbol{u} \tag{19.4-13}$$

$$\langle \boldsymbol{uuuu} \rangle_j = \int \boldsymbol{uuuu} f_j(\boldsymbol{u}, t) d\boldsymbol{u} \tag{19.4-14}$$

It is now convenient to introduce again the scaled distance along the chain $\sigma = j/N_\alpha$. One may then rewrite the stress tensor expression as

$$\boldsymbol{\pi} = \boldsymbol{\pi}_k + \frac{1}{2} kT \sum_\alpha n_\alpha N_\alpha \lambda_\alpha \int_0^1 \sigma(1-\sigma)\{\langle \boldsymbol{uu} \rangle_{(1)} + 2(1-\varepsilon)\langle \boldsymbol{uuuu} \rangle : \boldsymbol{\kappa}\} d\sigma \tag{19.4-15}$$

where the subscript on $\langle \boldsymbol{uu} \rangle_{(1)}$ indicates the convected derivative of $\langle \boldsymbol{uu} \rangle$, defined in Eq. D.2-4.

It may be shown from the diffusion equation for the single-link distribution function, Eq. 19.3-26, that the convected derivative is

$$\langle \boldsymbol{uu} \rangle_{(1)} = \frac{(1-\varepsilon')}{\lambda} \frac{\partial^2}{\partial \sigma^2} \langle \boldsymbol{uu} \rangle + \frac{2\varepsilon' N_\alpha^2}{\lambda} \boldsymbol{\delta} - \frac{6\varepsilon' N_\alpha^2}{\lambda} \langle \boldsymbol{uu} \rangle - 2\langle \boldsymbol{uuuu} \rangle : \boldsymbol{\kappa} \tag{19.4-16}$$

With this result the last expression for the stress tensor, Eq. 19.4-15, may be written in an alternative form. In developing this expression we integrate the term involving $(\partial^2/\partial\sigma^2)\langle \boldsymbol{uu} \rangle$ twice by parts assuming that the ends of the chains are oriented at random, that is,

$$f_\alpha(\boldsymbol{u}, 0, t) = f_\alpha(\boldsymbol{u}, 1, t) = \frac{1}{4\pi} \tag{19.4-17}$$

Thus one finds that

$$\boxed{\begin{aligned} \boldsymbol{\pi} = \boldsymbol{\pi}_k + kT \sum_\alpha n_\alpha N_\alpha \Bigg\{ & (1-\varepsilon') \left[\frac{1}{3} \boldsymbol{\delta} - \int \langle \boldsymbol{uu} \rangle \, d\sigma \right] \\ & + \varepsilon' N_\alpha^2 \left[\frac{1}{6} \boldsymbol{\delta} - 3 \int \sigma(1-\sigma) \langle \boldsymbol{uu} \rangle d\sigma \right] \\ & - \varepsilon \lambda_\alpha \boldsymbol{\kappa} : \int \sigma(1-\sigma) \langle \boldsymbol{uuuu} \rangle d\sigma \Bigg\} \end{aligned}} \tag{19.4-18}$$

where λ_α is the time constant of molecules of species α defined by Eq. 19.3-25.

Let us now return to the expression for $\boldsymbol{\pi}_k$, the contribution to the stress tensor of the Brownian motion of the centers of mass of the molecules as given by Eq. 19.4-10. First, we note that isotropic contributions to the stress tensor are of no rheological interest. Next we note that the diagonal terms in the double sum on j and k lead to a contribution to the stress tensor which is of the same form as the integral term at the end of the first line of Eq. 19.4-18 but smaller by a factor of $N_\alpha/2$. It appears reasonable to assume that the correlation

between the orientations of successive links falls off sufficiently rapidly with the difference $(j - k)$ that the off-diagonal terms do not contribute enough to overcome this factor. Thus in the subsequent development we neglect[2] π_k; when we do this $\tau = \pi - \pi_k$.

b. The Mass Flux Vector

The mass flux of species α is given by Eq. 17.6-12. If one uses the expression for the total hydrodynamic force on a molecule of this species, Eq. 19.1-7, in this expression one finds

$$\boldsymbol{j}_\alpha = -\frac{m^\alpha}{\zeta^\alpha}\int \boldsymbol{F}^{(h)\alpha}\Psi_\alpha\, dQ - \nabla\cdot\sum_\nu m_\nu \int \boldsymbol{R}_\nu[\![\dot{\boldsymbol{R}}_\nu]\!]\Psi_\alpha\, dQ \tag{19.4-19}$$

as the expression for the mass flux. Since the momentum average $[\![\dot{\boldsymbol{R}}_\nu]\!]$ is zero at equilibrium, the term in Eq. 19.4-19 containing this factor is second and higher order in the gradients of the macroscopic variables n_α and v; therefore this is a "nonlinear" term. In the present discussion we neglect this term, as well as higher order terms which were already neglected in developing Eq. 17.6-12 from Eq. 17.4-35.

The mass fluxes are defined so that the sum over all α is zero (see Eq. 17.2-15). Thus, if we neglect the last term in Eq. 19.4-19, this equation may be rewritten in the form

$$\boldsymbol{j}_\alpha = -\frac{\rho_\alpha}{\zeta^\alpha}\left[\langle \boldsymbol{F}^{(h)\alpha}\rangle^\alpha - \sum_\beta \frac{\zeta^\alpha\rho_\beta}{\zeta^\beta\rho}\langle \boldsymbol{F}^{(h)\beta}\rangle^\beta\right] \tag{19.4-20}$$

where the angular brackets, $\langle\cdots\rangle^\alpha$, indicate an average over the configuration space with respect to the distribution function Ψ_α. From the force balance, Eq. 17.5-18, one finds that the total hydrodynamic force is simply related to the sum of the total external and Brownian forces. Thus,

$$\bar{N}\langle \boldsymbol{F}^{(h)\alpha}\rangle = -\langle \boldsymbol{F}^{(b)\alpha}\rangle - \langle \boldsymbol{F}^{(e)\alpha}\rangle \tag{19.4-21}$$

The contribution to the mass flux arising from the external forces $\boldsymbol{F}^{(e)\alpha}$ is associated with the concept of mobility, and that arising from the Brownian forces $\boldsymbol{F}^{(b)\alpha}$ will be shown to be associated with the effects of concentration gradients.

An expression for the total Brownian force on the center of mass of a molecule is given by Eq. 17.5-17. The first term in this expression involves the momentum average, $[\![(\dot{\boldsymbol{r}}_c - \boldsymbol{v})(\dot{\boldsymbol{r}}_c - \boldsymbol{v})]\!]$, appearing on the left of Eq. 19.4-7, and which arose in the term π_k in the stress tensor (Eq. 19.4-5) describing the effect of this Brownian motion. As discussed in connection with π_k, the evaluation of this term using the reptation concept of Brownian motion requires a knowledge of the correlation among the directions of the links in the Kramers chain. Thus in the evaluation of this term we will assume equilibration in momentum space and use the expression for the Brownian force, $\boldsymbol{F}^{(b)\alpha}$, given by Eq. 18.3-6. With this expression, we find from Eq. 19.4-21 that

$$\bar{N}\langle \boldsymbol{F}^{(h)\alpha}\rangle = \frac{kT}{\rho_\alpha}\nabla\rho_\alpha - \langle \boldsymbol{F}^{(e)\alpha}\rangle^\alpha \tag{19.4-22}$$

[2] The center-of-mass motion was considered for the elastic dumbbell model by R. B. Bird and J. R. DeAguiar, *J. Non-Newtonian Fluid Mech.*, **13**, 149–160 (1983), Eqs. 3.8 and 3.9.

and thus

$$j_\alpha = -\frac{kT}{\bar{N}\zeta^\alpha}\left[\nabla\rho_\alpha - \frac{\rho_\alpha}{kT}\langle \boldsymbol{F}^{(e)\alpha}\rangle^\alpha - \sum_\beta \frac{\zeta^\alpha \rho_\alpha}{\zeta^\beta \rho}\left(\nabla\rho_\beta - \frac{\rho_\beta}{kT}\langle \boldsymbol{F}^{(e)\beta}\rangle^\beta\right)\right] \tag{19.4-23}$$

This expression may be rewritten as

$$j_\alpha = -\sum_\beta D_{\mathrm{tr}}^{\alpha\beta}\left[\nabla\rho_\beta - \frac{\rho_\beta}{kT}\langle \boldsymbol{F}^{(e)\beta}\rangle^\beta\right] \tag{19.4-24}$$

where the quantities

$$D_{\mathrm{tr}}^{\alpha\beta} = \frac{kT}{\bar{N}\zeta^\beta}\left(\delta_{\alpha\beta} - \frac{\rho_\alpha}{\rho}\right) \tag{19.4-25}$$

form a matrix of translational diffusion coefficients.

We now turn our attention to the mass flux of a species α which is present only in a trace amount, so that $\rho_\alpha/\rho \ll 1$. Then it follows from Eq. 19.4-25 that $D_{\mathrm{tr}}^{\alpha\beta}$ is diagonal ($D_{\mathrm{tr}}^{\alpha\beta} = D_{\mathrm{tr}}^{\alpha}\delta_{\alpha\beta}$) and

$$D_{\mathrm{tr}}^{\alpha} = \frac{kT}{\bar{N}\zeta^\alpha} \tag{19.4-26}$$

For this situation the mass flux becomes

$$\boxed{j_\alpha = -D_{\mathrm{tr}}^{\alpha}\left(\nabla\rho_\alpha - \frac{\rho_\alpha}{kT}\langle \boldsymbol{F}^{(e)\alpha}\rangle^\alpha\right)} \tag{19.4-27}$$

This equation has the same form as Eq. 18.4-32, although the averaging of $\boldsymbol{F}^{(e)\alpha}$ is different. If we now let $\zeta^\alpha = (N_\alpha^2/\bar{N})\zeta$, where ζ is the single-bead friction coefficient, then one finds from Eq. 19.4-26 that

$$\boxed{D_{\mathrm{tr}}^{\alpha} = \frac{kT}{N_\alpha^2\zeta}} \tag{19.4-28}$$

The above empiricism for ζ^α leads to an M_α^{-2} dependence for the self-diffusion of species α and also for a trace of polymer α diffusing in polymer β; this appears to describe the limited experimental data available[3]. A similar result has been obtained by "scaling arguments."[4]

[3] M. Tirrell, *Rubber Chem. and Tech.*, **57**, 523-556 (1984).

[4] P.-G. de Gennes and L. Léger, *Ann. Rev. Phys. Chem.*, **33**, 49 61 (1982); P.-G. de Gennes, *Phys. Today*, **36**, 33 39 (1983).

§19.5 SOLUTION OF THE DIFFUSION EQUATION FOR THE SINGLE-LINK DISTRIBUTION FUNCTION

In this section we discuss the solution of the diffusion equation for the single link distribution function, Eq. 19.3-26, which is consistent with the assumption that the end links are oriented randomly as described by Eqs. 19.4-17. For this purpose we first define a function $F(\boldsymbol{u}, t, t')$ as the solution of the equation

$$\frac{\partial}{\partial t}F = \frac{\varepsilon' N^2}{\lambda}\left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}}F\right) - \left(\frac{\partial}{\partial \boldsymbol{u}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{u} - \boldsymbol{\kappa}:\boldsymbol{uuu}]F\right) \tag{19.5-1}$$

subject to the "initial" condition that at $t = t'$

$$F(\boldsymbol{u}, t', t') = \frac{1}{4\pi} \tag{19.5-2}$$

It is to be noted that this equation is identical to that which determines the distribution function of rigid rods, Eq. 14.2-8, except that the time constant λ is replaced by $\lambda/6\varepsilon' N^2$. However, in this discussion the normalization condition, Eq. 14.1-3, is replaced by the initial condition, Eq. 19.5-2.

Next we will show that the required solution of the diffusion equation, Eq. 19.3-26, may be written as a time average of the function, $F(\boldsymbol{u}, t, t')$,

$$f(\boldsymbol{u}, \sigma, t) = \int_{-\infty}^{t} P(\varepsilon', \sigma, t - t')F(\boldsymbol{u}, t, t')dt' \tag{19.5-3}$$

involving the probability per unit time

$$P(\varepsilon', \sigma, s) = \frac{4(1-\varepsilon')}{\pi}\sum_{n,\text{odd}}\frac{1}{n\lambda_n^{(r)}}(\sin n\pi\sigma)e^{-(1-\varepsilon')s/\lambda_n^{(r)}} \tag{19.5-4}$$

and a series of time constants associated with the purely reptational motion

$$\lambda_n^{(r)} = \frac{\lambda}{\pi^2 n^2} \tag{19.5-5}$$

It may be shown from properties of Fourier series that

$$\int_0^{\infty} P(\varepsilon', \sigma, s)ds = \frac{4}{\pi}\sum_{n,\text{odd}}\frac{1}{n}(\sin n\pi\sigma) = 1 \tag{19.5-6}$$

We will next show that the expression on the right of Eq. 19.5-3 is (1) a solution of the diffusion equation, (2) properly normalized, and (3) consistent with the conditions that the ends of the chain are oriented randomly (as described by Eq. 19.4-17).

To show that the expression on the right of 19.5-3 is a solution of the diffusion equation we differentiate with respect to t to find that

$$\frac{\partial}{\partial t} f = \frac{(1-\varepsilon')}{\lambda} \sum_{n,\,\text{odd}} n(\sin n\pi\sigma)$$
$$- \frac{4(1-\varepsilon')^2}{\pi} \sum_{n,\,\text{odd}} \frac{1}{n\lambda_n^{(r)2}} (\sin n\pi\sigma) \int_{-\infty}^{t} e^{-(1-\varepsilon')(t-t')/\lambda_n^{(r)}} F(\boldsymbol{u}, t, t')\, dt'$$
$$+ \int_{-\infty}^{t} P(\varepsilon', \sigma, t-t') \left[\frac{\varepsilon' N^2}{\lambda} \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} F(\boldsymbol{u}, t, t') \right) \right.$$
$$\left. - \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}] F(\boldsymbol{u}, t, t') \right) \right] dt' \qquad (19.5\text{-}7)$$

The first term on the right arises from differentiating the upper limit of the integral and making use of the initial condition, Eq. 19.5-2; the second term arises from differentiating $P(\varepsilon', \sigma, t-t')$, and the third term from differentiating $F(\boldsymbol{u}, t, t')$ and using the defining equation, Eq. 19.5-1. The first term may be shown to be zero and the remaining terms lead to the terms on the right of the diffusion equation.

Next we show that the solution, Eq. 19.5-3, is properly normalized. For this purpose we first integrate Eq. 19.5-1 over $\boldsymbol{u}$ and make use of Eqs. E.7-1 and E.7-2 to find that

$$\frac{\partial}{\partial t} \int F(\boldsymbol{u}, t, t') d\boldsymbol{u} = 0 \qquad (19.5\text{-}8)$$

that is, the normalization of the function is independent of time, and thus from the initial condition, Eq. 19.5-2

$$\int F(\boldsymbol{u}, t, t') d\boldsymbol{u} = 1 \qquad (19.5\text{-}9)$$

Then on integrating the expression for $f(\boldsymbol{u}, \sigma, t)$, Eq. 19.5-3, and making use of the normalization of $P(\varepsilon', \sigma, s)$, Eq. 19.5-6, one finds that

$$\int f(\boldsymbol{u}, \sigma, t) d\boldsymbol{u} = 1 \qquad (19.5\text{-}10)$$

and thus the solution is normalized.

Finally, we consider the form of the solution, Eq. 19.5-3, near $\sigma = 0$ and $\sigma = 1$. Since at these points, $\sin n\pi\sigma = 0$, near these points only those terms with very large n contribute to the sum. In these terms if $\varepsilon' < 1$ the only contribution to the integrals arises from values of t' near t, where $F(\boldsymbol{u}, t, t') \doteq 1/4\pi$. Thus, for these values of σ,

$$f(\boldsymbol{u}, \sigma, t) \to \frac{1}{4\pi} \int_{-\infty}^{t} P(\varepsilon', \sigma, t-t') dt' = \frac{1}{4\pi} \qquad (19.5\text{-}11)$$

That is, if ε' is not exactly unity, the end links are oriented randomly;[1] it is clear from the form of the diffusion equation that for $\varepsilon' = 1$, the solution is independent of σ.

[1] The form of the distribution function near $\sigma = 0$ and 1 for steady flows to first order in $\dot{\gamma}$ is discussed in more detail near the end of this section (see Eqs. 19.5-21 and 24).

a. Exact Solution in the Pure Reptation Limit ($\varepsilon' = 0$)

Next we consider the solution of the equation for $F(\boldsymbol{u}, t, t')$ Eq. 19.5-1, in the pure reptation limit in which $\varepsilon' = 0$. For this purpose, we first consider the properties of the finite strain tensor, $\boldsymbol{\gamma}^{[0]}(t, t')$, which are discussed briefly in Appendix D. From Eq. D.3-3 it may be shown that

$$\frac{\partial}{\partial t}\boldsymbol{\gamma}^{[0]}(t, t') = -(\boldsymbol{\kappa} + \boldsymbol{\kappa}^\dagger) - \{\boldsymbol{\gamma}^{[0]} \cdot \boldsymbol{\kappa} + \boldsymbol{\kappa}^\dagger \cdot \boldsymbol{\gamma}^{[0]}\} \tag{19.5-12}$$

in which $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa}^\dagger$ may be functions of t. From this it follows that

$$\frac{\partial}{\partial t}[1 + (\boldsymbol{\gamma}^{[0]} : \boldsymbol{uu})]^{-3/2} = -\left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{u} - \boldsymbol{\kappa} : \boldsymbol{uuu}](1 + \boldsymbol{\gamma}^{[0]} : \boldsymbol{uu})^{-3/2}\right) \tag{19.5-13}$$

On comparing this equation with Eq. 19.5-1 one finds that in the limit that $\varepsilon' = 0$,

$$F(\boldsymbol{u}, t, t') = \frac{1}{4\pi(1 + \boldsymbol{\gamma}^{[0]} : \boldsymbol{uu})^{3/2}} \tag{19.5-14}$$[2]

When this expression is used in Eq. 19.5-3, with $\varepsilon' = 0$, one obtains the solution of the diffusion equation, in the "reptating" limit,

$$\boxed{f(\boldsymbol{u}, \sigma, t) = \frac{1}{4\pi}\int_{-\infty}^{t} \frac{P(\sigma, t - t')}{(1 + \boldsymbol{\gamma}^{[0]} : \boldsymbol{uu})^{3/2}}\, dt'} \tag{19.5-15}$$

where

$$\begin{aligned} P(\sigma, s) &= P(0, \sigma, s) \\ &= \frac{4\pi}{\lambda}\sum_{n,\,\text{odd}} n(\sin \pi n\sigma) \exp(-s/\lambda_n^{(r)}) \end{aligned} \tag{19.5-16}$$

[2] Equation 19.5-14 was first obtained by C. F. Curtiss and R. B. Bird [*J. Chem. Phys.*, **74**, 2016–2033 (1981)] by transforming the expression of M. Doi and S. F. Edwards [*J. Chem. Soc., Faraday Trans. II*, **74**, 1818–1832 (1978)]:

$$F(\boldsymbol{u}, t, t') = \frac{1}{4\pi}\int \delta(\boldsymbol{u} - \hat{\boldsymbol{u}})d\bar{\boldsymbol{u}} \tag{19.5-14a}$$

where

$$\hat{\boldsymbol{u}}(\bar{\boldsymbol{u}}, t, t') = \frac{[\mathbf{E}(t, t') \cdot \bar{\boldsymbol{u}}]}{|[\mathbf{E}(t, t') \cdot \bar{\boldsymbol{u}}]|} \tag{19.5-14b}$$

Here $\mathbf{E}(t, t')$ is the displacement-gradient tensor. See Example 8.3-2 for the transformation of coordinates needed to interrelate the two expressions for $F(\boldsymbol{u}, t, t')$. It is interesting that in the differential equation (Eq. 19.5-1) the flow field is described by the kinematic tensor $\boldsymbol{\kappa} = (\nabla \boldsymbol{v})^\dagger$, but that in the solution (Eq. 19.5-14 or 19.5-14a) the kinematic tensor $\boldsymbol{\gamma}^{[0]} = \{\boldsymbol{\Delta}^\dagger \cdot \boldsymbol{\Delta} - \boldsymbol{\delta}\}$ or $\mathbf{E}$ appears. The relations between $\boldsymbol{\Delta}$ or $\mathbf{E}$ and $\boldsymbol{\kappa}$ are quite complicated (see problem 8D.1).

A retarded-motion expansion for $f(\boldsymbol{u}, \sigma, t)$ can be obtained by expanding the denominator of the integral in Eq. 19.5-15 in a Taylor series and then expanding $\gamma^{[0]}(t, t')$ about $t' = t$ (see Problem 9B.2). Then the time integrals can be performed and one finally obtains

$$f(\boldsymbol{u}, \sigma, t) = \frac{1}{4\pi}\left[1 + \tfrac{3}{4}\lambda(\boldsymbol{\gamma}^{(1)} : \boldsymbol{uu})(\sigma - \sigma^2) + \frac{1}{32}\lambda^2(5\boldsymbol{\gamma}^{(1)}\boldsymbol{\gamma}^{(1)} \vdots \boldsymbol{uuuu} - 2\boldsymbol{\gamma}^{(2)} : \boldsymbol{uu})(\sigma - 2\sigma^3 + \sigma^4) + \cdots\right] \quad (19.5\text{-}17)$$

The λ^3-term has also been worked out but is not included here.[3]

b. Perturbation Solution for $\varepsilon' \neq 0$

As was pointed out earlier, if $\varepsilon' \neq 0$ Eq. 19.5-1 is essentially the rigid rod equation discussed in Chapter 14. Although no completely general solution of this equation is known some results in Chapter 14 may be used in the present discussion.

As an example of the use of the rigid rod results we consider the perturbation solution for arbitrary, irrotational, time-dependent flows discussed in §14.5. From Eqs. 14.5-4, 14, and 21 it follows that

$$F(\boldsymbol{u}, t, t') = \frac{1}{4\pi}\left\{1 + \frac{3}{2}\int_{t'}^{t} e^{-6\varepsilon' N^2(t-t'')/\lambda}(\dot{\boldsymbol{\gamma}}(t'') : \boldsymbol{uu})dt'' - \frac{3}{14}\int_{t'}^{t}\int_{t'}^{t''}(\dot{\boldsymbol{\gamma}}(t'') : \dot{\boldsymbol{\gamma}}(t''') - 3\{\dot{\boldsymbol{\gamma}}(t'') \cdot \dot{\boldsymbol{\gamma}}(t''')\} : \boldsymbol{uu})e^{-6\varepsilon' N^2(t-t')/\lambda}\, dt'''dt'' + \frac{3}{14}\int_{t'}^{t}\int_{t'}^{t''}\Big((\dot{\boldsymbol{\gamma}}(t'') : \dot{\boldsymbol{\gamma}}(t''') - 10\{\dot{\boldsymbol{\gamma}}(t'') \cdot \dot{\boldsymbol{\gamma}}(t''')\} : \boldsymbol{uu} + \frac{35}{2}(\dot{\boldsymbol{\gamma}}(t'') : \boldsymbol{uu})(\dot{\boldsymbol{\gamma}}(t''') : \boldsymbol{uu})\Big)e^{-2\varepsilon' N^2(10t - 7t'' - 3t''')/\lambda}\, dt'''\, dt'' + \cdots\right\} \quad (19.5\text{-}18)$$

This solution is consistent with the initial condition, Eq. 19.5-2, and becomes the solution discussed in §14.5 in the limit that $t' \to -\infty$. In a similar manner higher terms in the series may be obtained from the expressions given in §14.5. When this result is used in the expression for the distribution function, Eq. 19.5-3, one finds that

$$f(\boldsymbol{u}, \sigma, t) = \frac{1}{4\pi}\left\{1 + \frac{6}{\pi}\sum_{n,\,\text{odd}}\frac{1}{n}(\sin \pi n\sigma)\int_{-\infty}^{t} e^{-(t-t')/\lambda_n}(\dot{\boldsymbol{\gamma}}(t') : \boldsymbol{uu})dt' + \cdots\right\} \quad (19.5\text{-}19)$$

where the λ_n are a set of effective time constants

$$\lambda_n = \left[\frac{(1-\varepsilon')}{\lambda_n^{(r)}} + \frac{6\varepsilon' N^2}{\lambda}\right]^{-1} = \frac{\lambda}{(1-\varepsilon')\pi^2 n^2 + 6\varepsilon' N^2} \quad (19.5\text{-}20)$$

[3] C. F. Curtiss and R. B. Bird, *J. Chem Phys.*, **74**, p. 2024 (1981).

For steady flows $\dot{\gamma}$ is independent of time and

$$f(\boldsymbol{u}, \sigma, t) = \frac{1}{4\pi}\{1 + \lambda(\dot{\boldsymbol{\gamma}} : \boldsymbol{uu})g(\sigma) + \cdots\} \tag{19.5-21}$$

where

$$g(\sigma) = \frac{6}{\pi}\sum_{n,\,\text{odd}} \frac{\sin n\pi\sigma}{n[(1-\varepsilon')n^2\pi^2 + 6\varepsilon' N^2]} \tag{19.5-22}$$

This series may be written in the alternate form

$$g(\sigma) = -\frac{3}{2(1-\varepsilon')x^2}\sum_{n=1}^{\infty}\frac{x^{2n}}{(2n)!}E_{2n}(\sigma) \tag{19.5-23}$$

where $x = [6\varepsilon' N^2/(1-\varepsilon')]^{1/2}$ and the $E_{2n}(\sigma)$ are the[4] "Euler polynomials." Using the definition of these polynomials one may sum this series to find that

$$g(\sigma) = \frac{3[\sinh \tfrac{1}{2}x\sigma][\sinh \tfrac{1}{2}x(1-\sigma)]}{(1-\varepsilon')x^2 \cosh \tfrac{1}{2}x} \tag{19.5-24}$$

One then gets for small values of x (or ε')

$$g(\sigma) = \frac{3\sigma(1-\sigma)}{4(1-\varepsilon')}\left[1 - \frac{x^2}{12}(1 + \sigma - \sigma^2) + \cdots\right] \tag{19.5-25}$$

and for large x (or $\varepsilon' \to 1$)

$$g(\sigma) \to \frac{3}{2(1-\varepsilon')x^2} = \frac{1}{4N^2} \tag{19.5-26}$$

except at $\sigma = 0$ or 1. On the other hand, if ε' is not unity, $g(\sigma)$ as given by Eq. 19.5-24 is zero at $\sigma = 0$ and 1.

Thus one sees explicitly that for steady state flows to first order in $\dot{\gamma}$, the solution of the equation for the single-link distribution function, $f(\boldsymbol{u}, \sigma, t)$, as given by Eq. 19.5-3, is $1/(4\pi)$ at $\sigma = 0$ and 1, except in the limit that $\varepsilon' \to 1$, and that in this limit the function is discontinuous at these points.

§19.6 THE CONSTITUTIVE EQUATION

One may combine the formal solution of the diffusion equation for the single-link distribution function developed in the previous section with the expression for the stress tensor developed in §19.4 to obtain a constitutive equation in terms of the solution, $F(\boldsymbol{u}, t, t')$, of the rigid rod equation, Eq. 19.5-1.

[4] M. Abramowitz and I. A. Stegun (Eds.), *Handbook of Mathematical Functions*, National Bureau of Standards, Washington D. C. (1964), pp. 803 *et seq.*

First, we define a second-order tensor $\mathbf{A}^{(2)}$ and a fourth-order tensor $\mathbf{A}^{(4)}$ by

$$\mathbf{A}^{(2)}(t, t') = \int F(\boldsymbol{u}, t, t')\boldsymbol{uu}\, d\boldsymbol{u} \tag{19.6-1}$$

$$\mathbf{A}^{(4)}(t, t') = \int F(\boldsymbol{u}, t, t')\boldsymbol{uuuu}\, d\boldsymbol{u} \tag{19.6-2}$$

With these definitions it follows from the expression for the single-link distribution function, Eq. 19.5-3, that

$$\int_0^1 \langle \boldsymbol{uu} \rangle d\sigma = \int_{-\infty}^{t} \mu(t, t')\mathbf{A}^{(2)}(t, t')dt' \tag{19.6-3}$$

$$\int_0^1 \sigma(1 - \sigma)\langle \boldsymbol{uu} \rangle d\sigma = \int_{-\infty}^{t} \nu(t, t')\mathbf{A}^{(2)}(t, t')dt' \tag{19.6-4}$$

$$\int_0^1 \sigma(1 - \sigma)\langle \boldsymbol{uuuu} \rangle d\sigma = \int_{-\infty}^{t} \nu(t, t')\mathbf{A}^{(4)}(t, t')dt' \tag{19.6-5}$$

where

$$\mu(s) = \int_0^1 P(\varepsilon', \sigma, s)d\sigma = \frac{8(1 - \varepsilon')}{\lambda} \sum_{n,\,\text{odd}} e^{-(1-\varepsilon')s/\lambda_n^{(r)}} \tag{19.6-6}$$

$$\nu(s) = \frac{2(1 - \varepsilon')}{\lambda} \int_s^{\infty} \mu(s')ds' = \frac{16(1 - \varepsilon')}{\pi^2\lambda} \sum_{n,\,\text{odd}} \frac{1}{n^2} e^{-(1-\varepsilon')s/\lambda_n^{(r)}} \tag{19.6-7}$$

When these expressions are used in Eq. 19.4-18 for the stress tensor, one finds that

$$\boldsymbol{\tau} = kT \sum_{\alpha} n_\alpha N_\alpha \Bigg[\tfrac{1}{3}(1 - \varepsilon')\boldsymbol{\delta} + \tfrac{1}{6}\varepsilon' N_\alpha^2 \boldsymbol{\delta} - (1 - \varepsilon') \int_{-\infty}^{t} \mu_\alpha(t - t')\mathbf{A}_\alpha^{(2)}(t, t')dt' - 3\varepsilon' N_\alpha^2 \int_{-\infty}^{t} \nu_\alpha(t - t')\mathbf{A}_\alpha^{(2)}(t, t')dt' - \varepsilon\lambda_\alpha \boldsymbol{\kappa}(t) : \int_{-\infty}^{t} \nu_\alpha(t - t')\mathbf{A}_\alpha^{(4)}(t, t')dt' \Bigg] \tag{19.6-8}$$

where the sum over α is the sum over the various species of molecules. In the polydisperse liquid being considered here the molecules differ only in length, that is, in the value of N_α; there is a time constant λ_α associated with each species. In general, the functions $\mu(s)$ and $\nu(s)$, as well as the tensors $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(4)}$, depend on the value of λ_α.

a. Complete Constitutive Equation in the Pure Reptation Limit ($\varepsilon' = 0$)

In the limit that $\varepsilon' = 0$, the function $F(\boldsymbol{u}, t, t')$ is independent of λ_α, and as a consequence $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(4)}$ are also independent of λ_α. The stress tensor is then[1]

$$\boxed{\begin{aligned}\boldsymbol{\tau} = \left(\sum_\alpha n_\alpha N_\alpha\right) kT \Bigg[\tfrac{1}{3}\boldsymbol{\delta} - \int_{-\infty}^{t} \left(\sum_\alpha w_\alpha \mu_\alpha(t-t')\right) \mathbf{A}^{(2)}(t, t')\,dt' \\ - \tfrac{1}{2}\varepsilon\dot{\boldsymbol{\gamma}}(t) : \int_{-\infty}^{t} \left(\sum_\alpha w_\alpha \lambda_\alpha \nu_\alpha(t-t')\right) \mathbf{A}^{(4)}(t, t')\,dt' \Bigg]\end{aligned}} \tag{19.6-9}$$

in which $w_\alpha = n_\alpha N_\alpha / \sum_\beta n_\beta N_\beta$ is the mass fraction of species α, and[2]

$$\mathbf{A}^{(2)} = \frac{1}{4\pi} \int \frac{\boldsymbol{uu}\, du}{(1 + \boldsymbol{\gamma}^{[0]} : \boldsymbol{uu})^{3/2}} = \frac{1}{4\pi} \int \hat{\boldsymbol{u}}\hat{\boldsymbol{u}}\, du \tag{19.6-10}$$

$$\mathbf{A}^{(4)} = \frac{1}{4\pi} \int \frac{\boldsymbol{uuuu}\, du}{(1 + \boldsymbol{\gamma}^{[0]} : \boldsymbol{uu})^{3/2}} = \frac{1}{4\pi} \int \hat{\boldsymbol{u}}\hat{\boldsymbol{u}}\hat{\boldsymbol{u}}\hat{\boldsymbol{u}}\, du \tag{19.6-11}$$

with $\hat{\boldsymbol{u}}(\boldsymbol{u}, t, t')$ being defined in Eq. 19.5-14b. The two forms of $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(4)}$ result from the use of the alternative forms for $F(\boldsymbol{u}, t, t')$ given in Eqs. 19.5-14 and 14a (see Example 8.3-3 for the relation between the two forms).

In Eq. 19.6-9 we have then arrived at the complete constitutive equation[3] for the polydisperse polymer melt, modeled as a collection of interacting Kramers chains. Given the kinematics of the flow field one can obtain $\boldsymbol{\gamma}^{[0]}(t, t')$ and then $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(4)}$. Substitution of these kinematic tensors into Eq. 19.6-9 then gives the stress in the fluid, provided that the time constants λ_α for the chain are known.

The stress-tensor expression in Eq. 19.6-9 may be put into the form of a *retarded motion expansion* (see Eq. 6.2-1) by performing the following manipulations: expand the expressions for $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(4)}$ as Taylor series in $\boldsymbol{\gamma}^{[0]}(t, t')$; expand $\boldsymbol{\gamma}^{[0]}$ about $t' = t$ using Eq. 9B.2-1; use Problem 9B.1 to replace all $\boldsymbol{\gamma}^{(n)}$ by combinations of $\boldsymbol{\gamma}_{(n)}$; finally, do the

[1] The Doi Edwards constitutive equation [M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. II*, **74**, 1789 1832 (1978); see Eq. 3.15 on p. 1822] can be obtained from Eq. 19.6-9 by specializing to a monodisperse fluid, setting $\varepsilon = 0$, and replacing kT by $3kT$. As noted earlier, in connection with Eq. 19.3-25, there is also a difference in the time constants in the two theories. For polydisperse fluids the mixing rules given by Doi and Edwards [*J. Chem. Soc., Faraday Trans. II*, **74**, pp. 1828 1829 (1978)] are the same as those implied by Eq. 19.6-9, except that the λ_α needed for calculating $\mu_\alpha(t - t')$ and $\nu_\alpha(t - t')$ are defined differently: in the Doi Edwards theory $\lambda_\alpha \propto N_\alpha^3$, whereas Eq. 19.3-25 gives $\lambda_\alpha \propto N_\alpha^2 \bar{N}^{1+\beta}$ with $\bar{N} = \sum_\alpha x_\alpha N_\alpha$.

[2] The tensors $\mathbf{A}^{(2)}$ and $\mathbf{A}^{(4)}$ used here are simply related to the two second-order tensors $\boldsymbol{A}$ and $\boldsymbol{B}$ used by C. F. Curtiss and R. B. Bird [*J. Chem. Phys.*, **74**, 2016 2033 (1981)] as follows $\boldsymbol{A} = \mathbf{A}^{(2)}$, and $\boldsymbol{B} = \frac{1}{2}\lambda\{\dot{\boldsymbol{\gamma}} : \mathbf{A}^{(4)}\}$. P. K. Currie [*J. Non-Newtonian Fluid Mech.*, **11**, 53 68 (1982)] has shown that $\boldsymbol{A}$ and $\boldsymbol{B}$ are both derivable from a "potential function" (see Table 8.3-2 and Example 8.3-3).

[3] This constitutive equation has been used along with the equations of continuity and motion for making flow calculations [D. S. Malkus and B. Bernstein, *J. Non-Newtonian Fluid Mech.*, **16**, 77 116 (1984)].

integrations over t'. The result is

$$\tau = -\left(\sum_\alpha n_\alpha N_\alpha\right)kT\left[\left(\frac{1}{60}+\frac{\varepsilon}{90}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha\right)\gamma_{(1)} - \left(\frac{1-\varepsilon}{1050}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right)\{\gamma_{(1)}\cdot\gamma_{(1)}\}\right.$$
$$\left. - \left(\frac{1}{600}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right)\gamma_{(2)} + \cdots\right] \tag{19.6-12}$$

From this expansion, including the third-order terms which are also available,[4] we can get the following results (cf. Example 6.2-1 and Problem 6B.2):

Viscometric Functions:

$$\eta = \left(\sum_\alpha n_\alpha N_\alpha\right)kT\left[\frac{1}{60}\left(1+\frac{2}{3}\varepsilon\right)\left(\sum_\alpha w_\alpha\lambda_\alpha\right) - \frac{17}{70560}\left(1-\frac{2}{5}\varepsilon\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^3\right)\dot\gamma^2 + \cdots\right] \tag{19.6-13}$$

$$\Psi_1 = \left(\sum_\alpha n_\alpha N_\alpha\right)kT\left[\frac{1}{300}\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right) - \frac{341}{3492720}\left(1-\frac{1}{2}\varepsilon\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^4\right)\dot\gamma^2 + \cdots\right] \tag{19.6-14}[5]$$

$$\Psi_2 = -\left(\sum_\alpha n_\alpha N_\alpha\right)kT(1-\varepsilon)\left[\frac{1}{1050}\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right) - \frac{341}{9604980}\left(\sum_\alpha w_\alpha\lambda_\alpha^4\right)\dot\gamma^2 + \cdots\right] \tag{19.6-15}[5]$$

Elongational Viscosity:

$$\bar\eta = 3\left(\sum_\alpha n_\alpha N_\alpha\right)kT\left[\frac{1}{60}\left(1+\frac{2}{3}\varepsilon\right)\left(\sum_\alpha w_\alpha\lambda_\alpha\right) + \left(\frac{1}{1400}+\frac{\varepsilon}{1050}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^2\right)\dot\varepsilon\right.$$
$$\left. + \left(-\frac{17}{78400}+\frac{17\varepsilon}{58800}\right)\left(\sum_\alpha w_\alpha\lambda_\alpha^3\right)\dot\varepsilon^2 + \cdots\right] \tag{19.6-16}$$

In these expressions the time constants λ_α are given by $\lambda_\alpha = N_\alpha^2\bar N^{1+\beta}\zeta a^2/2kT$ and $\bar N = \sum_\alpha x_\alpha N_\alpha$; the x_α are mole fractions, the w_α are mass fractions, and the n_α are number densities. Note that the normal-stress ratio at $\dot\gamma = 0$ is given by

$$\frac{\Psi_{2,0}}{\Psi_{1,0}} = -\tfrac{2}{7}(1-\varepsilon) \tag{19.6-17}$$

for monodisperse and polydisperse fluids.[6] It is interesting to note that the "rod climbing" phenomenon occurs for small deformation rates only if $\Psi_{2,0}/\Psi_{1,0} > -\frac{1}{4}$ or $\varepsilon > \frac{1}{8}$; this means that the Doi–Edwards theory ($\varepsilon = 0$) does not predict rod climbing at the

[4] C. F. Curtiss and R. B. Bird, *J. Chem. Phys.*, **74**, p. 2029 (1981).

[5] The $\dot\gamma^2$-terms in the expression for Ψ_1 and Ψ_2 were not obtained from the fourth-order terms in Eq. 19.6-12, but rather by expanding the integrals in Eqs. 19.7-10 and 11.

[6] The quantity $\Psi_{2,0}/\Psi_{1,0}$ has been measured for linear polybutadienes and polystyrenes in normal butylbenzene and found to be about -0.29 [see S. Ramachandran, Ph.D. Thesis, University of Utah, Salt Lake City (1983), as cited in S. Ramachandran and E. B. Christiansen, *J. Non-Newtonian Fluid Mech.*, **13**, 21–32 (1983)]; the same authors reported $\Psi_{2,0}/\Psi_{1,0} \doteq -0.214$ for star polymers.

second-order fluid level, in conflict with known experimental facts (see Problem 6B.6), even if polydispersity is accounted for.[7]

b. Retarded-Motion Expansion and Linear Viscoelastic Reponse for $\varepsilon' \neq 0$

From the series expression for $F(\boldsymbol{u}, t, t')$ given by Eq. 19.5-18 one finds that for irrotational flows

$$\begin{aligned}\mathbf{A}^{(2)}(t, t') = &\frac{1}{3}\boldsymbol{\delta} + \frac{1}{5}\int_{t'}^{t} e^{-6\varepsilon' N^2 (t-t'')/\lambda}\dot{\boldsymbol{\gamma}}(t'')dt'' \\ &- \frac{1}{70}\int_{t'}^{t}\int_{t'}^{t''} e^{-6\varepsilon' N^2 (t-t'')/\lambda}[2(\dot{\boldsymbol{\gamma}}(t'') : \dot{\boldsymbol{\gamma}}(t'''))\boldsymbol{\delta} \\ &- 3\{\dot{\boldsymbol{\gamma}}(t'') \cdot \dot{\boldsymbol{\gamma}}(t''')\} - 3\{\dot{\boldsymbol{\gamma}}(t''') \cdot \dot{\boldsymbol{\gamma}}(t'')\}]dt'''dt'' + \cdots \end{aligned} \tag{19.6-18}$$

$$\begin{aligned}\mathbf{A}^{(4)}(t, t') = &\frac{1}{15}(\boldsymbol{\delta}\boldsymbol{\delta} + \mathbf{I} + \mathbf{I}^{\dagger}) \\ &- \frac{1}{35}\int_{t'}^{t} e^{-6\varepsilon' N^2 (t-t'')/\lambda}\{[\boldsymbol{\delta}\boldsymbol{\delta} + \mathbf{I} + \mathbf{I}^{\dagger}] \cdot \dot{\boldsymbol{\gamma}}(t'') \\ &+ \dot{\boldsymbol{\gamma}}(t'') \cdot [\boldsymbol{\delta}\boldsymbol{\delta} + \mathbf{I} + \mathbf{I}^{\dagger}]\}dt'' + \cdots \end{aligned} \tag{19.6-19}$$

where $\mathbf{I}$ is the isotropic fourth rank tensor defined in §E.9. When these series are used in the expression for the stress tensor, Eq. 19.6-8, one finds that

$$\begin{aligned}\boldsymbol{\tau} = &-\frac{8kT}{5\pi^4}\sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \sum_{n,\,\text{odd}} \frac{1}{n^4}\lambda_n \int_{-\infty}^{t}\Bigg[e^{-(t-t')/\lambda_n}\dot{\boldsymbol{\gamma}}(t') \\ &- \frac{1}{14}\int_{-\infty}^{t''} e^{-(t-t'')/\lambda_n}\{2(\dot{\boldsymbol{\gamma}}(t') : \dot{\boldsymbol{\gamma}}(t''))\boldsymbol{\delta} \\ &- 3\dot{\boldsymbol{\gamma}}(t') \cdot \dot{\boldsymbol{\gamma}}(t'') - 3\dot{\boldsymbol{\gamma}}(t'') \cdot \dot{\boldsymbol{\gamma}}(t')\}dt'' + \cdots\Bigg]dt' \\ &- \frac{16\varepsilon kT}{15\pi^4}\sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \sum_{n,\,\text{odd}} \frac{1}{n^4}\Bigg[\dot{\boldsymbol{\gamma}}(t) + \frac{3}{14}\int_{-\infty}^{t} e^{-(t-t')/\lambda_n}\{(\dot{\boldsymbol{\gamma}}(t) : \dot{\boldsymbol{\gamma}}(t'))\boldsymbol{\delta} \\ &+ 2\dot{\boldsymbol{\gamma}}(t) \cdot \dot{\boldsymbol{\gamma}}(t') + 2\dot{\boldsymbol{\gamma}}(t') \cdot \dot{\boldsymbol{\gamma}}(t)\}dt' + \cdots\Bigg] \end{aligned} \tag{19.6-20}$$

where the λ_n are the time constants defined by Eq. 19.5-20. From this it may be shown that the coefficients in the retarded motion expansion are

$$b_1 = \eta_0 = \frac{8kT}{5\pi^4}(1 + \tfrac{2}{3}\varepsilon)\sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \sum_{n,\,\text{odd}} \frac{1}{n^4} \tag{19.6-21}$$

$$b_2 = -\tfrac{1}{2}\Psi_{1,0} = -\frac{8kT}{5\pi^4}\sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \sum_{n,\,\text{odd}} \frac{\lambda_n}{n^4} \tag{19.6-22}$$

$$b_{11} = \Psi_{2,0} = \tfrac{4}{7}(1 - \varepsilon)b_2 \tag{19.6-23}$$

In the limit that $\varepsilon' \to 0$ these results are equivalent to the first terms in the series given by Eqs. 19.6-13 to 15. It is interesting to note that η_0 and the ratio $\Psi_{1,0}/\Psi_{2,0}$ are independent of ε'. For a monodisperse system, the value of $\Psi_{1,0}$ (or $\Psi_{2,0}$) when $\varepsilon' = 1$ differs from the value when $\varepsilon' = 0$ by a factor of $5/(3N^2)$. The explicit form of the dependence of these quantities on ε' is examined in Problem 19D.1.

It may also be shown from Eq. 19.6-20 that the relaxation modulus is

$$G(t) = kT \sum_{\alpha} n_\alpha N_\alpha \left[\frac{\varepsilon}{45} \lambda \delta(t) + \frac{8\lambda}{5\pi^4} \sum_{n,\text{odd}} \frac{e^{-t/\lambda_{\alpha,n}}}{n^4 \lambda_{\alpha,n}} \right] \tag{19.6-24}$$

From this it follows that the complex viscosity is

$$\eta^* = kT \sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \left[\frac{\varepsilon}{90} + \frac{8}{5\pi^4} \sum_{n,\text{odd}} \frac{1}{n^4(1 + i\omega\lambda_{\alpha,n})} \right] \tag{19.6-25}$$

and that

$$\lim_{\omega \to \infty} \frac{\eta'(\omega)}{\eta'(0)} = \frac{(2\varepsilon/3)}{1 + (2\varepsilon/3)} \tag{19.6-26}$$

$$\lim_{\omega \to \infty} \omega\eta''(\omega) = \tfrac{1}{5} kT \left(1 - \frac{\varepsilon'}{2}\right) \sum_{\alpha} n_\alpha N_\alpha \lambda_\alpha \tag{19.6-27}$$

Experimental data on $\eta'(\omega)$ for polymer melts at high ω when compared with Eq. 19.6-26 suggest that ε should be very small or zero.[8] However, we feel that it is inappropriate to draw this conclusion, since the Kramers bead-rod model is too crude to account for the very small-scale motions that are probed by high frequencies in the oscillatory-flow experiment.

EXAMPLE 19.6-1 Effect of Polydispersity on Rheological Properties

Use Eqs. 19.6-13 and 19.6-14 to obtain the zero-shear-rate viscosity and first normal-stress coefficient for a polydisperse polymer melt. Then obtain the steady-state compliance J_e^0 in terms of appropriate molecular weight averages. Finally as an illustration of using a two-parameter empiricism for the molecular weight distribution, use the logarithmic-normal distribution[9] to compare the theoretical result with the experimentally determined molecular-weight distribution dependence

$$J_e^0 \propto \left(\frac{\bar{M}_z}{\bar{M}_w} \right)^{3.7} \tag{19.6-28}$$

deduced from data on polydimethylsiloxane and polystyrene in the range $1 < \bar{M}_z/\bar{M}_w < 3$ by Mills.[10]

SOLUTION We approximate the molecular weight distribution by a continuous function $w(M)$, such that $w(M)\,dM$ is the weight fraction of polymer with molecular weight between M and $M + dM$. We define molecular weight averages as follows:

$$\bar{M}_{z+j} = \frac{\int_0^\infty M^{2+j} w(M)\,dM}{\int_0^\infty M^{1+j} w(M) dM} \tag{19.6-29}$$

[8] D. A. Bernard and J. Noolandi, *Macromolecules*, **16**, 1358 1366 (1983).

[9] H. Wesslau, *Makromolecule Chemie*, **20**, 111-142 (1956).

[10] N. J. Mills, *Nature* (London), **219**, 1249 1250 (1968); see also H. J. M. A. Mieras and C. F. H. van Rijn, *Nature*, **218**, 865-866 (1968).

For $j = -2$, -1, and 0 these quantities are generally called, respectively, the number-average molecular weight $\bar{M}_n$, the weight-average molecular weight $\bar{M}_w$, and the z-average molecular weight $\bar{M}_z$. Keep in mind that $\int_0^\infty w(M)\, dM = 1$.

Now we note that the sum $\sum_\alpha n_\alpha N_\alpha$ appearing in Eqs. 19.6-13 and 14 may be written as follows:

$$\sum_\alpha n_\alpha N_\alpha = \frac{\tilde{N}}{M_0} \sum_\alpha c_\alpha M_\alpha = \frac{\tilde{N}}{M_0} \rho \tag{19.6-30}$$

in which c_α is the molar concentration of species α, M_0 is the molecular weight of that part of the chain corresponding to one "bead", ρ is the mass density of the mixture, and $\tilde{N}$ is the Avogadro number. Next we note that the time constant λ_α, given in Eq. 19.3-25, can be rewritten in terms of molecular weights using $M_\alpha = N_\alpha M_0$, as follows:

$$\lambda_\alpha = \frac{\bar{N}^{1+\beta} N_\alpha^2 \zeta a^2}{2kT} = \frac{\bar{M}_n^{1+\beta} M_\alpha^2}{M_0^{3+\beta}} \left(\frac{\zeta a^2}{2kT} \right) \tag{19.6-31}$$

The sums, involving weight fractions w_α, appearing in Eqs. 19.6-13 and 14, may now be written as follows:

$$\begin{aligned} \sum_\alpha w_\alpha \lambda_\alpha &= \frac{\bar{M}_n^{1+\beta}}{M_0^{3+\beta}} \left(\frac{\zeta a^2}{2kT} \right) \int_0^\infty M^2 w(M) dM \\ &= \frac{\bar{M}_n^{1+\beta} \bar{M}_w \bar{M}_z}{M_0^{3+\beta}} \left(\frac{\zeta a^2}{2kT} \right) \end{aligned} \tag{19.6-32}$$

$$\begin{aligned} \sum_\alpha w_\alpha \lambda_\alpha^2 &= \left(\frac{\bar{M}_n^{1+\beta}}{M_0^{3+\beta}} \right)^2 \left(\frac{\zeta a^2}{2kT} \right)^2 \int_0^\infty M^4 w(M) dM \\ &= \frac{\bar{M}_n^{2+2\beta} \bar{M}_w \bar{M}_z \bar{M}_{z+1} \bar{M}_{z+2}}{M_0^{6+2\beta}} \left(\frac{\zeta a^2}{2kT} \right)^2 \end{aligned} \tag{19.6-33}$$

Therefore, the zero-shear-rate viscometric functions become

$$\eta_0 = \frac{\rho \tilde{N} kT}{60 M_0^{4+\beta}} (1 + \tfrac{2}{3}\varepsilon) \left(\frac{\zeta a^2}{2kT} \right) \bar{M}_n^{1+\beta} \bar{M}_w \bar{M}_z \tag{19.6-34}$$

$$\Psi_{1,0} = \frac{\rho \tilde{N} kT}{300 M_0^{7+2\beta}} \left(\frac{\zeta a^2}{2kT} \right)^2 \bar{M}_n^{2+2\beta} \bar{M}_w \bar{M}_z \bar{M}_{z+1} \bar{M}_{z+2} \tag{19.6-35}$$

and also

$$J_e^0 = \frac{\Psi_{1,0}}{2\eta_0^2} \propto \frac{\bar{M}_{z+1} \bar{M}_{z+2}}{\bar{M}_w \bar{M}_z} \tag{19.6-36}$$

Thus J_e^0 is predicted to be independent of molecular weight in a monodisperse system, but strongly dependent on molecular weight distribution in a polydisperse liquid, which is in qualitative agreement with experiment.

To go further one has to assume a form for the molecular-weight distribution $w(M)$. One two-parameter equation is the logarithmic-normal distribution

$$w(M) = \frac{\exp[-(\ln M - \ln \bar{M}_m)^2 / 2\sigma^2]}{\sqrt{2\pi}\, \sigma M} \tag{19.6-37}$$

in which σ and $\bar{M}_m$ are constants. It can be shown that for this distribution $\bar{M}_{z+j}/\bar{M}_{z+j-1} = \exp \sigma^2$. Using this result we then get[11]

$$J_e^0 \propto \left(\frac{\bar{M}_z}{\bar{M}_w}\right)^4 \tag{19.6-38}$$

which should be compared with the experimental result in Eq. 19.6-28.

Extensive comparisons[12] between experimental data and the mixture-theory results of Eqs. 19.6-36, 19.7-9, 19.7-10, and other equations for material functions suggest that the time constant λ_α of Eq. 19.3-25 is reasonable. This formula is, in turn, a consequence of the definition of $\boldsymbol{F}^{(h)\alpha}$ in Eqs. 17.5-10 through 12. The generally satisfactory agreement between theory and experiment provides some additional support for the method of incorporation of concentration and molecular weight dependence in Eq. 17.5-10 (see footnote 1 in §17.5).

§19.7 SHEAR-FLOW RHEOLOGICAL PROPERTIES[1,2]

In this section we use Eq. 19.6-9 to obtain some of the material functions for monodisperse fluids for shear flows of the form $v_x = 0$, $v_y = \dot{\gamma}_{yz}(t)z$, $v_z = 0$ in the pure reptation limit, $\varepsilon' = 0$. For such flows the kinematic tensors $\dot{\boldsymbol{\gamma}}(t)$ and $\mathbf{E}(t, t')$ are (see Appendix C)

$$\dot{\boldsymbol{\gamma}}(t) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \dot{\gamma}_{yz}(t), \qquad \mathbf{E}(t, t') = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & \Gamma \\ 0 & 0 & 1 \end{pmatrix} \tag{19.7-1}$$

in which $\Gamma(t, t') = -\gamma_{yz}(t, t') = \int_{t'}^{t} \dot{\gamma}_{yz}(t'')dt''$ is the negative of the shear strain from t to t'. Then the unit vector $\hat{\boldsymbol{u}}(t, t')$ appearing in Eqs. 19.6-10 and 11 is:

$$\hat{\boldsymbol{u}} = \frac{[\mathbf{E} \cdot \boldsymbol{u}]}{|\mathbf{E} \cdot \boldsymbol{u}|} = \frac{1}{\sqrt{1 + 2\Gamma u_y u_z + \Gamma^2 u_z^2}} \begin{pmatrix} u_x \\ u_y + \Gamma u_z \\ u_z \end{pmatrix} \tag{19.7-2}$$

Here $u_x = \sin\theta \cos\phi$, $u_y = \sin\theta \sin\phi$, and $u_z = \cos\theta$, where θ and ϕ are the polar angles describing $\boldsymbol{u}$; this expression for $\hat{\boldsymbol{u}}$ then has to be inserted into Eqs. 19.6-10 and 11. From the latter we get the yz-components of $\mathbf{A}^{(2)}$ and $\mathbf{B}^{(2)} = \frac{1}{2}\{\lambda\dot{\boldsymbol{\gamma}} : \mathbf{A}^{(4)}\}$, needed to get the shear stress

[11] The importance of polydispersity in polymer-melt kinetic theory was emphasized by M. Doi and S. F. Edwards [*J. Chem. Soc., Faraday Trans II*, **74**, 1818–1832 (1978), Eqs. 7.2-7.4]. Their recommended averaging procedure is different from ours and leads to

$$J_e \propto \frac{\bar{M}_{z+2}\bar{M}_{z+3}\bar{M}_{z+4}}{\bar{M}_w\bar{M}_z\bar{M}_{z+1}} \xrightarrow[\text{distribution}]{\text{logarithmic normal}} \left(\frac{\bar{M}_z}{\bar{M}_w}\right)^9 \tag{19.6-38a}$$

For more on this subject see M. Kurata, *Macromolecules*, **17**, 895–898 (1984) and W. W. Graessley, *J. Polymer Sci., Polymer Phys. Ed.*, **18**, 27–34 (1980).

[12] J. D. Schieber, C. F. Curtiss, and R. B. Bird, *Ind. Eng. Chem. Fundam.*, **25**, 471–475 (1986); J. D. Schieber *J. Chem. Phys.*, *87*, 4917–4936 (1987).

[1] R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4747–4757 (1982) and H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982); errata in this paper have been pointed out X.-J. Fan and R. B. Bird, *J. Non-Newtonian Fluid Mech.*, **15**, 341–373 (1984).

[2] H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

τ_{yz}, by doing the ϕ-integrations and changing the θ-integrations to integrations over $x = \cos\theta$

$$A_{yz}^{(2)} = \frac{1}{2\Gamma}\int_0^1 [1 + g^{-1}(\Gamma^2 x^2 - 1)]dx \tag{19.7-3}$$

$$B_{yz}^{(2)} = \frac{\lambda\dot{\gamma}_{yz}}{4\Gamma^2}\int_0^1 \{1 + g^{-3}[(3\Gamma^6 + 8\Gamma^4)x^6 - (7\Gamma^4 + 8\Gamma^2)x^4 + 5\Gamma^2 x^2 - 1]\}dx \tag{19.7-4}$$

in which $g = [(\Gamma^4 + 4\Gamma^2)x^4 - 2\Gamma^2 x^2 + 1]^{1/2}$. Next we give the corresponding quantities needed to get the first and second normal-stress differences:

$$A_{yy}^{(2)} - A_{zz}^{(2)} = \Gamma A_{yz}^{(2)} \tag{19.7-5}$$

$$A_{zz}^{(2)} - A_{xx}^{(2)} = -\frac{1}{2}\int_0^1 \{1 - g^{-1}[(\Gamma^2 + 6)x^2 - 1]\}dx \tag{19.7-6}$$

$$B_{yy}^{(2)} - B_{zz}^{(2)} = \frac{\lambda\dot{\gamma}_{yz}}{4\Gamma}\int_0^1 \left\{\frac{3 + 2\Gamma^2}{1 + \Gamma^2} + g^{-3}[(2\Gamma^6 + 2\Gamma^4 - 8\Gamma^2)x^6 - (7\Gamma^4 + 8\Gamma^2)x^4 + (6\Gamma^2 - 6)x^2 - 1]\right\}dx \tag{19.7-7}$$

$$B_{zz}^{(2)} - B_{xx}^{(2)} = -\frac{1}{2}\lambda\dot{\gamma}_{yz}\frac{d}{d\Gamma}(A_{zz}^{(2)} - A_{xx}^{(2)}) \tag{19.7-8}$$

The derivation of these equations is outlined in the original reference,[1] and tables of these quantities as functions of Γ are given.

When the components of $\mathbf{A}^{(2)}$ and $\mathbf{B}^{(2)}$ are substituted into Eq. 19.6-9 and the integration variable is changed to the dimensionless variable $s' = (t - t')/\lambda$, we get for the *steady shear flow* of monodisperse fluids:

$$\frac{\eta(\dot{\gamma})}{NnkT\lambda} = \frac{1}{\lambda\dot{\gamma}}\left[\int_0^\infty \lambda\mu(\lambda s')(A_{yz}^{(2)})_\Gamma\, ds' + \varepsilon\int_0^\infty \lambda\nu(\lambda s')(B_{yz}^{(2)})_\Gamma\, ds'\right] \tag{19.7-9}$$

$$\frac{\Psi_1(\dot{\gamma})}{NnkT\lambda^2} = \frac{1}{(\lambda\dot{\gamma})^2}\left[\int_0^\infty \lambda\mu(\lambda s')(A_{yy}^{(2)} - A_{zz}^{(2)})_\Gamma\, ds' + \varepsilon\int_0^\infty \lambda\nu(\lambda s')(B_{yy}^{(2)} - B_{zz}^{(2)})_\Gamma\, ds'\right] \tag{19.7-10}$$

$$\frac{\Psi_2(\dot{\gamma})}{NnkT\lambda^2} = \frac{1 - \varepsilon}{(\lambda\dot{\gamma})^2}\int_0^\infty \lambda\mu(\lambda s')(A_{zz}^{(2)} - A_{xx}^{(2)})_\Gamma\, ds' \tag{19.7-11}$$

In these equations the subscript Γ serves as a reminder that the components of $A^{(2)}$ and $B^{(2)}$ are functions of Γ, which is related to s' by $\Gamma = \dot{\gamma}(t - t') = \lambda\dot{\gamma}s'$; for steady shear flow we

drop the subscripts yz on $\dot{\gamma}_{yz}$. For very small $\lambda\dot{\gamma}$ the viscometric functions η, Ψ_1, and Ψ_2 may be expanded to give Eqs. 19.6-13 to 15 appropriately simplified for a monodisperse fluid. For very large $\lambda\dot{\gamma}$ it has been found[1] that

$$\frac{\eta}{NnkT\lambda} \sim \frac{\varepsilon}{\lambda\dot{\gamma}} \qquad (\varepsilon \neq 0) \tag{19.7-12}$$

$$\frac{\Psi_1}{NnkT\lambda^2} \sim \frac{2\varepsilon \ln \lambda\dot{\gamma}}{(\lambda\dot{\gamma})^2} \qquad (\varepsilon \neq 0) \tag{19.7-13}$$

$$\frac{\Psi_2}{NnkT\lambda^2} \sim -\frac{1.1619(1-\varepsilon)}{(\lambda\dot{\gamma})^{5/2}} \tag{19.7-14}$$

When $\varepsilon = 0$ (Doi Edwards theory) at very large $\dot{\gamma}$ it is found[3] that $\eta \propto \dot{\gamma}^{-3/2}$ and $\Psi_1 \propto \dot{\gamma}^{-2}$. The calculated curves of η, Ψ_1, and Ψ_2 are shown in Figs. 19.7-1 and 2.

Experimental data on η and Ψ_1 for well-fractionated melts and concentrated solutions can be reasonably well fit by the theoretical curves, as may be seen in Figs. 19.7-3 (polystyrene melts), 19.7-5 (poly-α-methylstyrene solutions), and 19.7-8 (polystyrene solutions). Values of ε in the range 0.3–0.5 seem to provide the best curve fits; the $\varepsilon = 0$ curve cannot describe the $\eta(\dot{\gamma})$ and $\Psi_1(\dot{\gamma})$ curves over a wide range of shear rates. In Figs. 19.7-4 and 6 we show how the values of η_0 and λ vary with the weight-averaged molecular weight. According to Eq. 19.6-13, η_0 and λ should have the same molecular weight dependence for monodisperse fluids ($\eta_0 \propto \lambda \propto M^{3+\beta}$) and the figures bear this out moderately well. In Fig. 19.7-7 we show how N increases with the molecular weight; note that N is not particularly large.

Finally in Fig. 19.7-9 we show the transient behavior at the inception of steady shear flow. For very small times the theory does not fit the data particularly well. This may in part

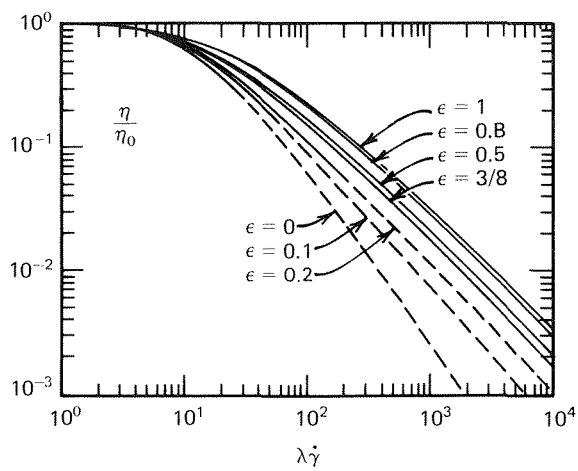


FIGURE 19.7-1. Viscosity as a function of shear rate $\dot{\gamma}$ for various values of the link tension coefficient ε. The time constant λ is $N^{3+\beta}\zeta a^2/2kT$ and the zero-shear-rate viscosity η_0 is $\frac{1}{60}(1+\frac{2}{3}\varepsilon)$ $NnkT\lambda$. The curves are dashed in the region where the slope is steeper than -1. The $\varepsilon = 0$ curve corresponds to the Doi–Edwards theory. Reproduced from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4747–4757 (1982).

[3] M. Doi and S. F. Edwards, *J. Chem. Soc., Faraday Trans. II*, **74**, 1789–1832 (1978); **75**, 38–54 (1979).

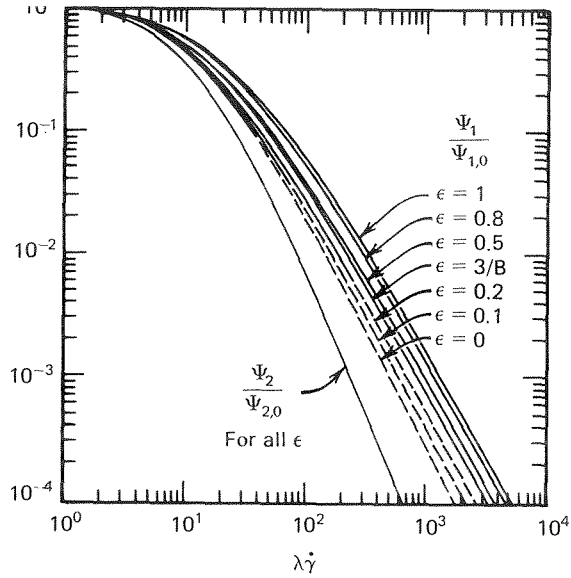


FIGURE 19.7-2. The normal-stress coefficients versus the dimensionless shear rate. The zero-shear-rate normal stress coefficients are $\Psi_{1,0} = (1/300)NnkT\lambda^2$ and $\Psi_{2,0} = -[(1-\varepsilon)/1050)]NnkT\lambda^2$. The dashed curves correspond to the region where the η/η_0 versus $\lambda\dot{\gamma}$ curves have a slope steeper than -1. The $\varepsilon = 0$ curve corresponds to the Doi-Edwards theory. Reproduced from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4747-4757 (1982).

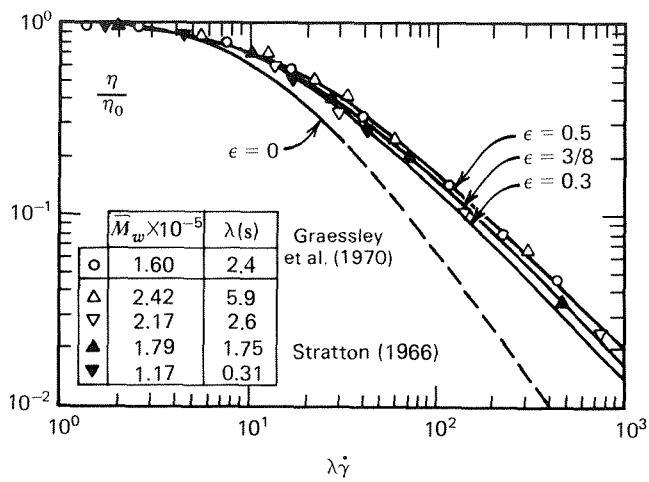


FIGURE 19.7-3. Comparison of the steady-state viscosity calculated from Eq. 19.7-9 with data on nearly monodisperse polystyrene melts of various molecular weights. The data of W. W. Graessley, S. D. Glasscock, and R. L. Crawley [*Trans. Soc. Rheol.*, **14**, 519-544 (1970)] are at 180°C, and those of R. A. Stratton [*J. Coll. Interf. Sci.*, **22**, 517-530 (1966)] are at 183°C. All the data are for samples with $\bar{M}_w/\bar{M}_n < 1.1$. The dashed part of the $\varepsilon = 0$ curve, corresponding to the Doi-Edwards theory, is unattainable, since the slope is steeper that -1. The experimental data extend well below the critical value of $\eta/\eta_0 \doteq 0.25$ of the $\varepsilon = 0$ curve. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4758-4766 (1982).

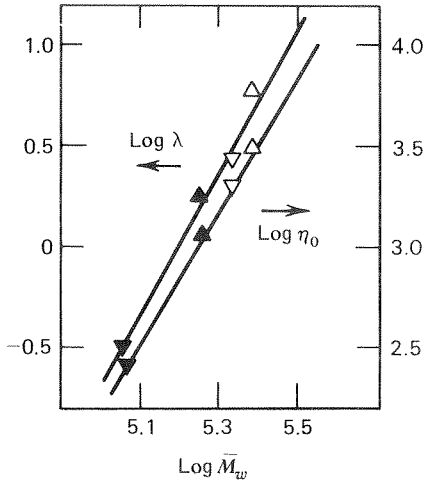


FIGURE 19.7-4. Plots of log η_0 and log λ versus log $\bar{M}_w$ from the data comparison of Fig. 19.7-3 for the data of Stratton. The quantities η_0(Pa · s) and λ(s) were determined by the best fit of the data with the theoretical curves in Fig. 19.7-1. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4758–4766 (1982).

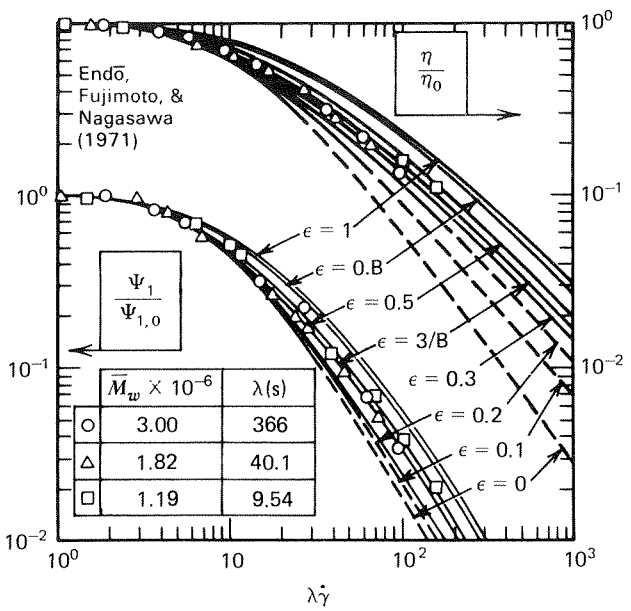


FIGURE 19.7-5. Data of H. Endō, T. Fujimoto, and M. Nagasawa, [*J. Polym. Sci.*, **A2**, **9**, 345-362 (1971)] on viscosity η and first normal stress coefficient Ψ_1 compared with curves of Figs. 19.7-1 and 2. The data are for 7% (by weight) solutions of poly-α-methylstrene of various molecular weights in Kanechlor at 25°C. All the polymer samples have $\bar{M}_w/\bar{M}_n < 1.01$. The same combinations of λ and ε fit both the η and Ψ_1 data. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, 77, 4758-4766 (1982).

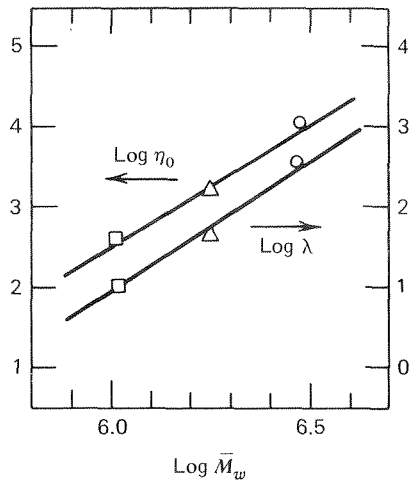


FIGURE 19.7-6. Plots of log η_0 and log λ vs. log $\bar{M}_w$ from the data comparison of Fig. 19.7-5 for the poly-α-methylstyrene solutions of Endō, Fujimoto and Nagasawa. The values of η_0(Pa·s) are the measured values and the values of λ(s) are those that give the best fit with the theoretical viscosity and normal-stress coefficient curves. Both lines have a slope of about 3.5, which corresponds to a value of 0.5 for β. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtis, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

be a result of the fact that the theoretical calculations do not account for the fluid inertia effects as the flow profiles are beginning to be established at the beginning of the experiment. On the other hand, it is more likely that the Kramers bead-spring chain model, with N not very large, is not capable of describing the rapid small-scale motions of the polymer molecules. This deficiency in the Kramers chain was also discussed in connection with the poor description of $\eta^*(\omega)$ at very high frequencies.

It must be borne in mind that the data comparisons given here are for monodisperse systems only. Even a small amount of polydispersity can have an appreciable effect. In Fig. 19.7-8, where the polymer being tested has $\bar{M}_w/\bar{M}_n = 1.25$, it was found that it was not

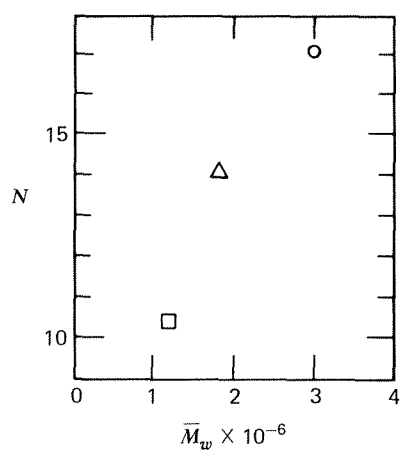


FIGURE 19.7-7. The number of beads per chain, N, versus the molecular weight from the data comparison in Fig. 19.7-6. The quantity N was determined from $\eta_0 = \frac{1}{60}(1 + \frac{2}{3}\varepsilon)N(\rho/\bar{M}_w)\tilde{N}kT\lambda$ of the solutions. $\rho = 1.3630$ g/cm^3 was given by M. Nagasawa (private communication (1982)). Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

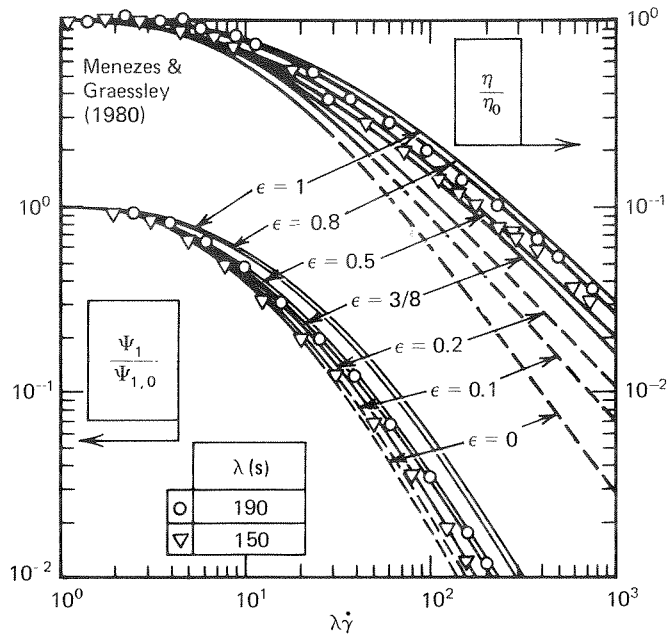


FIGURE 19.7-8. Data of E. V. Menezes and W. W. Graessley [*Rheol. Acta*, **19**, 38 50 (1980)] for viscosity η and first normal stress coefficient Ψ_1 compared with theoretical curves of Figs. 19.7-1 and 2. The data are for 12% (by weight) solutions of polystyrene ($\bar{M}_w = 1.8 \times 10^6$, $\bar{M}_w/\bar{M}_n = 1.25$) in tricresyl phosphate at 25°C. Because of polydispersity, it is not possible to fit both properties with a single combination of λ and ε: $\lambda = 150$s fits the η-data to the $\varepsilon = 0.5$ curve, whereas $\lambda = 190$s fits the Ψ_1-data to the $\varepsilon = 0.5$ curve. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758-4766 (1982).

possible to fit two material functions, namely η and Ψ_1, with a single value of the time constant λ. It is necessary to use the mixture formula in Eq. 19.6-9 to account for polydispersity.[4]

§19.8 ELONGATIONAL-FLOW RHEOLOGICAL PROPERTIES[1]

We conclude this chapter with a brief discussion of the theoretical predictions for elongational flow, using Eq. 19.6-9 as a starting point. The flow pattern under consideration is $v_x = -\frac{1}{2}\dot{\varepsilon}(t)x$, $v_y = -\frac{1}{2}\dot{\varepsilon}(t)y$, $v_z = \dot{\varepsilon}(t)z$, for which

$$\dot{\gamma}(t) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \dot{\varepsilon}(t), \qquad \gamma^{[0]} = \begin{pmatrix} \Lambda - 1 & 0 & 0 \\ 0 & \Lambda - 1 & 0 \\ 0 & 0 & \Lambda^{-2} - 1 \end{pmatrix} \quad (19.8\text{-}1)$$

where $\Lambda(t, t') = \lambda_z(t, t') = \exp \int_{t'}^{t} \dot{\varepsilon}(t'')dt''$ is the "elongation ratio" (see Appendix C). Then the components of the tensors $\mathbf{A}^{(2)}$ and $\mathbf{B}^{(2)} = \frac{1}{2}\{\dot{\gamma} : \mathbf{A}^{(4)}\}$ needed for getting the elongational

[4] One attempt to do this was that of Y.-H. Lin, *J. Rheol.*, **28**, 1-22 (1984), who used the Doi Edwards theory ($\varepsilon = 0$). For $\varepsilon \neq 0$ more satisfactory results are obtained, as may be seen in J. D. Schieber, C. F. Curtiss, and R. B. Bird, *Ind. Eng. Chem. Fundam.*, **25**, 471 475 (1986), J. D. Schieber, Univ. of Wisc. Rheology Research Center Reports Nos. 107 and 108 (1986).

[1] R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102 1106 (1982).

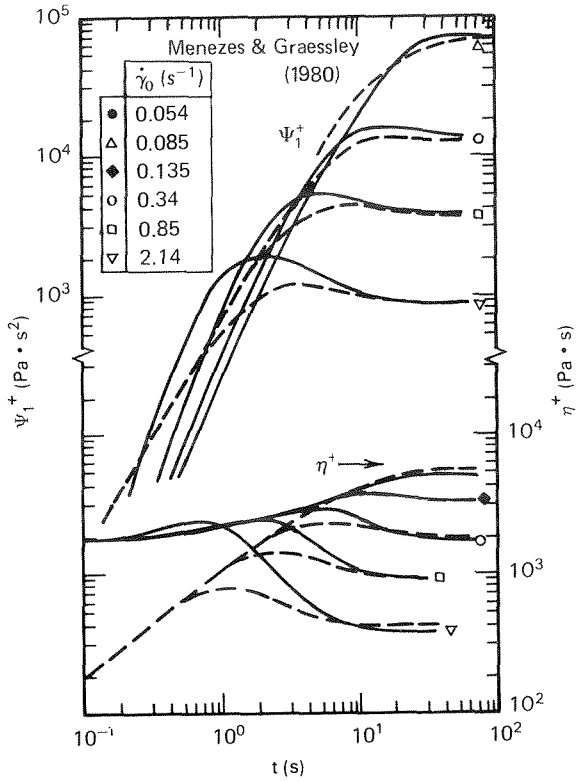


FIGURE 19.7-9. Data of E. V. Menezes and W. W. Graessley [*Rheol. Acta*, **19**, 38–50 (1980)] for η^+ and Ψ_1^+ at inception of steady shear flow (dashed lines) with the theoretical curves obtained from the kinetic theory (solid lines). The liquid used is the same as that described in the caption to Fig. 19.7-8. The theoretical curves for η^+ were calculated for $\lambda = 150$s, $\varepsilon = 0.5$, and for Ψ_1^+ with $\lambda = 190$s, $\varepsilon = 0.5$. Reproduced from H. H. Saab, R. B. Bird, and C. F. Curtiss, *J. Chem. Phys.*, **77**, 4758–4766 (1982).

viscosity may be found from Eqs. 19.6-10 and 11 to be

$$A_{zz}^{(2)} - A_{xx}^{(2)} = \frac{3}{2}\frac{\Lambda^3}{\Lambda^3 - 1}\left(1 - \frac{\arctan\sqrt{\Lambda^3 - 1}}{\sqrt{\Lambda^3 - 1}}\right) - \frac{1}{2}, \qquad \Lambda > 1 \tag{19.8-2}$$

$$A_{zz}^{(2)} - A_{xx}^{(2)} = \frac{3}{2}\frac{\Lambda^3}{1 - \Lambda^3}\left(\frac{\operatorname{arctanh}\sqrt{1 - \Lambda^3}}{\sqrt{1 - \Lambda^3}} - 1\right) - \frac{1}{2}, \qquad \Lambda < 1 \tag{19.8-3}$$

$$\frac{B_{zz}^{(2)} - B_{xx}^{(2)}}{\lambda\dot{\varepsilon}} = \frac{1}{8(\Lambda^3 - 1)^2}\left[8\Lambda^6 + 17\Lambda^3 + 2 - (15\Lambda^6 + 12\Lambda^3)\frac{\arctan\sqrt{\Lambda^3 - 1}}{\sqrt{\Lambda^3 - 1}}\right], \qquad \Lambda > 1 \tag{19.8-4}$$

$$\frac{B_{zz}^{(2)} - B_{xx}^{(2)}}{\lambda\dot{\varepsilon}} = \frac{1}{8(1 - \Lambda^3)^2}\left[8\Lambda^6 + 17\Lambda^3 + 2 - (15\Lambda^6 + 12\Lambda^3)\frac{\operatorname{arctanh}\sqrt{1 - \Lambda^3}}{\sqrt{1 - \Lambda^3}}\right], \qquad \Lambda < 1 \tag{19.8-5}$$

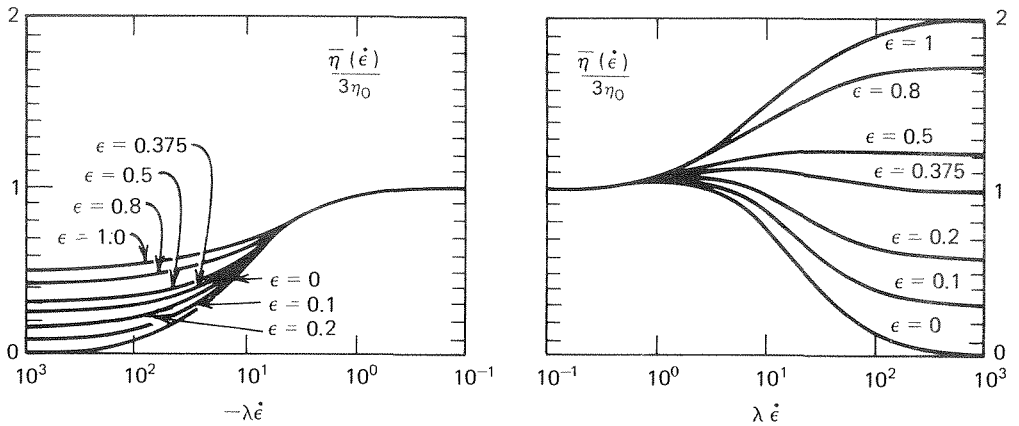


FIGURE 19.8-1. Elongational viscosity as a function of elongation rate $\dot{\varepsilon}$ for various values of the link tension coefficient ε. The time constant λ is $N^{3+\beta}\zeta a^2/2kT$. For small values of $|\lambda\dot{\varepsilon}|$, Eq. 19.6-16 can be used. Reprinted with permission from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1106 (1982). Copyright (1982) American Chemical Society.

With these quantities Eq. 19.6-9 may be used to get the normal stress differences in any time-dependent elongational flow.

Specifically for *steady elongational flow* Eq. 19.6-9 (written for a monodisperse fluid) can be integrated numerically. Then $\tau_{zz} - \tau_{xx}$, and hence $\bar{\eta}(\dot{\varepsilon})$, can be found. Figure 19.8-1 shows the behavior of $\bar{\eta}(\dot{\varepsilon})$ both for $\dot{\varepsilon} > 0$ (fiber stretching) and $\dot{\varepsilon} < 0$ (sheet stretching). Note that there is a nonzero slope at $\dot{\varepsilon} = 0$ and that the link tension coefficient ε has a substantial effect on the curves. For $\varepsilon = 3/8$ the elongational viscosity is very nearly constant for $\dot{\varepsilon} > 0$.

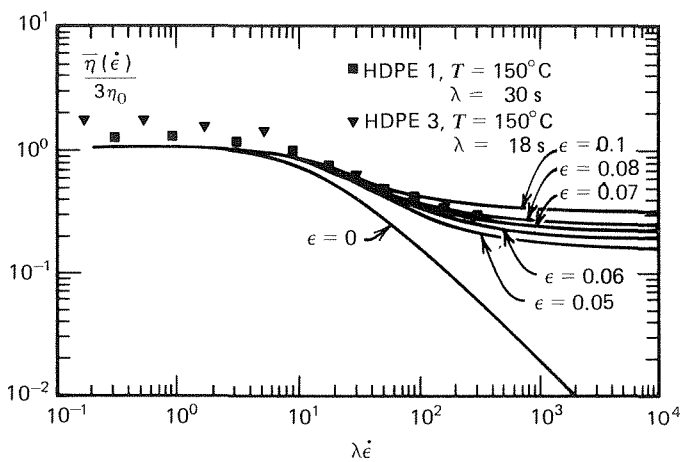


FIGURE 19.8-2. Comparison of experimental steady elongational viscosity data for high-density polyethylene melts with the calculated curves in Fig. 19.8-1; $\varepsilon = 0$ corresponds to the Doi–Edwards theory: (■) data of H. M. Laun [in G. Astarita, G. Marrucci, and L. Nicolais, eds., *Rheology*, Vol. 2, Plenum, New York (1980), pp. 419–424]; (▼) data of H. Münstedt and H. M. Laun [*Rheol. Acta*, **20**, 211–221 (1981)]. Note that in plotting the experimental values of $\bar{\eta}(\dot{\varepsilon})/3\eta_0$, the quantity η_0 is the zero-shear-rate viscosity, determined experimentally. Reprinted with permission from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1106 (1982). Copyright (1982) American Chemical Society.

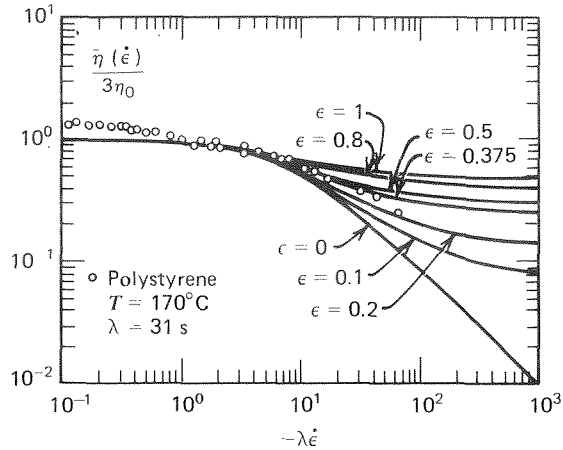


FIGURE 19.8-3. Comparison of the biaxial extension data for a polystyrene melt (Hostyren *N* 4000 V) of J. A. van Aken and H. Janeschitz-Kriegl [*Rheol. Acta*, **19**, 744–754 (1980); **21**, 388–393 (1982)] with the $\dot{\epsilon} < 0$ part of the $\bar{\eta}(\dot{\epsilon})$ curves in Fig. 19.8-1. The data have been temperature shifted to 170°C. In plotting the experimental values of $\bar{\eta}(\dot{\epsilon})/3\eta_0$, the quantity η_0 is the zero-shear-rate viscosity, determined experimentally. Reprinted with permission from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1106 (1982). Copyright (1982) American Chemical Society.

In Fig. 19.8-2 experimental data for $\bar{\eta}(\dot{\epsilon})$ with $\dot{\epsilon} > 0$ for polyethylene melts are shown. These are linear polyethylenes; unfortunately they are highly polydisperse, and this fact makes the data comparison of questionable value. Values of λ and ε ($= 0.08$) were chosen by fitting the experimental data. In Fig. 19.8-3 values of $\bar{\eta}(\dot{\epsilon})$ for $\dot{\epsilon} < 0$ inferred from birefringence data on polystyrene melts in biaxial extension are shown. Figures 19.8-2 and 3 by no means constitute a complete experimental test of the theory; however it can at least be seen that the theoretical curves exhibit the correct trends (except for $\varepsilon = 0$).

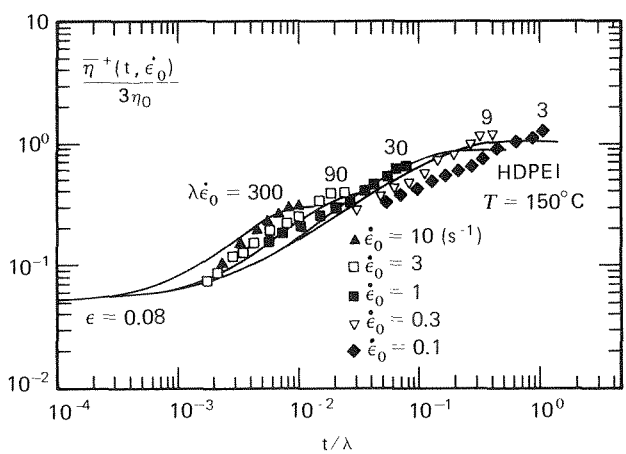


FIGURE 19.8-4. Comparison of experimental elongational growth viscosity with calculated curves based on Eqs. 19.6-9, and 19.8-2 to 5. The experimental data are those of H. M. Laun [in G. Astarita, G. Marrucci, and L. Nicolais, eds., *Rheology*, Plenum, New York (1980), Vol. 2, pp. 419–424]. The combination of λ and ε (30 s, 0.08) that gives the best fit with the steady elongational viscosity is used. Reprinted with permission from R. B. Bird, H. H. Saab, and C. F. Curtiss, *J. Phys. Chem.*, **86**, 1102–1106 (1982). Copyright (1982) American Chemical Society.

One additional test, also incomplete, is the comparison of elongational stress growth data with the theoretical curves shown in Fig. 19.8-4. Here the parameters $\lambda = 30$ s and $\varepsilon = 0.08$ were determined from steady elongational data, and no additional parameters were used in making the data comparison in the figure.

We conclude this section by reminding the reader that the experiments for measuring $\bar{\eta}$ and $\bar{\eta}^+$ are exceedingly difficult to perform. For testing the theory, data on monodisperse systems would be highly desirable; also more theoretical calculations taking into account the polydispersity effects, with Eq. 19.6-9, should be performed.[2]

PROBLEMS

19C.1 The Single-Link Distribution Function and the Constitutive Equation for $\varepsilon' = 0$.

a. Obtain the expansion in Eq. 19.5-17 from the expression for $f(\boldsymbol{u}, \sigma, t)$ in Eq. 19.5-15.
b. Verify that Eq. 19.5-21 simplifies to the lowest order terms in Eq. 19.5-17 when ε' is set equal to zero.
c. Substitute Eq. 19.5-17 for $f(\boldsymbol{u}, \sigma, t)$ into Eq. 19.4-18 and obtain the retarded motion expansion in Eq. 19.6-12.

19D.1 Retarded Motion Expansion

Show that the sums over n in Eqs. 19.6-21 and 22 are given by

$$\sum_{n,\text{odd}} \frac{1}{n^4} = \frac{\pi^4}{96} \tag{19D.1-1}$$

$$\sum_{n,\text{odd}} \frac{\lambda_n}{n^4} = \frac{\pi^4 \lambda_\alpha}{4(1-\varepsilon')x^5}\left[\frac{\sinh x}{1+\cosh x} - \frac{1}{2}x + \frac{1}{24}x^3\right] \tag{19D.1-2}$$

where $x = [6\varepsilon' N_\alpha^2/(1-\varepsilon')]^{1/2}$.

[2] J. D. Schieber, Univ. of Wisconsin Rheology Research Center Report No. 108 (1986).

PART VIII

ELEMENTARY KINETIC THEORY FOR NETWORK MODELS

In Chapter 19 we presented the "reptation" theories for concentrated solutions and melts. In these theories one focuses on a single macromolecule that is constrained to move in a confined region because of the other macromolecules in the immediate neighborhood. The interaction of the macromolecule with its neighbors is described in terms of an empirical relation similar to Stokes' law, and reptation is described by nonisotropic Brownian motion.

In Chapter 20 an alternative approach to concentrated solutions and melts is set forth. A polymeric liquid can be regarded as a sort of "liquefied" rubber, in which the permanent chemical junctions in rubber are replaced by temporary physical junctions in the liquid; these junctions are introduced to describe the interaction of a macromolecule with its neighbors. Then it is necessary to include some empirical statements about junction motion and about the rates at which the junctions are created and destroyed.

Hence in both the network and reptation approach to concentrated systems, it is necessary to introduce some empiricisms. The network theories have the advantage of simplicity; one can get from the model to the final constitutive equations rather quickly. The reptation theories have the advantage that they can be obtained as a special case of a general phase-space kinetic theory. Both approaches have advanced our understanding of constitutive equations and rheological responses.

CHAPTER 20

NETWORK THEORIES FOR POLYMER MELTS AND CONCENTRATED SOLUTIONS[1]

Most of this volume has focused on molecular theories of dilute solutions in which polymer–polymer interactions are neglected. All dilute solution theories predict that the viscosity should depend linearly on the polymer concentration. However, we know that the range in which the dilute solution assumption applies is limited to very small concentrations. At larger concentrations the zero-shear-rate viscosity increases much faster than linearly with concentration, indicating strong polymer–polymer interactions (see Eq. 3.6-15). The approach to the molecular description of concentrated solutions and melts taken in the previous chapter was to construct a systematic application of the general phase-space kinetic theory which included the interaction between two or more polymer molecules. There the polymer–polymer interactions were accounted for primarily by taking into account the constraints imposed on the motion of a polymer molecule resulting from the close proximity of the neighboring molecules. This is accomplished by requiring that Brownian motion be highly anisotropic ("reptation") and that the hydrodynamic drag on the beads also be anisotropic.

Here we take a different approach in modeling the interactions of the polymer molecules which builds on the classical network theories of rubber elasticity. In the network theories of macromolecular solids, chemical crosslinks are described as points, or junctions, at which connecting portions of molecules are forced to move together for all times. In adapting this theory to liquids we assume the junctions are not permanent, but are continually being created and destroyed. However, we apply the central idea from the solid theory and assert that polymer–polymer interactions are described by the temporary cooperative movement of molecular segments joined by these transient "crosslinks."

The theoretical development of the network theory is much simpler than that for the phase-space treatment in Chapter 19. The primary deficiency of the network approach taken here is that it does not provide the molecular description of the central process of junction formation and destruction. This means that the relaxation spectrum is not given explicitly by the theory in terms of molecular model parameters as was the case for the

[1] The authors are greatly indebted to Professor Arthur S. Lodge of the University of Wisconsin–Madison in connection with the preparation of this chapter. We have made considerable use of his research papers, unpublished lecture notes, and informal comments. The approach taken in this chapter is patterned after A. S. Lodge, R. C. Armstrong, M. H. Wagner, and H. H. Winter, *Pure Appl. Chem.*, **54**, 1349–1359 (1982).

For other general treatments of network theories see M. Yamamoto, *J. Phys. Soc. Japan*, **11**, 413–421 (1956); **12**, 1148–1158 (1957); **13**, 1200–1211 (1958); F. W. Wiegel, *Physica*, **42**, 156–164 (1969); F. W. Wiegel and F. Th. de Bats, *Physica*, **43**, 33–44 (1969).

phase-space theory. However, the constitutive equations obtained from the network theory are much simpler to use than the corresponding Chapter 19 results.

In the first section we introduce the terminology that is needed to describe the network models. Then in the next section we develop a balance equation for network segments, which allows us to describe the "configuration" of a polymer network undergoing flow. Then in §20.3, we derive an expression for the stress tensor in terms of the configuration of the network. It should be noted that §§20.2 and 3 are very similar to §§13.2 and 3 as to scope and general procedures. §§20.4 and 5 specialize the general network theory results to several models that have been studied extensively in the literature and to some new models which appear to be particularly promising.

§20.1 DESCRIPTIONS OF NETWORK MODELS

The central approximation in all network theories of macromolecular materials is that polymer–polymer interactions are localized at *junctions*. A junction is a strong local attraction between isolated points along two different polymer chains at which the interacting points are constrained to coincide. In macromolecular solids, the junction is the point at which there is a permanent *chemical* crosslink; in macromolecular fluids, junctions are temporary *physical* entanglements of various complexities and lifetimes. The macromolecular chain joining two successive junctions is called a network *segment*. A macromolecular chain which is connected to a junction at only one point is called a *loose end*, and a macromolecule not attached to the network is known as a *stray chain*. The totality of network segments is referred to as a molecular *network*, and *connectivity* is used to describe the organization of junctions tying the network together. A solid, crosslinked polymer is said to have constant connectivity, whereas a concentrated polymer solution or melt is said to have time-dependent connectivity.

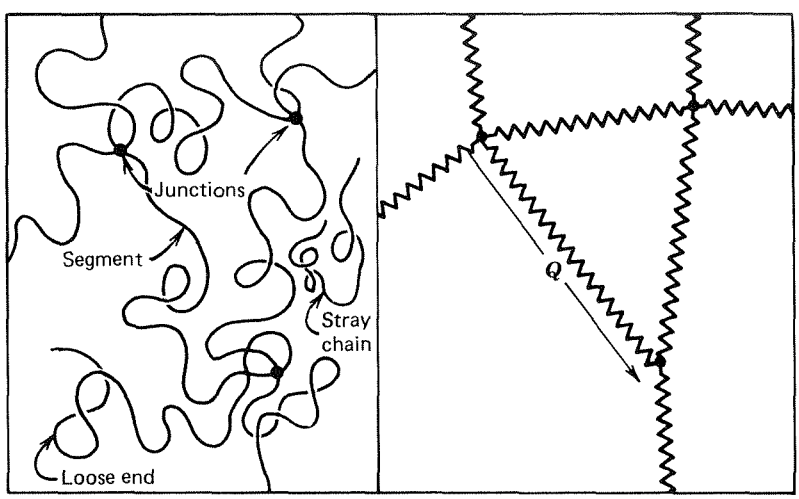


FIGURE 20.1-1. Small element of a macromolecular network. In (*a*) the "actual" molecular structure is shown; a segment, several junctions, a loose end, and a stray chain are labeled. The junctions could be either permanent crosslinks or temporary physical entanglements; the segments are composed of parts of macromolecules undergoing thermal motions. The statistical treatment of the system of part (*a*) replaces it by the classical system with Hookean springs shown in part (*b*). Part (*b*) also shows the segment vector $\boldsymbol{Q}$. Note that the loose end and stray chain of (*a*) are omitted from (*b*).

The definitions given above are illustrated in Fig. 20.1-1 which shows the idealization made in treating polymeric materials as networks. All polymeric chains that are not network segments, that is, all loose ends and stray chains are entirely neglected in the network theory. For example, the loose end and stray chain in Fig. 20.1-1(a) have no representation in the idealized network of Fig. 20.1-1(b).

The following six assumptions are common to network theories for both solids and liquids:

i. A concentrated polymer solution, polymer melt or crosslinked polymeric solid can be represented by a molecular network with polymer-polymer interactions occurring only as strong local interactions at isolated points along the chains. This network is *coherent* in the sense that each network point is connected by at least two continuous network paths to the bounding surface of a physically infinitesimal material element. This network alone is responsible for the rheological behavior of the material; loose ends and stray chains are neglected.

ii. The polymeric material is assumed to be incompressible, that is, we consider only deformations at constant volume.[2]

iii. The network junction points move *affinely*,[3] that is, as if they were material particles in an equivalent macroscopic continuum. The thermal motions of the junctions are neglected.

iv. The phase space distribution function for each segment is equilibrated at all times.

v. The polymeric material is subjected to either a homogeneous deformation or a homogeneous flow.

vi. Each network segment can be modeled as a *Gaussian* chain.[4] We take the segments to be freely jointed, bead-rod chains, in which the end-to-end distance of any segment is small compared with $a(N-1)$, where $N-1$ is the number of rods in the segment and a is the length of each rod. Together with assumption (iv) above this means that each segment can be modeled as a Hookean spring with spring constant $H_N = 3kT/(N-1)a^2$ (cf. Eq. 11.3-20).

Except as noted above, these assumptions may not be removed without fundamental changes in the theory. The network theory for solids rests essentially upon these assumptions with only very minor additional assumptions. The strikingly good agreement[5] between the predictions of the network theory for solids and experimental observations indicates that assumptions (i) to (vi) are valid for materials such as crosslinked rubber. It is not yet clear whether these same assumptions are equally valid for polymeric fluids.

For fluids we make the following additional assumptions:

vii. Segments are lost and created during flow. At any one time, the network will therefore consist of segments with a distribution of ages. The stress is assumed to be the sum of contributions from all segments existing at the present time, these having been created at various past times.

[2] A. S. Lodge, *Proc. VII International Cong. Rheology*, C. Klason and J. Kubát, eds. (Gothenburg), 79–84 (1976), has extended the network theory to allow for compressibility.

[3] The implications of nonaffine junction motion are explored in §20.5. An alternative to assuming that each junction point moves affinely is given in H. M. James, *J. Chem. Phys.*, **15**, 651–668 (1947) where the concept of "boundary points" is introduced. These are points of the network segments where the segments intersect the surface of a volume element enclosing the system under investigation. Instead of the affine junction motion assumption, James merely assumes that the boundary points also move affinely; he then calculated the motion of the junctions, thereby formulating a theory somewhat more general than the one considered here. However, this extra generality in the formulation does not lead to a more general constitutive equation.

[4] The removal of the Gaussian assumption has been shown by A. S. Lodge, *Rheol. Acta*, **7**, 379–392 (1968) to give no substantial improvement in the constitutive equation for polymeric liquids.

[5] L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed., Oxford University Press, London (1975).

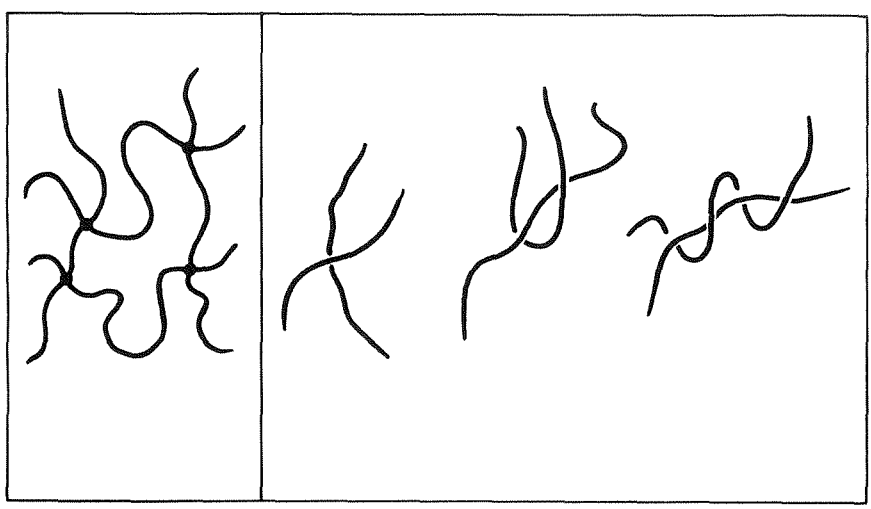
viii. It is assumed that the distribution function for the network segments at the moment of creation is identical to the equilibrium distribution function for a freely jointed, bead-rod chain with no constraints on the end points. The Gaussian distribution for newly created segments is sometimes referred to as the "Wall distribution."

ix. Segments may be characterized by a single positive integer i that indicates the "complexity" of the segment.

For fluids not much is known about the mechanisms of formation and loss of the temporary entanglements. Thus the theory focuses instead on the segments. It is expected that many different kinds of physical entanglements can be formed and that these will exhibit a wide range of degree of permanence. The idea of *segment complexity* is used to describe the relative permanence of different segments. The origin of segment complexity is illustrated in Fig. 20.1-2 where segments formed as a result of temporary physical entanglements are contrasted with those formed between permanent chemical crosslinks. For the solid, segments are all of the same complexity, since they are all permanent. For the fluid, the complexity of a segment is tied to the topology of the "knot" that is formed by Brownian motion and which constitutes the junction. As shown in Fig. 20.1-1(b) the end-to-end vector for a typical segment is given by $\boldsymbol{Q}$.

We will henceforth refer to segments of type i which are composed of $N-1$ equivalent random links as iN-segments. We now introduce a distribution function $\Psi_{iN}(\boldsymbol{Q}, t)$ which is defined such that

$$\Psi_{iN}(\boldsymbol{Q}, t)d\boldsymbol{Q} = \text{number of segments per unit volume at time } t \text{ that have complexity } i \text{ and } N-1 \text{ equivalent random links and that have end-to-end vector in the range } d\boldsymbol{Q} \text{ about } \boldsymbol{Q}. \tag{20.1-1}$$



(*a*) (*b*)

FIGURE 20.1-2. Junctions in (*a*) macromolecular solids and (*b*) macromolecular network fluids. The junctions in (*a*) are chemical crosslinks and result in permanent segments. The junctions in (*b*) are physical entanglements and result in temporary segments. As illustrated in (*b*) many different types of entanglements can be formed by Brownian motion and these will differ in longevity. The variability in junction durability leads to segments of varying complexity.

The distribution function is normalized as follows:

$$\int \Psi_{iN}(\boldsymbol{Q}, t)d\boldsymbol{Q} = n_{iN} \tag{20.1-2}$$

in which n_{iN} is the number density of iN-segments. We assume n_{iN} is independent of position. The number density of all segments at any time is

$$n = \sum_N n_N = \sum_i \sum_N n_{iN} \tag{20.1-3}$$

where n_N is the number density of segments of all complexities that have $N - 1$ equivalent random links. It is also sometimes convenient to assume that Ψ_{iN} can be factored as follows:

$$\Psi_{iN}(\boldsymbol{Q}, t) = n_{iN}\psi_N(\boldsymbol{Q}, t) \tag{20.1-4}$$

where

$$\psi_N(\boldsymbol{Q}, t)d\boldsymbol{Q} = \text{probability that a segment with } N \text{ equivalent random links has an end-to-end vector between } \boldsymbol{Q} \text{ and } \boldsymbol{Q} + d\boldsymbol{Q} \tag{20.1-5}$$

depends only on N and not on the complexity of the segment. We require

$$\int \psi_N(\boldsymbol{Q}, t)d\boldsymbol{Q} = 1 \tag{20.1-6}$$

to be consistent with the normalization of Ψ_{iN}.

§20.2 CONVECTION EQUATION FOR NETWORK SEGMENTS

In this section we derive an equation that determines the distribution function for the segments. This equation is derived by a method similar to that used for obtaining the diffusion equation for elastic dumbbell models in §13.2. For network models, the equation of motion is much simpler than that for the elastic dumbbells, but the continuity equation for the network is slightly more complicated because of the creation and destruction terms for the segments.

a. The Equation of Motion for Network Segments

Since it is assumed that the junction points move affinely, it follows that the segment vector $\boldsymbol{Q}$ which joins two junctions must also move affinely. This gives the equation of motion for a segment

$$\dot{\boldsymbol{Q}} = [\boldsymbol{\kappa} \cdot \boldsymbol{Q}] \tag{20.2-1}$$

where $\dot{\boldsymbol{Q}} = d\boldsymbol{Q}/dt$. Equation 20.2-1 can be integrated to give an explicit expression for $\boldsymbol{Q}(t)$,

$$\boldsymbol{Q} = [\mathbf{E} \cdot \boldsymbol{Q}'] \tag{20.2-2}$$

in which we have used the initial condition that at $t = t'$, $\boldsymbol{Q} = \boldsymbol{Q}(t') = \boldsymbol{Q}'$. $\mathbf{E}(t, t')$ is the deformation gradient between times t' and t (cf. Eq. D.1-6, Eq. 9.2-5).

b. The Equation of Continuity for $\Psi_{iN}(\boldsymbol{Q}, t)$

The configuration of a single segment is given by specifying the three Cartesian coordinates X, Y, Z of its end-to-end vector $\boldsymbol{Q}$. For a concentrated polymer solution or melt containing many segments, the time rate of change of iN-segments in the volume $\Delta X \Delta Y \Delta Z$ in configuration space is

$$\frac{\partial}{\partial t} \Psi_{iN}(\boldsymbol{Q}, t) \Delta X \Delta Y \Delta Z \tag{20.2-3}$$

The net rate at which segments enter the given configuration volume because of the flow of the liquid is

$$(\dot{X}\Psi_{iN})|_X \Delta Y \Delta Z - (\dot{X}\Psi_{iN})|_{X+\Delta X} \Delta Y \Delta Z \tag{20.2-4}$$

$$+2 \text{ additional pairs of terms for the } Y \text{ and } Z \text{ directions.}$$

Finally, it is possible that segments are created and destroyed by the flow, because of the temporary nature of the junctions in liquid polymers. Let the number per unit volume of iN-segments of length Q that are created per unit time at time t be denoted by $L_{iN}(Q, t)$. Next let us denote the probability per unit time that an iN-segment will be destroyed as $\lambda_{iN}^{-1}(Q, t)$. Then for the configuration volume $\Delta X \Delta Y \Delta Z$ the rate at which iN-segments are created minus the rate of destruction is

$$\left(L_{iN}(Q, t) - \frac{\Psi_{iN}}{\lambda_{iN}(Q, t)} \right) \Delta X \Delta Y \Delta Z \tag{20.2-5}$$

Combining Eqs. 20.2-3 through 5 gives in the limit as $\Delta X \Delta Y \Delta Z$ goes to zero a continuity equation for Ψ_{iN}

$$\frac{\partial \Psi_{iN}}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot [\dot{\boldsymbol{Q}} \Psi_{iN}] \right) + L_{iN}(Q, t) - \frac{\Psi_{iN}}{\lambda_{iN}(Q, t)} \tag{20.2-6}$$

This result differs from Eq. 13.2-12, obtained for dilute solutions of elastic dumbbells, in that creation and destruction terms are included. This latter distinction makes it more convenient to work in terms of Ψ_{iN} rather than the probability density ψ_N, which corresponds to ψ used in Chapter 13. Also the velocity space average $[\![\dot{\boldsymbol{Q}}]\!]$ in the elastic dumbbell theory is replaced by $\dot{\boldsymbol{Q}}$ in the network theory, since no account is taken of Brownian motion in the equation of motion for the segment vector.

c. The "Convection" Equation for $\Psi_{iN}(\boldsymbol{Q}, t)$

If we use Eq. 20.2-1 to replace $\dot{\boldsymbol{Q}}$ in Eq. 20.2-6 we obtain the *convection equation*

$$\boxed{\frac{\partial \Psi_{iN}}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{Q}]\Psi_{iN}\right) + L_{iN}(Q, t) - \frac{\Psi_{iN}}{\lambda_{iN}(Q, t)}} \tag{20.2-7}$$

This is a first-order partial differential equation that describes how the segment distribution function Ψ_{iN} changes in time when the flow field is described by $\boldsymbol{\kappa}(t)$. Note that the corresponding "diffusion equation" in Eq. 13.2-13 is of second order.

By multiplying Eq. 20.2-7 by any function B of the segment vector $\boldsymbol{Q}$ and then integrating over all configuration space, we obtain an *equation of change* for $\langle B \rangle_{iN}$:

$$\frac{d}{dt}\langle B \rangle_{iN} = \boldsymbol{\kappa} : \left\langle \boldsymbol{Q}\frac{\partial B}{\partial \boldsymbol{Q}} \right\rangle_{iN} + \int L_{iN} B \, d\boldsymbol{Q} - \left\langle \frac{B}{\lambda_{iN}} \right\rangle_{iN} \tag{20.2-8}$$

where $\langle B \rangle_{iN} = \int B\Psi_{iN}\, d\boldsymbol{Q} = n_{iN} \int B\psi_N \, d\boldsymbol{Q}$ (*caution*: $\langle B \rangle_{iN}$ differs by a factor n_{iN} from the $\langle B \rangle$ defined in §12.4 and Eq. 13.1-5). The details of the integration follow closely those given in Example 13.2-1. If we generalize to the particular choice where **B** is a second-order tensor $\boldsymbol{QQ}$ then we find (see Example 20.2-1):

$$\langle \boldsymbol{QQ} \rangle_{iN(1)} = \bar{L}_{iN}(t)\boldsymbol{\delta} - \left\langle \frac{\boldsymbol{QQ}}{\lambda_{iN}} \right\rangle_{iN} \tag{20.2-9}$$

$$\bar{L}_{iN}(t) = \frac{4\pi}{3}\int_0^\infty L_{iN}(Q, t) Q^4 \, dQ \tag{20.2-10}$$

The derivation of Eq. 20.2-9 is given in Example 20.2-1 where this result is specialized to systems in which the probability of destruction λ_{iN} depends on time but not on the segment length Q. In Eq. 20.2-9 the subscript $_{(1)}$ notation denotes the convected time derivative defined in Eq. D.2-4a (note that the flow is homogeneous, so that the $\{\boldsymbol{v} \cdot \nabla \langle \boldsymbol{QQ} \rangle_{iN}\}$ contribution to the convected derivative is zero). We note that at equilibrium the creation and loss terms balance one another so that

$$\bar{L}_{iN,\,\mathrm{eq}}\boldsymbol{\delta} = \left\langle \frac{\boldsymbol{QQ}}{\lambda_{iN}} \right\rangle_{iN,\,\mathrm{eq}} \tag{20.2-11}$$

This result is used later to evaluate the pressure contribution from iN-segments.

EXAMPLE 20.2-1 Time Rate of Change of $\langle \boldsymbol{QQ} \rangle_{iN}$

Derive Eq. 20.2-9 by beginning with Eq. 20.2-8 written for the tensor $\mathbf{B} = \boldsymbol{QQ}$. Specialize this result for a network model in which the segment destruction probability is independent of Q, that is, $\lambda_{iN} = \lambda_{iN}(t)$.

SOLUTION For $\mathbf{B} = \boldsymbol{QQ}$ the equation of change Eq. 20.2-8 is rewritten

$$\frac{d}{dt}\langle \boldsymbol{QQ}\rangle_{iN} = \left\{\boldsymbol{\kappa}:\left\langle \boldsymbol{Q}\frac{\partial}{\partial \boldsymbol{Q}}\boldsymbol{QQ}\right\rangle_{iN}\right\} + \int L_{iN}(Q,t)\boldsymbol{QQ}\,d\boldsymbol{Q} - \left\langle \frac{\boldsymbol{QQ}}{\bar{\lambda}_{iN}(Q,t)}\right\rangle_{iN}$$

$$= \{\boldsymbol{\kappa}\cdot\langle \boldsymbol{QQ}\rangle_{iN} + \langle \boldsymbol{QQ}\rangle_{iN}\cdot\boldsymbol{\kappa}^{\dagger}\} + \int L_{iN}(Q,t)Q^4\,dQ\int \boldsymbol{uu}\,d\boldsymbol{u} - \left\langle \frac{\boldsymbol{QQ}}{\bar{\lambda}_{iN}}\right\rangle_{iN} \tag{20.2-12}$$

where we have rewritten the integral involving the creation term in spherical coordinates (Q, θ, ϕ). The vector $\boldsymbol{u} = \boldsymbol{Q}/Q$ is a unit vector in the direction of $\boldsymbol{Q}$, and $d\boldsymbol{u}$ denotes $\sin\theta\,d\theta\,d\phi$, where θ and ϕ are the spherical polar angles describing the orientation of $\boldsymbol{Q}$. The integral over $\boldsymbol{u}$ is easily done (cf. Eq. E.7-4)

$$\int \boldsymbol{uu}\,d\boldsymbol{u} = \frac{4\pi}{3}\boldsymbol{\delta} \tag{20.2-13}$$

and when this is combined with the definition for $\bar{L}_{iN}$ in Eq. 20.2-10, Eq. 20.2-9 is obtained.

We now consider the simplification in Eq. 20.2-9 that results when the segment loss rate is independent of Q. In this limit λ_{iN} can be taken outside of the configuration space average to give the following differential equation for $\langle \boldsymbol{QQ}\rangle_{iN}$:

$$\langle \boldsymbol{QQ}\rangle_{iN(1)} + \frac{1}{\bar{\lambda}_{iN}(t)}\langle \boldsymbol{QQ}\rangle_{iN} = \bar{L}_{iN}(t)\boldsymbol{\delta} \tag{20.2-14}$$

By using the methods of Chapter 9 (cf. Example 9.4-1) it is straightforward to integrate this result to get an explicit formula for $\langle \boldsymbol{QQ}\rangle_{iN}$. To do this we follow Example 9.4-1 and note that Eq. 20.2-14 can be rewritten as

$$\boldsymbol{\alpha}_{[1]}(t,t') + \frac{1}{\bar{\lambda}_{iN}(t')}\boldsymbol{\alpha}_{[0]}(t,t') = -\bar{L}_{iN}(t')\mathbf{B}(t,t') \tag{20.2-15}$$

where each term is understood to be evaluated at $t' = t$. Here we have abbreviated $\langle \boldsymbol{QQ}\rangle_{iN}$ by $\boldsymbol{\alpha}$, and we have replaced the unit tensor by[1]

$$\boldsymbol{\delta} = \mathbf{E}\cdot\mathbf{E}^{\dagger}|_{t'=t} = \mathbf{B}(t,t')|_{t'=t} \tag{20.2-16}$$

in which $\mathbf{E}$ is the deformation gradient (Eq. D.1-6) and $\mathbf{B}$ is the Finger strain tensor (Eq. D.3-4). We next replace $\boldsymbol{\alpha}_{[1]}$ by $\partial\boldsymbol{\alpha}_{[0]}/\partial t'$, and this gives a first order differential equation for $\boldsymbol{\alpha}_{[0]}$ that can be solved to give

$$\langle \boldsymbol{QQ}\rangle_{iN} = \int_{-\infty}^{t} \bar{L}_{iN}(t')\exp\left(\int_{t}^{t'} \bar{\lambda}_{iN}^{-1}(t'')dt''\right)\mathbf{B}(t,t')dt' \tag{20.2-17}$$

Notice that the average value $\langle \boldsymbol{QQ}\rangle_{iN}$ depends on the history of the deformation weighted by the creation and loss rates for the segments.

[1] The unit tensor could also be written as $\mathbf{B}^{-1}(t,t)$. That this is not the proper substitution is best seen by writing Eq. 20.2-14 in a convected coordinate system by using the outermost columns of Tables 9.3-1 and 9.4-1. In making this transformation, $\boldsymbol{\alpha}$ is treated like $\boldsymbol{\tau}$ in Table 9.4-1. Since the $_{(1)}$ notation denotes the convected derivative of the contravariant components of the tensor $\boldsymbol{\alpha}$, the inverse of the convected metric $\hat{g}^{ij}$ must be introduced on the right side of the equation during the coordinate transformation. Following the integration with respect to t', transformation back to the space fixed coordinate system transforms $\hat{g}^{ij}(t')$ to $\mathbf{B}(t,t')$.

EXAMPLE 20.2-2 The Distribution Function for a Network Solid

Determine the distribution function $\psi_N(\boldsymbol{Q}, t)$ for a solid polymer in which the network junctions are permanent chemical bonds. Use this distribution function to determine $\langle \boldsymbol{QQ} \rangle_N$. Note that for solids the subscript i, designating the segment complexity, is dropped. Since all segments are permanent, there is only one type of complexity.

SOLUTION For a solid, the convection equation, Eq. 20.2-7 simplifies considerably since segments are not destroyed, so that $\lambda_N \to \infty$; also all junctions are presumed to have been simultaneously created at time t_0. In keeping with assumption **(viii)** we take the distribution function for the network segments at the instant of creation to be the same as that of a set of freely jointed bead-rod chains with no constraints on the end points (that is, Gaussian). Thus from Eq. 11.3-21

$$L_N(t) = n_N \psi_{N,\text{eq}}(\boldsymbol{Q}_0)\delta(t - t_0) \tag{20.2-18}$$

where

$$\psi_{N,\text{eq}}(\boldsymbol{Q}_0) = \left(\frac{H_N}{2\pi kT}\right)^{3/2} e^{-(H_N/2kT)(\boldsymbol{Q}_0 \cdot \boldsymbol{Q}_0)} \tag{20.2-19}$$

Then the convection equation is

$$\frac{\partial \psi_N}{\partial t} = -\left(\frac{\partial}{\partial \boldsymbol{Q}} \cdot [\boldsymbol{\kappa} \cdot \boldsymbol{Q}]\psi_N\right) + \psi_{N,\text{eq}}(\boldsymbol{Q}_0)\delta(t - t_0) \tag{20.2-20}$$

where we have divided by the constant number density n_N.

The solution to Eq. 20.2-20 for $t > t_0$ may be obtained by inspection by noting that

$$\psi_{N,\text{eq}}(\boldsymbol{Q}_0)d\boldsymbol{Q}_0 = \psi_N(\boldsymbol{Q}, t)d\boldsymbol{Q} \qquad (t > t_0) \tag{20.2-21}$$

since the distortion of the segment vectors is equivalent to a change of variables in the distribution function. Thus the distribution function is (cf. Eq. 12.3-4b)

$$\begin{aligned}\psi_N(\boldsymbol{Q}, t) &= \psi_{N,\text{eq}}(\boldsymbol{Q}_0)\left|\frac{\partial}{\partial \boldsymbol{Q}}\boldsymbol{Q}_0\right| \\ &= \psi_{N,\text{eq}}(\boldsymbol{Q}_0)\det \boldsymbol{\Delta}(t, t_0) \\ &= \left(\frac{H_N}{2\pi kT}\right)^{3/2} e^{-(H_N/2kT)(\mathbf{B}^{-1}:\boldsymbol{QQ})} \qquad (t > t_0)\end{aligned} \tag{20.2-22}$$

where $\boldsymbol{\Delta} = \mathbf{E}^{-1}$ arises in the Jacobian of the transformation because of Eq. 20.2-2 (with $t' = t_0$). Since the deformation is at constant volume $\det \boldsymbol{\Delta} = 1$. Also in replacing $\boldsymbol{Q}_0$ by $\boldsymbol{Q}$ we introduce the Cauchy strain tensor $\mathbf{B}^{-1} = \{\boldsymbol{\Delta}^\dagger \cdot \boldsymbol{\Delta}\}$. If we now consider $t \le t_0$ as well as $t > t_0$, the δ-function in Eq. 20.2-18 causes a Heaviside unit step H function to be introduced into ψ_N:

$$\psi_N(\boldsymbol{Q}, t) = \left(\frac{H_N}{2\pi kT}\right)^{3/2} e^{-(H_N/2kT)(\mathbf{B}^{-1}:\boldsymbol{QQ})} H(t - t_0) \tag{20.2-23}$$

That Eq. 20.2-23 satisfies the convection equation Eq. 20.2-20 is easy to verify by direct substitution (see Problem 20B.4).

We next use the distribution function Eq. 20.2-22 to calculate $\langle \boldsymbol{QQ} \rangle_N$ for $t > t_0$. This is given by

$$\begin{aligned}
\langle \boldsymbol{QQ} \rangle_N &= \int \boldsymbol{QQ}\, \Psi_N(\boldsymbol{Q}, t) d\boldsymbol{Q} \\
&= n_N \int \boldsymbol{QQ}\, \psi_N(\boldsymbol{Q}, t) d\boldsymbol{Q} \\
&= n_N \int [\mathbf{E} \cdot \boldsymbol{Q}_0][\mathbf{E} \cdot \boldsymbol{Q}_0] \psi_{N,\mathrm{eq}}(\boldsymbol{Q}_0) d\boldsymbol{Q}_0 \\
&= n_N \{ \mathbf{E} \cdot \int \boldsymbol{Q}_0 \boldsymbol{Q}_0 \left(\frac{H_N}{2\pi kT} \right)^{3/2} \exp(-(H_N/2kT)(\boldsymbol{Q}_0 \cdot \boldsymbol{Q}_0)) d\boldsymbol{Q}_0 \cdot \mathbf{E}^\dagger \} \\
&= n_N (\tfrac{1}{3}(N-1)a^2) \mathbf{B}(t, t_0) \qquad (t \geq t_0)
\end{aligned} \tag{20.2-24}$$

Note that in computing this average it is simpler to change the integration variable to the undeformed state $\boldsymbol{Q}_0$, where the distribution function is that for equilibrium. This result could also be obtained by combining Eqs. 20.2-18 and 19 for $L_N(t)$ with Eq. 20.2-17 (with $\lambda_N^{-1} = 0$).

§20.3 THE EXPRESSION FOR THE STRESS TENSOR

According to the assumptions given in §20.1, the stress is produced solely by the network structure. In this section we use a simple physical argument similar to that given in §13.3 to deduce the expression for the stress tensor.

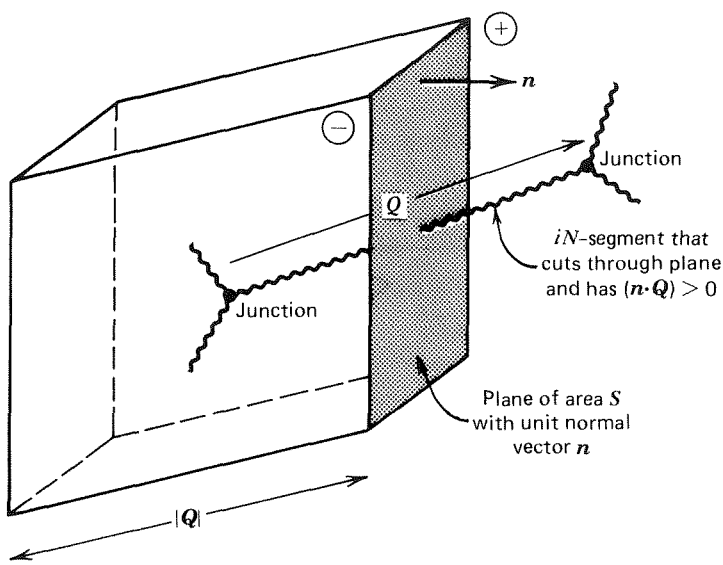


FIGURE 20.3-1. Physical argument used in calculating the contribution π_{iN} of segments of type iN to the stress tensor. The force per unit area exerted by − material ("behind" $\boldsymbol{n}$) on + material ("in front" of $\boldsymbol{n}$) is denoted by $[\boldsymbol{n} \cdot \boldsymbol{\pi}_{iN}]$. The tension in the strand $\boldsymbol{F}_N^{(c)} = F_N^{(c)}\, \boldsymbol{Q}/Q$ depends on the number of equivalent random links $(N-1)$ in the chain.

Consider an arbitrary plane of area S moving with the local material velocity that divides the material into two regions (Fig. 20.3-1). The only mechanism for the material on one side of this plane to transmit a force to the material on the other side is through the tension in the network segments that pass through the plane. To calculate this force we first note that the number of iN-network strands in the configuration range $\boldsymbol{Q}$ to $\boldsymbol{Q} + d\boldsymbol{Q}$ that intersect the plane is given by

$$|\boldsymbol{n} \cdot \boldsymbol{Q}| S \Psi_{iN}(\boldsymbol{Q}, t) d\boldsymbol{Q} \tag{20.3-1}$$

where $\boldsymbol{n}$ is the unit normal vector giving the orientation of the plane. The tension in the strand is $\boldsymbol{F}_N^{(c)} = F_N^{(c)} \boldsymbol{Q}/Q$ so that the force exerted by the material on the negative side of the plane on the positive side is

$$-\boldsymbol{F}_N^{(c)}, \quad \text{for} \quad (\boldsymbol{n} \cdot \boldsymbol{Q}) \geq 0; \qquad \boldsymbol{F}_N^{(c)}, \quad \text{for} \quad (\boldsymbol{n} \cdot \boldsymbol{Q}) < 0 \tag{20.3-2}$$

To get the total force per unit area of $-$ material on $+$ material due to iN-segments we take the product of the number of strands and the force from each strand divided by the area S and integrate over all configurations:

$$\begin{aligned}
[\boldsymbol{n} \cdot \boldsymbol{\pi}_{iN}] &= \int_{(\boldsymbol{n} \cdot \boldsymbol{Q}) > 0} (\boldsymbol{n} \cdot \boldsymbol{Q})(-\boldsymbol{F}_N^{(c)}) \Psi_{iN}(\boldsymbol{Q}, t) d\boldsymbol{Q} \\
&\quad + \int_{(\boldsymbol{n} \cdot \boldsymbol{Q}) < 0} (-\boldsymbol{n} \cdot \boldsymbol{Q})(\boldsymbol{F}_N^{(c)}) \Psi_{iN}(\boldsymbol{Q}, t) d\boldsymbol{Q} \\
&= -[\boldsymbol{n} \cdot \int \boldsymbol{Q} \boldsymbol{F}_N^{(c)} \Psi_{iN}(\boldsymbol{Q}, t) d\boldsymbol{Q}] \\
&= -[\boldsymbol{n} \cdot \langle \boldsymbol{Q} \boldsymbol{F}_N^{(c)} \rangle_{iN}]
\end{aligned} \tag{20.3-3}$$

Therefore the contribution to the total stress tensor from iN-segments is identified as

$$\begin{aligned}
\boldsymbol{\pi}_{iN} &= -\langle \boldsymbol{Q} \boldsymbol{F}_N^{(c)} \rangle_{iN} \\
&= -H_N \langle \boldsymbol{Q} \boldsymbol{Q} \rangle_{iN}
\end{aligned} \tag{20.3-4}$$

and the total stress tensor is

$$\boxed{\boldsymbol{\pi} = \sum_i \sum_N \boldsymbol{\pi}_{iN} = -\sum_i \sum_N H_N \langle \boldsymbol{Q} \boldsymbol{Q} \rangle_{iN}} \tag{20.3-5}$$

This expression for the total stress tensor is very similar to the intramolecular force contribution to the total stress tensor for elastic dumbbells (Eq. 13.3-5) and bead-spring chain models (Eq. 15.2-1).

To get the extra stress we write the total stress tensor as the sum of two parts:

$$\boldsymbol{\pi}_{iN} = p_{iN} \boldsymbol{\delta} + \boldsymbol{\tau}_{iN} \tag{20.3-6}$$

By definition $\boldsymbol{\tau}_{iN}$ is zero at equilibrium so that pressure p_{iN} is given by

$$p_{iN} \boldsymbol{\delta} = -\langle \boldsymbol{Q} \boldsymbol{F}^{(c)}(Q) \rangle_{iN, \text{eq}} = -H_N \langle \boldsymbol{Q} \boldsymbol{Q} \rangle_{iN, \text{eq}} \tag{20.3-7}$$

where we have used the Gaussian assumption in replacing $\boldsymbol{F}_N^{(c)}$ in the last equality above.

EXAMPLE 20.3-1 Constitutive Equation for a Macromolecular Solid

(a) Show how Eqs. 20.3-4 and 5 can be specialized for a crosslinked polymeric solid. (b) Use this constitutive equation to calculate the stress-strain behavior in simple shear, pure shear, and elongation (Fig. 20.3-2).

SOLUTION (a) As in Example 20.2-2 we drop the subscript i on the stress tensor equation for a crosslinked solid with permanent junctions. The contribution to the stress tensor by an N-chain is easily evaluated with the aid of Eq. 20.2-24 in Example 20.2-2:

$$\pi_N = -H_N\langle \underline{QQ}\rangle_N = -\tfrac{1}{3}n_N H_N(N-1)a^2\mathbf{B}(t,t_0) = -n_N kT\mathbf{B}(t,t_0) \tag{20.3-8}$$

In the last step, Eq. 11.3-20 has been used. The total stress tensor is then of the form

$$\pi = -G_0\mathbf{B} \tag{20.3-9}$$

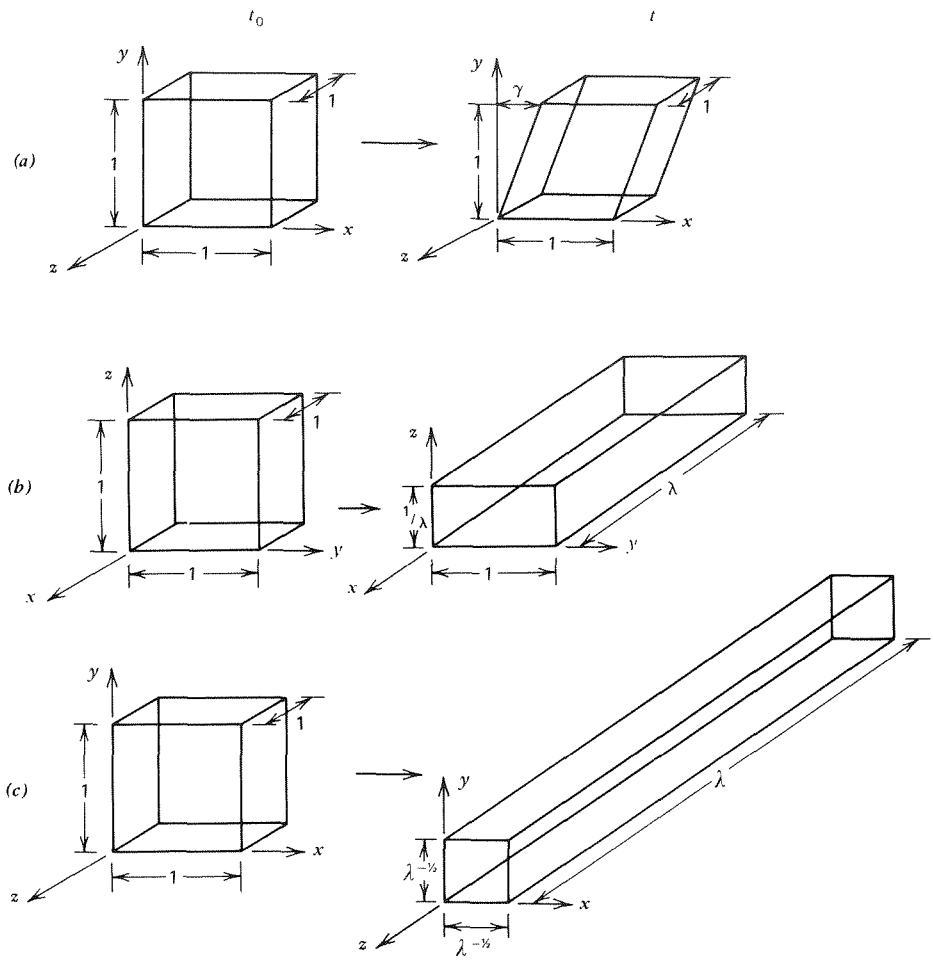


FIGURE 20.3-2. Deformations of a unit cube in (*a*) simple shear, (*b*) pure shear, and (*c*) elongation. The undeformed states t_0 are shown on the left and the deformed states t on the right. The orientation of the Cartesian axes in each part corresponds to the usage in part (*b*) of Example 20.3-2.

where the modulus G_0 is

$$\boxed{G_0 = \sum_N n_N kT = n_0 kT} \tag{20.3-10}$$

n_0 being the total number density of segments.

To get the extra stress τ we note that the pressure is from Eq. 20.3-7

$$p = -G_0 \tag{20.3-11}$$

and we obtain the constitutive equation for the elementary network model of a polymeric solid

$$\boxed{\tau = G_0 \gamma_{[0]}(t, t_0)} \tag{20.3-12}$$

For later comparison with the constitutive equations for network fluids, we note that Eq. 20.3-12 can be written in the equivalent differential form

$$\tau_{(1)}(t) = -G_0 \gamma_{(1)}(t) \tag{20.3-13}$$

This result is easily obtained with the aid of Problem 9B.5.

The modulus G_0 is often expressed in terms of the number density of junctions $n_0^\times$ rather than in terms of the number density of segments n_0. It is generally assumed that n_0 will be a small multiple s, say, of $n_0^\times$ such that

$$G_0 = s n_0^\times kT \tag{20.3-14}$$

The factor s will depend on the nature of the crosslinks introduced. For a network in which four segments meet at each junction, the factor s will be 2. In any event, s will seldom differ by very much from 2.

The constitutive equation Eq. 20.3-12 is often referred to as the equation of a "neo-Hookean" material. It is indeed quite remarkable that we have been able to obtain so easily a complete constitutive equation for the network model in a closed form. This equation provided the basis for the early work of Rivlin[1] on finite deformations of solids, and extensive[2] investigations have shown that the predictions are in excellent agreement with experimental results for moderate deformations.

Although the neo-Hookean solid is in good agreement with experimental observations at moderate deformations, it does not provide a complete description of the stress-strain relations for macromolecular solids. However, continuum mechanical arguments have been used to formulate a complete theory for large elastic deformations of solids. This development is primarily due to the theoretical and experimental works of Rivlin.[3]

(b) In order to be slightly more general in illustrating the material properties of network solids, we use in this part a generalization of the constitutive equation, Eq. 20.3-12, proposed originally by Mooney:[4]

$$\tau = G_0[(1 - q)\gamma_{[0]}(t, t_0) + q\gamma^{[0]}(t, t_0)] \tag{20.3-15}$$

[1] R. S. Rivlin, *Phil. Trans. Roy. Soc.* (London) **A240**, 459-490 (1948); **A240**, 491-508 (1948); **A240**, 509-525 (1948).

[2] The reader wishing a more comprehensive treatment with detailed comparisons with experiments is referred to L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd. ed., Oxford University Press, London (1975). This book is attractively arranged to give a clear overview of the kinetic theory of rubber in the first five chapters. A useful review can be found in L. R. G. Treloar, *Rep. Progr. Phys.*, **36**, 755-826 (1973).

[3] A summary of this development is given by R. S. Rivlin, in F. R. Eirich, ed., *Rheology*, Vol. 1, Academic Press, New York (1956), pp. 351-385.

[4] M. Mooney, *J. Appl. Phys.*, **11**, 582-592 (1940).

Solids that follow Eq. 20.3-15 are called "Mooney" materials. When $q = 0$, the stress tensor depends linearly on the $\gamma_{[0]}$ tensor, and the Mooney equation reduces to the neo-Hookean equation. When $q = 1$, the stress tensor depends linearly on $\gamma^{[0]}$ defined in Eq. D.3-3. The inclusion of the $\gamma^{[0]}$ term in the equation, with q approximately equal to 0.1, gives improved agreement with experimental observations; however, the molecular origin of the $\gamma^{[0]}$ term is not clear.

(i) *Simple Shear*: Let the coordinates of a typical particle be x_0, y_0, z_0 in the undeformed state t_0 and x, y, z in the deformed state t. The displacement functions (Eq. D.1-4) relating the two sets of coordinates for simple shear are

$$\begin{cases} x = x_0 + \gamma y_0 \\ y = y_0 \\ z = z_0 \end{cases} \tag{20.3-16}$$

$$\begin{cases} x_0 = x - \gamma y \\ y_0 = y \\ z_0 = z \end{cases} \tag{20.3-17}$$

where γ is the "magnitude of shear" which is equal to the negative of the shear strain from state t to t_0 defined in Table C.1 as $\gamma_{yx}(t, t_0) = \int_t^{t_0} \dot{\gamma}_{yx}(t'')dt''$. From Table C.1 we see the deformation tensors are

$$\gamma_{[0]} = -\begin{pmatrix} \gamma^2 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{20.3-18}$$

$$\gamma^{[0]} = -\begin{pmatrix} 0 & \gamma & 0 \\ \gamma & -\gamma^2 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{20.3-19}$$

When these expressions are inserted into Eq. 20.3-15, we find the following nonzero stress components

$$\begin{aligned} \tau_{yx} = \tau_{xy} &= -G_0\gamma \\ \tau_{xx} - \tau_{yy} &= -G_0\gamma^2 \\ \tau_{yy} - \tau_{zz} &= qG_0\gamma^2 \end{aligned} \tag{20.3-20}$$

Note that the shear modulus is G_0, which is independent of q and of the magnitude of shear. In addition, we see that this macromolecular solid exhibits normal stress differences in shear, just as many macromolecular fluids exhibit normal stress differences in shear flow.

(ii) *Pure Shear*: The displacement functions are in pure shear (cf. Table C.1 with $b = 1$, and $\lambda_x = \lambda$, $\lambda_y = 1$, $\lambda_z = \lambda^{-1}$)

$$\begin{cases} x = \lambda x_0 \\ y = y_0 \\ z = \lambda^{-1} z_0 \end{cases} \tag{20.3-21}$$

$$\begin{cases} x_0 = \lambda^{-1} x \\ y_0 = y \\ z_0 = \lambda z \end{cases} \tag{20.3-22}$$

This deformation is obtained if a thin sheet of material oriented normal to the z-axis is clamped along two planes of constant x and then stretched by a factor of λ in the x-direction (Fig. 20.3-2b). From Table C.1 the deformation tensors are

$$\boldsymbol{\gamma}_{[0]} = \begin{pmatrix} 1-\lambda^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1-\lambda^2 \end{pmatrix} \tag{20.3-23}$$

$$\boldsymbol{\gamma}^{[0]} = \begin{pmatrix} \lambda^{-2}-1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \lambda^2-1 \end{pmatrix} \tag{20.3-24}$$

We then find the following nonzero stress differences

$$\tau_{xx} - \tau_{yy} = G_0[(1-2q) - (1-q)\lambda^2 - q\lambda^{-2}] \tag{20.3-25}$$

$$\tau_{xx} - \tau_{zz} = G_0[\lambda^{-2} - \lambda^2] \tag{20.3-26}$$

Hence if we let the surfaces of constant z be at atmospheric pressure p_a, we find that we must apply a force per unit area (measured in the stretched state) in the x-direction $-\pi_{xx}$ given by

$$\pi_{xx} = (\tau_{xx} - \tau_{zz}) + p_a = G_0(\lambda^{-2} - \lambda^2) + p_a \tag{20.3-27}$$

Note that π_{xx} is independent of q.

(iii) *Elongation*: The displacement functions are in elongation (cf. Table C.1 with $b = 0$, and $\lambda_x = \lambda_y = \lambda^{-1/2}$, $\lambda_z = \lambda$)

$$\begin{cases} x = \lambda^{-1/2} x_0 \\ y = \lambda^{-1/2} y_0 \\ z = \lambda z_0 \end{cases} \tag{20.3-28}$$

$$\begin{cases} x_0 = \lambda^{1/2} x \\ y_0 = \lambda^{1/2} y \\ z_0 = \lambda^{-1} z \end{cases} \tag{20.3-29}$$

This deformation is obtained if a long slender rod oriented in the z-direction is stretched by a ratio λ in the z-direction. The deformation tensors are

$$\boldsymbol{\gamma}_{[0]} = \begin{pmatrix} 1-\lambda^{-1} & 0 & 0 \\ 0 & 1-\lambda^{-1} & 0 \\ 0 & 0 & 1-\lambda^2 \end{pmatrix} \tag{20.3-30}$$

$$\boldsymbol{\gamma}^{[0]} = \begin{pmatrix} \lambda-1 & 0 & 0 \\ 0 & \lambda-1 & 0 \\ 0 & 0 & \lambda^{-2}-1 \end{pmatrix} \tag{20.3-31}$$

We then find the following stress differences:

$$\tau_{zz} - \tau_{xx} = G_0[(1-q)\lambda + q](\lambda^{-2} - \lambda) \tag{20.3-32}$$

$$\tau_{xx} - \tau_{yy} = 0 \tag{20.3-33}$$

Hence if the rod of material is surrounded by atmospheric pressure, we must apply a force per unit area (measured in the stretched state) in the z-direction $-\pi_{zz}$ given by

$$\pi_{zz} = (\tau_{zz} - \tau_{xx}) + p_a = G_0[(1-q)\lambda + q](\lambda^{-2} - \lambda) + p_a \tag{20.3-34}$$

in order to hold the material in the stretched state.

§20.4 THE LODGE NETWORK MODEL[1]

The Lodge network model is a generalization to multiple time constants of the single exponential constitutive equation of Green and Tobolsky. It is obtained by adding to the list of assumptions given in §20.1 that

x. (Lodge network model) The creation rates are independent of time $L_{iN} = L_{iN}(Q)$; the loss rates λ_{iN} are constants.

With L_{iN} and λ_{iN} given as above, Eq. 20.2-14 gives for $\langle \boldsymbol{QQ} \rangle_{iN}$:

$$\langle \boldsymbol{QQ} \rangle_{iN} + \lambda_{iN} \langle \boldsymbol{QQ} \rangle_{iN(1)} = \bar{L}_{iN} \lambda_{iN} \boldsymbol{\delta} \tag{20.4-1}$$

where $\bar{L}_{iN}$ given by Eq. 20.2-10 is now constant. In view of Eqs. 20.3-4 and 5, the stress tensor is then

$$\boldsymbol{\pi} = \sum_N \sum_i \boldsymbol{\pi}_{iN} \tag{20.4-2}$$

$$\boldsymbol{\pi}_{iN} + \lambda_{iN} \boldsymbol{\pi}_{iN(1)} = -H_N \bar{L}_{iN} \lambda_{iN} \boldsymbol{\delta} \tag{20.4-3}$$

By paralleling the development leading to Eq. 20.2-17 we can integrate Eq. 20.4-3 to get an explicit expression for the stress tensor:

$$\boldsymbol{\pi} = -\int_{-\infty}^{t} M(t-t') \mathbf{B}(t, t') dt' \tag{20.4-4}$$

$$M(t-t') = \sum_N H_N \sum_i \bar{L}_{iN} e^{-(t-t')/\lambda_{iN}} \tag{20.4-5}$$

In Eqs. 20.4-3 and 5 the spring constant H_N is given by $3kT/(N-1)a^2$ because of the assumption of Gaussian chains.

[1] A. S. Lodge, *Trans. Faraday Soc.*, **52**, 120-130 (1956); *Elastic Liquids*, Academic Press, New York (1964), pp. 118-120; *Rheol. Acta*, 7, 379 392 (1968). The pioneering paper on the development of a constitutive equation for arbitrary deformations of a network model for fluids is that of M. S. Green and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 80-92 (1946); see particularly Appendix B of this reference.

In order to write the constitutive equations for the extra stress τ we must subtract off the pressure contribution. This is found by evaluating Eq. 20.4-3 at equilibrium

$$p_{iN} = -H_N \bar{L}_{iN} \lambda_{iN} \tag{20.4-6}$$

The quantity $\bar{L}_{iN}$ can be evaluated since by assumption (viii) we take the Q-dependence of the creation rate to be the same as that for the equilibrium distribution function for freely jointed bead-rod chains with no constraints on the end points (Eq. 20.2-19). Thus if we denote by $\hat{L}_{iN}$ the constant creation rate of all iN-segments independent of segment length, then $L_{iN}(Q)$ is equal to $\hat{L}_{iN}\psi_{N,\mathrm{eq}}(Q)$ and we have

$$\begin{aligned}
\bar{L}_{iN} &= \frac{4\pi}{3} \hat{L}_{iN} \int_0^{\infty} \psi_{N,\mathrm{eq}}(Q) Q^4 \, dQ \\
&= \frac{4\pi}{3} \hat{L}_{iN} \left(\frac{H_N}{2\pi kT} \right)^{3/2} \int_0^{\infty} Q^4 e^{-(H_N/2kT)Q^2} \, dQ \\
&= \frac{1}{3} \hat{L}_{iN} \int Q^2 \psi_{N,\mathrm{eq}} \, d\boldsymbol{Q} \\
&= \frac{1}{3} \hat{L}_{iN} (N-1) a^2
\end{aligned} \tag{20.4-7}$$

Therefore

$$p_{iN} = -\hat{L}_{iN} kT \lambda_{iN} \tag{20.4-8}$$

and

$$p = \sum_N \sum_i p_{iN} \tag{20.4-9}$$

The constitutive equation for the extra stress tensor is then

$$\boxed{\boldsymbol{\tau} = \sum_j \boldsymbol{\tau}_j, \qquad \boldsymbol{\tau}_j + \lambda_j \boldsymbol{\tau}_{j(1)} = -\eta_j \boldsymbol{\gamma}_{(1)}} \tag{20.4-10}$$

or

$$\boxed{\begin{aligned} \boldsymbol{\tau} &= \int_{-\infty}^{t} M(t-t') \boldsymbol{\gamma}_{[0]}(t, t') \, dt' \\ M(t-t') &= \sum_j \frac{\eta_j}{\lambda_j^2} e^{-(t-t')/\lambda_j} \end{aligned}} \tag{20.4-11}$$

Here we have introduced $\sum_j$ to denote $\sum_N \sum_i$ and have rewritten the constant creation rate in terms of constants η_j with dimensions of viscosity

$$kT\hat{L}_j = \frac{\eta_j}{\lambda_j^2} \tag{20.4-12}$$

Equation 20.4-10 is identical to the generalized Maxwell model presented in Chapter 7 (Eqs. 7.6-1 and 7.6-2), and Eq. 20.4-11 was previously used in Chapter 8 (Eqs. 8.2-1 and 4).

The constants η_j (or $\hat{L}_j$) and λ_j are left undetermined by the theory. Note, however, that the relaxation modulus of linear viscoelasticity corresponding to $M(s)$ is

$$\boxed{G(s) = \sum_j \frac{\eta_j}{\lambda_j} e^{-s/\lambda_j}} \tag{20.4-13}$$

Hence the constants η_j and λ_j may be determined from the linear viscoelastic properties of a material (see Example 5.3-7).

It is clear that eventually the constants η_j (or $\hat{L}_j$) and λ_j, or appropriate replacements, should be obtained from detailed molecular calculations of the motions of the constituent macromolecules. In this way the dependence of the calculated material functions on molecular structure (for example, molecular weight, molecular weight distribution, and branching), which is presently missing in the network models, could be determined. Without developing such extensions of the theory, we can note a few features of the structure dependence. First, to the extent that the creation and loss of junctions are governed by thermal motions of the macromolecules (and it seems reasonable that this is the dominant mechanism at least for small deformations), $1/\lambda_j$ and $\hat{L}_j$ should depend on the equivalent number of random links (molecular weight) and temperature in the same way. One simple way to indicate this dependence is to let

$$\lambda_j \propto M^{\beta} a_T \tag{20.4-14}$$

$$\eta_j \propto M^{\beta} a_T \qquad (\hat{L}_j \propto M^{-\beta} a_T^{-1}) \tag{20.4-15}$$

where β is an unknown constant and a_T is a function of temperature. The function a_T is the "shift factor" in the method of time-temperature superposition (see §3.6 and Eqs. 15.3-31 through 33), and its inclusion in Eq. 20.4-14 is consistent with its normal use to scale time constants. The exponent β is expected to be positive, since the time required for overall macromolecular configuration changes increases with molecular weight.

It is interesting to note that the constitutive equation for the Lodge network model is very similar to the constitutive equations for chainlike bead-spring models of Rouse and Zimm for dilute solutions in Eqs. 15.3-17 and 15.4-21. The only difference is that the bead spring models give the relaxation modulus explicitly in terms of model parameters, whereas the network theory leaves the relaxation modulus undetermined. We can therefore easily adapt the material functions obtained for the Rouse–Zimm models (but not their molecular weight dependence).

In steady shear flow we find by analogy with Eqs. 15.3-25 through 27

$$\begin{aligned} \eta &= \eta_0 = \sum_j \eta_j \\ \Psi_1 &= \Psi_{10} = \sum_j 2\eta_j \lambda_j \\ \Psi_2 &= \Psi_{20} = 0 \end{aligned} \tag{20.4-16}$$

that is, the Lodge network model predicts shear-rate-independent viscometric functions, and the second normal stress coefficient is zero. Note that if Eqs. 20.4-14 and 15 are combined with Eqs. 20.4-16 we obtain

$$\eta_0 \propto M^{\beta}$$
$$\Psi_{10} \propto M^{2\beta} \tag{20.4-17}$$

A value of β equal to 3.4 gives good agreement with structure property data on these material functions (cf. Figs. 3.6-4 and 7).

An exhaustive exploration of the predictions of the Lodge network model for a large number of homogeneous deformations has been given by Lodge.[2] In particular we call attention to the calculation[3] of the lateral expansion and longitudinal contraction exhibited by the Lodge network model if, at any instant in steady shear flow, all forces are suddenly removed from the fluid. Another interesting property of the Lodge network model is the prediction of stress relaxation upon cessation of steady shear flow that the shear stress should relax faster than the first normal stress difference, in agreement with experimental observations (§3.4, Experiment d). For elongational flow, the Lodge network model suffers from the same defect as the Rouse–Zimm models or the Hookean dumbbell: when the elongation rate equals $1/2\lambda_{\max}$, the elongational viscosity becomes infinite. Here $\lambda_{\max}$ is the largest of the λ_j. Moreover for $\dot{\varepsilon} > 1/2\lambda_{\max}$, start-up of steady elongational flow will never approach a steady state.

Finally we note that if it is desired to have information about molecular (segment) stretching and orientation, the distribution function Ψ_{iN} is available (Example 20.4-1). If it is desired to know how much the iN-segments are stretched by a flow, this can be obtained directly from Eq. 20.2-17:

$$\langle Q^2 \rangle_{iN} = \tfrac{1}{3}(N-1)a^2\hat{L}_{iN}\int_{-\infty}^{t} e^{-(t-t')/\lambda_{iN}}\,\mathrm{tr}\,\mathbf{B}(t,t')dt'$$
$$= (N-1)a^2\left[\hat{L}_{iN}\lambda_{iN} - \frac{1}{3kT}\,\mathrm{tr}\,\boldsymbol{\tau}_{iN}\right] \tag{20.4-18}$$

The first line of Eq. 20.4-18 is more convenient if the deformation field is given. The second form is useful in suggesting ways to let the segment loss rates depend on the mean extension of segments through the trace of the stress tensor. We will investigate this latter possibility further in the next section.

EXAMPLE 20.4-1 The Segment Distribution Function for the Lodge Network Model

Find the segment distribution function Ψ_{iN} for the Lodge network model.

SOLUTION The convection equation for Ψ_{iN} for the Lodge network model is

$$\frac{\partial \Psi_{iN}}{\partial t} = -\frac{\partial}{\partial \boldsymbol{Q}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\Psi_{iN} + L_{iN}(Q) - \frac{\Psi_{iN}}{\lambda_{iN}} \tag{20.4-19}$$

[2] A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), Chapters 6 and 7.

[3] A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), pp. 131–139; see problem 20C.3.

where the λ_{iN} are constants. Since segments are assumed to be produced at a constant rate and with a distribution of configurations identical to an unconstrained bead-rod chain at equilibrium we have (cf. Eq. 20.2-18)

$$L_{iN}(Q) = \hat{L}_{iN}\psi_{N,\mathrm{eq}}(Q) = \hat{L}_{iN}\left(\frac{H_N}{2\pi kT}\right)^{3/2} e^{(H_N/2kT)(\boldsymbol{Q}\cdot\boldsymbol{Q})} \tag{20.4-20}$$

Note that, in contrast to Eq. 20.2-18, the above result involves only a single time t, at which the segments are created.

To solve Eq. 20.4-19, let us introduce two new terms

$$\dot{n}_{iN}(t, t')\,dt' = \text{number density of } iN\text{-segments created between time } t' \text{ and } t' + dt' \text{ that survive to time } t \tag{20.4-21}$$

$$\psi_N(\boldsymbol{Q}, t, t')\,d\boldsymbol{Q} = \text{fraction of segments with } (N-1) \text{ equivalent random links created at time } t' \text{ which are in the configuration range } \boldsymbol{Q} \text{ to } \boldsymbol{Q} + d\boldsymbol{Q} \text{ at time } t \tag{20.4-22}$$

In terms of these, Ψ_{iN} is

$$\Psi_{iN}(\boldsymbol{Q}, t) = \int_{-\infty}^{t} \dot{n}_{iN}(t, t')\psi_N(\boldsymbol{Q}, t, t')dt' \tag{20.4-23}$$

When Eq. 20.4-23 is put into Eq. 20.4-19 we see that

$$\hat{L}_{iN}\psi_{N,\mathrm{eq}}(Q) + \int_{-\infty}^{t} \frac{\partial}{\partial t}[\dot{n}_{iN}(t, t')\psi_N(\boldsymbol{Q}, t, t')]dt' = \int_{-\infty}^{t}\left[-\frac{\partial}{\partial \boldsymbol{Q}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{Q}](\dot{n}_{iN}(t, t')\psi_N(\boldsymbol{Q}, t, t')) - \frac{\dot{n}_{iN}(t, t')\psi_N(\boldsymbol{Q}, t, t')}{\lambda_{iN}}\right]dt' + \hat{L}_{iN}\psi_{N,\mathrm{eq}}(Q) \tag{20.4-24}$$

where we have identified $\dot{n}_{iN}(t, t) = \hat{L}_{iN}$ as the constant creation rate of iN-segments.

Equation 20.4-24 can be satisfied provided that

$$\frac{\partial}{\partial t}\dot{n}_{iN}(t, t')\psi_N(\boldsymbol{Q}, t, t') = -\dot{n}_{iN}(t, t')\frac{\partial}{\partial \boldsymbol{Q}}\cdot[\boldsymbol{\kappa}\cdot\boldsymbol{Q}]\psi_N(\boldsymbol{Q}, t, t') - \frac{\dot{n}_{iN}(t, t')\psi_N(\boldsymbol{Q}, t, t')}{\lambda_{iN}} \tag{20.4-25}$$

It seems reasonable to postulate that (cf. Eq. 20.2-22)

$$\psi_N(\boldsymbol{Q}, t, t') = \left(\frac{H_N}{2\pi kT}\right)^{3/2} e^{-(H_N/2kT)(\mathbf{B}^{-1}(t,t'):\boldsymbol{QQ})} \tag{20.4-26}$$

whereupon in view of Eq. 20.2-20, $\dot{n}_{iN}(t, t')$ must satisfy

$$\frac{\partial}{\partial t}\dot{n}_{iN}(t, t') = -\frac{\dot{n}_{iN}(t, t')}{\lambda_{iN}} \tag{20.4-27}$$

subject to the initial condition

$$\dot{n}_{iN}(t', t') = \hat{L}_{iN} \tag{20.4-28}$$

The solution to Eqs. 20.4-27 and 28 is easily found:

$$\dot{n}_{iN}(t, t') = \hat{L}_{iN} e^{-(t-t')/\lambda_{iN}} \tag{20.4-29}$$

This means that the total number of iN-segments present at any time is

$$n_{iN}(t) = \int_{-\infty}^{t} \dot{n}_{iN}(t, t')dt' = \hat{L}_{iN}\lambda_{iN} \tag{20.4-30}$$

Finally, the segment distribution function is

$$\boxed{\Psi_{iN}(\underline{Q}, t) = \hat{L}_{iN}\left(\frac{H_N}{2\pi kT}\right)^{3/2} \int_{-\infty}^{t} e^{-(t-t')/\lambda_{iN}} e^{-(H_N/2kT)(\mathbf{B}^{-1}:\underline{Q}\underline{Q})}\, dt'} \tag{20.4-31}$$

Note that once Ψ_{iN} is available, it is possible to calculate the stress tensor directly from Eq. 20.3-4. This is easily done either by interchanging the order of the time and $\underline{Q}$-integrations and then performing the configuration average by using the steps shown in Eq. 20.2-24, or by using Eq. E.3-3.

§20.5 MODIFIED NETWORK MODELS FOR MACROMOLECULAR FLUIDS

Several modified network models have been proposed to improve on the rheological predictions of the Lodge rubberlike liquid. A first group of modifications has focused on using more realistic segment kinetics assumptions. Indeed the assumption used in the previous section that the segment creation and loss rates are entirely independent of the deformation history seems rather unlikely, particularly for the destruction term. It seems plausible that large deformations and stresses would influence the rates at which segments are created and lost. For example, the infinite elongational viscosity of the Lodge model is easily shown to correspond to the fact that the segments are stretched to infinite length, in the same way as Hookean dumbbells were found to stretch infinitely far in elongational flows (Eqs. 13.4-34 and 35). We intuitively feel that one or both of the end junctions for these segments should break and that the segments should be lost from the network, rather than be allowed to stretch this drastically. A second modification of the rubberlike liquid model relaxes the affine motion assumption.

Below we give a brief discussion of several network models that illustrate these two kinds of modifications of the rubberlike liquid model. The discussion is not exhaustive, but is rather intended to give the reader an introduction to the research activities in this area. We discuss the nonaffine motion first, since it is somewhat simpler to treat, and it can then be used together with any modifications to the segment kinetics.

a. Non-Affine Motion

Here we consider a modification, which was proposed by Phan-Thien and Tanner,[1] to assumption (iii) that the junctions move affinely. We continue to neglect the thermal motions of the junctions.

[1] N. Phan-Thien and R. I. Tanner, *J. Non-Newtonian Fluid Mech.*, **2**, 353–365 (1977); N. Phan-Thien, *J. Rheol.*, **22**, 259–283 (1978); R. I. Tanner, *J. Non-Newtonian Fluid Mech.*, **5**, 103–112 (1979).

Let us denote by $\boldsymbol{r}_\nu$ the position of an arbitrary junction ν. Phan-Thien and Tanner proposed that the motion of this junction be given by

$$\dot{\boldsymbol{r}}_\nu = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}_\nu] - \tilde{\boldsymbol{v}}(\boldsymbol{r}_\nu) \tag{20.5-1}$$

where $\tilde{\boldsymbol{v}}(\boldsymbol{r})$ is a "slip velocity" that accounts for the inability of the junctions to follow the macroscopically imposed velocity field exactly. Now let $\boldsymbol{r}_\mu$ be the position of a second junction connected to $\boldsymbol{r}_\nu$ by the segment with end-to-end vector $\boldsymbol{Q}$:

$$\boldsymbol{r}_\mu - \boldsymbol{r}_\nu = \boldsymbol{Q} \tag{20.5-2}$$

The velocity of $\boldsymbol{r}_\mu$ is also given by Eq. 20.5-1. Subtracting the equation for $\dot{\boldsymbol{r}}_\nu$ from that for $\dot{\boldsymbol{r}}_\mu$ gives

$$\begin{aligned} \dot{\boldsymbol{Q}} &= [\boldsymbol{\kappa} \cdot \boldsymbol{Q}] - [\tilde{\boldsymbol{v}}(\boldsymbol{r}_\mu) - \tilde{\boldsymbol{v}}(\boldsymbol{r}_\nu)] \\ &= [\boldsymbol{\kappa} \cdot \boldsymbol{Q}] - [\nabla \tilde{\boldsymbol{v}}^\dagger \cdot \boldsymbol{Q}] + \cdots \\ &\doteq [\hat{\boldsymbol{\kappa}} \cdot \boldsymbol{Q}] \end{aligned} \tag{20.5-3}$$

In going from the first to the second line of Eq. 20.5-3 we have expanded the slip velocity at junction $\boldsymbol{r}_\mu$ in a Taylor series about $\boldsymbol{r}_\nu$ and kept only the first two terms. This truncation should be a reasonable approximation if Q is small compared to the macroscopic length scale over which $\tilde{\boldsymbol{v}}$ varies. In the last line above we have introduced the "effective velocity gradient tensor" (cf. Problem 13B.2)

$$\begin{aligned} \hat{\boldsymbol{\kappa}} &= \boldsymbol{\kappa} - \nabla \tilde{\boldsymbol{v}}^\dagger \\ &= \boldsymbol{\kappa} - \tilde{\boldsymbol{\kappa}} \end{aligned} \tag{20.5-4}$$

of the effective macroscopic velocity field

$$\hat{\boldsymbol{v}} = \boldsymbol{v}_0 + [\boldsymbol{\kappa} \cdot \boldsymbol{r}] - \tilde{\boldsymbol{v}} \tag{20.5-5}$$

Finally, we assume that the "slip tensor" $\tilde{\boldsymbol{\kappa}}$ can be given by[2]

$$\tilde{\boldsymbol{\kappa}} = \tfrac{1}{2}\xi\dot{\boldsymbol{\gamma}} \tag{20.5-6}$$

in which ξ is an arbitrary "slip constant" and $\dot{\boldsymbol{\gamma}} = \boldsymbol{\kappa} + \boldsymbol{\kappa}^\dagger$ is the rate of strain tensor for the macroscopically imposed velocity field.

When Eqs 20.5-3 through 6 are combined we get the equation of motion for the segment vector

$$\dot{\boldsymbol{Q}} = [\boldsymbol{\kappa} \cdot \boldsymbol{Q}] - \tfrac{1}{2}\xi[\dot{\boldsymbol{\gamma}} \cdot \boldsymbol{Q}] \tag{20.5-7}$$

Equation 20.5-7 replaces Eq. 20.2-1 in the non-affine motion modification to the network theory. Note that slip is completely described by ξ.

[2] Phan-Thien and Tanner (*op.cit.*) assume a slightly different form for $\tilde{\boldsymbol{\kappa}}$ which leads to an additional term $-\sigma\boldsymbol{Q}$ on the right of Eq. 20.5-7. This term must be excluded, since for a fluid at rest ($\boldsymbol{v} = \boldsymbol{0}$), the modified Eq. 20.5-7 would give $Q \to 0$ or ∞ depending on whether $\sigma > 0$ or $\sigma < 0$. Both alternatives are physically unreasonable.

The entire development leading up to the constitutive equaiton for the Lodge network model can now be paralleled by simply replacing $\boldsymbol{v}$ everywhere by $\hat{\boldsymbol{v}}$ (and $\boldsymbol{\kappa}$ by $\hat{\boldsymbol{\kappa}}$). This leads to the following differential form of the extra stress tensor (cf. Eq. 20.4-10):

$$\boxed{\boldsymbol{\tau} = \sum_j \boldsymbol{\tau}_j} \tag{20.5-8}$$

$$\boldsymbol{\tau}_j + \lambda_j \left\{ \frac{\partial}{\partial t} \boldsymbol{\tau}_j - \hat{\boldsymbol{\kappa}} \cdot \boldsymbol{\tau}_j - \boldsymbol{\tau}_j \cdot \hat{\boldsymbol{\kappa}}^\dagger \right\} = -\eta_j (\hat{\boldsymbol{\kappa}} + \hat{\boldsymbol{\kappa}}^\dagger) \tag{20.5-9}$$

When $\hat{\boldsymbol{\kappa}}$ is rewritten in terms of $\boldsymbol{\kappa}$ and $\frac{1}{2}\xi\dot{\boldsymbol{\gamma}}$ we obtain

$$\boxed{\begin{aligned} &\boldsymbol{\tau}_j + \lambda_j \boldsymbol{\tau}_{j(1)} + \tfrac{1}{2}\lambda_j \xi \{\dot{\boldsymbol{\gamma}} \cdot \boldsymbol{\tau}_j + \boldsymbol{\tau}_j \cdot \dot{\boldsymbol{\gamma}}\} = -\hat{\eta}_j \dot{\boldsymbol{\gamma}} \\ &\text{or} \\ &\boldsymbol{\tau}_j + \lambda_j \boldsymbol{\tau}_{j(\hat{1})} = -\hat{\eta}_j \dot{\boldsymbol{\gamma}} \end{aligned}} \tag{20.5-10}$$

where

$$\hat{\eta}_j = \eta_j (1 - \xi) \tag{20.5-11}$$

gives the relation between the creation rate constants η_j in the Lodge network model and the coefficients appearing naturally in Eq. 20.5-10. In the second form of Eq. 20.5-10, the notation $_{(\hat{1})}$ denotes the convected derivative calculated with the effective velocity gradient $\hat{\boldsymbol{\kappa}}$. The integral form of the constitutive equation with non-affine motion can also be written down immediately from Eq. 20.4-11:

$$\boxed{\begin{aligned} \boldsymbol{\tau} &= \int_{-\infty}^{t} M(t - t')(1 - \xi)^{-1} \hat{\boldsymbol{\gamma}}_{[0]}(t, t') dt' \\ M(t - t') &= \sum_j \frac{\hat{\eta}_j}{\lambda_j^2} e^{-(t - t')/\lambda_j} \end{aligned}} \tag{20.5-12}$$

The tensor $\hat{\boldsymbol{\gamma}}_{[0]}$ is a modified finite strain tensor which is computed from the velocity field $\hat{\boldsymbol{v}}$ rather than from $\boldsymbol{v}$. The factor of $(1 - \xi)^{-1}$ is included in Eq. 20.5-12, because $(1 - \xi)^{-1}\hat{\boldsymbol{\gamma}}_{[0]}$ simplifies to the infinitesimal strain tensor in the limit of small deformations. If linear viscoelastic data are used to determine the $\hat{\eta}_j$ and λ_j in Eqs. 20.5-10 or 12, then the resulting values will be numerically equal to the η_j and λ_j found for the Lodge network model.

The differential form of the constitutive equation[3] is a special case of the Oldroyd 8-constant model discussed in detail in §7.3 (cf. Eq. 7.3-2). As is shown in Example 20.5-1, the non-affine motion assumption leads to a shear-rate-dependent viscosity. However, the viscosity decreases too rapidly with shear rate, and the negative of the shear stress goes through a maximum with increasing shear rate, which is physically unreasonable. In addition, the elongational viscosity becomes infinite at finite elongation rates. Although these critical elongation rates are slightly different than those found for the Lodge network

[3] A similar model was developed from purely continuum arguments by M. W. Johnson, Jr. and D. Segalman, *J. Non-Newtonian Fluid Mech.*, **2**, 255-270 (1977).

model, the infinite value of $\bar{\eta}$ is unrealistic. Thus modification of only the affine motion assumption in the Lodge network model (at least in the way done here) does not lead to substantial improvements in the rheological predictions, so we turn in the next subsection to consideration of non-constant segment creation rates and loss probabilities.

EXAMPLE 20.5-1 Rheological Properties of a Non-Affine Lodge Network Model

Consider the constitutive equations obtained from relaxing the affine motion assumption in the Lodge network model (Eqs. 20.5-8, 10 and 12). Determine the (a) viscometric properties and (b) elongational viscosity for this model.

SOLUTION **(a)** Steady Shear Flow

For steady shear flow with shear rate $\dot{\gamma}$ we can use the entries in Table C.1 to write Eq. 20.5-10 in matrix form:

$$\begin{pmatrix} \tau_{jxx} & \tau_{jyx} & 0 \\ \tau_{jyx} & \tau_{jyy} & 0 \\ 0 & 0 & \tau_{jzz} \end{pmatrix} - \lambda_j\dot{\gamma}\begin{pmatrix} 2\tau_{jyx} & \tau_{jyy} & 0 \\ \tau_{jyy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$+ \tfrac{1}{2}\xi\lambda_j\dot{\gamma}\begin{pmatrix} 2\tau_{jyx} & (\tau_{jxx}+\tau_{jyy}) & 0 \\ (\tau_{jxx}+\tau_{jyy}) & 2\tau_{jyx} & 0 \\ 0 & 0 & 0 \end{pmatrix} = -\hat{\eta}_j\dot{\gamma}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{20.5-13}$$

The equations for the stress components are then

$$\tau_{jxx} - 2\lambda_j\dot{\gamma}\,\tau_{jyx}(1 - \tfrac{1}{2}\xi) = 0 \tag{20.5-14}$$

$$\tau_{jyx} - \lambda_j\dot{\gamma}(\tau_{jyy} - \tfrac{1}{2}\xi(\tau_{jxx} + \tau_{jyy})) = -\hat{\eta}_j\dot{\gamma} \tag{20.5-15}$$

$$\tau_{jyy} + \lambda_j\xi\dot{\gamma}\,\tau_{jyx} = 0 \tag{20.5-16}$$

$$\tau_{jzz} = 0 \tag{20.5-17}$$

When these are solved we get the viscometric functions

$$\eta(\dot{\gamma}) = -\sum_j \frac{\tau_{jyx}}{\dot{\gamma}} = \sum_j \frac{\hat{\eta}_j}{[1 + \xi(2-\xi)(\lambda_j\dot{\gamma})^2]} \tag{20.5-18}$$

$$\Psi_1(\dot{\gamma}) = -\sum_j \frac{(\tau_{jxx} - \tau_{jyy})}{\dot{\gamma}^2} = \sum_j \frac{2\lambda_j\hat{\eta}_j}{[1 + \xi(2-\xi)(\lambda_j\dot{\gamma})^2]} \tag{20.5-19}$$

$$\Psi_2(\dot{\gamma}) = -\sum_j \frac{(\tau_{jyy} - \tau_{jzz})}{\dot{\gamma}^2} = -\frac{\xi}{2}\Psi_1 \tag{20.5-20}$$

At high shear rates it is seen that $\eta \propto \dot{\gamma}^{-2}$ which is physically impossible; however, this asymptotic behavior is not reached until $\dot{\gamma} \gg 1/\lambda_{\min}$ where $\lambda_{\min}$ is the smallest of the empirically fit time constants. The asymptotic behavior of Ψ_1 is also proportional to $\dot{\gamma}^{-2}$, which is much closer to experimental observations at high shear rates. From Eq. 20.5-20 we see that if Ψ_2 can be measured, then its ratio to Ψ_1 can be used to determine the slip parameter ξ. Experimental data on polymer melts and concentrated solutions suggests a value of ξ in the range $0.1 < \xi < 0.5$.

In the absence of experimental data on Ψ_2, ξ can be estimated from comparisons of $\eta(\dot{\gamma})$ and $\eta'(\omega)$. For small rates of deformation, Eqs. 20.5-8 and 10 reduce to the Lodge network model Eq. 20.4-10 (with η_j replaced by $\hat{\eta}_j$) which is the same as the Rouse model Eq. 15.3-17 (with $\eta_s = 0$ $\eta_j = nkT\lambda_j$ and the λ_j undetermined). The small amplitude oscillatory shearing properties are then given by Eqs. 15.3-29 and 30. For η' we have

$$\eta' = \sum_j \frac{\hat{\eta}_j}{[1 + (\lambda_j\omega)^2]} \tag{20.5-21}$$

Comparing η and η' shows

$$\eta(\dot{\gamma}) = \eta'(\omega)|_{\omega = \sqrt{\xi(2-\xi)}\dot{\gamma}} \tag{20.5-22}$$

Thus the viscosity curve is identical to the η' curve except that it is shifted to the right on the shear rate/frequency axis by a factor of $\sqrt{\xi(2-\xi)}$. This horizontal displacement is not actually observed experimentally. Although η does lie above η' at high frequencies and shear rates, the two curves have different slopes with η' decreasing more rapidly than η. Nonetheless, the difference in η and η' at large $\dot{\gamma}$ and ω can be approximated by a horizontal shift, and the magnitude of the shift gives ξ.

(b) Elongational Flow

For steady elongational flow with elongation rate $\dot{\varepsilon}$ we can again use Table C.1 to find the contributions to the constitutive equation Eq. 20.5-10. When these are combined we have

$$\begin{pmatrix} \tau_{jxx} & 0 & 0 \\ 0 & \tau_{jyy} & 0 \\ 0 & 0 & \tau_{jzz} \end{pmatrix} - \lambda_j\dot{\varepsilon}(1-\xi)\begin{pmatrix} -\tau_{jxx} & 0 & 0 \\ 0 & -\tau_{jyy} & 0 \\ 0 & 0 & 2\tau_{jzz} \end{pmatrix} = -\hat{\eta}_j\dot{\varepsilon}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{20.5-23}$$

The stress components are given by

$$\tau_{jxx} = \tau_{jyy} = \frac{\hat{\eta}_j\dot{\varepsilon}}{[1 + (1-\xi)\lambda_j\dot{\varepsilon}]} \tag{20.5-24}$$

$$\tau_{jzz} = \frac{-2\hat{\eta}_j\dot{\varepsilon}}{[1 - 2(1-\xi)\lambda_j\dot{\varepsilon}]} \tag{20.5-25}$$

Thus the elongational viscosity is given by

$$\bar{\eta} = -\frac{\tau_{zz} - \tau_{xx}}{\dot{\varepsilon}} = 3\sum_j \frac{\hat{\eta}_j}{[1 + (1-\xi)\lambda_j\dot{\varepsilon}][1 - 2(1-\xi)\lambda_j\dot{\varepsilon}]} \tag{20.5-26}$$

An infinite value of $\bar{\eta}$ is found when either

$$\dot{\varepsilon} = -\frac{1}{(1-\xi)\lambda_{\max}} \quad \text{or} \quad \dot{\varepsilon} = \frac{1}{2(1-\xi)\lambda_{\max}} \tag{20.5-27}$$

For values of ξ between 0.1 and 0.5, these critical strain rates are within a factor of two of the critical elongation rates found for Hookean dumbbells (cf. Eq. 13.4-36).

b. Time-Dependent Segment Creation and Loss Rates

Let us replace assumption (x) used in the Lodge network model by:

x′. The creation and loss rates can be functions of time.

With this additional generality most of the development leading up to the constitutive equation in §20.4 can be taken over with only slight modification. This leads to the following constitutive equation for the contribution of iN-segments to the total stress tensor

$$\boxed{\boldsymbol{\pi}_{iN} + \lambda_{iN}(t)\boldsymbol{\pi}_{iN(1)} = -kT\hat{L}_{iN}(t)\lambda_{iN}(t)\boldsymbol{\delta}} \tag{20.5-28}$$

which is equivalent to Eq. 20.4-3 with λ_{iN} and $\hat{L}_{iN}$ allowed to depend on time. Also in writing Eq. 20.5-28 we have assumed that segments are created with a Gaussian distribution so that $\bar{L}_{iN}$ can be replaced by the rate of creation of all iN-segments $\hat{L}_{iN}$ by means of Eq. 20.4-7. The pressure contribution, obtained by evaluating the above at equilibrium, is

$$p_{iN} = -kT\hat{L}_{iN,\,\mathrm{eq}}\lambda_{iN,\,\mathrm{eq}} = -n_{iN,\,\mathrm{eq}}kT \tag{20.5-29}$$

in which the subscript $_{\mathrm{eq}}$ denotes an equilibrium value. By subtracting $p_{iN}\boldsymbol{\delta}$ from $\boldsymbol{\pi}_{iN}$ we get a constitutive equation for the extra stress

$$\boxed{\boldsymbol{\tau}_{iN} + \lambda_{iN}(t)\boldsymbol{\tau}_{iN(1)} = -kT\hat{L}_{iN,\,\mathrm{eq}}\lambda_{iN,\,\mathrm{eq}}\lambda_{iN}(t)\dot{\boldsymbol{\gamma}} - kT[\hat{L}_{iN}(t)\lambda_{iN}(t) - \hat{L}_{iN,\,\mathrm{eq}}\lambda_{iN,\,\mathrm{eq}}]\boldsymbol{\delta}} \tag{20.5-30}$$

The integral forms of Eqs. 20.5-28 and 30 give the following constitutive equations for the total stress tensor and the extra stress tensor, respectively:

$$\boxed{\boldsymbol{\pi} = -\int_{-\infty}^{t} M(t, t')\mathbf{B}(t, t')dt'} \tag{20.5-31}$$

$$\boxed{\boldsymbol{\tau} = \sum_j n_{j,\,\mathrm{eq}}kT\boldsymbol{\delta} - \int_{-\infty}^{t} M(t, t')\mathbf{B}(t, t')dt'} \tag{20.5-32}$$

where

$$M(t, t') = kT\sum_j \hat{L}_j(t')\exp\left[-\int_{t'}^{t}\lambda_j^{-1}(t'')dt''\right] \tag{20.5-33}$$

where the sums on i and N have again been abbreviated as a single sum on j. Two differences between these results and Eqs. 20.4-4, 5 and 11 are evident. First, the memory function M now depends on t and t' separately, rather than only on their difference, $t - t'$. Second, the equation for the extra stress is now written more conveniently in terms of $\mathbf{B}$ than in terms of $\boldsymbol{\gamma}_{[0]}$, because of the time dependence of $\hat{L}_{iN}$ and λ_{iN}. If information is desired about the deformation of the segments during flow, this can be obtained from Eq. 20.2-17 with $\bar{L}_{iN}$ replaced by $\frac{1}{3}(N-1)a^2\hat{L}_{iN}$.

We now describe three models which can be obtained from the general constitutive equations above by making specific assumptions about the segment kinetics. These are the models of Acierno, La Mantia, Marrucci, and Titomanlio, of Wagner, and of Phan-Thien and Tanner.

The Acierno, La Mantia, Marrucci, and Titomanlio Model[4]

Although not originally developed as a molecular network theory, it has been shown by Jongschaap[5] that this model can be derived from a network theory in which the creation and loss rates are given by

$$\hat{L}_j(t) \equiv \int L_j(Q, t)dQ = \frac{n_j(t)}{\nu_j(t)} \tag{20.5-34}$$

$$\frac{1}{\lambda_j(t)} = \frac{1}{\nu_j(t)}\left(\alpha\sqrt{\frac{-\text{tr}\,\tau_j}{2G_j}} - \frac{1}{x_j} + 2\right) \tag{20.5-35}$$

in which $\nu_j(t)$ is a time "constant" for creation, α is an adjustable constant, and x_j is the number density of j-segments at time t divided by the equilibrium number density

$$x_j = \frac{n_j}{n_{j,\text{eq}}} \tag{20.5-36}$$

The G_j are moduli given by

$$G_j = n_j kT \tag{20.5-37}$$

The functions ν_j describing creation are assumed to depend on x_j as follows:

$$\nu_j(t) = \nu_{j,\text{eq}} x_j(t)^{1.4} \tag{20.5-38}$$

The exponent of 1.4 on x_j in this equation is chosen so that the zero-shear-rate viscosity is proportional to $n^{3.4}$ where n is the total number density of segments. Allowing the segment loss rates to depend on the trace of the extra stress tensor as is done in Eq. 20.5-35 would seem to be a reasonable postulate in view of the connection between segment stretching and $\text{tr}\,\tau_j$ (cf. Eq. 20.4-18).

To obtain the memory function for this model we begin by integrating the convection equation, Eq. 20.2-7, over all configurations Q. If we use the divergence theorem on the first term on the right side of Eq. 20.2-7 and assert that $\Psi_j \to 0$ as $Q \to \infty$ then we obtain[6]

$$\frac{\partial n_j}{\partial t} = \hat{L}_j - \frac{n_j}{\lambda_j} = n_j\left(\frac{1}{\nu_j} - \frac{1}{\lambda_j}\right) \tag{20.5-39}$$

[4] D. Acierno, F. P. La Mantia, G. Marrucci, and G. Titomanlio, *J. Non-Newtonian Fluid Mech.*, **1**, 125–146 (1976); see also H. Janeschitz-Kriegl, *Polymer Melt Rheology and Flow Birefringence*, Springer, Berlin (1983), §2.5.5. The differential form of the model as originally proposed is given as Eq. E in Table 7.6-1.

[5] R. J. J. Jongschaap, *J. Non-Newtonian Fluid Mech.*, **8**, 183–190 (1983).

[6] Equation 20.5-39 corresponds to Acierno et al.'s equation for the "structure" variable x_j. Their equation is obtained from Eq. 20.5-39 by replacing n_j by x_j (Eq. 20.5-36) and by using Eq. 20.5-35 for λ_j.

The solution for the number density of segments is

$$n_j(t) = n_j(t') \exp\left[\int_{t'}^{t}\left(\frac{1}{\nu_j(t'')} - \frac{1}{\lambda_j(t'')}\right)dt''\right]$$
$$= \hat{L}_j(t')\nu_j(t') \exp\left[\int_{t'}^{t}\left(\frac{1}{\nu_j(t'')} - \frac{1}{\lambda_j(t'')}\right)dt''\right] \tag{20.5-40}$$

where in the second line we have used Eq. 20.5-34 to write the number density at t' in terms of the creation rate. Finally we solve Eq. 20.5-40 for $\hat{L}_j$ and combine this result with Eq. 20.5-33 to get the memory function

$$M(t, t') = kT \sum_j \hat{L}_j(t') \exp\left[-\int_{t'}^{t} \frac{1}{\lambda_j(t'')}\, dt''\right]$$
$$= \frac{n_j(t)kT}{\nu_j(t')} \exp\left[-\int_{t'}^{t} \frac{1}{\nu_j(t'')}\, dt''\right] \tag{20.5-41}$$

When written as in the bottom line above, the relaxation times for the model are seen to be associated with segment creation rates rather than segment loss rates as found in the Lodge network model or the Wagner or Phan-Thien–Tanner models to be discussed next. Acierno, La Mantia, Marrucci, and Titomanlio[7] report that good fits to low density polyethylene data can be obtained with Eqs. 20.5-32 and 41.

Phan-Thien–Tanner Model

Another model in which segment kinetics are allowed to depend on $\operatorname{tr}\boldsymbol{\tau}_j$ is the Phan-Thien–Tanner model[8] which was discussed previously in connection with non-affine segment motion. Phan-Thien and Tanner assume that both the creation and loss rates depend on the mean squared segment vector $\langle Q^2\rangle_j$:

$$L_j = \hat{L}_j(\langle Q^2\rangle_j)\psi_{N,\mathrm{eq}} \tag{20.5-42}$$

$$\lambda_j = \lambda_j(\langle Q^2\rangle_j) \tag{20.5-43}$$

The constitutive equation and pressure are then given by Eqs., 20.5-28, 29, 42, and 43. To evaluate $\langle Q^2\rangle_j$ we note that since $\boldsymbol{\pi}_j = -H_N\langle \boldsymbol{QQ}\rangle_j$ we must have

$$\langle Q^2\rangle_j = -\frac{1}{H_N}\operatorname{tr}\boldsymbol{\pi}_j$$
$$= -\frac{1}{H_N}(\operatorname{tr}\boldsymbol{\tau}_j + 3p_j)$$
$$= (N-1)a^2\left(\hat{L}_{j,\mathrm{eq}}\lambda_{j,\mathrm{eq}} - \frac{1}{3kT}\operatorname{tr}\boldsymbol{\tau}_j\right) \tag{20.5-44}$$

The differential equation for the extra stress is Eq. 20.5-30.

[7] Acierno et al., *op. cit.*

[8] N. Phan-Thien and R. I. Tanner, *J. Non-Newtonian Fluid Mech.*, **2**, 353–365 (1977); N. Phan-Thien, *J. Rheol.*, **22**, 259–283 (1978); R. I. Tanner, *J. Non-Newtonian Fluid Mech.*, **5**, 103–112 (1979).

To simplify Eq. 20.5-30 we next assume that λ_j^{-1} and $\hat{L}_j$ both have the same dependence on $\text{tr}\,\tau_j$. We write this as

$$\hat{L}_j(\text{tr}\,\tau_j) = \frac{G_0}{kT\lambda_j(\text{tr}\,\tau_j)} \tag{20.5-45}$$

where G_0 is a constant modulus. It then follows that

$$\hat{L}_{j,\text{eq}}\lambda_{j,\text{eq}} = \hat{L}_j\lambda_j = \frac{G_0}{kT} \tag{20.5-46}$$

so that the extra stress is given by[9]

$$\tau_j + \lambda_j(\text{tr}\,\tau_j)\tau_{j(1)} = -G_0\lambda_j(\text{tr}\,\tau_j)\dot{\gamma} \tag{20.5-47}$$

Finally, we let

$$\lambda_j = \frac{\lambda_{j0}}{Y(\text{tr}\,\tau_j)} \tag{20.5-48}$$

where λ_{j0} is a constant with units of time and Y is a dimensionless function of τ_j. The same function Y is used for all j. The constitutive equation then becomes

$$Y(\text{tr}\,\tau_j)\tau_j + \lambda_{j0}\tau_{j(1)} = -\eta_j\dot{\gamma} \tag{20.5-49}$$

where $\eta_j = G_0\lambda_{j0}$. Finally, in the Phan-Thien–Tanner model, the segment kinetics that lead to Eq. 20.5-49 are combined with the non-affine motion assumption that leads to Eq. 20.5-10. In this way we obtain

$$\tau = \sum_j \tau_j \tag{20.5-50}$$

$$Y(\text{tr}\,\tau_j)\tau_j + \lambda_{j0}\tau_{j(1)} + \tfrac{1}{2}\lambda_{j0}\xi\{\dot{\gamma}\cdot\tau_j + \tau_j\cdot\dot{\gamma}\} = -\hat{\eta}_j\dot{\gamma} \tag{20.5-51}$$

$\hat{\eta}_j$ being given by Eq. 20.5-11. To complete the model an expression for Y must be postulated. Phan-Thien and Tanner have suggested two empirical forms

$$Y = \begin{cases} 1 - \varepsilon\lambda_{j0}(\text{tr}\,\tau_j)/\hat{\eta}_j & \text{(20.5-52a)} \\ \exp(-\varepsilon\lambda_{j0}(\text{tr}\,\tau_j)/\hat{\eta}_j) & \text{(20.5-52b)} \end{cases}$$

in which $\varepsilon \geq 0$ is an adjustable constant. The difference in the choice of Y can be seen in the elongational viscosity. For Eq. 20.5-52a, $\bar{\eta}$ is a monotone increasing function of $\dot{\varepsilon}$ which approaches a constant value as $\dot{\varepsilon} \to \infty$. For Eq. 20.5-52b, $\bar{\eta}$ goes through a maximum with increasing $\dot{\varepsilon}$.

[9] Note that Eq. 20.5-47 is very similar to the White-Metzner model, Eq. 7.3-1. The difference is that in the Phan-Thien and Tanner model the time constant is allowed to depend on $\text{tr}\,\tau$ whereas in the White Metzner model the time constant depends on $\dot{\gamma}$.

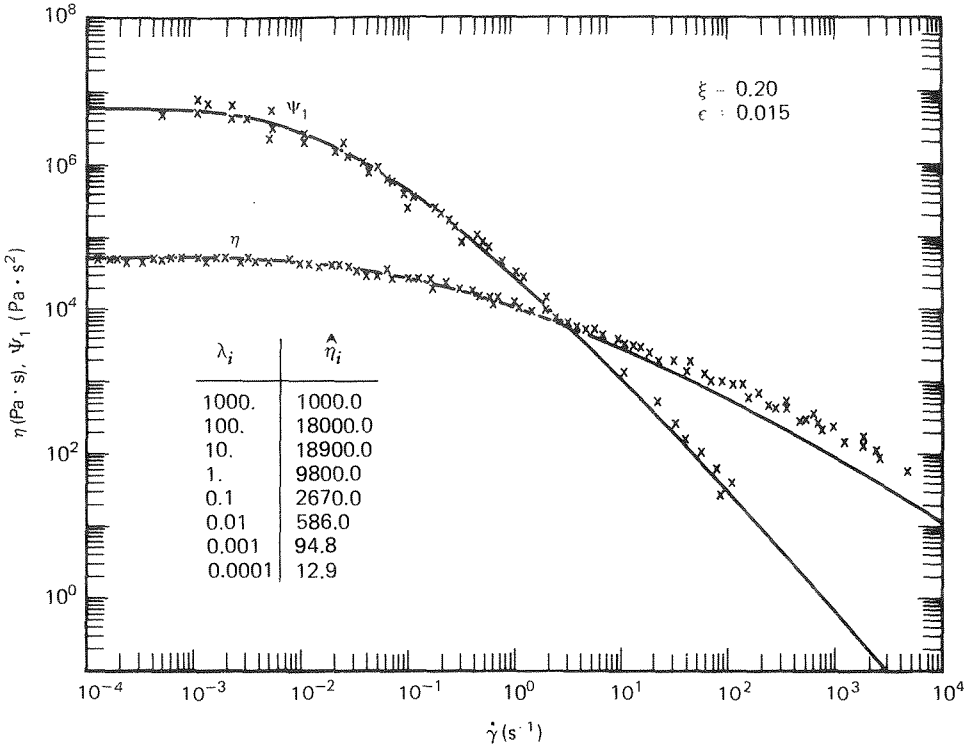


FIGURE 20.5-1. Comparison of predictions of the Phan-Thien Tanner model, Eqs. 20.5-50, 51 and 52b, with η and Ψ_1 data for a low density polyethylene melt. The constants λ_{0j} and $\hat{\eta}_j$ were fit with linear viscoelastic data (cf. Example 5.3-7); the constants ξ and ε were chosen to be 0.2 and 0.015, respectively, in order to achieve a best fit of the data. Data from H. M. Laun, *Rheol. Acta*, **17**, 1-15 (1978).

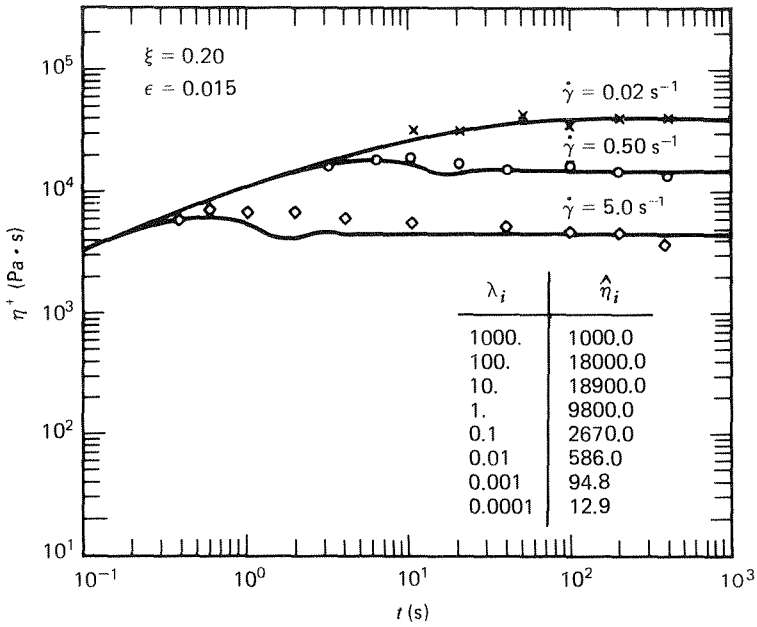


FIGURE 20.5-2. Comparison of the Phan-Thien Tanner model predictions with low density polyethylene data for η^+ in the start-up of steady shear flow. The model parameters are the same as in Fig. 20.5-1. Data as reported by M. H. Wagner, *Rheol. Acta*, **15**, 136-142 (1976).

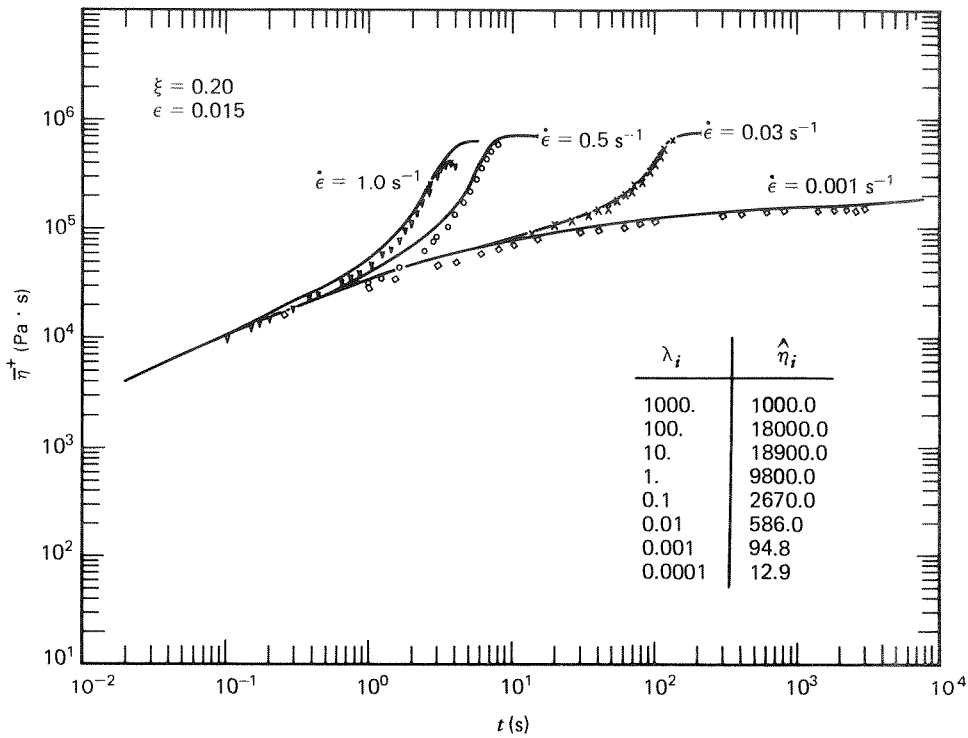


FIGURE 20.5-3. Comparison of the Phan-Thien–Tanner model predictions with low density polyethylene data for $\bar{\eta}^+$ in the start-up of steady elongational flow. The model parameters are the same as in Fig. 20.5-1. Data as reported by M. H. Wagner, *Rheol. Acta*, **18**, 39–50 (1979).

A comparison of the Phan-Thien–Tanner model (with Y given by Eq. 20.5-52b) predictions with rheological properties of low density polyethylene is shown in Figs. 20.5-1 to 3. In making these fits, the linear viscoelastic properties η' and η'' were first used to determine the λ_{j0} and $\hat{\eta}_j$. This procedure is illustrated in Example 5.3-7 and the values for λ_{j0} and $\hat{\eta}_j$ are those given in Table 5.3-7 (in this table λ_{j0} is listed as λ_j). After the λ_{j0} and $\hat{\eta}_j$ are determined, there are only two adjustable constants, ξ and ε, to be used in fitting nonlinear material functions. The choices of $\xi = 0.015$ and $\varepsilon = 0.2$ used here represent best fits of the low-density polyethylene data. In fitting these parameters it is found that the shear-flow properties are insensitive to ε and the shearfree flow properties are insensitive to ξ. Thus ξ and ε can be determined from separate sets of experiments. The fits are seen to be quite good, although it is not possible to fit exactly both η and Ψ_1 in the high shear rate region with the same value of ξ.

Wagner Model

An even more successful equation of the form of Eqs. 20.5-32 and 33 for describing rheological properties of molten polymers is one in which the memory function includes a scalar function of strain between times t' and t as a factor. Step-strain experiments[10] (cf.

[10] H. M. Laun, *Rheol. Acta*, **17**, 1–15 (1978); Y. Einaga, K. Osaki, M. Kurata, and M. Tamura, *Polymer J.*, **2**, 550–552 (1971).

Figs. 3.4-15 and 16) have given compelling evidence for such a "strain/time" factorization, at least in the terminal zone of the relaxation spectrum.

Wagner[11] assumes that the creation rates $\hat{L}_j$ are constant and that there are two *independent* mechanisms for segment loss:

(1) one, due to Brownian motion, as described by constant loss probabilities $1/\lambda_j$, and

(2) another, due to "rupture by deformation." For this mechanism, the probability that a segment will survive from the instant of creation t' to the present time t is the same for all segments and is denoted by $1/\lambda_d(t', t)$.

Since the two loss mechanisms are independent, the total loss probability $1/\lambda_j(t', t)$ is given

$$\frac{1}{\lambda_j(t', t)} = \frac{1}{\lambda_j} + \frac{1}{\lambda_d(t', t)} \tag{20.5-53}$$

The molecular weight and temperature dependence of λ_j and $\hat{L}_j$ are the same as for the Lodge network model, Eqs. 20.4-14 and 15. The deformation dependent term $\lambda_d(t', t)$ is independent of molecular weight and temperature.

The constitutive equation is then given by Eqs. 20.5-31 and 32 with

$$\begin{aligned} M(t, t') &= kT \sum_j \hat{L}_j e^{-(t-t')/\lambda_j} \exp\left(- \int_{t'}^{t} \frac{1}{\lambda_d(t'', t)}\, dt'' \right) \\ &= kTh(I_w(t', t)) \sum_j \hat{L}_j e^{-(t-t')/\lambda_j} \end{aligned} \tag{20.5-54}$$

in which the *damping function* h is defined by

$$h(I_w(t', t)) = \exp\left(- \int_{t'}^{t} \frac{1}{\lambda_d(t'', t)}\, dt'' \right) \tag{20.5-55}$$

I_w is a generalized strain invariant, formed from the first and second invariants of $\mathbf{B}$ (cf. Eqs. 8.3-1 and 2)

$$\begin{aligned} I_1 &= \text{tr } \mathbf{B} \\ I_2 &= \text{tr } \mathbf{B}^{-1} \end{aligned} \tag{20.5-56}$$

The specific dependence of I_w on I_1 and I_2 is determined empirically.

For small strains it is assumed that no segments are broken by the deformation, so that $\lambda_d \to \infty$ and $h \to 1$. Thus the constants $\hat{L}_j$ ($\equiv \eta_j/kT\lambda_j^2$) and λ_j can be determined from linear viscoelastic data in the same way as for the Lodge network model. The damping function h was fit by Wagner to stress relaxation data for single-step, shear strain experiments and stress growth data in the start-up of steady elongational flow experiments for a low density polyethylene melt. This led to the following form for h

$$h = \exp\left[-\beta\sqrt{\alpha I_1 + (1-\alpha)I_2 - 3} \right] \tag{20.5-57}$$

[11] M. H. Wagner, *Rheol. Acta*, **18**, 33–50 (1979).

with $\beta = 0.18$ and $\alpha = 0.032$. Note that h in Eq. 20.5-57 is equivalent to a deformation loss probability

$$\frac{1}{\lambda_d(t', t)} = -\frac{\beta}{2\sqrt{I_w}} \frac{dI_w}{dt'} \tag{20.5-58}$$

where

$$I_w = \alpha I_1 + (1 - \alpha) I_2 - 3 \tag{20.5-59}$$

The resulting constitutive equation, a particular case of the Rivlin–Sawyers class of equations, gives an excellent description of a variety of experiments in shear and elongation, but it significantly overestimates the free recovery following elongation at constant rates.[12] The agreement with shear recovery data (following shear flow) is satisfactory, however.

To remedy the errors in free recovery following start-up of steady elongational flow, Wagner and Stephenson[13] revised the second mechanism for segment loss as follows:

(2′) Segments are lost *irreversibly* during a nondecreasing deformation and are not recreated during subsequent decreasing deformation; the deformation-dependent survival function h in Eq. 20.5-54 should be replaced by a functional H of strain given by

$$H(t, t') = \underset{t''=t'}{\overset{t''=t}{\text{Min}}} \{h(I_w(t', t''))\} \tag{20.5-60}$$

where "Min" denotes the minimum value assumed by the function h over the interval indicated.

The terms decreasing and non-decreasing as applied to the deformations here are defined by

$$\text{A deformation is } \left\{\begin{matrix}\text{non-decreasing} \\ \text{decreasing}\end{matrix}\right\} \text{ throughout an interval } (t', t) \text{ where } t' < t$$

$$\text{provided that } h(I_w(t', t'')) \text{ is } \left\{\begin{matrix}\text{increasing} \\ \text{non-increasing}\end{matrix}\right\} \text{ for } t' < t'' < t \tag{20.5-61}$$

With these modifications, network segments that are lost during elongation from deformation-induced rupture are not recreated during recovery. Much better agreement with recovery data following elongation is then obtained.

An interesting consequence of the appearance of two times in $\lambda_j(t', t)$ in the Wagner model is that it is not in general possible to find an equivalent differential form for the constitutive equation, as we have been able to do for the other network models discussed in this chapter. A further discussion of the Wagner model and its material functions is given in Example 8.3-2.

[12] M. H. Wagner, *I. U. T. A. M. Conf.*, Louvain, Belgium (1978).
[13] M. H. Wagner and S. E. Stephenson, *J. Rheol.*, **23**, 491–504 (1979).

PROBLEMS

20A.1 Elongation of a Rubber Band

A slender rubber band has an equilibrium length of 0.60 m. One end of the rubber band is held fixed, while a weight of mass 0.050 kg is attached to the other end. Under this weight the rubber band is stretched to a total length of 0.80 m. Assume that the rubber is a neo-Hookean material, and calculate the weight necessary to stretch the rubber band to 1.00 m.

20A.2 Determination of Parameters in the Mooney Equation

A rectangular strip of crosslinked rubber sheet has equilibrium dimensions given by $x_0 = 0.30$ m, $y_0 = 0.02$ m, and $z_0 = 0.001$ m (Fig. 20A.2). A first test is performed on the sample by applying tensile forces of 10 N parallel to the x-axis to the ends of the material that are initially located at $x = 0$ and $x = x_0$. Under the action of this load, the strip undergoes a homogeneous elongation that increases its length by 71% in the x-direction. The material is then allowed to return to its equilibrium shape. A second experiment is then performed by clamping the edges at $y = 0$ and $y = y_0$; in this way the dimension of the strip in the x-direction is held fixed at x_0. Tensile forces of 50 N are now applied to the sample parallel to the y-axis by means of the clamps, and the strip undergoes homogeneous pure shear that increases its y-dimension by 12%. Assume that the rubber is described by the Mooney equation given in Eq. 20.3-15, and estimate the modulus G_0 and the parameter q.

20B.1 Estimation of Segment Number Density

Consider the elementary network model for a macromolecular fluid described in §20.4. Assume that there is only one kind of segment.

a. Show that the total number density of segments is given as follows in terms of the viscometric functions.

$$n = \frac{2[\eta(\dot{\gamma})]^2}{kT\Psi_1(\dot{\gamma})} \tag{20B.1-1}$$

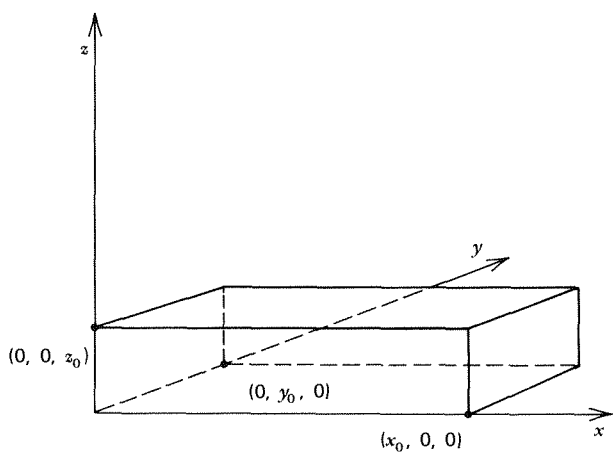


FIGURE 20A.2. A rectangular strip of rubber sheet with dimensions $x_0 = 0.30$ m, $y_0 = 0.02$ m, and $z_0 = 0.001$ m.

b. From the data[1] in Figs. 3.3-3 and 5 plot $2[\eta(\dot{\gamma})]^2/kT\Psi_1(\dot{\gamma})$ as a function of the shear rate $\dot{\gamma}$ for the 1.5% polyacrylamide solution.

c. Use Eq. 20B.1-1 and the plot to make a rough estimate of the total number density of segments in the solution. Are the data consistent with the theory?

20B.2 Strain Increment Test of a Network Model[2]

It is desired to test whether a given polymer material can be described by the generalization of the Lodge network model, Eq. 20.5-32, in which $M(t, t')$ is allowed to be any scalar functional of the deformation history. Specifically consider a shear flow that is arbitrary up to a certain time t_0. Let x', y', z' denote the past coordinates of a typical particle that just prior to time t_0 has coordinates x^-, y^-, z^-. Then at time t_0 an additional shear strain γ_0 is imposed on the material. Denote the new coordinates of the particle by x^+, y^+, z^+. In other words we consider the following deformation history:

For $t < t_0^-$:

$$x = x' - \gamma_{yx}(t, t')y' \qquad y = y' \qquad z = z' \tag{20B.2-1}$$

For $t = t_0^+$:

$$x^+ = x' + (\gamma_0 - \gamma_{yx}(t_0^-, t'))y' \qquad y^+ = y' \qquad z^+ = z' \tag{20B.2-2}$$

where $\gamma_{yx}(t, t') = \int_t^{t'} \dot{\gamma}_{yx}(t'')dt''$ is the shear strain from time t to time t'. Note that $\gamma_0 = -\int_{t_0^-}^{t_0^-} \dot{\gamma}_{yx}(t'')dt''$.

a. Assume that M is unchanged by the instantaneous deformation at time t_0, and derive expressions for τ_{yx}^-, $(\tau_{xx} - \tau_{yy})^-$, τ_{yx}^+, and $(\tau_{xx} - \tau_{yy})^+$ where the superscripts "$-$" and "$+$" indicate that the stress-tensor components are to be evaluated just prior to and just after the instantaneous deformation, respectively.

b. Let n denote the total number density of segments at time t_0. By using the results of Problem 20B.5 for $\dot{n}_j(t, t')$ and Eq. 20.4-30, show that

$$\tau_{yx}^+ = \tau_{yx}^- - nkT\gamma_0 \tag{20B.2-3}$$

$$(\tau_{xx} - \tau_{yy})^+ = (\tau_{xx} - \tau_{yy})^- + \gamma_0(\tau_{yx}^+ + \tau_{yx}^-) \tag{20B.2-4}$$

Equations 20B.2-3 and 4 combined represent a test (albeit not a sufficient condition) of the validity of the assumptions leading to Eq. 20.5-32, as well as a method for estimating the number density of segments n in any shear flow experiment.

20B.3 Start-Up of Shear Flow of the Lodge Network Model

Consider the constitutive equation given by Eq. 20.4-11 in which the memory function M is a function of $(t - t')$ only.

a. Derive expressions for the growth functions η^+, Ψ_1^+, and Ψ_2^+ in terms of $M(t - t')$.

[1] J. D. Huppler, E. Ashare, and L. A. Holmes, *Trans. Soc., Rheol.*, **11**, 159–179 (1967).

[2] A. S. Lodge and J. Meissner, *Rheol. Acta*, **11**, 351–352 (1972).

b. From the expressions for η^+ and Ψ_1^+ show that:

$$\Psi_1^+(t, \dot{\gamma}) = 2\left[t\eta^+(t, \dot{\gamma}) - \int_0^t \eta^+(t', \dot{\gamma})dt'\right] \tag{20B.3-1}$$

c. Derive expressions for η^+, Ψ_1^+, and Ψ_2^+ corresponding to the memory function M given in Eq. 20.4-11.

Answer: **c.** $\eta^+ = \sum_j \eta_j[1 - e^{-t/\lambda_j}]$

$$\Psi_1^+ = 2\sum_j \eta_j\lambda_j[1 - (1 + t/\lambda_j)e^{-t/\lambda_j}]$$

$$\Psi_2^+ = 0$$

20B.4 Verification of the Distribution Function Obtained from the Network Theory for Solids

a. Show that Eq. 20.2-23 is the correct distribution function for a network solid by substituting it into the convection equation.

b. By taking the convected derivative of Eq. 20.3-12, show that Eq. 20.3-13 is the differential form of the constitutive equation for a macromolecular network solid.

20B.5 Alternative Form for the Fluid Network Model Constitutive Equation

It is desired to rewrite the constitutive equation for the network model for polymeric fluids given in Eqs. 20.5-31 through 33 in terms of the number density of segments. By paralleling the development that led to Eq. 20.4-29, but allowing for time-dependent segment creation and loss rates, show that the memory function in Eq. 20.5-33 can be written as

$$M(t, t') = \sum_j \dot{n}_j(t, t')kT \tag{20B.5-1}$$

where $\dot{n}_j(t, t')$ is defined in Eq. 20.4-21.

20C.1 Constrained Recoil after Steady Shear Flow of the Lodge Rubberlike Liquid[3]

Consider a fluid described by the constitutive equation given by Eq. 20.4-11 with the assumption that the memory function, M, is a function of $t - t'$ only. The fluid is contained between two parallel plates, and has prior to time $t = 0$ been undergoing a steady shear flow with shear rate $\dot{\gamma}_0$. At time $t = 0$ the shear stress is suddenly removed. The fluid then recoils, and the magnitude of shear from time $t = 0$ is designated by $\gamma(t) = \int_0^t \dot{\gamma}(t'')dt''$. It is assumed that inertial effects are negligible and that the flow during recoil is homogeneous.

a. Show that for time $t \geq 0$ the magnitude of shear satisfies the integral equation:

$$M_0\gamma(t) + \dot{\gamma}_0 \int_t^\infty M(s)(t - s)ds = \int_0^t M(t - s)\gamma(s)ds \tag{20C.1-1}$$

Here and in the following we use the notation:

$$M_r = \int_0^\infty M(s)s^r\, ds \tag{20C.1-2}$$

[3] A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), pp. 144–147. See also Examples 6.2-5 and 6.3-2.

b. From Eq. 20C.1-1 show that the "instantaneous recoil," that is $\gamma_0 = \lim_{t \to 0} \gamma(t)$, is given by:

$$\gamma_0 = \frac{\dot{\gamma}_0 M_1}{M_0} \tag{20C.1-3}$$

c. Take the Laplace transform of Eq. 20C.1-1 by using the convolution theorem. Show that the Laplace transform $\bar{\gamma}(p)$ of $\gamma(t)$ is given by

$$\bar{\gamma}(p) = \dot{\gamma}_0 \frac{M_0 p^{-2} - M_1 p^{-1} - \bar{M}(p) p^{-2}}{\bar{M}(p) - M_0} \tag{20C.1-4}$$

where $\bar{M}(p)$ is the Laplace transform of $M(s)$.

d. Expand $\bar{M}(p)$ in powers of p, and use the final value theorem to show that the "ultimate recoil," that is, $\gamma_\infty = \lim_{t \to \infty} \gamma(t)$ is given by

$$\gamma_\infty = \dot{\gamma}_0 \frac{M_2}{2M_1} \tag{20C.1-5}$$

e. Discuss a form of $M(s)$ for which $\gamma_\infty = \gamma_0$ and a form for which $\gamma_\infty > \gamma_0$.

20C.2 Rapid Deformations of the Lodge Rubberlike Liquid[4]

Consider a network model given by Eq. 20.4-11, where M is a function of $t - t'$ only and is continuous at $t' = t$. The liquid has been undergoing an arbitrary homogeneous deformation at constant volume up to a time t_1. The position vector of a typical particle P at time t_1 is designated by $\boldsymbol{r}_1$. Similarly at a past time t' the position vector of P is designated by $\boldsymbol{r}'$.

a. At time t_1 the stress is suddenly made isotropic, and the liquid "instantaneously" undegoes a homogeneous deformation at constant volume, such that the position vector of P is given by $\boldsymbol{r}_0$. Show that the position vector $\boldsymbol{r}_0$ satisfies the following equations:

$$G_0 \left(\frac{\partial}{\partial \boldsymbol{r}_0} \boldsymbol{r}_1\right) \cdot \left(\frac{\partial}{\partial \boldsymbol{r}_0} \boldsymbol{r}_1\right)^\dagger = \int_{-\infty}^{t_1} M(t_1 - t') \left(\frac{\partial}{\partial \boldsymbol{r}'} \boldsymbol{r}_1\right) \cdot \left(\frac{\partial}{\partial \boldsymbol{r}'} \boldsymbol{r}_1\right)^\dagger dt' \tag{20C.2-1}$$

$$\det\left\{\left(\frac{\partial}{\partial \boldsymbol{r}_0} \boldsymbol{r}_1\right) \cdot \left(\frac{\partial}{\partial \boldsymbol{r}_0} \boldsymbol{r}_1\right)^\dagger\right\} = 1 \tag{20C.2-2}$$

Here G_0 is a constant that depends on the deformation history up to time t_1 as given by Eq. 20C.2-1.

b. Instead of the deformation described under part a, we now assume that at time t_1 the liquid is suddenly subjected to an arbitrary, rapid, homogeneous deformation at constant volume to a state t. Show that for such rapid deformations, the liquid model behaves as a solid described by:

$$\tau(t) = G_0 \gamma_{[0]}(t, t_0) \tag{20C.2-3}$$

The modulus G_0 and the isotropic stress state t_0 are those determined by Eqs. 20C.2-1 and 2. That is for rapid deformations the Lodge network model behaves as a neo-Hookean solid with modulus and isotropic stress state determined by the past history of deformation.

[4] This problem is patterned after the development by A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), pp. 124–129.

20C.3 Free Recovery after Steady-Shear Flow of the Lodge Rubberlike Liquid[5]

Consider the network model given by Eqs. 20.4-11, in which M is taken to be a function of $t - t'$ only. Assume that the liquid model has been undergoing a steady shear flow of shear rate $\dot{\gamma}_0$ up to time $t = t_1$. Then the stress is suddenly made isotropic. The subsequent deformation of the liquid is called a free recovery. For the present model the free recovery consists of an "instantaneous recovery" and a time-dependent "delayed recovery." During the delayed recovery the fluid slowly settles to an equilibrium shape. It is desired to use the results of Problem 20C.2 part (**a**) to calculate the instantaneous recovery.

Introduce a rectangular Cartesian coordinate system, such that the steady shear flow is given by $v_1 = \dot{\gamma}_0 x_2$, $v_2 = 0$, and $v_3 = 0$. For purposes of computation we assume that the instantaneous recovery may be decomposed artificially as follows:

First, imagine a shearfree deformation in which a typical particle P changes position vector from $\boldsymbol{r}_1$ to $\tilde{\boldsymbol{r}}$, such that

$$\tilde{\boldsymbol{r}} = [\boldsymbol{\Lambda}_1 \cdot \boldsymbol{r}_1] \tag{20C.3-1}$$

where

$$\boldsymbol{\Lambda}_1 = \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{pmatrix} \tag{20C.3-2}$$

Then imagine a shear flow in which P further changes position vector from $\tilde{\boldsymbol{r}}$ to the position $\boldsymbol{r}_0$ in the state after the instantaneous recovery, such that

$$\boldsymbol{r}_0 = [\boldsymbol{\Lambda}_2 \cdot \tilde{\boldsymbol{r}}] \tag{20C.3-3}$$

where

$$\boldsymbol{\Lambda}_2 = \begin{pmatrix} 1 & -\gamma & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{20C.3-4}$$

a. Show that

$$\alpha_2 = \alpha_3 = \alpha_1^{-1/2} = \alpha \tag{20C.3-5}$$

$$\alpha = [1 + \dot{\gamma}_0^2(M_0 M_2 - M_1^2)/M_0^2]^{1/6} \tag{20C.3-6}$$

$$\gamma = \dot{\gamma}_0 M_1/(M_0 \alpha^3) \tag{20C.3-7}$$

$$G_0 = M_0 \alpha^2 \tag{20C.3-8}$$

$$\alpha \geq 1 \tag{20C.3-9}$$

Here G_0 is the modulus defined by Eq. 20C.2-1 and the M_r are constants defined by Eq. 20C.1-2.

[5] This problem is patterned after the development by A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), pp. 131–139.

b. Show that the results of the above analysis alternatively may be expressed by the following statements concerning instantaneous recovery following shear flow of the Lodge network model:

1. The separation of each pair of material shearing planes increases by the factor α given above.
2. Each material line in the shearing planes, perpendicular to the direction of shear, increases in length by the factor α.
3. Each material line in the shearing planes, parallel to the direction of shear, is contracted by a factor of α^2.
4. Each material line that is normal to the shearing planes just prior to the moment of recovery is tilted backwards with respect to the original shear direction through an angle ε where $\tan \varepsilon = \gamma$ and γ is given above.

c. For a memory function of the form

$$M(s) = \frac{\eta}{\lambda^2} e^{-s/\lambda} \tag{20C.3-10}$$

show that

$$\alpha = [1 + (\lambda\dot{\gamma}_0)^2]^{1/6} \tag{20C.3-11}$$

$$\tan \varepsilon = \gamma = (\lambda\dot{\gamma}_0)[1 + (\lambda\dot{\gamma}_0)^2]^{-1/2} \tag{20C.3-12}$$

$$\frac{\lambda G_0}{\eta} = [1 + (\lambda\dot{\gamma}_0)^2]^{1/3} \tag{20C.3-13}$$

Here G_0 is the modulus given by Eq. 20C.2-1. Prepare plots to show α, $\tan \varepsilon$ and $\lambda G_0/\eta$ as functions of $\lambda\dot{\gamma}_0$.

20D.1 General Solution to the Convection Equation[6]

Assume that the loss probability λ_{iN} is a function of time alone, that is λ_{iN} is independent of $\boldsymbol{Q}$. Show that the convection equation, Eq. 20.2-7, is satisfied by

$$\Psi_{iN} = \int_{-\infty}^{t} \exp\left(\int_{t}^{t'} \lambda_{iN}^{-1}(t'')\, dt''\right) L_{iN}(\boldsymbol{\Delta}(t, t') \cdot \boldsymbol{Q}, t')dt' \tag{20D.1-1}$$

where L_{iN} depends on $[\boldsymbol{\Delta} \cdot \boldsymbol{Q}]$ as well as on t'.

[6] This problem is due to J. M. Wiest (personal communication).

APPENDIX D

SUMMARY OF CONTINUUM MECHANICS NOTATION AND RESULTS

Here we summarize some of the most important continuum mechanics ideas and notation from Volume 1 that are needed for the kinetic theory development in Volume 2: the kinematics of flow fields, various kinds of time derivatives, the most important kinematic tensors, commonly used constitutive equations, definitions of experimentally measured material functions, and the equations of change (or "conservation equations"). Of particular importance are the rather general constitutive equations in §D.4, since these provide a framework for displaying kinetic theory results. In the first two sections equations are given both in (Gibbs) tensor notation and in Cartesian component form; in the former we generally use boldface Italic symbols for vectors and boldface Greek symbols for second-order tensors.

§D.1 DESCRIPTION OF FLOW FIELDS

The motion of a fluid may be described in two ways: (a) in terms of the fluid velocity field, or (b) in terms of the fluid particle trajectories. Both descriptions are used in the definitions of kinematic tensors.

a. The Fluid Velocity Field and Closely Related Quantities

The *velocity* of a fluid at position $\boldsymbol{r}$ at time t is denoted by $\boldsymbol{v}(\boldsymbol{r}, t)$. A flow is said to be *homogeneous* if the velocity gradients are the same at all points in the fluid so that,

$$\boldsymbol{v} = \boldsymbol{v}_0 + [\boldsymbol{\kappa}(t)\cdot\boldsymbol{r}] \tag{D.1-1a}$$

$$v_i = v_{0i} + \sum_j \kappa_{ij}(t) x_j \tag{D.1-1b}$$

where $\boldsymbol{v}_0$ and $\boldsymbol{\kappa}$ are independent of position but may be functions of time. For incompressible fluids $\operatorname{tr}\boldsymbol{\kappa} = \sum_i \kappa_{ii} = 0$.

For any velocity field $\boldsymbol{v}$, the *rate-of-strain tensor* (or *rate-of-deformation tensor*) $\dot{\boldsymbol{\gamma}}$ is defined by

$$\dot{\boldsymbol{\gamma}} = \nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^{\dagger} \tag{D.1-2a}$$

$$\dot{\gamma}_{ij} = \frac{\partial}{\partial x_i} v_j + \frac{\partial}{\partial x_j} v_i \tag{D.1-2b}$$

where $\dagger$ indicates the transpose of the tensor. The magnitude of $\dot{\boldsymbol{\gamma}}$ is defined to be $\dot{\gamma} = \sqrt{\frac{1}{2}(\dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}})}$; in shear flows this quantity is called the "shear rate." Sometimes $\dot{\boldsymbol{\gamma}}$ is designated by $\boldsymbol{\gamma}^{(1)}$ or $\boldsymbol{\gamma}_{(1)}$ for reasons explained in §D.3.

The *vorticity tensor* is defined by

$$\boldsymbol{\omega} = \nabla \boldsymbol{v} - (\nabla \boldsymbol{v})^{\dagger} \tag{D.1-3a}$$

$$\omega_{ij} = \frac{\partial}{\partial x_i} v_j - \frac{\partial}{\partial x_j} v_i \tag{D.1-3b}$$

(*Caution*: Many authors define $\dot{\boldsymbol{\gamma}}$ and $\boldsymbol{\omega}$ with a factor of $\frac{1}{2}$ on the right side of the defining equations; sometimes $\boldsymbol{\omega}$ is defined with the opposite sign.)

b. The Fluid Particle Trajectories and Closely Related Quantities

Let a fluid particle be at position $\boldsymbol{r}$ at time t and at position $\boldsymbol{r}'$ at some other time t'. Then the motion of the fluid particle is given by the *displacement functions*

$$\boldsymbol{r} = \boldsymbol{r}(\boldsymbol{r}', t', t) \quad \text{or} \quad \boldsymbol{r}' = \boldsymbol{r}'(\boldsymbol{r}, t, t') \tag{D.1-4a}$$

$$x_i = x_i(x_1', x_2', x_3', t', t) \quad \text{or} \quad x_i' = x_i'(x_1, x_2, x_3, t, t') \tag{D.1-4b}$$

Specification of the displacement functions for all fluid particles is equivalent to giving the velocity field for all points in space and all times.

The *displacement gradient tensors* $\boldsymbol{\Delta}$ and $\mathbf{E}$ are given by:

$$\boldsymbol{\Delta} = \left(\frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{r}'\right)^{\dagger} \qquad \text{or} \qquad \Delta_{ij}(\boldsymbol{r}, t, t') = \frac{\partial x_i'}{\partial x_j} \tag{D.1-5}$$

$$\mathbf{E} = \left(\frac{\partial}{\partial \boldsymbol{r}'} \boldsymbol{r}\right)^{\dagger} \qquad \text{or} \qquad E_{ij}(\boldsymbol{r}, t, t') = \frac{\partial x_i}{\partial x_j'} \tag{D.1-6}$$

The tensors $\boldsymbol{\Delta}$ and $\mathbf{E}$ are inverse to one another, and are both equal to the unit tensor when $t' = t$. For incompressible fluids $\det \boldsymbol{\Delta} = 1$ and $\det \mathbf{E} = 1$.

§D.2 TIME DERIVATIVES

Four different kinds of time derivatives are encountered in continuum mechanics; we illustrate these in terms of derivatives of a second-order tensor $\mathbf{\Lambda}$:

a. The *partial derivative* $\partial\mathbf{\Lambda}/\partial t$, with Cartesian components $\partial\Lambda_{ij}/\partial t$, is a derivative with respect to time, the position in space being held fixed. Higher-order derivatives are $\partial^2\mathbf{\Lambda}/\partial t^2$, $\partial^3\mathbf{\Lambda}/\partial t^3$, and so on.

b. The *substantial* (or *material*) *derivative* gives the time rate of change following a fluid particle (i.e., following the "substance" or "material"):

$$\frac{D}{Dt}\mathbf{\Lambda} = \frac{\partial}{\partial t}\mathbf{\Lambda} + \{\boldsymbol{v}\cdot\nabla\mathbf{\Lambda}\} \tag{D.2-1a}$$

$$\frac{D}{Dt}\Lambda_{ij} = \frac{\partial}{\partial t}\Lambda_{ij} + \sum_k v_k \frac{\partial}{\partial x_k}\Lambda_{ij} \tag{D.2-1b}$$

Higher-order derivatives are designated by $D^2\mathbf{\Lambda}/Dt^2 = (D/Dt)(D\mathbf{\Lambda}/Dt)$, and so on.

c. The (*Jaumann*) *corotational derivative* gives the time rate of change, following a particle, in a coordinate frame rotating with the instantaneous fluid angular velocity at the particle:

$$\frac{\mathscr{D}}{\mathscr{D}t}\mathbf{\Lambda} = \frac{D}{Dt}\mathbf{\Lambda} + \frac{1}{2}\{\boldsymbol{\omega}\cdot\mathbf{\Lambda} - \mathbf{\Lambda}\cdot\boldsymbol{\omega}\} \tag{D.2-2a}$$

$$\frac{\mathscr{D}}{\mathscr{D}t}\Lambda_{ij} = \frac{D}{Dt}\Lambda_{ij} + \frac{1}{2}\sum_n (\omega_{in}\Lambda_{nj} - \Lambda_{in}\omega_{nj}) \tag{D.2-2b}$$

Higher-order derivatives are designated by $\mathscr{D}^2\mathbf{\Lambda}/\mathscr{D}t^2 = (\mathscr{D}/\mathscr{D}t)(\mathscr{D}\mathbf{\Lambda}/\mathscr{D}t)$, and so on.

d. The (*Oldroyd*) *convected derivatives* (or *codeformational derivatives*) give the time rate of change, following the particle, in a local coordinate system embedded in the fluid and moving along with it. Two such derivatives can be obtained, $\mathbf{\Lambda}^{(1)}$ and $\mathbf{\Lambda}_{(1)}$, the first corresponding to describing $\mathbf{\Lambda}$ in terms of its covariant components and the second corresponding to the use of contravariant components (see §9.4):

$$\mathbf{\Lambda}^{(1)} = \frac{\mathscr{D}}{\mathscr{D}t}\mathbf{\Lambda} + \tfrac{1}{2}\{\hat{\boldsymbol{\gamma}}\cdot\mathbf{\Lambda} + \mathbf{\Lambda}\cdot\hat{\boldsymbol{\gamma}}\} = \frac{D}{Dt}\mathbf{\Lambda} + \{(\nabla\boldsymbol{v})\cdot\mathbf{\Lambda} + \mathbf{\Lambda}\cdot(\nabla\boldsymbol{v})^{\dagger}\} \tag{D.2-3a}$$

$$\Lambda^{(1)}_{ij} = \frac{D}{Dt}\Lambda_{ij} + \sum_n \left(\frac{\partial v_n}{\partial x_i}\Lambda_{nj} + \Lambda_{in}\frac{\partial v_n}{\partial x_j}\right) \tag{D.2-3b}$$

$$\mathbf{\Lambda}_{(1)} = \frac{\mathscr{D}}{\mathscr{D}t}\mathbf{\Lambda} - \tfrac{1}{2}\{\hat{\boldsymbol{\gamma}}\cdot\mathbf{\Lambda} + \mathbf{\Lambda}\cdot\hat{\boldsymbol{\gamma}}\} = \frac{D}{Dt}\mathbf{\Lambda} - \{(\nabla\boldsymbol{v})^{\dagger}\cdot\mathbf{\Lambda} + \mathbf{\Lambda}\cdot(\nabla\boldsymbol{v})\} \tag{D.2-4a}$$

$$\Lambda_{(1)ij} = \frac{D}{Dt}\Lambda_{ij} - \sum_n \left(\frac{\partial v_i}{\partial x_n}\Lambda_{nj} + \Lambda_{in}\frac{\partial v_j}{\partial x_n}\right) \tag{D.2-4b}$$

Higher-order convected derivatives are defined as $\mathbf{\Lambda}^{(2)} = (\mathbf{\Lambda}^{(1)})^{(1)}$, $\mathbf{\Lambda}_{(2)} = (\mathbf{\Lambda}_{(1)})_{(1)}$, and so on. The convected derivatives are encountered in numerous discussions in Volumes 1 and 2.

§D.3 KINEMATIC TENSORS

Only the most commonly encountered kinematic tensors are summarized here. A more exhaustive listing may be found in Table 9.3-1, and tabulations of these quantities for shear and shearfree flows are given in Appendix C; the tables for cylindrical and spherical coordinates are to be found in Appendix B.

a. Higher Order Rate-of-Strain Tensors (Obtained from the Velocity Field)

The rate of strain tensor $\dot{\gamma}$ is defined in Eq. D.1-2. When used in equations along with its convected derivatives we usually use the notation $\gamma^{(1)}$ or $\gamma_{(1)}$ for this quantity; but we must emphasize that the index "(1)" in this case does *not* refer to the first convected derivative of the infinitesimal strain tensor γ. The higher-order convected derivatives are called the *second, third, ..., rate-of-strain tensors*:

$$\gamma^{(2)} = (\gamma^{(1)})^{(1)}, \qquad \gamma^{(3)} = (\gamma^{(2)})^{(1)}, \qquad \text{and so on.} \tag{D.3-1}$$

$$\gamma_{(2)} = (\gamma_{(1)})_{(1)}, \qquad \gamma_{(3)} = (\gamma_{(2)})_{(1)}, \qquad \text{and so on.} \tag{D.3-2}$$

The $\gamma^{(n)}$ are sometimes called the *Rivlin-Ericksen tensors*, $\mathbf{A}_n$, and are equal to two times *Oldroyd's nth rate-of-strain tensors*, $e^{(n)}$.

b. Finite Strain Tensors (Obtained from the Displacement Functions)

Many different *finite strain tensors* have been defined in the literature. In this volume we have restricted ourselves to three tensors $\gamma^{[0]}$, $\gamma_{[0]}$, and $\mathbf{B}$ defined by

$$\gamma^{[0]}(\boldsymbol{r}, t, t') = \mathbf{B}^{-1} - \boldsymbol{\delta} = \{\boldsymbol{\Delta}^{\dagger} \cdot \boldsymbol{\Delta} - \boldsymbol{\delta}\} \tag{D.3-3}$$

$$\gamma_{[0]}(\boldsymbol{r}, t, t') = \boldsymbol{\delta} - \mathbf{B} = (\boldsymbol{\delta} - \mathbf{E} \cdot \mathbf{E}^{\dagger}\} \tag{D.3-4}$$

in which $\boldsymbol{\Delta}$ and $\mathbf{E}$ are the tensors whose Cartesian components were given in Eqs. D.1-5 and 6, and $\mathbf{B}$ is called the *Finger strain tensor*. The tensors $\gamma^{[0]}$ and $\gamma_{[0]}$ are convenient, since they both simplify to the infinitesimal strain tensor γ for vanishingly small displacement gradients. Higher order time derivatives are designated as $\gamma^{[n]}(\boldsymbol{r}, t, t') = \partial^n \gamma^{[0]}/\partial t'^n$ and $\gamma_{[n]}(\boldsymbol{r}, t, t') = \partial^n \gamma_{[0]}/\partial t'^n$. Furthermore,

$$\gamma^{[n]}(\boldsymbol{r}, t, t) = \gamma^{(n)}(\boldsymbol{r}, t); \qquad \gamma_{[n]}(\boldsymbol{r}, t, t) = \gamma_{(n)}(\boldsymbol{r}, t) \tag{D.3-5}$$

gives the relation between the [ ] and ( ) quantities.

§D.4 CONSTITUTIVE EQUATIONS FOR INCOMPRESSIBLE FLUIDS

As pointed out in §9.6 a very general expression for the stress tensor is the *memory-integral expansion*

$$\tau(r, t) = \int_{-\infty}^{t} M_I(t - t')\gamma'_{[0]}\, dt'$$

$$+ \int_{-\infty}^{t}\int_{-\infty}^{t} M_{II}(t - t', t - t'')\{\gamma'_{[0]} \cdot \gamma''_{[0]} + \gamma''_{[0]} \cdot \gamma'_{[0]}\}dt''\, dt' + \cdots \quad \text{(D.4-1)}$$

in which $\gamma'_{[0]} \equiv \gamma_{[0]}(r, t, t')$; keep in mind that to get the stress at position r at time t, we are integrating over past times following the fluid particle that ends up at position r at time t. If the double-, triple-, ... integral terms are neglected, the remaining single-integral expression (with $M_I \equiv M$) is the *Lodge rubberlike liquid* (Eq. 8.2-1). Equation D.4-1 becomes the *general linear viscoelastic fluid* (Eqs. 5.2-18, 19) in the limit of vanishingly small displacement gradients

$$\tau(r, t) = \int_{-\infty}^{t} M(t - t')\gamma(r, t, t')dt'$$

$$= -\int_{-\infty}^{t} G(t - t')\dot{\gamma}(r, t')dt' \quad \text{(D.4-2)}$$

in which M is the "memory function" and G is the "relaxation modulus." The functions M and G are related by $M(t - t') = \partial G(t - t')/\partial t'$, and the infinitesimal strain tensor γ is given by $\gamma(r, t, t') = \int_{t}^{t'} \dot{\gamma}(r, t'')dt''$.

For flows that are slowly varying in space and time, $\gamma_{[0]}(r, t, t')$ can be expanded about $t' = t$ and Eq. D.4-1 takes the form of the *retarded-motion expansion* (Eq. 6.2-1)

$$\tau(r, t) = -[b_1\gamma_{(1)} + b_2\gamma_{(2)} + b_{11}\{\gamma_{(1)} \cdot \gamma_{(1)}\}$$

$$+ b_3\gamma_{(3)} + b_{12}\{\gamma_{(1)} \cdot \gamma_{(2)} + \gamma_{(2)} \cdot \gamma_{(1)}\}$$

$$+ b_{1;11}(\gamma_{(1)} : \gamma_{(1)})\gamma_{(1)} + \cdots] \quad \text{(D.4-3)}$$

in which the b's are constants related to integrals over the M's in Eq. D.4-1; furthermore $b_1 = \eta_0$, $b_2 = -\frac{1}{2}\Psi_{1,0}$, and $b_{11} = \Psi_{2,0}$, where η_0, $\Psi_{1,0}$, and $\Psi_{2,0}$ are the zero-shear-rate viscometric functions defined in Eqs. D.5-1 to 3. If only the dashed-underlined terms are retained in Eq. D.4-3, the constitutive equation is referred to as the *second-order fluid.*

For "viscometric flows" (steady unidirectional shear flows, as defined in §3.7), Eqs. D.4-1 and D.4-3 collapse to the very simple *Criminale-Ericksen-Filbey* (*CEF*) *equation*:

$$\tau = -\eta\gamma_{(1)} + \tfrac{1}{2}\Psi_1\gamma_{(2)} - \Psi_2\{\gamma_{(1)} \cdot \gamma_{(1)}\} \quad \text{(D.4-4)}$$

in which the $\eta(\dot{\gamma})$, $\Psi_1(\dot{\gamma})$, and $\Psi_2(\dot{\gamma})$ are the "viscometric functions"—functions of the "shear rate" $\dot{\gamma} = \sqrt{\frac{1}{2}(\gamma_{(1)} : \gamma_{(1)})}$.

In addition to the above constitutive equations which result from making a very general postulate about the form of the stress tensor and then exploring special forms that

result from restrictions on the kinematics of the flow field, one can also propose empirical expressions. One widely used differential model is the *Oldroyd 8-constant model* (Eq. 7.3-2)

$$\boldsymbol{\tau} + \lambda_1\boldsymbol{\tau}_{(1)} + \tfrac{1}{2}\lambda_3\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\tau} + \boldsymbol{\tau}\cdot\boldsymbol{\gamma}_{(1)}\} + \tfrac{1}{2}\lambda_5(\text{tr}\,\boldsymbol{\tau})\boldsymbol{\gamma}_{(1)} + \tfrac{1}{2}\lambda_6(\boldsymbol{\tau}:\boldsymbol{\gamma}_{(1)})\boldsymbol{\delta}$$
$$= -\eta_0[\boldsymbol{\gamma}_{(1)} + \lambda_2\boldsymbol{\gamma}_{(2)} + \lambda_4\{\boldsymbol{\gamma}_{(1)}\cdot\boldsymbol{\gamma}_{(1)}\} + \tfrac{1}{2}\lambda_7(\boldsymbol{\gamma}_{(1)}:\boldsymbol{\gamma}_{(1)})\boldsymbol{\delta}] \qquad \text{(D.4-5)}$$

in which η_0 is the zero-shear-rate viscosity and the λ_i are time constants. This constitutive equation is linear in $\boldsymbol{\tau}$ and contains all possible terms quadratic in the stress components and the velocity-gradient components consistent with giving a symmetric stress tensor. Equation D.4-5 contains a number of well-known equations as special cases.

Newtonian fluid	All λ_i are zero
Second-order fluid	$\lambda_2 \neq 0$, $\lambda_4 \neq 0$; all other λ_i are zero
Convected Maxwell model	$\lambda_1 \neq 0$; all other λ_i are zero
Convected Jeffreys model	$\lambda_1 \neq 0$, $\lambda_2 \neq 0$; all other λ_i are zero
Oldroyd 6-constant model	Only λ_6 and λ_7 are zero

There are relations between the six constants in the Oldroyd 6-constant model and the six constants in the third-order fluid (see Table 6.2-2). Other empirical differential models can be found in Chapter 7.

Among empirical integral models the most popular is the *factorized K-BKZ model* (Eq. 8.3-7):

$$\boldsymbol{\tau} = \int_{-\infty}^{t} M(t-t')\left[\frac{\partial W}{\partial I_1}\boldsymbol{\gamma}_{[0]}(\boldsymbol{r},t,t') + \frac{\partial W}{\partial I_2}\boldsymbol{\gamma}^{[0]}(\boldsymbol{r},t,t')\right]dt' \qquad \text{(D.4-6)}$$

in which W is a function of the two strain invariants $I_1 = \text{tr}\,\mathbf{B}$ and $I_2 = \text{tr}\,\mathbf{B}^{-1}$. The Lodge rubberlike liquid is obtained by setting W equal to I_1.

§D.5 DEFINITIONS OF MATERIAL FUNCTIONS FOR INCOMPRESSIBLE FLUIDS

Many experiments have been performed to determine the mechanical behavior of polymeric liquids in various flow situations. Each experiment gives rise to one or more "material functions." In Chapter 3 sample data are presented for polymer melts, concentrated polymer solutions, and dilute polymer solutions; the experimental arrangements are described in Chapter 10. Here we summarize the definitions of some of the more important material functions.

For *steady-shear flow* of the form $v_x = \dot{\gamma}y$, $v_y = 0$, $v_z = 0$, three combinations of stresses can be measured for an incompressible fluid:

$$\tau_{yx} = \tau_{xy} = -\eta\dot{\gamma} \qquad \text{(D.5-1)}$$

$$\tau_{xx} - \tau_{yy} = -\Psi_1\dot{\gamma}^2 \qquad \text{(D.5-2)}$$

$$\tau_{yy} - \tau_{zz} = -\Psi_2\dot{\gamma}^2 \qquad \text{(D.5-3)}$$

These relations define three material functions: η, the (*non-Newtonian*) *viscosity*; Ψ_1, the *first normal stress coefficient*; and Ψ_2, the *second normal stress coefficient*. All three of these are functions of the shear rate $\dot{\gamma}$ (see §3.3). At low shear rates η, Ψ_1, and Ψ_2 approach constants known as their zero-shear-rate values; these are denoted by η_0, $\Psi_{1,0}$, and $\Psi_{2,0}$. For dilute solutions the *intrinsic viscosity* (with dimensions of reciprocal concentration):

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_s}{c\eta_s} = \lim_{n \to 0} \frac{\tilde{N}}{M} \frac{\eta - \eta_s}{n\eta_s} \tag{D.5-4}$$

is frequently used. Here η_s is the solvent viscosity, c is the mass concentration of the solute, n is the number density of the solute, M is the solute molecular weight, and $\tilde{N}$ is Avogadro's number.

For *small-amplitude oscillatory shear flow* of the form[1] $v_x = (\dot{\gamma}^0 \cos \omega t)y$, $v_y = 0$, $v_z = 0$, the stresses depend on the time t:

$$\tau_{yx} = -\eta' \dot{\gamma}^0 \cos \omega t - \eta'' \dot{\gamma}^0 \sin \omega t \tag{D.5-5}$$

Here the material functions η' and η'' are functions of the frequency ω. Sometimes these oscillatory phenomena are described in terms of complex functions; then $\eta^* = \eta' - i\eta''$, the *complex viscosity*, is used. Many authors use $G^* = i\omega\eta^* = G' + iG''$ where $G' = \omega\eta''$ is the *storage modulus* and $G'' = \omega\eta'$ is the *loss modulus*. (For further information see §3.4.)

For stress relaxation following a sudden shearing displacement γ_0, the relaxing shear stress is described by the *relaxation modulus* $G(t, \gamma_0)$

$$\tau_{yx} = -G(t, \gamma_0)\gamma_0 \tag{D.5-6}$$

In the limit of small applied strains γ_0, we have

$$\lim_{\gamma_0 \to 0} G(t, \gamma_0) = G(t) \tag{D.5-7}$$

so that the relaxation modulus (cf. Eq. D.4-2) of linear viscoelasticity is recovered. The linear relaxation modulus $G(t)$ contains the same information as $\eta'(\omega)$ and $\eta''(\omega)$.

Another time-dependent shear flow is the *stress growth* experiment in which the fluid is at rest for $t < 0$, and in a state of flow $v_x = \dot{\gamma}_0 y$, $v_y = 0$, $v_z = 0$ for $t > 0$. Then for $t > 0$ the functions η^+, Ψ_1^+, and Ψ_2^+ are defined by

$$\tau_{yx} = -\eta^+(t, \dot{\gamma}_0)\dot{\gamma}_0 \tag{D.5-8}$$

$$\tau_{xx} - \tau_{yy} = -\Psi_1^+(t, \dot{\gamma}_0)\dot{\gamma}_0^2 \tag{D.5-9}$$

$$\tau_{yy} - \tau_{zz} = -\Psi_2^+(t, \dot{\gamma}_0)\dot{\gamma}_0^2 \tag{D.5-10}$$

The "growth functions" are thus functions of time and depend parametrically on $\dot{\gamma}_0$.

[1] In some developments we write $v_x = \mathscr{R}e\{\dot{\gamma}^0 e^{i\omega t}\}y$ and allow $\dot{\gamma}^0$ to be complex. In addition, the shear stress may be written $\tau_{yx} = \mathscr{R}e\{\tau^0 e^{i\omega t}\}$, where τ^0 is also complex. The complex viscosity is then defined by $\tau^0 = -\eta^*\dot{\gamma}^0$.

The inverse experiment is *stress relaxation* after sudden cessation (at time $t = 0$) of steady-state shear flow $v_x = \dot{\gamma}_0 y$, $v_y = 0$, and $v_z = 0$. For $t > 0$ the functions η^-, Ψ_1^-, and Ψ_2^- are defined by

$$\tau_{yx} = -\eta^-(t, \dot{\gamma}_0)\dot{\gamma}_0 \tag{D.5-11}$$

$$\tau_{xx} - \tau_{yy} = -\Psi_1^-(t, \dot{\gamma}_0)\dot{\gamma}_0^2 \tag{D.5-12}$$

$$\tau_{yy} - \tau_{zz} = -\Psi_2^-(t, \dot{\gamma}_0)\dot{\gamma}_0^2 \tag{D.5-13}$$

These "relaxation functions" are simply related to the growth functions only in the limit as $\dot{\gamma}_0 \to 0$ (linear viscoelasticity).

For *steady-state elongational flow* $v_x = -\frac{1}{2}\dot{\varepsilon}x$, $v_y = -\frac{1}{2}\dot{\varepsilon}y$, $v_z = +\dot{\varepsilon}z$, the only experimentally accessible combination of stresses for incompressible fluids is:

$$\tau_{zz} - \tau_{xx} = -\bar{\eta}\dot{\varepsilon} \tag{D.5-14}$$

in which $\bar{\eta}$ is the *elongational viscosity*, which is a function of the elongation rate $\dot{\varepsilon}$ (see §3.5). Note that positive $\dot{\varepsilon}$ corresponds to "fiber-stretching," whereas negative $\dot{\varepsilon}$ corresponds to biaxial "sheet-stretching."

Stress growth and stress relaxation experiments may also be performed in elongational flow. If the liquid sample is at rest for time $t < 0$ and elongated at an elongation rate of $\dot{\varepsilon}_0$ for $t > 0$, then $\bar{\eta}^+$ is defined analogously to Eq. D.5-8 by

$$\tau_{zz} - \tau_{xx} = -\bar{\eta}^+(t, \dot{\varepsilon}_0)\dot{\varepsilon}_0 \tag{D.5-15}$$

Similarly when a steady elongational flow is suddenly stopped at $t = 0$, we define $\bar{\eta}^-$ by

$$\tau_{zz} - \tau_{xx} = -\bar{\eta}^-(t, \dot{\varepsilon}_0)\dot{\varepsilon}_0 \tag{D.5-16}$$

which describes the stress relaxation after cessation of elongational flow (see Table 3.5-1).

§D.6 THE EQUATIONS OF CHANGE AND THE FLUXES

For the flow of a fluid mixture at constant temperature, the velocity, concentration, and pressure distributions are given by the solution of a set of *equations of change*, which describe the conservation of mass and momentum:

Equation of continuity for species i:
$$\frac{\partial}{\partial t}\rho_i = -(\nabla \cdot \rho_i \boldsymbol{v}) - (\nabla \cdot \boldsymbol{j}_i) + r_i \tag{D.6-1}$$

Equation of continuity for the mixture:
$$\frac{\partial}{\partial t}\rho = -(\nabla \cdot \rho \boldsymbol{v}) \tag{D.6-2}$$

Equation of motion for the mixture:
$$\frac{\partial}{\partial t}\rho \boldsymbol{v} = -[\nabla \cdot \rho \boldsymbol{v}\boldsymbol{v}] - [\nabla \cdot \boldsymbol{\pi}] + \sum_i \rho_i \boldsymbol{g}_i \tag{D.6-3}$$

Here ρ_i is the mass concentration of species i, and $\rho = \sum_i \rho_i$ is the density of the fluid mixture; $\boldsymbol{v} = (1/\rho)\sum \rho_i \boldsymbol{v}_i$ is the mass-average velocity of the fluid, where $\boldsymbol{v}_i$ is the mean velocity of species i. The mass flux $\boldsymbol{j}_i = \rho_i(\boldsymbol{v}_i - \boldsymbol{v})$ describes the diffusion of species i with respect to the mass-average velocity, and $\boldsymbol{\pi}$ is the momentum flux tensor or (total) stress tensor. The symbol r_i stands for the mass rate of production of i by chemical reactions and $\boldsymbol{g}_i$ is the external force per unit mass acting on species i; if the only external force is gravity, then the last term in Eq. D.6-3 is just $\rho\boldsymbol{g}$, where $\boldsymbol{g}$ is the gravitational acceleration.

To understand the physical interpretation of the fluxes $\boldsymbol{j}_i$ and $\boldsymbol{\pi}$, we consider an element of surface dS moving with the mass average velocity of the fluid, with a unit vector $\boldsymbol{n}$ describing its orientation. We refer to the material on that side of dS into which $\boldsymbol{n}$ points, as the "positive material," and that on the other side of dS as the "negative material." Then $(\boldsymbol{n}\cdot\boldsymbol{j}_i)dS$ gives the rate of mass flow of species i from the negative side of dS to the positive side of dS. Similarly $[\boldsymbol{n}\cdot\boldsymbol{\pi}]$ is the force exerted by the negative material on the positive material across dS. We often write the total stress tensor $\boldsymbol{\pi}$ as

$$\boldsymbol{\pi} = p\boldsymbol{\delta} + \boldsymbol{\tau} \tag{D.6-4}$$

where p is an isotropic pressure, and $\boldsymbol{\tau}$ is that part of the total stress tensor that is zero at equilibrium. When incompressibility is assumed, p is not uniquely determined and only normal stress differences can be measured. For an incompressible Newtonian liquid with viscosity μ, the stress $\boldsymbol{\tau}$ is just $-\mu\dot{\gamma}$.

APPENDIX E

USEFUL MATHEMATICAL FORMULAS

Here we collect together for easy reference some mathematical results that are used in the kinetic theory discussions of Volume 2.

§E.1 THE CHAIN RULE FOR PARTIAL DIFFERENTIATION

If two sets of independent variables $x_1, x_2, \ldots, x_N$ and $y_1, y_2, \ldots, y_N$ are related by equations of the form $y_i = y_i(x_1, x_2, \ldots, x_N)$, then a function of the x_i may be written as a different function of the y_i: $f(x_1, x_2, \ldots, x_N) = g(y_1, y_2, \ldots, y_N)$. Then the partial derivatives are related by the "chain rule:"

$$\frac{\partial f}{\partial x_j} = \sum_{k=1}^{N} \frac{\partial y_k}{\partial x_j} \frac{\partial g}{\partial y_k} \qquad (j = 1, 2, \ldots, N) \tag{E.1-1}$$

Similarly if $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N) = g(\boldsymbol{s}_1, \boldsymbol{s}_2, \ldots, \boldsymbol{s}_N)$ and if the components of $\boldsymbol{r}_i$ and $\boldsymbol{s}_i$ are x_{in} and y_{in} respectively (with $n = 1, 2, 3$), then the chain rule is given in vector form by

$$\frac{\partial}{\partial \boldsymbol{r}_j} f = \sum_{k=1}^{N} \left[\left(\frac{\partial}{\partial \boldsymbol{r}_j} \boldsymbol{s}_k \right) \cdot \frac{\partial}{\partial \boldsymbol{s}_k} g \right] \qquad (j = 1, 2, \ldots, N) \tag{E.1-2}$$

or in component form

$$\frac{\partial f}{\partial x_{jn}} = \sum_{k=1}^{N} \sum_{m=1}^{3} \frac{\partial y_{km}}{\partial x_{jn}} \frac{\partial g}{\partial y_{km}} \qquad \begin{pmatrix} j = 1, 2, \ldots, N \\ n = 1, 2, 3 \end{pmatrix} \tag{E.1-3}$$

Note that the operator $\partial/\partial \boldsymbol{r}_j$ is just a ∇-operator: $\partial/\partial \boldsymbol{r}_j = \sum_{n=1}^{3} \boldsymbol{\delta}_n \partial/\partial x_{jn}$, where $\boldsymbol{\delta}_n$ is the unit vector in the nth Cartesian coordinate direction.

§E.2 GENERALIZED TAYLOR THEOREM

If $f(x)$ is any sufficiently well-behaved function then

$$f(x + y) = f(x) + y \frac{\partial}{\partial x} \int_0^1 f(x + \xi y) d\xi \tag{E.2-1}$$

This may be verified by expanding $f(x + \xi y)$ in a conventional Taylor series about $\xi y = 0$ and then performing the ξ-integrations.

If the independent variable is a vector, then

$$f(\boldsymbol{r} + \boldsymbol{s}) = f(\boldsymbol{r}) + \left(\boldsymbol{s} \cdot \frac{\partial}{\partial \boldsymbol{r}} \int_0^1 f(\boldsymbol{r} + \xi \boldsymbol{s}) d\xi \right) \tag{E.2-2}$$

is the appropriate generalization of Eq. E.2-1.

§E.3 INTEGRALS OVER ALL THREE-DIMENSIONAL SPACE

Several three-dimensional integrals arise at many places in the text; in these α is a positive, real number, $\boldsymbol{\alpha}$ is a positive-definite, second-order tensor, and both $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are symmetric tensors

$$\int e^{-\alpha r^2} d\boldsymbol{r} = \left(\frac{\pi}{\alpha} \right)^{3/2} \tag{E.3-1}$$

$$\int \frac{1}{r} e^{-\alpha r^2} d\boldsymbol{r} = \frac{2\pi}{\alpha} \tag{E.3-2}$$

$$\int \frac{1}{r^3} \boldsymbol{r}\boldsymbol{r} e^{-\alpha r^2} d\boldsymbol{r} = \frac{2\pi}{3\alpha} \boldsymbol{\delta} \tag{E.3-3}$$

$$\int e^{-(\boldsymbol{\alpha}:\boldsymbol{r}\boldsymbol{r})} d\boldsymbol{r} = \frac{\pi^{3/2}}{\sqrt{\det \boldsymbol{\alpha}}} \tag{E.3-4}^{1}$$

$$\int \boldsymbol{r}\boldsymbol{r} e^{-(\boldsymbol{\alpha}:\boldsymbol{r}\boldsymbol{r})} d\boldsymbol{r} = \frac{\pi^{3/2} \boldsymbol{\alpha}^{-1}}{2\sqrt{\det \boldsymbol{\alpha}}} \tag{E.3-5}^{1}$$

$$\int e^{-\alpha(\boldsymbol{r}\cdot\boldsymbol{r}) - \beta(\boldsymbol{r}\cdot\boldsymbol{s})} d\boldsymbol{r} = \left(\frac{\pi}{\alpha} \right)^{3/2} e^{(\beta^2/4\alpha)(\boldsymbol{s}\cdot\boldsymbol{s})} \tag{E.3-6}$$

$$\int e^{-(\boldsymbol{\alpha}:\boldsymbol{r}\boldsymbol{r}) - (\boldsymbol{\beta}:\boldsymbol{r}\boldsymbol{s})} d\boldsymbol{r} = \frac{\pi^{3/2}}{\sqrt{\det \boldsymbol{\alpha}}} e^{(1/4)((\boldsymbol{\alpha}^{-1}\cdot\boldsymbol{\beta}^2):\boldsymbol{s}\boldsymbol{s})} \tag{E.3-7}$$

In all of these integrals $\int \ldots d\boldsymbol{r}$ stands for $\iiint \ldots dx\, dy\, dz$ with the integrals going from $x = -\infty$ to $x = \infty$, $y = -\infty$ to $y = \infty$, and $z = -\infty$ to $z = \infty$.

[1] Equations E.3-4 and 5 can be generalized from 3 to d dimensions as follows:

$$\int \exp\left(-\sum_s \sum_t \alpha_{st} x_s x_t \right) dx = \frac{\pi^{d/2}}{\sqrt{\det (\alpha_{st})}} \tag{E.3-4a}$$

$$\int x_u x_v \exp\left(-\sum_s \sum_t \alpha_{st} x_s x_t \right) dx = \frac{\pi^{d/2} \alpha_{uv}^{-1}}{2\sqrt{\det (\alpha_{st})}} \tag{E.3-5a}$$

in which α_{uv}^{-1} is the uv-element of the inverse matrix, and $\int \ldots dx$ implies a d-fold integral over $x_1, x_2, \ldots, x_d$, with the integrals going from $-\infty$ to $+\infty$.

§E.4 THE DIRAC DELTA FUNCTION[2]

We use the following representation of the Dirac delta function[3]

$$\delta(x) = \lim_{n \to \infty} \sqrt{\frac{n}{\pi}}\, e^{-nx^2} \tag{E.4-1}$$

from which it follows that

$$\int_{-b}^{+a} f(x)\delta(x)dx = 2\int_{0}^{a} f(x)\delta(x)dx = f(0) \tag{E.4-2}$$

$$\int_{-b}^{+a} f(x)\delta'(x)dx = -f'(0) \tag{E.4-3}$$

in which $a > 0$ and $b > 0$, and the prime denotes differentiation with respect to x.

Similarly, for a vector $\boldsymbol{r}$ in three dimensions with components x, y, z:

$$\delta(\boldsymbol{r}) = \lim_{n \to \infty} \left(\frac{n}{\pi}\right)^{3/2} e^{-n(\boldsymbol{r}\cdot\boldsymbol{r})}$$

$$= \delta(x)\delta(y)\delta(z) \tag{E.4-4}$$

Another useful representation is

$$\delta(\boldsymbol{r}) = \frac{1}{(2\pi)^3}\int_{-\infty}^{\infty} e^{i(\boldsymbol{r}\cdot\boldsymbol{s})}\, d\boldsymbol{s} \tag{E.4-5}$$

From either Eq. E.4-4 or Eq. E.4-5 it follows that

$$\int f(\boldsymbol{r})\delta(\boldsymbol{r})d\boldsymbol{r} = f(\boldsymbol{0}) \tag{E.4-6}$$

In these expressions $\int \ldots d\boldsymbol{r}$ is understood to mean $\iiint \ldots dx\, dy\, dz$.

§E.5 UNIT VECTORS IN SPHERICAL COORDINATES

In §A.6 unit vectors in the spherical coordinate system are referred to as $\boldsymbol{\delta}_r$, $\boldsymbol{\delta}_\theta$, $\boldsymbol{\delta}_\phi$. In Volume 2 we often use $\boldsymbol{u}$, $\boldsymbol{s}$, $\boldsymbol{t}$ in order to eliminate the need for subscripts. We also find it useful to introduce vectors $\boldsymbol{c}_n$ and $\boldsymbol{d}_n$ ($n = 1, 2$) which are related to the base vectors and reciprocal base vectors respectively. The notation is summarized in Table E.5-1. In the discussion of bead-rod chains these various vectors may be associated with each link; then the additional index k, indicating the kth link, may be appended thus: $\boldsymbol{u}_k$, $\boldsymbol{s}_k$, $\boldsymbol{t}_k$ and $\boldsymbol{c}_{kn}$, $\boldsymbol{d}_{kn}$.

[2] P. A. M. Dirac, *The Principles of Quantum Mechanics*, 3rd ed., Oxford University Press, London (1947), pp. 58-61.

[3] For a more general definition of the delta function see M. J. Lighthill, *Fourier Analysis and Generalised Functions*, Cambridge University Press, Cambridge (1964), p. 17.

TABLE E.5-1

Unit Vectors and Related Quantities in Spherical Coordinates

	Radial	Polar	Azimuthal
Unit vectors (§A.6)	δ_r	δ_θ	δ_ϕ
Unit vectors (Vol. 2)	$\boldsymbol{u}$	$\boldsymbol{s}$	$\boldsymbol{t}$
Base vectors (§A.8)	$\boldsymbol{g}_r = \delta_r$	$\boldsymbol{g}_\theta = r\delta_\theta$	$\boldsymbol{g}_\phi = r \sin\theta\, \delta_\phi$
Reciprocal base vectors (§A.8)	$\boldsymbol{g}^r = \delta_r$	$\boldsymbol{g}^\theta = (1/r)\delta_\theta$	$\boldsymbol{g}^\phi = (1/r \sin\theta)\, \delta_\phi$
Unit sphere base vectors		$\boldsymbol{c}_1 = \boldsymbol{s}$	$\boldsymbol{c}_2 = \sin\theta\, \boldsymbol{t}$
Unit sphere reciprocal base vectors		$\boldsymbol{d}_1 = \boldsymbol{s}$	$\boldsymbol{d}_2 = (1/\sin\theta)\, \boldsymbol{t}$

In Table E.5-2 we give additional information about the unit vectors: their Cartesian components, and their derivatives with respect to θ and ϕ.

§E.6 THE DIFFERENTIAL OPERATOR $\partial/\partial\boldsymbol{u}$

The operator $\partial/\partial\boldsymbol{u}$ is defined by

$$\frac{\partial}{\partial \boldsymbol{u}} = r[(\boldsymbol{\delta} - \boldsymbol{uu})\cdot\nabla] = \boldsymbol{s}\frac{\partial}{\partial\theta} + \boldsymbol{t}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi} \tag{E.6-1}$$

in which $\boldsymbol{s}$ and $\boldsymbol{t}$ are the unit vectors in Table E.5-1. This corresponds to a ∇-operator on the surface of a sphere (cf. Eq. A.7-9). The operation analogous to ∇^2 is

$$\Lambda \equiv \left(\frac{\partial}{\partial \boldsymbol{u}}\cdot\frac{\partial}{\partial \boldsymbol{u}}\right) = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{E.6-2}$$

This should be compared with Eq. B of Table A.7-3.

TABLE E.5-2

Components and Derivatives of Unit Vectors in Spherical Coordinates

Unit Vector	Cartesian Components of Unit Vectors			Derivatives of Unit Vectors	
	x	y	z	$\partial/\partial\theta$	$\partial/\partial\phi$
$\boldsymbol{s}$	$\cos\theta\cos\phi$	$\cos\theta\sin\phi$	$-\sin\theta$	$-\boldsymbol{u}$	$\boldsymbol{t}\cos\theta$
$\boldsymbol{t}$	$-\sin\phi$	$\cos\phi$	0	$\boldsymbol{0}$	$-\boldsymbol{u}\sin\theta - \boldsymbol{s}\cos\theta$
$\boldsymbol{u}$	$\sin\theta\cos\phi$	$\sin\theta\sin\phi$	$\cos\theta$	$\boldsymbol{s}$	$\boldsymbol{t}\sin\theta$

Note: If $Q_1 = \theta$ and $Q_2 = \phi$, then $\sum_{n=1}^{2}\frac{\partial}{\partial Q_n}(\boldsymbol{d}_n \sin\theta) = -2\boldsymbol{u}\sin\theta$

The following identities are useful:

$$\frac{\partial}{\partial \boldsymbol{u}}\boldsymbol{u} = \boldsymbol{ss} + \boldsymbol{tt} = \boldsymbol{\delta} - \boldsymbol{uu} \tag{E.6-3}$$

$$\begin{aligned}\frac{\partial}{\partial \boldsymbol{u}}\boldsymbol{uu} &= (\boldsymbol{ss} + \boldsymbol{tt})\boldsymbol{u} + \boldsymbol{sus} + \boldsymbol{tut} \\ &= (\boldsymbol{\delta} - \boldsymbol{uu})\boldsymbol{u} + [(\boldsymbol{\delta} - \boldsymbol{uu})\boldsymbol{u}]^{\dagger} \\ &= (\boldsymbol{\delta} - \boldsymbol{uu})\boldsymbol{u} + {}^{\dagger}[\boldsymbol{u}(\boldsymbol{\delta} - \boldsymbol{uu})]\end{aligned} \tag{E.6-4}$$

in which † preceding/following a tensor indicates transposition of the first/last two indices. That is, ${}^{\dagger}[\boldsymbol{u}(\boldsymbol{\delta} - \boldsymbol{uu})]_{ijk} = u_j(\delta_{ik} - u_i u_k)$.

In the following equations $\boldsymbol{\alpha}$ is a second order tensor independent of $\boldsymbol{u}$, and F is a scalar function of $\boldsymbol{u}$:

$$\left[\frac{\partial}{\partial \boldsymbol{u}} \cdot \{\boldsymbol{\alpha} \cdot \boldsymbol{uu}\}\right] = [\boldsymbol{\alpha} : (\boldsymbol{\delta u} + \boldsymbol{u\delta})] - 2[\boldsymbol{\alpha} : \boldsymbol{uuu}] \tag{E.6-5}$$

$$\left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\alpha} : \boldsymbol{uuu}]\right) = 2(\boldsymbol{\alpha} : \boldsymbol{uu}) \tag{E.6-6}$$

$$\left(\frac{\partial}{\partial \boldsymbol{u}} \cdot [\boldsymbol{\alpha} \cdot \boldsymbol{u}]F\right) = (\boldsymbol{\alpha} : (\boldsymbol{\delta} - \boldsymbol{uu}))F + \left(\boldsymbol{\alpha} : \boldsymbol{u}\frac{\partial}{\partial \boldsymbol{u}}F\right) \tag{E.6-7}$$

§E.7 THE INTEGRAL OPERATION $\int \ldots d\boldsymbol{u}$

The integral operation $\int \ldots d\boldsymbol{u}$ is equivalent to $\iint \ldots \sin\theta d\theta d\phi$ with integration range $0 < \theta \leq \pi$ and $0 < \phi \leq 2\pi$. In the following integrals the scalars A and B, as well as the vector $\boldsymbol{A}$ are functions of θ and ϕ, and are periodic in ϕ:

$$\int \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \boldsymbol{A}\right) B \, d\boldsymbol{u} = -\int \left(\boldsymbol{A} \cdot \left(\frac{\partial}{\partial \boldsymbol{u}} B - 2\boldsymbol{u}B\right)\right) d\boldsymbol{u} \tag{E.7-1}$$

$$\int \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} A\right) B \, d\boldsymbol{u} = \int \left(\frac{\partial}{\partial \boldsymbol{u}} \cdot \frac{\partial}{\partial \boldsymbol{u}} B\right) A \, d\boldsymbol{u} \tag{E.7-2}$$

$$\int \boldsymbol{u}\left(\frac{\partial}{\partial \boldsymbol{u}} A\right) d\boldsymbol{u} = \int (3\boldsymbol{uu} - \boldsymbol{\delta}) A \, d\boldsymbol{u} \tag{E.7-3}$$

These equations are obtained by performing integrations by parts on θ and ϕ.

The averages of products of $\boldsymbol{u}$ are

$$\frac{1}{4\pi}\int \boldsymbol{uu} \, d\boldsymbol{u} = \tfrac{1}{3}\boldsymbol{\delta} \tag{E.7-4}$$

$$\frac{1}{4\pi}\int \boldsymbol{uuuu} \, d\boldsymbol{u} = \tfrac{1}{15}(\boldsymbol{\delta\delta} + \mathbf{I} + \mathbf{I}^{\dagger}) \tag{E.7-5}$$

and in general:[4]

$$\frac{1}{4\pi}\int \underbrace{\boldsymbol{uuu}\cdots\boldsymbol{u}}_{p\text{-times}}\, d\boldsymbol{u} = \frac{1}{(p+1)!}\underbrace{\boldsymbol{\nabla\nabla\nabla}\cdots\boldsymbol{\nabla}}_{p\text{-times}} r^p \quad (p \text{ even}) \tag{E.7-6}$$

For p odd these integrals are zero. The tensors $\mathbf{I}$ and $\mathbf{I}^{\dagger}$ are defined in Eq. E.9-1. Equations E.7-4 and 5 are special cases of Eqs. E.11-3 and 4.

§E.8 SPHERICAL HARMONICS AND LEGENDRE POLYNOMIALS[5]

The spherical harmonics are generated when Laplace's equation $\nabla^2\Psi = 0$ is solved by the method of separation of variables in spherical coordinates, using $\Psi = R(r)\Theta(\theta)\Phi(\phi)$. This leads to three ordinary differential equations:

$$\Phi'' + m^2\Phi = 0 \tag{E.8-1}$$

$$(\sin\theta)^{-1}(\Theta'\sin\theta)' + [n(n+1) - m^2(\sin\theta)^{-2}]\Theta = 0 \tag{E.8-2}$$

$$(r^2R')' - n(n+1)R = 0 \tag{E.8-3}$$

The constants m and n appearing in these equations arise in the separation-of-variables procedure; they are integers and $0 \le m \le n$. The solutions of the Φ equation are $\cos m\phi$ and $\sin m\phi$, and the solutions of the Θ equation are the Legendre polynomials $P_n^m(\cos\theta)$. The first few P_n^m with even indices are

$$\begin{aligned} P_0^0 &= 1 & P_4^0 &= \tfrac{1}{8}(35C^4 - 30C^2 + 3) \\ P_2^0 &= \tfrac{1}{2}(3C^2 - 1) & P_4^2 &= \tfrac{15}{2}(1 - C^2)(7C^2 - 1) \\ P_2^2 &= 3(1 - C^2) & P_4^4 &= 105(1 - C^2)^2 \end{aligned} \tag{E.8-4}$$

in which $C = \cos\theta$. The products $P_n^m \sin m\phi$ and $P_n^m \cos m\phi$ are referred to as *spherical harmonics*.

The spherical harmonics obey the relations

$$\Lambda P_n^m \sin m\phi = -n(n+1)P_n^m \sin m\phi \tag{E.8-5}$$

$$\Lambda P_n^m \cos m\phi = -n(n+1)P_n^m \cos m\phi \tag{E.8-6}$$

[4] H. Brenner, *Chem. Eng. Sci.*, **19**, 519 539 (1964).

[5] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1964), second printing, pp. 905 912.

in which Λ is the operator defined in Eq. E.6-2. In addition the spherical harmonics have the following orthogonality relations:

$$\int_0^{2\pi}\int_0^{\pi} P_n^m \begin{Bmatrix}\cos m\phi\\ \sin m\phi\end{Bmatrix} P_{n'}^{m'} \begin{Bmatrix}\cos m'\phi\\ \sin m'\phi\end{Bmatrix} \sin\theta\, d\theta\, d\phi = \frac{2\pi(n+m)!}{(2n+1)(n-m)!}\delta_{nn'}\delta_{mm'}(1 \pm \delta_{m0}) \tag{E.8-7}$$

where the positive sign in the factor $(1 \pm \delta_{m0})$ is to be used when $\cos m\phi$ and $\cos m'\phi$ appear in the integrals, and the negative sign when $\sin m\phi$ and $\sin m'\phi$ appear. Note that the product of two spherical harmonics integrated over the surface of a unit sphere is zero unless the two spherical harmonics are *identical.*

§E.9 FOURTH-ORDER ISOTROPIC TENSORS

We define three fourth-order, isotropic tensors in terms of their Cartesian components as follows:

$$(\delta\delta)_{mnpq} = \delta_{mn}\delta_{pq}, \qquad \mathsf{I}_{mnpq} = \delta_{mq}\delta_{np}, \qquad \mathsf{I}^{\dagger}_{mnpq} = \delta_{mp}\delta_{nq} \tag{E.9-1}$$

These tensors have the property that for any tensor $\mathbf{A}$ of order greater than or equal to 2:

$$\mathsf{I}:\mathbf{A} = \mathbf{A}:\mathsf{I} = \mathbf{A}, \qquad \mathsf{I}^{\dagger}:\mathbf{A} = {}^{\dagger}\mathbf{A}, \qquad \mathbf{A}:\mathsf{I}^{\dagger} = \mathbf{A}^{\dagger} \tag{E.9-2}$$

Sometimes it is convenient to use an alternative set of isotropic, fourth-order tensors:

$$\mathsf{I}_0 = \tfrac{1}{3}\delta\delta, \qquad \mathsf{I}_1 = \frac{1}{2\sqrt{3}}(\mathsf{I} - \mathsf{I}^{\dagger}), \qquad \mathsf{I}_2 = \frac{1}{2\sqrt{5}}(\mathsf{I} + \mathsf{I}^{\dagger}) - \frac{1}{3\sqrt{5}}\delta\delta \tag{E.9-3}$$

Note finally that the tensors I_J are orthogonal in the following sense:

$$(\mathsf{I}_J \vdots \mathsf{I}_K) = \sum_m\sum_n\sum_p\sum_q (\mathsf{I}_J)_{mnpq}(\mathsf{I}_K)_{qpnm} = \delta_{JK} \qquad (J, K = 0, 1, 2) \tag{E.9-4}$$

The "nesting convention" is used for multiple dot products.

§E.10 SURFACE SPHERICAL HARMONICS[6]

The *jth surface spherical harmonic* is a tensor of order j defined by

$$\mathbf{S}_j = r^{j+1}\underbrace{\nabla\nabla\cdots\nabla}_{j \text{ times}}\left(\frac{1}{r}\right) \qquad (j = 0, 1, 2, \ldots) \tag{E.10-1}$$

[6] G. K. Batchelor, *An Introduction to Fluid Dynamics*, Cambridge University Press (1970), p. 121; H. Jeffreys and B. S. Jeffreys, *Methods of Mathematical Physics*, 3rd ed., Cambridge University Press (1972), Chapter 24. See H. Brenner, *Chem. Eng. Sci.*, **19**, 519-539 (1964), Sec. 6 for an elegant method for computing surface averages of the $\mathbf{S}_j$.

Here r is the radial spherical coordinate $r = \sqrt{x^2 + y^2 + z^2}$. By using this definition, the first few even surface spherical harmonics can be worked out:

$$\mathbf{S}_0 = 1 \tag{E.10-2}$$

$$\mathbf{S}_2 = 3\boldsymbol{uu} - \boldsymbol{\delta} \tag{E.10-3}$$

$$\begin{aligned}\mathbf{S}_4 = {} & 105\boldsymbol{uuuu} - 15[\boldsymbol{\delta uu} + \boldsymbol{u\delta u} \\ & + \boldsymbol{uu\delta} + {}^{\dagger}(\boldsymbol{u\delta u}) + (\boldsymbol{u\delta u})^{\dagger} + {}^{\dagger}(\boldsymbol{u\delta u})^{\dagger}] \\ & + 3(\boldsymbol{\delta\delta} + \mathbf{I} + \mathbf{I}^{\dagger})\end{aligned} \tag{E.10-4}$$

The fourth-order isotropic tensors $\boldsymbol{\delta\delta}$, $\mathbf{I}$, and $\mathbf{I}^{\dagger}$ have been discussed in §E.9; below Eq. E.6-4 the convention regarding the transpose symbol † is given.

The $\mathbf{S}_j$ satisfy the differential relation (cf. Eqs. E.8-5 and 6)

$$\Lambda \mathbf{S}_j = -j(j+1)\mathbf{S}_j \tag{E.10-5}$$

as well as the orthogonality relation (cf. Eq. E.8-7):

$$\int \mathbf{S}_j \mathbf{S}_k \, d\boldsymbol{u} = \mathbf{0} \qquad (j \neq k) \tag{E.10-6}$$

The products $r^{-(j+1)}\mathbf{S}_j$ are called the *solid spherical harmonics* and are solutions to Laplace's equation.

§E.11 EULER ANGLES[7]

We start with a Cartesian coordinate frame xyz shown in Fig. E.11-1. We now want to describe a second coordinate frame $\check{x}\check{y}\check{z}$ with the same origin O but tilted with respect to the original frame. The orientation of the second frame with respect to the first is specified by giving three angles α, β, and γ; these are called the *Euler angles*. [WARNING! Not all authors use the same definition of the Euler angles; see, for example, the discussion by Margenau and Murphy.[8]] The sequence of rotations that define Euler angles used in this book is described in Fig. E.11-1. The ranges of the Euler angles are as follows: $0 \leq \alpha < 2\pi$; $0 \leq \beta \leq \pi$; $0 \leq \gamma < 2\pi$.

The unit vectors $\boldsymbol{\delta}_i$ along the coordinate axes in the xyz-system and the corresponding unit vectors $\check{\boldsymbol{\delta}}_i$ in the $\check{x}\check{y}\check{z}$-system are related as follows:

$$\check{\boldsymbol{\delta}}_m = \sum_{n=1}^{3} \Omega_{mn} \boldsymbol{\delta}_n \qquad (m = 1, 2, 3) \tag{E.11-1}$$

[7] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1964), p. 908.

[8] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, 2nd ed., Van Nostrand, Princeton (1956), pp. 286–289.

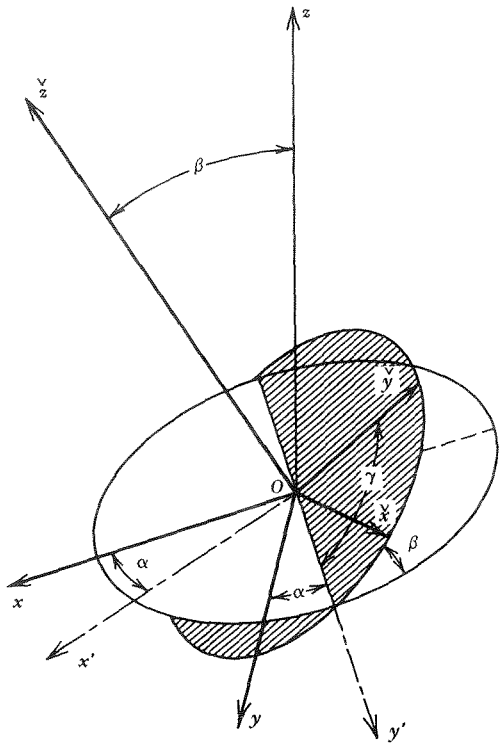


FIGURE E.11-1. Definition of the Euler angles, α, β, and γ. The following procedure is carried out to rotate the xyz-system into the $\check{x}\check{y}\check{z}$-system: (1) rotate the x- and y-axes about the z-axis by an angle α to the axes marked x' and y', so that y' lies in the $\check{x}\check{y}$-plane; (2) tilt about the y'-axis so that the z-axis moves through an angle β to the axis marked $\check{z}$; (3) rotate about the $\check{z}$-axis so that the y'-axis moves through an angle γ to the axis labeled $\check{y}$. Note that the unshaded plane contains the axes x, y, x', y', and that α is measured in this plane. The shaded plane contains the $\check{x}$- and $\check{y}$-axes, and γ is measured in this plane.

where the Ω_{mn} are given in terms of the Euler angles:

$$(\Omega_{mn}) = \begin{pmatrix} cC\not{c} - s\$ & sC\not{c} + c\$ & -S\not{c} \\ -cC\$ - s\not{c} & -sC\$ + c\not{c} & S\$ \\ cS & sS & C \end{pmatrix} \tag{E.11-2}$$

in which s, S, and $\$$ are $\sin\alpha$, $\sin\beta$, $\sin\gamma$, and c, C, $\not{c}$ are $\cos\alpha$, $\cos\beta$, $\cos\gamma$.

Let $\boldsymbol{a}_n$ be unit vectors in three-space that are functions of the Euler angles. If we use an overbar to indicate $(1/8\pi^2)\iiint \ldots \sin\beta\, d\alpha\, d\beta\, d\gamma$, then

$$\overline{\boldsymbol{a}_m\boldsymbol{a}_n} = \tfrac{1}{3}\overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_n)}\boldsymbol{\delta} \tag{E.11-3}$$

$$\begin{aligned}\overline{\boldsymbol{a}_m\boldsymbol{a}_n\boldsymbol{a}_p\boldsymbol{a}_q} = {}& \tfrac{1}{30}[4\overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_n)(\boldsymbol{a}_p\cdot\boldsymbol{a}_q)} - \overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_q)(\boldsymbol{a}_n\cdot\boldsymbol{a}_p)} - \overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_p)(\boldsymbol{a}_n\cdot\boldsymbol{a}_q)}]\boldsymbol{\delta}\boldsymbol{\delta} \\ & + \tfrac{1}{30}[4\overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_q)(\boldsymbol{a}_n\cdot\boldsymbol{a}_p)} - \overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_n)(\boldsymbol{a}_p\cdot\boldsymbol{a}_q)} - \overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_p)(\boldsymbol{a}_n\cdot\boldsymbol{a}_q)}]\mathbf{I} \\ & + \tfrac{1}{30}[4\overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_p)(\boldsymbol{a}_n\cdot\boldsymbol{a}_q)} - \overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_n)(\boldsymbol{a}_p\cdot\boldsymbol{a}_q)} - \overline{(\boldsymbol{a}_m\cdot\boldsymbol{a}_q)(\boldsymbol{a}_n\cdot\boldsymbol{a}_p)}]\mathbf{I}^{\dagger}\end{aligned} \tag{E.11-4}$$

The isotropic, fourth-order tensors appearing here ($\delta\delta$, $\mathbf{I}$, $\mathbf{I}^{\dagger}$) are defined in §E.9. Equations E.11-3 and 4 are special cases of relations for an arbitrary, second-order tensor Λ, and an arbitrary, fourth-order tensor $\mathbf{A}$:

$$\bar{\Lambda} = \tfrac{1}{3}\overline{(\Lambda:\delta)}\delta \tag{E.11-5}$$

$$\bar{\mathbf{A}} = \sum_{J=0}^{2} \overline{(\mathbf{A} \vdots \mathbf{I}_J)}\mathbf{I}_J \tag{E.11-6}$$

in which the $\mathbf{I}_J$ are the fourth-order tensors of Eq. E.9-3.

§E.12 THE FUNCTIONS $D^J(\alpha, \beta, \gamma)_{KM}$

A set of functions $D^J(\alpha, \beta, \gamma)_{KM}$ of the three Euler angles have been defined,[9] and these are the solutions of the Helmholtz equation (Eq. 16.7-5):

$$\left[\frac{\partial^2}{\partial\beta^2} + \frac{C}{S}\frac{\partial}{\partial\beta} + \frac{1}{S^2}\frac{\partial}{\partial\alpha^2} + \left(\frac{C^2}{S^2} + \varepsilon\right)\frac{\partial^2}{\partial\gamma^2} - \frac{2C}{S^2}\frac{\partial^2}{\partial\alpha\partial\gamma}\right]D^J(\alpha, \beta, \gamma)_{KM}$$
$$= -[J(J+1) + (\varepsilon - 1)K^2]D^J(\alpha, \beta, \gamma)_{KM} \tag{E.12-1}$$

where $S = \sin\beta$ and $C = \cos\beta$. These functions are finite everywhere and periodic in α and γ (with periods of 2π). The indices are integers such that $J \geq 0$, $-J \leq K \leq J$, and $-J \leq M \leq J$. When Eq. E.12-1 is solved by the method of separation of variables the solution is independent of the parameter ε and has the form:

$$D^J(\alpha, \beta, \gamma)_{KM} = e^{iM\alpha}d^J(\beta)_{KM}e^{iK\gamma} \tag{E.12-2}$$

where the $d^J(\beta)_{KM}$ are solutions of the equation

$$\left(\frac{\partial^2}{\partial\beta^2} + \frac{C}{S}\frac{\partial}{\partial\beta} - \frac{1}{S^2}(M^2 - 2CMK + K^2)\right)d^J(\beta)_{KM} = -J(J+1)d^J(\beta)_{KM} \tag{E.12-3}$$

A comparison of this equation with Eq. E.8-2 shows that the functions d^J_{KM}, with either K or M equal to zero, are solutions of the same equation as that for the $P_J^{|M-K|}(\cos\beta)$, and, since both functions are nonsingular, they are the same functions (aside from the normalization). For arbitrary choices of K and M, the $d^J(\beta)_{KM}$ are closely related to the Jacobi polynomials of $\cos\beta$.

The D^J_{KM} functions are orthogonal in that

$$\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \overline{D^{J'}(\alpha, \beta, \gamma)_{K'M'}}D^J(\alpha, \beta, \gamma)_{KM} \sin\beta\, d\alpha\, d\beta\, d\gamma = [8\pi^2/(2J+1)]\delta_{J'J}\delta_{K'K}\delta_{M'M} \tag{E.12-4}$$

In this section the overbar indicates the complex conjugate.

[9] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1964), p. 909.

The functions, $D^J(\alpha, \beta, \gamma)_{KM}$, are frequently referred to as representations of the three dimensional rotation group, since, when considered as matrices with the indices K and M indicating the components, they are irreducible representations of the group. In particular, the functions with $J = 1$ are closely related to the elements of the rotation matrix, Ω_{mn}, defined by Eq. 16.1-2.

$$D^1(\alpha, \beta, \gamma)_{KM} = \sum_{m=1}^{3} \sum_{n=1}^{3} T_{Km} \Omega_{mn} \bar{T}_{Mn} \tag{E.12-5}$$

where the T_{Km} are the elements of the matrix

$$(T_{Km}) = \begin{pmatrix} T_{-1,1} & T_{-1,2} & T_{-1,3} \\ T_{01} & T_{02} & T_{03} \\ T_{11} & T_{12} & T_{13} \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} -1 & -i & 0 \\ 0 & 0 & \sqrt{2} \\ 1 & -i & 0 \end{pmatrix} \tag{E.12-6}$$

which is unitary, so that

$$\sum_{K=-1}^{1} \bar{T}_{Km} T_{Kn} = \delta_{mn} \qquad (m, n = 1, 2, 3) \tag{E.12-7}$$

$$\sum_{m=1}^{3} T_{Km} \bar{T}_{Mm} = \delta_{KM} \qquad (K, M = -1, 0, 1) \tag{E.12-8}$$

The matrix (T_{Km}) describes relations between the unit vectors $\boldsymbol{\delta}_m$ of a Cartesian coordinate system $(m = 1, 2, 3)$ and the "complex unit vectors" $\boldsymbol{\varepsilon}_K$ of an associated "complex-spherical" system $(K = -1, 0, 1)$

$$\boldsymbol{\varepsilon}_K = \sum_{m=1}^{3} \bar{T}_{Km} \boldsymbol{\delta}_m \tag{E.12-9}$$

The complex unit vectors satisfy the orthogonality relations $(\boldsymbol{\varepsilon}_K \cdot \bar{\boldsymbol{\varepsilon}}_{K'}) = \delta_{KK'}$; combination of Eq. E.12-9 with Eqs. A.6-31 to 33 gives the $\boldsymbol{\varepsilon}_K$ in terms of the usual unit vectors used in spherical coordinates.

$$\boldsymbol{\varepsilon}_0 = \boldsymbol{\delta}_r \cos\theta - \boldsymbol{\delta}_\theta \sin\theta \tag{E.12-10}$$

$$\boldsymbol{\varepsilon}_{\pm 1} = \pm \frac{1}{\sqrt{2}} e^{\pm i\phi} (\boldsymbol{\delta}_r \sin\theta + \boldsymbol{\delta}_\theta \cos\theta \pm i\boldsymbol{\delta}_\phi) \tag{E.12-11}$$

Just as an arbitrary vector $\boldsymbol{v}$ may be decomposed into its Cartesian components $v_m = (\boldsymbol{v} \cdot \boldsymbol{\delta}_m)$, so also it may be decomposed into its "complex-spherical components" $v_K = (\boldsymbol{v} \cdot \bar{\boldsymbol{\varepsilon}}_K)$. Similarly the components of a second-order tensor may be obtained by forming the double-dot products of the tensor with the dyads $\boldsymbol{\delta}_m \boldsymbol{\delta}_n$ in the Cartesian system or with the dyads $\bar{\boldsymbol{\varepsilon}}_J \bar{\boldsymbol{\varepsilon}}_K$ in the complex-spherical system.

TABLE E.12-1

Tabulation of the Tensors $\Theta_{JM} = \sum_p \sum_q \Theta_{JM,pq}\delta_p\delta_q$

$$\Theta_{00} = -\frac{1}{\sqrt{3}}\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix} \tag{A}$$

$$\Theta_{10} = \frac{1}{\sqrt{2}}\begin{pmatrix}0 & -i & 0\\ i & 0 & 0\\ 0 & 0 & 0\end{pmatrix} \tag{B}$$

$$\Theta_{1,\pm1} = \frac{1}{2}\begin{pmatrix}0 & 0 & 1\\ 0 & 0 & \mp i\\ -1 & \pm i & 0\end{pmatrix} \tag{C}$$

$$\Theta_{20} = \frac{1}{\sqrt{6}}\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2\end{pmatrix} \tag{D}$$

$$\Theta_{2,\pm1} = \frac{1}{2}\begin{pmatrix}0 & 0 & \pm 1\\ 0 & 0 & -i\\ \pm 1 & -i & 0\end{pmatrix} \tag{E}$$

$$\Theta_{2,\pm2} = \frac{1}{2}\begin{pmatrix}1 & \mp i & 0\\ \mp i & -1 & 0\\ 0 & 0 & 0\end{pmatrix} \tag{F}$$

However, rather than using the dyads $\bar{\varepsilon}_J\bar{\varepsilon}_K$ it is more convenient to use the linear combinations Θ_{JK}, which are defined in terms of the "3-j symbols"[10]

$$\Theta_{JK} = \sqrt{2J+1}\sum_{K'=-1}^{1}\sum_{K''=-1}^{1}\begin{pmatrix}1 & 1 & J\\ K' & K'' & K\end{pmatrix}\varepsilon_{K'}\varepsilon_{K''}$$

$$= \sum_{m=1}^{3}\sum_{n=1}^{3}\Theta_{JK,mn}\delta_m\delta_n \tag{E.12-12}$$

where the Cartesian components $\Theta_{JK,mn}$ are given by

$$\Theta_{JK,mn} = \sqrt{2J+1}\sum_{K'=-1}^{1}\sum_{K''=-1}^{1}\begin{pmatrix}1 & 1 & J\\ K' & K'' & K\end{pmatrix}\bar{T}_{K'm}\bar{T}_{K''n} \tag{E.12-13}$$

[10] The 3-j symbol $\begin{pmatrix}j_1 & j_2 & j_3\\ m_1 & m_2 & m_3\end{pmatrix}$ arises in the quantum mechanical theory of angular momenta. It is associated with the coupling of two angular momentum states (j_1, m_1) and (j_2, m_2) to form a third (j_3, m_3). See for example, U. Fano and G. Racah, *Irreducible Tensorial Sets*, Academic Press, New York (1959); C. F. Curtiss, *J. Chem. Phys.*, **48**, 1725-1731 (1968).

These tensors, which are nonzero only for $0 \leq J \leq 2$ and $-J \leq K \leq J$, have the property that

$$(\bar{\Theta}^{\dagger}_{J'K'} : \Theta_{JK}) = \delta_{J'J}\delta_{K'K} \tag{E.12-14}$$

The Cartesian components of the Θ_{JK} tensors are displayed in Table E.12.1.

Note that any second-order tensor Λ can be written as the sum of an isotropic tensor, an antisymmetric tensor, and a traceless symmetric tensor

$$\Lambda = (\tfrac{1}{3}\,\mathrm{tr}\,\Lambda)\delta + \tfrac{1}{2}(\Lambda - \Lambda^{\dagger}) + \tfrac{1}{2}[\Lambda + \Lambda^{\dagger} - (\tfrac{2}{3}\,\mathrm{tr}\,\Lambda)\delta] \tag{E.12-15}$$

Under a coordinate rotation there is no mixing of components from these three terms, which may be said to be "rotationally invariant". The tensors Θ_{JK} have the property that they "project" from any second-order tensor Λ the complex-spherical components of its rotationally invariant parts

$$(\Lambda : \bar{\Theta}^{\dagger}_{00}) = (\tfrac{1}{3}\,\mathrm{tr}\,\Lambda)(\delta : \bar{\Theta}^{\dagger}_{00}) \tag{E.12-16}$$

$$(\Lambda : \bar{\Theta}^{\dagger}_{1K}) = (\tfrac{1}{2}(\Lambda - \Lambda^{\dagger}) : \bar{\Theta}^{\dagger}_{1K}) \tag{E.12-17}$$

$$(\Lambda : \bar{\Theta}^{\dagger}_{2K}) = (\tfrac{1}{2}[\Lambda + \Lambda^{\dagger} - (\tfrac{2}{3}\,\mathrm{tr}\,\Lambda)\delta] : \bar{\Theta}^{\dagger}_{2K}) \tag{E.12-18}$$

Finally, we note that the isotropic, fourth-order tensors introduced in §E.9 are related to the Θ_{JK}:

$$\mathbf{I}_J = \frac{1}{\sqrt{2J+1}} \sum_{K=-J}^{J} \bar{\Theta}^{\dagger}_{JK}\Theta_{JK} \qquad (J = 0, 1, 2) \tag{E.12-19}$$

and thus

$$\{\Lambda : \mathbf{I}_J\} = \frac{1}{\sqrt{2J+1}} \sum_{K=-J}^{J} (\Lambda : \bar{\Theta}^{\dagger}_{JK})\Theta_{JK} \qquad (J = 0, 1, 2) \tag{E.12-20}$$

It may also be shown that

$$\Lambda = \sum_{J=0}^{2} \sqrt{2J+1}\,\{\Lambda : \mathbf{I}_J\} = \sum_{J=0}^{2} \sum_{K=-J}^{J} (\Lambda : \bar{\Theta}^{\dagger}_{JK})\Theta_{JK} \tag{E.12-21}$$

That is in Eq. E.12-20, the $\mathbf{I}_J$ "project" from Λ, the three rotationally invariant parts given in Eq. E.12-15, and the Θ_{JK} project the complex-spherical components of these parts.

AUTHOR INDEX

FOR VOLUME 2

Abdel-Khalik, S. I., 127, 131, 145, 210
Abramowitz, M., 127, 332
Acierno, D., 379, 380
Altenberger, A. R., 124, 300
Armstrong, R. C., 21, 76, 90, 91, 127, 131, 146, 148, 353
Ashare, E., 387
Astarita, G., 87, 347, 348
Atkinson, J. D., 105
Attane, P., 174
Auer, P. L., 118, 133

Basaran, O., 90, 91
Batchelor, G. K., 409
Bazua, E. R., 105, 172
Beals, E., 172
Bernard, D. A., 337
Bernstein, B., 334
Berry, G. C., 172
Billmeyer, F. W., Jr., 162
Bird, R. B., 26, 41, 57, 62, 64, 69, 76, 82, 84, 85, 89, 92, 95, 96, 98, 100, 118, 119, 121, 124–127, 131, 133, 145–149, 154, 156, 163, 166, 172, 178, 196, 204, 210, 218, 237, 239, 245, 258, 291, 300, 309, 311, 324, 326, 331, 334, 335, 339, 341–348, 408, 410, 412
Bloomfield, V., 172
Booij, H. C., 71, 105, 108, 151, 157
Brenner, H., 289, 304, 408, 409
Brunn, P., 81, 175
Bueche, F., 161
Burdette, S. R., 172, 210
Burgers, J. M., 92

Casassa, E. F., 172
Cerf, R., 105, 172
Christiansen, E. B., 174, 335
Christiansen, R. L., 76, 82, 84
Coleman, B. D., 127, 173
Cottrell, F. R., 72
Cragg, L. H., 83
Crawley, R. L., 342
Currie, P. K., 334
Curtiss, C. F., 26, 57, 62, 64, 69, 100, 118, 133, 156, 196, 204, 210, 218, 237, 239, 245, 291, 300, 309, 311, 324, 331, 334, 335, 339, 341–347, 408, 410, 412, 414

Dahler, J. S., 124, 300
DeAguiar, J. R., 64, 98, 291, 326
de Bats, F. T., 353
de Gennes, P.-G., 85, 307, 322, 327
Denn, M. M., 100
DeWames, R. E., 94, 133, 161
Dirac, P. A. M., 405
Doi, M., 307, 322, 334, 339, 341
Dotson, P. J., 41, 89, 163, 164, 172
Durst, F., 87

Edwards, S. F., 172, 307, 322, 334, 339, 341
Einaga, Y., 383
Eirich, F. R., 106, 365
Endō, H., 343
Epstein, L. F., 170
Erpenbeck, J. J., 286
Evans, D. C., 64, 118, 119, 121, 124, 145, 149, 210, 237
Eyring, H., 11, 226

Fan, X. J., 21, 57, 81, 83, 85, 98, 120, 163, 178, 210, 226–228, 291, 309, 339
Fano, U., 414
Ferry, J. D., 132, 151, 163, 170, 176
Fisher, R. J., 100
Fixman, M., 36, 81, 157, 172, 232 233, 277
Flory, P. J., 9, 10, 11, 14, 26, 162 178, 226
Fox, T. G., 178
Fraenkel, G. K., 19, 21
Freed, K. F., 172
Fujimoto, T., 176, 343
Fukatsu, M., 172
Fuller, G. G., 85, 105
Fulton, R. W., 132

Gao, H. W., 174
Georgescu, A. G., 172
Giesekus, H., 69–71, 85, 97, 118 120, 131, 133, 145, 156, 210, 237
Glasscock, S. D., 342
Gordon, R. J., 100
Gottlieb, M., 41
Graessley, W. W., 99, 178, 339, 342, 345, 346
Green, M. S., 368
Grimm, R. J., 91
Gupta, S. K., 90, 91

Haas, R., 87
Hall, W. F., 94, 133, 161
Ham, J. S., 172
Harris, E. K., Jr., 174
Harris, R. A., 172
Hassager, O., 24, 64, 127, 131, 145, 147, 154, 156, 166, 204, 210, 221, 222, 229, 232, 234, 237–239, 245, 336
Hayashi, S., 56
Hearst, J. E., 172
Hermans, J. J., 4, 19, 164
Heuer, W., 162
Higashitani, K., 81
Hildebrand, F. B., 24, 139
Hinch, E. J., 85
Hirschfelder, J. O., 300, 408, 410. 412

Holmes, L. A., 387
Huglin, M. B., 72
Huppler, J. D., 387

Imai, S., 172
Inagaki, H., 83
Interthal, W., 87
Irving, J. H., 245, 277
Ishikawa, S., 90, 146

James, D. F., 151, 157, 355
Jamieson, A. M., 176
Janeschitz-Kriegl, H., 348, 379
Jeffreys, B. S., 409
Jeffreys, H., 409
Johnson, M. W., Jr., 62, 100, 125, 126, 375
Johnson, N. L., 89, 172
Jongschaap, R. J. J., 379

Kato, T., 176
Keck, T., 87
Keentok, M., 172
Kiefer, J., 94, 133
Kilb, R. W., 172
Kim, S., 120
King, D. H., 151, 157
Kirkwood, J. G., 10, 69, 70, 92, 94, 106, 118, 120, 133, 140, 156, 164, 175, 245, 277, 286
Kleintjens, L. A., 92
Kotaka, T., 83, 120, 133
Kovac, J., 157, 232, 233
Kramers, H. A., 11, 24, 27, 40, 64, 69, 101, 118, 156
Kratky, O., 11
Krigbaum, W. R., 162
Kuhn, H., 19, 105
Kuhn, W., 19, 105
Kurata, M., 162, 172, 339, 383

La Mantia, F. P., 379
Landau, L., 108
Landel, R. F., 87, 163, 222
Laun, H. M., 347, 348, 382, 383
Leal, L. G., 85, 100, 105
Léger, L., 307, 322, 327
Leider, P. J., 91
Lemstra, P. J., 92
LeRoy, P., 174
Lifshitz, E. M., 108
Lightfoot, E. N., 95, 258, 300
Lighthill, M. J., 405
Liouville, J., 255
Liu, T. W., 5, 172, 210, 226–228
Lodge, A. S., 70, 71, 151, 157, 166, 170, 353, 355, 368, 371, 387–390

Malkus, D. S., 334
Manero, O., 85, 100
Manke, C. W., 105
Margenau, H., 410
Markovitz, H., 173
Marrucci, G., 87, 100, 108, 347, 348, 379
Massa, D. J., 84
Mayer, J. E., 39
Mayer, M. G., 39
Mazo, R. M., 210, 237
Meissner, J., 387
Menezes, E. V., 345, 346
Merrill, E. W., 72
Mieras, H. J. M. A., 337
Mills, N. J., 337
Mizutani, K., 176
Mochimaru, Y., 91
Mooney, M., 365
Morrison, J. D., 170
Mou, C. Y., 237
Münstedt, H., 347
Murphy, G. M., 410

Nagasawa, M., 83, 176, 343
Nemoto, N., 132
Nicolais, L., 87, 347, 348
Noda, I., 83, 172, 176
Noolandi, J., 337

Onogi, S., 125, 126
Osaki, K., 170, 176, 383
Oseen, C. W., 92
Öttinger, H. C., 94

Paul, E., 210, 237
Peng, S. T. J., 87, 222
Perena, J. M., 83
Peterlin, A., 76, 81, 92, 105, 161, 169, 172
Phan-Thien, N., 85, 100, 105, 373, 374, 380
Pierrard, J. M., 174
Plock, R. J., 118, 120
Porod, G., 11
Prager, S., 94, 118, 120, 131, 133
Prigogine, I., 237
Pyun, C. W., 172

Racah, G., 414
Ramachandran, S., 174, 335
Rayleigh, Lord (J. W. Strutt), 50
Reihanian, H., 176
Reinhold, C., 105, 172
Rektorys, K., 90
Renardy, M., 85
Riande, E., 83
Rice, S. A., 237
Riseman, J., 92, 106, 140
Rivlin, R. S., 210, 218, 365
Roe, G. M., 170
Roitman, D. B., 210
Rotne, J., 94, 133
Rouse, P. E., Jr., 17, 24, 151, 159

Saab, H. H., 163, 164, 178, 309, 339, 341–348
Sammler, R. L., 170
Sarti, G. C., 108
Schieber, J. D., 5, 339, 345
Schowalter, W. R., 100
Schrag, J. L., 132, 170, 176
Segalman, D., 100, 375
Shafer, R. H., 172
Shen, M. C., 94, 133, 161
Sherwood, A. A., 172
Smith, K. A., 72
Sørensen, J. P., 123, 138, 141, 142
Staudinger, H., 162
Stegun, I. A., 127, 332
Stehrenberger, W., 21, 144
Stevenson, J. F., 62, 76, 125, 126
Stewart, W. E., 95, 123, 138, 141, 142, 258, 300
Stidham, H. D., 172
Stockmayer, W. H., 50, 81, 162, 172
Stratton, R. A., 342
Suzuki, H., 83

Takserman-Krozer, R., 151
Tamura, M., 383
Tanaka, G., 21, 172
Tanner, R. I., 21, 72, 85, 90, 104, 105, 144, 172, 373, 374, 380
Thurston, G. B., 169, 170
Tirrell, M., 326
Titomanlio, G., 379
Tobolsky, A. V., 368
Tolman, R. C., 39, 108
Treloar, L. R. G., 10, 11, 13, 226, 355, 365
Truesdell, C., 127
Tschoegl, N. W., 172
Turrel, G., 174

van Aken, J. A., 348
van Kampen, N., 47
van Oene, H., 83
van Rijn, C. F. H., 337
van Wiechen, P. H., 71, 105, 151, 157
Verdier, P. H., 157
Volkenstein, M., 226

Wada, E., 123, 124
Wagner, M. H., 353, 382–385
Wall, F. T., 11
Wang, F. W., 107, 172
Warner, H. R., Jr., 16, 21, 64, 76, 118, 119, 121, 124, 133, 145, 149, 210, 237

Wedgewood, L. E., 92
Weiss, G. H., 94, 133
Wesslau, H., 337
Wiegel, F. W., 353
Wiest, J. M., 85, 96, 172, 210, 291, 391
Wilemski, G., 21
Williams, M. C., 17, 105, 151, 161, 172
Williams, M. L., 163
Winter, H. H., 353
Wu, Y., 70, 71, 151, 157, 166, 170

Yamada, Y., 83
Yamakawa, H., 11, 14, 62, 94, 133, 140, 161, 172, 175, 178, 226
Yamamoto, M., 353
Yang, J. T., 123, 124
Yu, T. L., 176

Zimm, B. H., 17, 50, 94, 107, 151, 157, 164, 170, 172, 210
Zwanzig, R., 94, 133

SUBJECT INDEX

FOR VOLUMES 1 AND 2

Page numbers following (1) refer to Volume 1, "Fluid Mechanics."
Page numbers following (2) refer to Volume 2, "Kinetic Theory."

Acierno–LaMantia–Marrucci–Titomanlio equation, (1)411
Acoustic streaming, (1)71
Admissibility, (1)293, 482, 497
Affine motion, (2)355
  deviations from, (2)373
Aluminum soap solutions, (1)79, 106, 108, 118, 121, 125, 172
Angular momentum equation of change, (1)8
Annular flow, axial:
  Bingham fluid, (1)249
  Ellis model, (1)231
  Newtonian fluid, (1)44
  power–law model, (1)176, 181, 202, 238
  second normal-stress difference and, (1)519
  viscoelastic fluid, (1)98
  see also Eccentric annuli, axial flow
Annular flow, helical, (1)160
  power–law model, (1)184
Annular flow, radial, (1)41
Annular flow, tangential, (1)160, 333
  Bingham fluid, (1)228
  Newtonian fluid, (1)35
  normal stress effects, (1)96
  oscillatory, (1)279
  power–law model, (1)176, 239
  see also Eccentric annuli, axial flow
Arrhenius expression, (1)140
Associative law, (1)556
Attenuation of velocity wave, (1)276
Average molecular weights, (1)49, 59, 144, (2)337
Average number of beads, (2)273
Average value, (2)12, 41, 58, 113
  over cross section, (1)14
  of kinetic energy, (2)43
  in momentum space, (2)42, 263
  in network theories, (2)359
  in phase space, (2)256
  of reciprocal of interbead distance, (2)46
  over time, (1)187, 375
  time rate of change of, (2)62, 116, 154, 256, 359
  over unit sphere, (2)411
Axisymmetric flow, (1)25

Base vectors, (2)33, 406
  bead-rod-spring models, (2)185, 186, 248
  differentiation of, (1)602
  Kramers chain, (2)35, 217
  modified reciprocal, (2)188
  multibead-rod model, (2)189
  multirod-rod model, (2)300
  in nonorthogonal coordinates, (1)598
  reciprocal, (1) 597, 599
  Rouse chain, (2)36
  special relation for system with no constraints, (2)51
  in spherical coordinates, (1)597
  transformation rules for, (1)605
  two-needle model, (2)253
Bead-rod models, (2)117, 136, 222, 229
Bead-rod-spring models:
  diffusion equation, (2)193
  generalized forces, (2)192
  geometry of, (2)182
  high-frequency dynamic viscosity, (2)240
  hydrodynamic interaction, (2)185
  index convention for, (2)249
  second-order fluid constants, (2)204, 238
  stress tensor, (2)198, 283
  thermodynamic quantities, (2)241
  third-order fluid constants for, (1)302
  translational diffusivity, (2)295
Bead-spring chain, (2)18
  diffusion equation, (2)152–155
  stress tensor, (2)155
  translational diffusivity, (2)174
  see also Rouse model; Zimm model
Bead-string model, (2)209

Bestul–Belcher equation, (1)244
Biaxial stretching flow, (1)101, 437, 533
Bingham fluid, (1)61, 228, 229
  axial annular flow, (1)249
  flow around sphere, (1)235
  tangential annular flow, (1)228
  tube flow, (1)244
Bipolar coordinates, (1)312, 595
  del operations in, (1)592
Bird–Carreau model, (1)467
Birefringence, (1)509
Bitumen, (1)74
BKZ model, *see* K-BKZ model
Bogue–Chen model, (1)467
Boltzmann's superposition principle, (1)263
Boundary-layer flows, (1)235
Branched polymers, (1)56
Brinkman number, (1)207
Brownian force:
  anisotropic, (2)96, 310
  approximations for, (2)291, 314
  equilibration in momentum space and, (2)292
  in melts, (2)314
  on polymer molecule, (2)292
  for systems with no constraints, (2)293
  see also Forces in kinetic theory
Bubble, deforming, (1)31, 325
  converging flow field and, (1)76
Bubble, translating:
  Newtonian flow around, (1)29
  second-order fluid, (1)318, 321
  shape of, (1)83
Bubble inflation, (1)533
Bubbles, Uebler effect, (1)74
Buckingham–Reiner equation, (1)229

Calculus of variations, (1)192–205
Capillary number, (1)31, 324
Capillary viscometer, *see* Tube flow
Carboxymethylcellulose, (1)61, 78, 236, 537, 547
Carboxypolymetheylene, (1)61, 208
Carreau–Yasuda model, (1)171
Cartesian tensor notation, (1)607
Casson equation, (1)227, 243
Cauchy tensor, (1)427. *See also* Strain tensors
Cayley–Hamilton theorem, (1)298, 435
  statement of, (1)569
CEF equation, *see* Criminale–Ericksen–Filbey ("CEF") equation
Cellulose, (2)83
Center of mass, (2)32
  motion of, (2)38, 60, 95, 115, 134, 152, 174, 273, 296
Center of resistance, (2)166
  motion of, (2)168, 288, 305
  weight tensors, (2)187, 286
Centripetal pumping between parallel disks, (1)551
Chain constraint exponent, (2)311
Chain models, (2)9–19
  generalized coordinates, (2)32
  geometry of, (2)22, 153, 167
  hydrodynamic interaction and, (2)164–175
  index conventions for, (2)33
  infinitely stiffened springs, (2)46
  second-order fluid constants, (2)208
  see also Kirkwood–Riseman model; Kramers model; Rouse model; Zimm model
Chain rule of partial differentiation, (1)579, (2)60, 403
Christoffel symbols, (1)602, 603
Circular tube, *see* Tube flow
Coat-hangar die, (1)245
Coaxial cylinders, *see* Annular flow, tangential
Codeformational derivatives, *see* Convected derivative
Collocation method, (1)199
Commutative law, (1)556
Complex modulus, (1)115
  plateau modulus, (1)147
  temperature dependence, (1)142
  see also Complex viscosity
Complex quantities:
  complex spherical components, (2)413
  product rule for real parts of, (1)188
  representation of oscillations, (1)116, 163
Complex viscosity:
  bead-rod-spring model, (2)240
  concentration dependence of, (1)147
  from cone-and-plate instrument, (1)549
  definition, (1)115, (2)399
  from eccentric rotating disk viscometer, (1)512, 516
  high-frequency expressions, (1)286
  linear viscoelastic fluid, (1)265, 287
  melt kinetic theory and, (2)337
  memory function and, (1)287
  parallel-disk viscometer, (1)510
  rigid dumbbell model, (1)286
  sample experimental data, (1)118
  third-order fluid and, (1)329
  from torsional viscometer, (1)282
  see also Material functions
Computer simulations, (2)41
Concentration, kinetic theory expression, (2)257, 264
Concentration dependence, (1)143–150
Concentric cylinder viscometer, *see* Couette viscometer
Cone-and-plate viscometer, (1)18, 517
  complex viscosity from, (1)549
  inertial effects in, (1)549
  Newtonian fluid, (1)18, 34
  power-law fluid, (1)223
  secondary flows in, (1)327
  sources of error, (1)523
  truncated, (1)520, 551
  viscometric functions from, (1)110, 518, 521, 548
  viscous heating in, (1)223, 523
Configurational distribution function, (2)12, 262, 272
  bead-rod models, (2)231
  change of coordinates, (2)40, 49
  elastic dumbbells, (2)21, 48, 56

equilibrium, (2)39
FENE dumbbells, (2)77
Hookean dumbbells, (2)72, 101
Kirkwood–Riseman chain, (2)226
Kramers chain, (2)40
in network theories, (2)356, 371
pair, (2)263
potential flow, (2)62
random walk distribution, (2)12
rigid dumbbells, (2)112, 121, 127
Rouse chain, (2)41, 161
Connector force:
elastic dumbbells, (2)60, 76
see also Forces in kinetic theory
Connector vector, (2)23
Conservation laws in fluid dynamics, (1)3
Consistency index, (1)173
Constitutive equations, (1)10
Acierno–LaMantia–Marrucci–Titomanlio equation, (1)411
chart showing interrelations among, (1)500
construction of admissible equations, (1)497
convected Jeffreys model, (1)345, (2)398
convected Maxwell model, (1)346, (2)398
Criminale–Ericksen–Filbey ("CEF") equation, (1)503, (2)397
Curtiss–Bird, (1)440, (2)334
Doi–Edwards, (1)440, (2)334
elastic solid, (2)364
factorized K-BKZ model, (1)437, (2)398
FENE dumbbells, (1)410, (2)88–91, 99
FENE-P, (1)410
Fraenkel dumbbells, (2)104
generalized Newtonian fluid, (1)169–253
general linear viscoelastic fluid, (1)263, (2)397
Giesekus equation, (1)303, 353, 361, 412, 417, 625, (2)97
Gordon–Schowalter equation, (1)355
Hand equation, (1)422
Hassager equation, (1)442
Hookean dumbbells, (2)71, 100
Johnson–Segalman equation, (1)355
K-BKZ equation, (1)436, 466, (2)398
Leal–Hinch equation, (1)422
Leonov model, (1)361
Lodge network model, (1)433, (2)368
Lodge rubberlike liquid, (1)431, (2)397
Marrucci, et al., (1)411, (2)379
Maxwell model, (1)258
for melts, (2)333
memory-integral expansion, (1)499, (2)397
nearly Hookean dumbbell model, (1)410
Newtonian fluid, (2)398
non-affine Lodge network model, (2)376
Oldroyd 4-constant model, (1)354, 356, 423
Oldroyd 6-constant model, (1)303, 416, (2)100, 144, 398
Oldroyd 8-constant model, (1)352, 353, 415, 420, 625, (2)398
Oldroyd's admissibility criteria, (1)482, 497
Papanastasiou–Scriven–Macosko equation, (1)441
Phan–Thien and Tanner, (1)411, (2)375, 380
Phillips equation, (1)441
recommendations for use of, (1)468
Reiner–Rivlin equation, (1)504
retarded-motion expansion, (1)298, (2)397
Rouse chains, (1)440, (2)159
second-order fluid, (2)398
Tanner model, (1)410
Tanner–Simmons equation, (1)440
Wagner model, (1)451, (2)383
White–Metzner model, (1)350, 371, 377, 415
Zimm chains, (1)440, (2)169
see also Stress tensor *and under name of equation or model*
Constrained recoil, *see* Recoil
Constraints:
bead-rod-spring models, (2)182
generalized coordinates and, (2)32
generalized forces, (2)192
Hamilton's equations and, (2)38
rigid dumbbell model, (2)115, 134
stress tensor and, (2)199, 201, 283
Continuity equation, *see Equation of continuity in kinetic theory*
Continuum mechanics, 477–508
summary of notation, (2)293
Contraction flow, (1)76
Deborah number, (1)93
torsional oscillations in, (1)95
Contravariant components, (1)597, 600
Convected base vectors, (1)480, 483
reciprocal, (1)485
time dependence of, (1)486
Convected coordinates, (1)480, 483
Convected derivatives:
definition, (1)342, 491, 494, 495, 496, (2)395
higher order, (1)495
in kinetic theory, (2)63
of product, (1)495
of rate-of-strain tensor, (1)297, 491, 492
rules for, (1)495
of stress tensor, (1)324, 622, 623
of unit tensor, (1)495
Convected integration, (1)496
Convected Jeffreys model, (1)345–350, 419, 483, (2)398
Hookean dumbbells and, (2)72, 107
integral form of, (1)432, 496
line sink, (1)458
oscillatory flow, (1)414
Rayleigh problem, (1)369
spherical film inflation, (1)458
torsional flow, (1)400
Convected Maxwell model, (1)346, 387, 418, (2)398
generalized, (1)409, 432
integral form of, (1)432
line sink, (1)458
modification of, (1)506
Convection equation in network theories, (2)357, 391

Converging flow, use for studying elongational flow, (1)532
Coordinates:
cylindrical, (1)578
nonorthogonal, (1)599
spherical, (1)578
transformation of, (1)605
Copolymers, (1)56
Corner:
Newtonian flow near, (1)46
second-order fluid flow near, (1)339
Corotational derivative, (1)324, 507, (2)395
Corotational Jeffreys model, (1)355
Couette flow:
Newtonian fluid, (1)13
power-law fluid, (1)180, 224
with viscous heating, (1)224
Couette viscometer, (1)519, 548
end corrections for, (1)550
viscous heating in, (1)551
wide-gap, (1)552
Coupling tensors, (2)187, 194, 288, 294, 301, 313
Covariant components, (1)597, 600
Covariant differentiation, (1)604
Cox-Merz rule, (1)150
Creep, (1)113, 128
elongational, (1)133, 137
linear viscoelastic fluid, (1)270
Creep compliance, (1)128
Creeping flow, (1)23, 316
Creep recovery, (1)131
Criminale-Ericksen-Filbey ("CEF") equation, (1)233, 397, 503, 521, (2)397
use in describing squeezing flow, (1)539
Critical molecular weight, (1)144
Critical shear rate, (1)146
Crosslinks, (1)56, (2)354, 365
Cross product:
of base vectors, (1)600
of tensor with vector, (1)568
of unit dyads, (1)565
of unit vectors, (1)560
of vectors, (1)558, 562, 602
Curl, (1)572
Currie potential, (1)454
Curtiss-Bird theory of melts, (1)468, (2)309, 316
hole-pressure effect and, (1)462
rod-climbing and, (1)330
third-order fluid constants from, (1)302
Curvilinear coordinates, (1)577-596
Cylinder, transverse flow around, (1)40
Cylindrical coordinates, (1)578
Christoffel symbols in, (1)603
del operations in, (1)582, 585, 588
equation of motion in, (1)612, 613
kinematic tensors in, (1)614-620
metric components in, (1)603
Cylindrical tank with rotating lid, (1)69

Damping function, (1)106, (2)384
Deborah number, (1)92
in fiber spinning, (1)383
for generalized Newtonian fluids, (1)234
in journal-bearing flow, (1)392
for retarded motion expansion, (1)301, 316
in spherical film inflation, (1)461
in torsional flow, (1)402
Deformation history, (1)481
Delayed swell, (1)73
Del operator, (1)571
in curvilinear coordinates, (1)582, 583
identities involving, (1)574
in nonorthogonal coordinates, (1)602
in spherical coordinates, (1)583, 597
tables of del operations, (1)586-593
Delta, *see* Dirac delta function; Kronecker delta
Density of polymer melts, (1)209
Die swell, (1)72
Differential constitutive equations, (1)345, 350, 408-413
Differential operators:
curl, (1)572, 604
del operator, (1)571, 582, 583, 584, 586-593, 597 602, 604
divergence, (1)571, 573, 604, 606
gradient, (1)571, 572
Laplacian, (1)573, 604, 606
operator Λ, (2)119, 125, 230, 406
operator $\partial/\partial \boldsymbol{r}$, (2)403
operator $\partial/\partial \boldsymbol{u}$, (2)114, 406
Diffusion equation in configuration space:
bead-rod-spring models, (2)193, 194, 290, 294
bead-spring chains, (2)154, 168
elastic dumbbells, (2)59-62, 96
in melts, (2)313, 317, 328
multibead-rod, (2)195
multirod-rod, (2)300
rigid dumbbells, (2)114-117, 119, 127, 134
see also Convection equation in network theories
Diffusion tensors, (2)165, 185, 188, 286
multibead-rod, (2)195
Diffusivity, *see* Rotatory diffusivity; Translational diffusivity
Dilatancy, (1)61, 105, 173
Dilatational viscosity, (1)10
Dimensionless groups, (1)12, 92, 207, 212, 213
Dirac delta function, (1)261, (2)14, 405
Displacement functions, (1)428, 484
definition, (1)425, (2)394
in eccentric disk viscometer, (1)513
Displacement gradient tensors, (1)485
components in curvilinear coordinates, (1)620
definition, (1)426, (2)394
in eccentric disk rheometer, (1)513
incompressibility and, (1)476
in linear viscoelasticity, (1)257
in shear flows, (1)623
in shearfree flows, (1)623
time derivatives of, (1)486, 507
in turntable problem, (1)289

Distribution function:
contracted, (2)44, 261
equilibrium, (2)38
for interbead vector, (2)45
pair, (2)261
for segments, (2)356, 371
time-evolution of, (2)271
see also Configurational distribution function; Momentum space distribution function; Phase space distribution function; Single-link distribution function; Velocity space distribution function
Distributive law, (1)556
Divergence, (1)571, 573, 595, 596, 604, 606
Doi–Edwards theory of melts, (2)307, 311, 314, 316, 322
constitutive equation, (1)453
Currie's approximate potential for, (1)454
relation to generalized Maxwell model, (1)262, 287
relation to K-BKZ model, (1)440
relaxation modulus from, (1)287
rod-climbing and, (1)330
third-order fluid constants from, (1)302
Domain perturbation approach, (1)387
Dot product:
of base vectors, (1)600
of tensors, (1)567, 601
of unit dyads, (1)565
of unit vectors, (1)560
of vectors, (1)557, 562, 601
Double-dot product, (1)565, 567
Drag force:
on bubble, (1)30, 323
on sphere, (1)28, 464
Drag reduction, (1)88
Draw ratio in fiber spinning, (1)379, 384
Drift velocity, *see* Center of mass
Dumbbell model, (2)19. *See also* Elastic dumbbell; FENE dumbbell; Hookean dumbbell; Rigid dumbbell
Dyadic product, (1)566
Dynamic moduli:
bead-rod models, (2)232, 238
definitions, (2)399
Dynamic viscosity, (1)122. *See also* Complex viscosity

Eccentric annuli, axial flow:
power-law fluid, (1)204
second-order fluid, (1)311
Eccentric annuli, tangential flow:
CEF equation, (1)397
convected Maxwell fluid, (1)387
Deborah number, (1)93
Newtonian fluid, (1)48
second-order fluid, (1)314
Weissenberg number, (1)94
White–Metzner equation, (1)397
Eccentric disk rheometer, (1)163, 166, 417, 512, (2)57
convected Maxwell model, (1)418
retarded-motion expansion and, (1)328
Rivlin–Sawyers model, (1)471
schematic diagram, (1)164
Effective forces, *see* Forces in kinetic theory
Effective-velocity-gradient assumption, (2)100, 374
Elastic dumbbell, (2)20
anisotropic effects, (2)96
configurational distribution function, (2)62
diffusion equation for, (2)62
effective-velocity-gradient assumption, (2)100
end-to-end distance, (2)28
equations of motion for, (2)59
equilibrium properties of, (2)47
force laws, (2)21
forces in, (2)58
stress tensor, (2)64–71
Elastic effects, (1)56, 69, 72
in line-sink flow, (1)458
second-order fluids and, (1)301, 318
in squeezing flow, (1)191, 539
stress ratio and, (1)110
see also Deborah number
Elastic modulus, (1)257, (2)365, 389
Elastic rhombus model, (2)209, 215, 239
Elastic solids:
configurational distribution for, (2)361
constitutive equation, (2)364
elastic modulus, (2)365
modeling of, (2)355
Elliptical tube, (1)327
Ellis model, (1)228, 229, 236
axial annular flow, (1)231
slit flow, (1)243
temperature dependence, (1)210
tube flow, (1)243
Elongation, (2)364, 367
uniaxial, (1)437
Elongational flow, (1)38, 101, (2)400
Elongational viscosity:
definition, (1)38, 132, (2)400
FENE dumbbell, (2)85–88
Kirkwood–Riseman chain, (2)229
Kramers chain, (2)219
measurement of, (1)530
melt kinetic theory for, (2)345
non-affine Lodge network model, (2)377
rigid dumbbell, (2)125, 145
sample experimental data, (1)133
second-order fluid, (1)300
see also Material functions
Elongation rate, (1)101
Embedded vectors, (2)182, 410
End effects in tube flow, (1)528, 551
End-to-end distance:
elastic dumbbells, (2)28, 72
FENE dumbbells, (2)89, 107
Hookean dumbbells, (2)73, 75, 101, 107
Kirkwood–Riseman chain, (2)13, 228
Kramers chain, (2)12

End-to-end distance (*Continued*)
Rouse chain, (2)18, 163
End-to-end vector, (2)12
distribution function, (2)13, 28
Kramers chain, (2)49
random-walk chain, (2)49
Rouse model, (2)19
Energy dissipation:
in Hookean dumbbell solutions, (2)106
in rigid dumbbell, (2)144
see also Viscous dissipation heating
Entanglements, (2)354
Entropy, (2)108, 241
Epprecht viscometer, (1)548
Equation of change for angular momentum, (1)8
Equation of change for enthalpy, (1)40
Equation of change for kinetic energy, (1)8
Equation of change in kinetic theory:
bead-spring chains, (2)154
elastic dumbbells, (2)62
general, (2)256
networks, (2)359
rigid dumbbells, (2)114
Equation of continuity in fluid dynamics, (1)4, (2)400
for incompressible fluids, (1)12, 206
kinetic theory derivation, (2)257, 269
for mixtures, (2)400
Equation of continuity in kinetic theory, (2)61, 116, 152, 168, 193, 255, 271, 272, 274, 358
Equation of energy, (1)9
alternative form for, (1)40
for generalized Newtonian fluids, (1)206
for incompressible fluids, (1)12
Equation of motion in fluid dynamics, (1)6, (2)400
for generalized Newtonian fluids, (1)206
for incompressible fluids, (1)12
kinetic theory derivation, (2)258, 269
tables in curvilinear coordinates, (1)612, 613
in terms of stream function, (1)24
Equation of motion in kinetic theory, (2)272, 274, 277, 295
bead-rod-spring models, (2)193, 194
bead-spring chains, (2)152, 164, 168
elastic dumbbells, (2)59, 92
in melts, (2)313
network segments, (2)357, 374
rigid dumbbells, (2)114
Equation of state, (1)10
Equations of change in fluid dynamics, (2)400
for generalized Newtonian fluids, (1)206
for incompressible fluids, (1)11, 12, 206
integrated forms of, (1)36
in terms of fluxes, (1)3
in terms of transport properties, (1)10
Equilibration in momentum space, (2)279, 291, 314, 355. *See also* Maxwellian velocity distribution
Essential boundary conditions, (1)194
Euler angles, (2)182, 410
functions of, (2)412
Eulerian technique, (1)455, 461
Euler–Lagrange equations, (1)194
Euler–Maclaurin expansion, (1)286
Excluded volume, (2)81, 172
Extensional viscosity, *see* Elongational viscosity
External force, translational diffusivity and, (2)95, 140, 174, 299, 327. *See also* Forces in kinetic theory
Extrudate swell, (1)72
Eyring model, (1)228, 229

Factorization, in linear viscoelasticity, (1)263
Factorized K-BKZ model, *see* K-BKZ model
Fading memory, (1)263
Falling-ball viscometer, (1)536
Falling cylinder viscometer, (1)45, 248
Falling film, *see* Film flow, power-law model
Falling-sphere viscometer, (1)521
FENE dumbbell, (2)76–92, 99
anisotropic effects, (2)98
constitutive equation, (2)79, 90, 98, 104
distribution function, (2)21, 29, 48
end-to-end distance, (2)28, 107
force law, (2)21
retarded-motion constants for, (1)302
FENE-P model, (1)410, (2)88
FENE springs, (2)16
Fiber-spinning, (1)235, 469
Newtonian fluid, (1)51
stability of, (1)79
White–Metzner fluid, (1)377
Fick's law of diffusion, (1)7, (2)299
Filament drawing, *see* Fiber-spinning
Film flow, power-law model, (1)179
Finger tensor, (1)427
invariants of, (1)435, 624
see also Strain tensors
Finite beads, (2)246, 252, 284, 289, 300
Finite linear viscoelasticity, (1)431
Finite strain tensors, *see* Relative (finite) strain tensors; Strain tensors
Flory–Fox equation, (2)178
Flow enhancement:
in helical annular flow, (1)184
by pulsatile pressure drop, (1)187, 371
Force balance in kinetic theory, *see* Equation of motion in kinetic theory
Forces in kinetic theory, (2)58, 191, 250
stress tensor and, (2)64
tables of notation, (2)192, 266, 273, 277, 283
see also Brownian force; Connector force; External force; Hydrodynamic force; Intramolecular force; Spring force
Fourier's law of heat conduction, (1)7, 11
Fraenkel dumbbell:
force law, (2)21
rigid dumbbell and, (2)104, 143
zero-shear-rate viscosity, (2)104
Free-draining assumption, (2)92
Freely jointed bead-rod chain, *see* Kramers model
Freely rotating chain, *see* Kirkwood–Riseman model

Free recovery, (1)131
after elongational flow, (1)133
Friction coefficient, (2)60, 188, 311
rotational, (2)289, 304
translational diffusivity and, (2)95
Friction tensor, (2)60, 97, 285, 300
effective, (2)188, 286
in melts, (2)311
modified effective, (2)187
total effective, (2)187, 286
Froude number, (1)12, 207

Galerkin's method, (1)200
Gaussian distribution, (2)14
Gaussian spring, (2)16, 355
Generalized coordinates, (2)31, 182, 248
Generalized forces, *see* Forces in kinetic theory
Generalized Maxwell model, (1)262
convected, (1)409, 432
fitting linear viscoelastic data, (1)117
stress growth, (1)269
stress relaxation, (1)268
Generalized momenta, (2)31, 34, 249
Generalized Newtonian fluid, (1)169–253
Deborah number, (1)234
equations of change for, (1)206
limitations of, (1)233
Nusselt numbers for, (1)212, 213
slit flow, (1)242
tube low, (1)242
variational principle for, (1)201, 252
Generalized velocities, (2)34, 248
General linear viscoelastic model, (1)263, 511
Generation number, (1)207
Giesekus constitutive equation, (1)353, 361, 412, 417
kinetic theory derivation, (2)97
for shear and shearfree flow, (1)625, 626
third-order constants for, (1)303
Giesekus equation for kinematic tensors, (1)305
Giesekus's three-dimensional flow theorem, (1)306
Giesekus stress tensor, *see* Stress tensor
Gleissele's mirror relations, (1)150, 153
Gordon–Schowalter equation, (1)355
Gradient, (1)571, 572
Graetz number, (1)212, 213

Hagen–Poiseuille equation, (1)15, 177
Hamiltonian, (2)15, 37, 249
Hamilton's equations, (2)37, 251
Hand equation, (1)422
Hassager equation, (1)442
Heat capacity, (1)209
Heat flux, (1)9, 11
Heat transfer, *see* Nonisothermal flow problems
Heat-transfer coefficient, (1)89, 215, 216
Heaviside unit step function, (1)123, 286, (2)75
definition, 286
Helical flow, *see* Annular flow, helical
Helmholtz equation, (2)230, 234
Helmholtz free energy, (2)15, 109, 241
Helmholtz–Korteweg variational principle, (1)201
Hencky strain, (1)135, 430, 531, 624
Herschel–Bulkley equation, (1)227
Heterogeneity index, (1)59, 96
Higashitani–Pritchard equation, (1)68, 463
Hole-pressure effect, (1)67, 97, 521
Curtiss–Bird model, (1)462
Higashitani–Pritchard relation, (1)68, 463
second-order fluid, (1)337
Tanner–Pipkin relation, (1)463
Homogeneous velocity fields, (2)57, 286, 393
Homopolymers, (1)56
Hookean dumbbell:
constitutive equation, (2)71, 100
distribution function, (2)21, 29
end-to-end distance, (2)28, 107
energy dissipation, (2)106
force law, (2)21
material functions for, (2)73–76
memory function for, (2)72
nearly Hookean dumbbell, (1)410
nondilute solutions, (2)107
nonisothermal flow, (2)100
retarded-motion constants for, (1)302, (2)105
second-order-fluid constants, (2)208
thermodynamic quantities, (2)108
time constants, (2)71
Hookean solid, (1)257
Hookean spring, (2)15
Huggins coefficient, (1)109
Hydrodynamic force:
bead-rod-spring model, (2)199
kinetic theory definition, (2)273
in melts, (2)311
table of notation, (2)283
see also Forces in kinetic theory; Stokes' law
Hydrodynamic interaction:
bead-rod-spring models, (2)185, 285
bead-spring chains, (2)164–173
elastic dumbbells, (2)59, 92
equilibrium-averaged, (2)94, 164, 185, 204, 213
Hookean dumbbells, (2)94
multibead-rod, (2)195
nondilute solutions, (2)107
notation for, (2)188
rigid dumbbells, (2)133
stress tensor with, (2)135, 198
tensors, (2)285
Zimm matrix, (2)165
see also Oseen–Burgers tensor; Rotne–Prager–Yamakawa tensor
Hydrodynamic interaction parameter, (2)133, 169, 177
Hydroxyethylcellulose, (1)175, 191, 446, (2)91

Incompressibility, (1)5, 11, 435, 476, (2)393
Indices, conventions for, (2)33, 249
Inelastic fluids, *see* Generalized Newtonian fluid
Infinite-shear-rate viscosity, (1)107

Infinitesimal strain tensor, (1)257
  additivity of, (1)258
  derived from finite strain tensors, (1)489
  see also Strain tensors
Instability problems, (1)235
Integral constitutive equations, (1)425–476
Integral operations:
  over all space, (2)404
  over unit sphere, (2)497
Internal degrees of freedom, (2)4
  chain models, (2)32
  equations of motion for, (2)38, 251, 272
  freezing out, (2)41, 46, 104, 143, 218, 226
Internal energy:
  bead-rod-spring models, (2)241
  equation of change for, (1)9
  Hookean dumbbell solution, (2)108
Internal viscosity, (2)105, 172
Intramolecular force, *see* Forces in kinetic theory
Intrinsic viscosity, (2)81, 123, 162, 205, 399
  complex viscosity, (1)117
  definition, (1)109
  Mark–Houwink exponent, (1)143
  see also Material functions
Invariance, rheological, (1)482
Invariants, (1)568
  joint, (1)569
  of rate-of-strain tensor, (1)170, 351
  of strain tensors, (1)435, 437, 624
Inverse Langevin force law, (2)16
Irrotational fields, (1)575

Jacobian of transformation, (2)40
Jaumann derivative, (1)342, 507, (2)395
Jeffreys model, (1)261, 285. *See also* Convected Jeffreys model
Jet emerging from tube:
  extrudate swell, (1)72
  Newtonian fluid, (1)36
  polymer additives and jet breakup, (1)91
  see also Fiber-spinning
Johnson–Segalman equation, (1)355
Journal-bearing problem, *see* Eccentric annuli, tangential flow
Junctions in networks, (2)354

Kaye model, (1)467
K-BKZ model, (1)436, 466, (2)398
  factorized, (1)437, 475, (2)398
  relation to molecular theories, (1)440
  retarded motion expansion and, (1)438
  third-order fluid and, (1)303
Kinematics, (1)100–103, 153–163
Kinematic tensors, (1)294, 296, (2)396
  operations with, (1)506
  relations among, (1)504
  table of notation for, (1)492
  tables in curvilinear coordinates, (1)614–620
  see also Rate-of-strain tensor; Strain tensors; Vorticity tensor
Kinetic energy, (2)33, 35
  average value of, (2)43
  elastic dumbbells, (2)48
  equation of change for, (1)8
  internal, (2)248
  rotational, (2)247
Kirkwood equation for translational diffusivity, (2)174, 299
Kirkwood–Riseman model, (2)10
  elongational viscosity, (2)229
  end-to-end distance, (2)13, 228
  equilibrium distribution function, (2)226
  generalized coordinates, (2)32
  geometry of, (2)25, 223
  radius of gyration, (2)27
  second-order fluid constants, (2)209, 228
Kramers–Kronig relations, (1)265, 284, 291
Kramers matrix, (2)23, 37
  modified, (2)166, 217
  relations for, (2)179
Kramers model, (2)11
  base vectors, (2)35, 217
  configurational distribution function, (2)40, 49
  dynamic moduli, (2)232
  elongational viscosity, (2)219
  end-to-end vector probability, (2)49
  generalized coordinates, (2)32
  geometry of, (2)23, 217
  melt kinetic theory and, (1)302, (2)309
  metric matrix, (2)35, 217
  radius of gyration, (2)27
  relation to bead-spring chain, (2)46
  second-order fluid constants, (2)208, 218
  three-bead, (2)35, 49, 189, 232
Kramers stress tensor, *see* Stress tensor
Kramers tensors, (2)218, 313
Kronecker delta, (1)559, (2)13

Lagrange's identity, (1)564
Lagrangian technique, (1)456, 461
Langevin function, (2)16
Langlois–Rivlin–Pipkin theorem, (1)309
Laplace transform, (1)289, 370
Laplacian, (1)573, 596, 604, 606
Laun's rule, (1)150
Leal–Hinch equation, (1)422
Legendre polynomials, (1)324, (2)408
Leibniz formula for differentiating an integral, (1)525
  three-dimensional, (1)576
Leonov model, (1)361, 413
Linear-locked dumbbell, (2)21
Linear viscoelasticity, (1)255–291
  finite, (1)431
  flow problems, (1)275
  limitations of, (1)282
  measurements, (1)510
  table of analogous quantities, (1)272
Line sink:
  Hookean dumbbell solutions, (2)107
  kinematics of, (1)162

Lodge rubberlike liquid, (1)456, 473
third-order fluid, (1)329
Lines of shear, (1)155, 158
Link tension coefficient, (2)311, 313
Liouville equation, (2)255
Lodge–Meissner rule, (1)125
Lodge network model, (1)432, 433, (2)368
inception of shear flow, (2)387
non-affine modification, (2)376
relation to K-BKZ model, (1)440
Lodge rubberlike liquid, (1)431, 483, 499, (2)397
comparison with experimental data, (1)122
eccentric disk rheometer, (1)513
filament stretching, (1)469
line sink, (1)456
rapid deformations of, (2)389
recoil, (2)388, 390
shear flow, (1)432
spherical film inflation, (1)458
Loss modulus, *see* Dynamic moduli
Loss tangent, (1)116
Lubricated squeezing flow, (1)533
Lubrication approximation, (1)13, 18, 19, 176, 189

Macromolecule, *see* Polymer
Mark–Houwink exponent, (1)143
Martin equation, (1)144
Mass flux, (2)299, 401
kinetic theory expression, (2)258, 264, 270, 278, 296
through surface, (1)559
Material derivative, (1)9, (2)395
Material functions, (1)99–153
convected Jeffreys model, (1)349
correlations for, (1)139–153
definitions of, (1)114, 132
Giesekus equation, (1)361–368
Hassager model, (1)446–449
K-BKZ model, (1)439
and linear viscoelasticity, (1)264–275
Lodge rubberlike liquid, (1)432
Oldroyd 4-constant model, (1)356–360
Oldroyd 8-constant model, (1)356
from rheometric measurements, (1)509–553
Rivlin–Sawyers model, (1)439
Wagner model, (1)451
Material functions from kinetic theory:
definitions, (2)398
FENE dumbbell, (2)80–88, 90
Fraenkel dumbbell, (2)104
Hookean dumbbell, (2)73–76, 94, 101
Kramers chain, (2)219
Lodge network model, (2)370, 387, 388
in melts, (2)335, 339–349
multibead-rods, (2)136
non-affine Lodge network model, (2)376
Phan-Thien and Tanner model, (2)382
rigid dumbbell, (2)123, 132, 138, 144, 145, 148
Rouse model, (2)161
see also Complex viscosity; Elongational viscosity; Normal-stress coefficients; Viscosity
Material (time) derivative, (2)395
Mathematical formulary, (2)403
Matrizant, (1)508
Maxwellian velocity distribution, (2)57
anisotropic modification of, (2)96
Maxwell model, (1)258, 278, 285. *See also* Convected Maxwell model
Maxwell orthogonal rheometer, *see* Eccentric disk rheometer
Mechanical energy balance, (1)552
Melts:
kinetic theory of, (2)307
modeling of, (2)310, 354
network theories of, (2)353
stress tensor, (2)325
Memory function:
complex viscosity and, (1)287
definition, (1)263, (2)397
generalized Maxwell model, (1)262
general network theory, (2)378
Hookean dumbbells, (2)72
Jeffreys model, (1)262
Lodge network model, (2)368
Lodge rubberlike liquid, (1)431
Marrucci et al., model, (2)380
Maxwell model, (1)260
Phan-Thien and Tanner equation, (2)375
Rouse chain, (2)159
Wagner model, (2)384
Memory-integral expansion, (1)498, (2)397
Oldroyd model and, (1)502
relation to retarded motion expansion, (1)501
rigid-dumbbell model and, (2)131
Memory in viscoelastic fluids, (1)56, 60, 73, 79, 263
Metric coefficients, (1)481, 600, 604
covariant, (1)481
table of, (1)603
Metric matrix, (2)33
bead-rod-spring models, (2)184, 248
differential relations, (2)292
elastic dumbbells, (2)47
inverse of, (2)34
Kramers chain, (2)35, 217
modified for hydrodynamic interaction, (2)187, 288, 294, 300
modified for melts, (2)312
multibead-rod, (2)189
rigid bead-rod-model, (2)234
Rouse chain, (2)36
two-needle model, (2)253
Mild-curvature approximation, (2)310, 318, 324
Mixtures:
bead-rod-spring models for, (2)181
kinetic theory results for, (2)193, 198
phase-space theory for, (2)245
rigid dumbbell model, (2)148
see also Polydispersity
Mobility factor, (1)353

Mobility tensors, (2)185, 188, 286, 305
multibead-rod, (2)195
Models for polymer molecules, (2)3, 247
bead-rod models, (2)229
bead-rod-spring models, (2)181
bead-spring chain, (2)18, 151
elastic dumbbell, (2)20, 55
elastic rhombus, (2)209, 215
freely jointed chain, (2)10, 217, 309
freely rotating chain, (2)10, 222
Gaussian chain, (2)16, 355
geometry of, (2)22, 153, 167, 186
multibead-rod, (2)26, 113
multirod-rod, (2)300
rigid dumbbell, (2)20, 111
second-order fluid constants, (2)208
three-bead-two-rod model, (2)190
two-needle model, (2)252
Modified pressure, (1)12, 14
Modulus of elasticity, (1)257, (2)365, 389
Molecular weight averages, (1)49, 59, 144, (2)337
Molecular weight dependence, (1)143
Molecular weight distribution, (2)4
logarithmic-normal, (2)338
Moment of inertia, (2)233
generalized, (2)184, 190, 225
tensor, (1)570
Momentum flux, (1)6
Momentum flux tensor, *see* Stress tensor
Momentum space average, (2)42
Momentum space distribution function, *see* Velocity space distribution function
Monodisperse, (1)57, (2)4
Mooney equation, (2)365, 386
Multibead-rod model, (2)26, 113
configurational quantities, (2)187
diffusion equation, (2)195
dynamic moduli, (2)232
elongational viscosity, (2)147
second-order fluid constants, (2)211
stress tensor, (2)117, 136, 202
third-order fluid constants, (1)302
Multirod-rod model, (2)300, 302

Nabla operator, *see* Del operator
Nahme–Griffith number, (1)207, 225
Natural boundary conditions, (1)194
Nearly Hookean dumbbell, (1)410, (2)90
Neo-Hookean solid, (2)365
Nernst-Einstein equation, (2)95, 140, 174, 299, 311
Network rupture model, (1)472
Network structure, (1)56
Network theories:
constitutive equations, (2)364
convection equation for segments, (2)357
equation of continuity, (2)358
Lodge network model, (1)433, (2)368
modeling of networks, (2)354
with non-affine motion, (2)273
stress tensor, (2)362
Newtonian flow problems, (1)12–53, 279, 537
Newtonian fluids, equation of motion for, (1)613
Newton's law of viscosity, (1)7, 10, 256
Nonisothermal flow problems, (1)205–227
equations of change for, (1)206
role of axial conduction, (1)251
tube flow, (1)210, 216, 218
Nonlinear viscoelasticity:
kinematic tensors used in, (1)294, 427
see also Constitutive equations
Non-Newtonian viscosity, (1)60
Bestul–Belcher equation, (1)244
Bingham model, (1)227
from capillary viscometer, (1)528
Carreau–Yasuda model, (1)171
Casson equation, (1)227, 243
concentration dependence, (1)144
from cone-and-plate viscometer, (1)111, 522
dimensionless plot for, (1)146
Ellis model, (1)210, 227
empiricisms for, (1)169–175, 227–233
Eyring model, (1)227
Herschel–Bulkley equation, (1)227
sample experimental data, (1)105–107
temperature dependence of, (1)139, 244
truncated power law, (1)227
see also Criminale–Ericksen–Filbey ("CEF") equation; Generalized Newtonian fluid; Viscometric functions
Nonorthogonal coordinates, (1)598–606
Normal coordinates, (2)156
Normal-stress coefficients:
bead-spring-rod models, (2)205, 238
from cone-and-plate viscometer, (1)111, 523
definition, (1)105, (2)399
Kirkwood–Riseman chain, (2)228
molecular weight dependence in melt, (1)148, (2)341, 371
from parallel-disk instrument, (1)526
in polydisperse melts, (2)338
sample experimental data, (1)108–112
stress relaxation and, (1)417
temperature dependence, (1)142
see also Criminale–Ericksen–Filbey ("CEF") equation; Material functions; Viscometric functions
Normal-stress differences, (1)62
index convention for, (1)62
rod-climbing and, (1)64
in shear flow, (1)104
in shearfree flows, (1)104
sign of, (1)62
stress growth, (1)118
stress relaxation, (1)122
in tangential annular flow, (1)333
tilted-trough experiment and, (1)65
Normal stresses:
and flow phenomena, (1)62
in Newtonian fluids, (1)12
in second-order fluids, (1)307, 309

Normal-stress ratio, (1)109
for melts, (2)335
osculating multibead-rod model and, (2)138
rod-climbing and, (2)335
Nusselt number, (1)212, 213, 215, 217

Oldroyd-A model, (1)498
Oldroyd-B model, *see* Convected Jeffreys model
Oldroyd 4-constant model, (1)354, 356–360, 423
Oldroyd 6-constant model, (2)398
Hookean dumbbells and, (2)100
memory integral expansion and, (1)502
retarded-motion constants for, (1)303, 416
rigid dumbbells and, (2)144
Oldroyd 8-constant model, (1)352, 354, 415, 416, 420, (2)398
Phan-Thien and Tanner model and, (2)385
for shear and shearfree flows, (1)625, 626
Oldroyd's admissibility criteria, (1)480, 497
Oldroyd's convected derivatives, *see* Convected derivatives
Oldroyd's nth rate-of-strain tensors, *see* Rate-of-strain tensors
Ordered fluids, *see* Retarded motion expansion
Order of magnitude analysis, (1)16
Orientational distribution function, *see* Configurational distribution function
Orientation vector, (2)405
operator $\partial/\partial \boldsymbol{u}$, (2)114, 406
time derivative of, (2)114
Orthogonal matrix, (2)157
Oscillating cylinder, (1)71
Oscillatory motion in annulus, (1)279
Oscillatory motion in semi-infinite medium, (1)275
Oscillatory motion in slit, (1)113
convected Jeffreys model, (1)347, 414
linear viscoelastic fluid, (1)264
Newtonian fluid, (1)52
viscous heating in, (1)53
Oscillatory motion in tubes, (1)187, 277
Oseen–Burgers tensor, (2)93, 133, 164, 195, 213
derivation of, (1)28
Ostwald–de Waele model, *see* Power–law model

Papanastasiou–Scriven–Macosko model, (1)441
Parallel-disk viscometer:
centripetal pumping, (1)551
convected derivative of stress tensor, (1)343
convected Jeffreys fluid, (1)400
inertial effects in, (1)549
Newtonian fluid, (1)37
second-order fluid, (1)335
viscometric functions from, (1)518, 520, 524
Parallel-plate plastometer, *see* Squeezing flow
Parallel-plate viscometer, (1)521
Particle label, (1)484
Particle motion in fluids, (1)85
Partition function, (2)15
Pawlowski's variational principle, (1)201
Pearl-necklace model, *see* Kramers model
Peclet number, (1)12, 207
Permutation symbol, (1)559, 600, (2)183
Perturbation method, (1)32, 316, 540
Phan-Thien and Tanner model, (1)411, 467, (2)373, 380
Phase shift in oscillatory testing, (1)115
Phase-space distribution function, (2)38, 255
elastic dumbbells, (2)56
rigid dumbbells, (2)112
Phase-space kinetic theory, (2)245, 279, 307
Phillips model, (1)441
Pipe flow, *see* Tube flow
Planar elongational flow, (1)101, 437, 471
Plane flow, (1)22, 24
Plateau modulus, (1)147
Polyacrylamide, (1)58, 61, 63, 70, 71, 76, 77, 82, 84, 86, 87, 106, 108, 118, 121, 125, 126, 163, 172, 236, 380, 465, 537, 548, (2)91
Poly-α-methylstyrene, (1)120, (2)83, 171, 175, 343
Polybutadiene, (1)117, 145
Polydimethylsiloxane, (1)58, 145, 208
Polydispersity, (1)59, (2)4
melt kinetic theory and, (2)337
Polyethylene, (1)57, 58, 60, 79, 105, 112, 117, 120, 127, 128, 131, 135, 139, 141, 145, 173, 208, 209, 274, 277, 412, 446, (2)6, 8, 347, 348, 382
Polyethylene glycol, (1)145
Polyethyleneoxide, (1)58, 82, 88, 90, 110, 175, (2)5, 91
Polyethylene terephthalate, (1)58
Poly-γ-benzyl-L-glutamate, (2)124, 143
Polyhexamethylene adipamide, (1)58
Polyisobutylene, (1)58, 65, 80, 81, 106, 108, 118, 121, 124, 125, 126, 136, 145, 172, 191, 284, 413, 446, 546, (2)91
Polyisoprene, (1)58, 117, 236
Polymer:
additives, (1)87
structure, (1)56, (2)4
Polymethylmethacrylate, (1)72, 145, 208
Polypeptide, (1)56
Polypropylene, (1)61, 208, 236, 446
Polystyrene, (1)58, 107, 117, 127, 133, 134, 137, 141, 143, 145, 146, 148, 149, 151, 152, 172, 173, 174, 208, 446, (2)7, 83, 84, 171, 175, 176, 342, 345, 348
Polyvinyl acetate, (1)145
Polyvinylchloride, (1)58, 208, 209
Potential energy, (2)37, 250, 265, 281
elastic dumbbells, (2)62
Potential flow, (2)57
bead-rod-spring models, (2)195
elastic dumbbells, (2)62, 102
rigid dumbbells, (2)116, 143
Rouse model, (2)154
Potential function, (1)438, 469
Powell–Eyring model, (1)228
Power–law model, (1)172
axial annular flow, (1)176, 181, 202, 238
axial eccentric annular flow, (1)204

Power–law model (*Continued*)
coat-hangar die, (1)245
cone-and-plate viscometer, (1)223
distributor design, (1)240
falling cylinder viscometer, (1)248
flow of immiscible fluids, (1)242
helical annular flow, (1)184
nonisothermal flow, (1)210, 216, 217, 223
pulsatile pressure drop, (1)187
radial flow between disks, (1)176, 240
Rayleigh problem, (1)248
shortcomings of, (1)175
with slip at wall, (1)247
slit flow, (1)176
square tube, (1)251
squeezing flow, (1)176, 189
tangential annular flow, (1)176, 239
tapered tube, (1)178, 241
temperature dependence of constants, (1)210
with third invariant, (1)250
tube flow, (1)175, 187, 210, 216, 218, 247
variational method, (1)202, 204
Power–law viscosity, (1)107
from rigid dumbbell model, (2)123, 140
Prandtl number, (1)90
Pressure, (1)10
modified, (1)12, 14
Pressure tensor, *see* Stress tensor
Pressure transducers, hole-pressure effect and, (1)67
Principal axes of rate of strain, (1)162
Principal elongation ratios, (1)430, 623
Proudman–Pearson equation, (1)28
Pseudoplastic fluids, (1)60, 173
Pulsatile tube flow, (1)187, 234, 277, 371
Purely viscous fluids, *see* Generalized Newtonian fluid
Pure shear, (2)364, 366

Quasilinear differential models, (1)345
Quasilinear integral models, (1)431
Quasi-steady-state approximation, (1)13, 20, 176, 189
Quelleffekt, (1)63

Radial flow between disks, (1)165
convected Maxwell model, (1)418
power–law model, (1)176, 240
second-order fluid, (1)318
third-order fluid, (1)330
Radius of gyration, (2)27
effect of ring closure, (2)50
Random walk distribution, (2)12
deviations from, (2)40, 47
equilibrium averages, (2)28
and probability of end-to-end vector, (2)49
Rate-of-deformation tensor, *see* Rate-of-strain tensor
Rate-of-strain tensor, (1)622, (2)64
components in curvilinear coordinates, (1)614
definition of, (1)11, 256, 296, (2)394
higher-order, (1)296, 491, 622, (2)396
invariants of, (1)170
relations among, (1)492, 504, 507
in shear flow, (1)297, 622
in shearfree flow, (1)622
transformation rules for, (1)488
Rayleigh problem:
convected Jeffreys model, (1)369
Newtonian fluid, (1)38
power–law fluid, (1)248
Rayleigh's equation, (2)50
Reciprocal base vectors, (1)597, 599, 602
Recoil:
in circular tube, (1)78
comparison with data, (1)130
constrained, (1)113, 129
extrudate swell and, (1)73
linear viscoelastic fluid, (1)269, 289
Lodge rubberlike liquid and, (2)388, 390
recoverable shear, (1)130
ultimate, (1)130
use of Laplace transform, (1)289
Recoverable shear, (1)130, 153
Reduced variables, (1)108, 139, (2)163
Reiner–Rivlin equation, (1)504
Reiner–Riwlin equation, (1)231
Relative (finite) strain tensors:
components in curvilinear coordinates, (1)616–619
definition, (1)427, (2)396
in eccentric disk rheometer, (1)513
and infinitesimal strain tensor, (1)489
in shear and shearfree flows, (1)623
Relative viscosity, (1)108
Relaxation modulus:
bead-rod models, (2)231, 233
Curtiss–Bird theory, (2)337
definition, (1)263, (2)399
determination from data, (1)273
Doi–Edwards theory and, (1)287
generalized Maxwell model, (1)262
Jeffreys model, (1)262
linear viscoelasticity and, (2)397
Lodge network model, (2)370
Maxwell model, (1)260
melt kinetic theory and, (2)337
rigid bead-rod models, (2)237
rigid dumbbell model, (1)285, (2)131, 237
sample experimental data, (1)127
Segalman empiricism, (1)285
step-strain experiment and, (1)124
zero-shear-rate viscosity and, (1)264
Relaxation spectrum, (1)285
Relaxation time, (1)259, 261, 442. *See also* Time constants
Renardy condition, (1)440
Reptation coefficient, (2)316, 322
Reptation, (1)146, (2)291, 310, 315
Retardation time, (1)261
Retarded motion expansion, (1)295–339, (2)397
boundary conditions and, (1)317
complex viscosity for, (1)329

constants in, (1)301–303
creeping flows, (1)316
definition, (1)298
eccentric-disk rheometer, (1)328
FENE dumbbells, (2)80
flow near a corner, (1)339
flow into a slit, (1)332
flow systems analyzed for, (1)318, 326
hole-pressure effect, (1)337
Hookean dumbbells, (2)105
limitations of, (1)325
line sink, (1)329
for melts, (2)335
Oldroyd 6-constant model and, (1)416
parallel disk viscometer, (1)335
radial flow between parallel disks, (1)330
relation to empirical constitutive equations, (1)303
relation to integral models, (1)438
relation to kinetic theory, (1)302
relation to memory integral expansion, (1)501
rigid dumbbells, (2)131
rod-climbing, (1)318, 330
shearfree flows, (1)329
stability of flow, (1)337
turntable experiment, (1)333
uses of, (1)326
viscometric functions for, (1)299
Reynolds number, (1)12, 207
Rheological equations of state, *see* Constitutive equations
Rheological invariance, (1)482
Rheologically steady shear flow, (1)157
Rheometry, (1)509–553
instruments for measurement of viscometric functions, (1)518–520
Ricci's lemma, (1)604
Riemann zeta function, (1)266
Rigid dumbbell, (2)20
diffusion equation, (2)116, 119, 127
distribution functions for, (2)112
Fraenkel dumbbell and, (2)104, 143
hydrodynamic interaction, (2)133, 213
lopsided, (2)208
mixtures, (2)148
relaxation modulus, (1)285, (2)131, 237
second-order fluid constants, (2)208
stress tensor, (2)117, 135
Ring models, (2)50, 209, 215
Rivlin–Ericksen tensors, *see* Rate-of-strain tensor
Rivlin–Sawyers model, (1)436, 441, 467, 499
eccentric disk rheometer, (1)471
factorized, (1)437
third-order fluid and, (1)303, 506
Rod-climbing, (1)163
experiments on, (1)62
melt kinetic theory and, (1)330, (2)335
second-order fluid, (1)318, 330
Rodlike polymers, models for, (2)112. *See also* Multibead-rod; Multirod-rod; Rigid dumbbell
Rolling-ball viscometer, (1)537
Rotational isomeric state model, (2)10
Rotation matrices, (2)26, 157, 182, 223, 235, 410
Rotatory diffusivity, (2)62
Rotne–Prager–Yamakawa tensor, (2)94, 133, 137, 142, 195, 213
Rouse matrix, (2)23, 37
eigenvalues of, (2)24, 27
modified, (2)166, 169, 217
Rouse model, (2)17
base vectors, (2)36
configurational distribution function, (2)41, 154, 157
constitutive equation, (2)159
diffusion equation, (2)152–155, 157, 239
distribution function for interbead vector, (2)45
end-to-end distance, (2)18
generalized coordinates, (2)32
generalized Maxwell model and, (1)262
geometry of, (2)23
material functions, (2)161
metric matrix, (2)36
normal coordinates, (2)156
radius of gyration, (2)27
relation to K-BKZ model, (1)440
second-order fluid constants, (2)208
single-link distribution function, (2)178
stress tensor, (2)156, 239
two-link distribution function, (2)49

Scale factors, (1)584, 597, 598
Scott equation, (1)190, 234
deviations from, (1)545
Secondary flows, (1)69
in disk-cylinder system, (1)69, 327
in elliptical tube, (1)327
near oscillating cylinder, (1)71
near rotating sphere, (1)69
Second-order fluid, (1)299, 355, 483, (2)397
bead-rod-spring models, (2)204, 207–210, 238
eccentric annuli flows, (1)311, 314
elastic rhombus, (2)215
elongational viscosity for, (1)300
forces on solid surfaces, (1)307, 309
Giesekus's flow theorem, (1)306
Kirkwood–Riseman chain, (2)228
Kramers chain, (2)218
Langlois–Rivlin–Pipkin theorem, (1)309
melt kinetic theory and, (2)336
multibead-rod, (2)211
multirod-rod, (2)304
Tanner–Pipkin plane-flow theorem, (1)306
tridumbbell, (2)213
useful theorems for, (1)304
wire-coating, (1)311
see also Retarded-motion expansion
Segalman memory function, (1)442, 473
Segment, in network theory, (2)354
complexity, (2)356
contribution to stress tensor, (2)362
distribution function, (2)356, 371

Segment, in network theory (*Continued*)
equation of continuity, (2)358
equation of motion for, (2)357
kinetics, (2)358, 368, 378, 380, 384
Shear axes, (1)156, 158
Shear flow, (2)398
classification, (1)153, 154
convected derivative of stress tensor, (1)343, 622
convected Jeffreys model, (1)346
form of stress tensor, (1)103, 622
Giesekus model, (1)625
homogeneous, (1)100, 154
kinematic tensors, (1)622
material functions, (1)104–132
nonhomogeneous, (1)154
Oldroyd model, (1)625
oscillatory, (2)399
particle separations in, (1)100
rate-of-strain tensors in, (1)297, 622
rectilinear, (1)154
rheologically steady, (1)157
simple, (1)154
table of kinematic tensors, (1)622–624
unidirectional, (1)154, 156, 164
unsteady-state experiments, (1)113
Shearfree flows, (2)57
convected Jeffreys model, (1)349
form of stress tensor, (1)104, 165, 622
Giesekus model, (1)625
homogeneous, (1)100, 162
kinematics of, (1)162
kinematic tensors, (1)622
material functions, (1)132–139
measurements, (1)529
Oldroyd model, (1)625
particle separation in, (1)103
table of kinematic tensors, (1)622–624
types of, (1)101
White–Metzner model, (1)415
Shearing plane, (1)154
Shearing surface, (1)155, 158
Shear rate, (2)57
definition, (1)100, 155, (2)394, 397
Shear strain, (1)623
Shear stress, (1)104
Shear-thickening fluids, (1)61, 105, 173
Shear-thinning, (1)60, 105, 173. *See also* Non-Newtonian viscosity; Viscometric functions
Shift factor, (1)107, 139
Short-range-force approximation, (2)279, 281, 310
Silicone, (1)72, 191
Silly putty, (1)73, 95
Simple shear, (2)364, 367
Simple shear flow, (2)57, 119, 138, 161
Single-link distribution function, (2)317, 322, 328, 330
Sinusoidal motion, *see* Oscillatory motion in annulus; Oscillatory motion in semi-infinite medium; Oscillatory motion in slit; Oscillatory motion in tubes
Slip at solid surface, (1)12, 247
Slip velocity, (2)374
Slit, flow into:
Newtonian fluid, (1)42, 43
second-order fluid, (1)332
Slit flow:
base vectors in, (1)505
Bingham model, (1)229
convected coordinates in, (1)487
Ellis model, (1)229
Eyring model, (1)229
generalized Newtonian fluid, (1)242
kinematic tensors, (1)505
Nusselt numbers for, (1)213
power–law model, (1)176, 229
truncated power law, (1)229
see also Couette flow
Sphere, rotating:
Deborah number, (1)93
Newtonian fluid, (1)31, 34
second-order fluid, (1)318
viscoelastic fluids, (1)69
Sphere, translating, (1)235
convected Maxwell, (1)464
Deborah number, (1)93
Newtonian fluid, (1)23
Oldroyd model, (1)414
Spherical coordinates, (1)580, 585
Christoffel symbols in, (1)603
del operator in, (1)583, 590
equation of motion in, (1)612, 613
kinematic tensors in, (1)614–620
metric coefficients in, (1)603
unit vectors in, (1)581, 591, (2)405
Spherical film inflation, (1)148
Spherical harmonics, (2)120, 128, 138, 408, 409
Spriggs–Bird model, (1)421
Spring force, (2)21. *See also* Forces in kinetic theory
Square duct, (1)251
Squeezing flow:
CEF equation, (1)539
inertial effects, (1)22
lubricated, (1)533
Newtonian fluid, (1)20
parallel-plate plastometer, (1)537
power–law model, (1)176, 189
Stability, (1)337, 405
Stanton number, (1)89
Star polymer model, (2)28
Staudinger's rule, (1)143, (2)176
Steady-state compliance:
bead-rod-spring models, (2)205
linear viscoelasticity, (1)270
melt kinetic theory and, (2)337
Stefan equation, (1)22
Step-strain experiment, (1)113, 124, 266, 286, 415
Stodola and Vianello method, (1)217
Stokes' law, (2)58, 115, 152, 193, 199, 279, 285
anisotropic, (2)97, 311
derivation of, (1)23

see also Forces in kinetic theory; Hydrodynamic force
Storage modulus, *see* Dynamic moduli
Strain history, (1)481
Strain tensors:
Cauchy tensor, (1)427
components in curvilinear coordinates, (1)616–619
definition of, (1)425, (2)396
eigenvalues of, (1)435
expansion in Taylor series, (1)505
Finger tensor, (1)427
finite, (1)425, 470
infinitesimal, (1)257, 489
invariants of, (1)435, 437, 624
in kinetic theory, (2)72, 159, 334, 378
reference state, (1)257, 260
relative, (1)427, 489
in shear flows, (1)429, 623
in shearfree flows, (1)429, 623
transformation rules for, (1)488
Strain-time factorization, (1)437, 451
Stream function:
definition, (1)22
differential equations for, (1)24
Stress growth, (1)113, (2)399
convected Jeffreys model, (1)348
in elongational flow, (1)135, (2)400
sample experimental data, (1)120–123
in shear flow, (1)118
see also Material functions
Stress history, (1)482
Stress ratio, (1)110
Stress relaxation after shear flow, (1)113, (2)400
bead-spring chains, (2)173
convected Jeffreys model, (1)348
in elongational flow, (2)400
linear viscoelastic fluid, (1)267
normal stress coefficient and, (1)417
rigid dumbbells, (2)145, 147
sample experimental data, (1)124
see also Material functions
Stress relaxation after step strain, (1)113, 124
linear viscoelastic fluid, (1)266
Stress tensor:
antisymmetric contribution to, (2)303
bead-rod-spring models, (2)198
bead-spring chains, (2)155, 169
bead-spring models, (2)285
contravariant components, (1)493
convected derivative of, (1)342, 343, 493
covariant components, (1)493
definition, (2)401
elastic dumbbells, (2)64–71, 97
FENE dumbbells, (2)79
Giesekus expression for, (2)69, 103, 118, 156, 202, 303
hydrodynamic interaction and, (2)94, 103, 135
kinetic contribution to, (2)259, 264
kinetic theory expressions, (2)259, 264, 269, 275, 277, 295
Kramers expression for, (2)69, 118, 156, 201
Kramers–Kirkwood expression for, (2)69, 118, 156, 199, 283
Lodge elastic liquid, (2)368
for melts, (2)322–326
molecular mechanisms and, (2)270
multibead-rods, (2)117, 202
multirod-rods, (2)302
for networks, (2)362, 368, 378
Phan-Thien and Tanner equation, (2)375, 380
rigid dumbbells, (2)117, 131, 135, 143
in shear flows, (1)103, 622
in shearfree flows, (1)104, 622
sign convention, (1)7
symmetry of, (1)6, 103
transformation rules for, (1)493
see also Constitutive equations
Stretching of polymer molecules, *see* End-to-end distance
Structure tensor, (2)194
second-order fluid constants and, (2)204
thermodynamic quantities and, (2)241
Substantial (time) derivative, (2)395
definition of, (1)9
Surface spherical harmonics, (2)128, 409
Sutterby model, (1)228

Tanner model, (1)377, 410
Tanner–Pipkin plane-flow theorem, (1)306, 314
Tanner–Simmons network-rupture model, (1)440, 472
Tapered tube:
Newtonian fluid, (1)16
power-law model, (1)178, 241
retarded-motion expansion and, (1)327
Taylor theorem, (2)403
Temperature dependence, (1)139–143
Temperature history, (1)482
Tension:
in link, (2)313
in polymer chain, (2)15
Tensors, (1)555–609
addition of, (1)567
antisymmetric, (1)566
Cartesian tensor notation, (1)607
characteristic equation of, (1)569
components of, (1)567
contravariant components of, (1)597, 600
covariant components of, (1)597, 600
curvilinear coordinates, (1)577
eigenvalues of, (1)569
fourth-order isotropic, (2)409, 412, 415
Gibbs notation, (1)607
integral theorems for, (1)576
invariants of, (1)568
magnitude of, (1)566
matrix representation, (1)608
moment-of-inertia tensor, (1)570
multiplication of, (1)567
notation, (1)555, 607

Tensors (*Continued*)
symmetric, (1)566
transformation rules, (1)605
transpose, (1)566
unit tensor, (1)566, 600
Terminal velocity of sphere, (1)34
Thermal conductivity, (1)11, 206, 208
Thermodynamic quantities, (2)108, 241
Third-order fluid, (1)299, (2)397. *See also* Retarded motion expansion
Three-bead-two-rod model, *see* Kramers model
Three-*j* symbols, (2)414
Thurston's equation, (2)170
Tilted-trough experiment, (1)65, 97
Time constants, (1)60
and Deborah number, (1)93, 234
in generalized Newtonian models, (1)228
spectrum of, (1)60
Time constants in molecular models, (1)302
bead-rod models, (2)231
FENE dumbbells, (2)76, 81
Hookean dumbbells, (2)71
in melts, (2)321, 328, 331
molecular weight dependence in melts, (2)343, 344, 370
multibead-rods, (2)117, 136, 198
multirod-rods, (2)301, 304
in network models, (2)358, 370, 379, 380, 384
in polydisperse melts, (2)338
rigid dumbbells, (2)123
Rouse chains, (2)159
Zimm chains, (2)169
Time derivatives:
convected, (1)342, 491, 494–496
corotational (Jaumann), (1)324, 507
substantial, (1)9
types of, (2)395
Time–temperature superposition, (1)108, (2)163
Tobacco mosaic virus, (2)22, 124, 132, 143
Torque:
in coaxial cylinder system, (1)230
molecular models and, (2)284, 289
in parallel-disk viscometer, (1)511
on rotating sphere, (1)33, 43, 321
Torsional flow, *see* Parallel disk viscometer
Torsional oscillatory viscometer, (1)279
Translational diffusivity:
bead-spring chains, (2)174, 176
bead-spring models, (2)299
elastic dumbbells, (2)62, 95
frictional coefficient and, (2)95
hydrodynamic force and, (2)273
Kirkwood equation, (2)174, 299
in melts, (2)327
molecular weight dependence of, (2)179, 273, 299
rigid dumbbells, (2)140
Triangular duct, (1)36
Tridumbbell model, (2)210, 213, 237
Triple-jet method, (1)532
Trouton viscosity, *see* Elongational viscosity
Truncated cone-and-plate instrument, (1)520, 551
Truncated power law, (1)228, 229, 236, 245
Tube flow:
Bingham model, (1)229, 244
capillary viscometer data, (1)547
Casson equation, (1)243
Ellis fluid, (1)229
end effects, (1)528
Eyring model, (1)229
generalized Newtonian fluid, (1)242, 518
kinematics of, (1)160
Newtonian fluid, (1)14, 34
nonisothermal flow, (1)210, 216, 218
normal-stress measurements in, (1)517
Nusselt numbers for, (1)212
Oldroyd model, (1)420
power–law model, (1)175, 187, 210, 216, 218, 229, 247
pulsatile pressure drop, (1)187, 234
recoil in, (1)78
with sinusoidally varying cross section, (1)35
with slip, (1)247
tapered tube, (1)16, 178
truncated power law, (1)229, 245
viscosity from, (1)527
Tubeless siphon, (1)74
use for studying elongational flow, (1)532
Tubes in kinetic theory, (2)307
Turbulent flow, (1)87, 235
drag reduction, (1)88
heat transfer, (1)89
laminar-turbulent transition, (1)177
Turntable experiment, (1)283
convected derivative of stress tensor, (1)344
displacement gradients in, (1)289
finite strain tensors and, (1)431
linear viscoelastic fluid, (1)283
second order fluid, (1)333
Two-needle model, (2)252

Uebler effect, (1)74
Ultimate recoil, (1)130, 269
elongational, (1)138
Undiluted polymers, *see* Melts
Uniaxial stretching, (1)437
Unit dyads, (1)564, 565
Unit tensor, (1)566, 600
convected derivative of, (1)495
Unit vectors, (1)560, 579, 580, 581
change with position, (1)582, 583, 594

Variational methods, (1)192–205, 252
collocation method and, (1)199
Galerkin's method and, (1)200
for generalized Newtonian fluids, (1)201
weighted residuals and, (1)199
Vectors, (1)555–609
addition and subtraction, (1)556, 561
base, (1)597–602, 605, (2)33, 35, 51, 184, 406
complex unit vectors, (2)413

components of, (1)561
contravariant components, (1)597, 600
covariant components, (1)597, 600
curvilinear coordinates, (1)577
derivatives of unit vectors, (2)406
embedded vectors, (2)182
integral theorems, (1)576
magnitude of, (1)556
modified reciprocal base, (2)188, 200
multiplication by scalar, (1)557, 562
notation, (1)555, 607
physical components of, (1)597
position vectors, (1)563, 575, 578, 594, (2)183
reciprocal base, (1)597–602, 605, (2)406
scalar product of, (1)557, 562
transformation rules, (1)605
unit vectors, (1)560, 580, 581, (2)405
vector product of, (1)558, 562
Velocity:
fields, (2)393
kinetic theory expression, (2)257, 264
Velocity gradient tensor, (1)296, 622
Velocity space distribution function:
anisotropic, (2)96
averages with respect to, (2)58
elastic dumbbells, (2)56
at equilibrium, (2)57
rigid dumbbells, (2)112
Viscoelasticity, (1)56
Viscometer:
coaxial cylinder, (1)35, 548
cone-and-plate, (1)18, 223, 521
Epprecht, (1)548
falling cylinder, (1)45, 248
falling sphere, (1)23
parallel-disk, (1)37, 335, 400, 510
squeezing flow, (1)20
torsional oscillatory, (1)279
truncated cone-and-plate instrument, (1)520
tube, (1)14
Viscometric flow, (1)100, 154, 157
examples of, (1)158
Viscometric functions:
CEF equation and, (1)503
convected Jeffreys model, (1)347
definition of, (1)105, (2)397
functional forms for, (1)165
measurement of, (1)517
sample experimental data, (1)105–112
temperature dependence, (1)139
third-order fluid, (1)299
Viscoplastic fluids, (1)61, 227. *See also* Bingham fluid
Viscosity:
bead-spring-rod models, (2)205
from capillary rheometer, (1)527
complex, (1)115, (2)399
concentration dependence, (1)143
from cone-and-plate instrument, (1)522
definition, (1)105, (2)399
dilatational, (1)10
intrinsic, (2)81, 123, 162, 205, 399
Kirkwood–Riseman chain, (2)228
molecular weight dependence in melt, (1)143, (2)341, 371
non-Newtonian, (1)60
from parallel-disk viscometer, (1)525
in polydisperse melts, (2)338
relative, (1)108
temperature dependence of, (1)139
see also Complex viscosity; Material functions; Non-Newtonian viscosity; Viscometric functions
Viscous dissipation heating, (1)11, 206
in cone-plate system, (1)223, 523
in oscillatory flow, (1)53
in tube flow, (1)218
see also Energy dissipation
Vortex inhibition, (1)81
rigid dumbbell model and, (2)146
Vorticity tensor, (1)615
definition, (1)296, (2)394

Wagner model, (1)439, 441, 451, 473, (2)383
comparison with experimental data, (1)106, 128, 131
with damping functional, (1)467
Wake behind particles, (1)85
Warner force law, (2)16
Wave transmission, (1)275
Weighted residuals, (1)199
Weissenberg effect, *see* Rod-climbing
Weissenberg hypothesis, (1)62, 109
Weissenberg number, (1)94, 392
Weissenberg–Rabinowitsch equation, (1)528
White–Metzner model, (1)351, 395–400
fiber spinning, (1)377
pulsatile flow, (1)371
shearfree flows, (1)415
Wire coating, (1)204, 239
second-order fluid, (1)311
WKBJ method, (1)223
WLF equation, (1)140, 141, (2)163
Wormlike chain, (2)11

Yield stress, (1)61, 227
Bingham fluids, (1)61

Zero-elongation-rate properties, (1)132
Zero-shear-rate properties, (1)105
blending law for, (1)147
second-order fluid constants and, (2)397
Zimm model, (2)18, 169–175
Flory–Fox relation and, (2)178
hydrodynamic interaction matrix, (2)165