SYMPOSIUM ON MACROMOLECULES

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PART I.   Properties of Macromolecules

The General Theory of Irreversible Processes in Solutions of Macromolecules

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INTRODUCTION

The course of irreversible processes in solutions of macromolecules is determined by the hydrodynamic forces which the large molecules exert on the solvent and by the Brownian drift in configuration which the molecules experience under the combined action of the frictional hydrodynamic forces and of external fields of force, gravitational, centrifugal, electric, or magnetic.   Perturbations in the flow pattern of the solvent by the macromolecules, which determine the visco-elastic behavior of their solutions, are most conveniently treated by the Oseen method[1] which is based upon solutions of the Navier-Stokes equation possessing singularities appropriate to the frictional forces exerted on the solvent by the segments of a macromolecule.   Macromolecular Brownian motion may be described by a distribution function satisfying a generalized equation of forced diffusion in molecular configuration space.

In an earlier investigation,[2] we have endeavored to formulate a unified statistical mechanical theory of irreversible processes in solutions of macromolecules, based upon these concepts.   Following Kramers,[3] the methods of Riemannian geometry were employed to formulate a generalized theory of Brownian motion in molecular configuration space leading to a generalized diffusion equation.   The Oseen method was used in the analysis of the perturbations produced in the flow pattern of the solvent and for the determination of the components of the molecular diffusion tensor.   The molecular relaxation time spectrum was constructed from the eigenvalues of the diffusion operator, and the perturbations in the distribution function in molecular configuration space were expanded in the corresponding eigenfunctions.   It is our purpose here to review the general theory and to outline its application to the analysis of a set of structurally significant

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phenomena, visco-elastic response to applied stresses, flow birefringence
and the Kerr effect, and dielectric polarization and dispersion.

Since we shall not attempt to take molecular interaction into account,
the applicability of our results is limited to highly dilute solutions. Further-
more, the schematic character of the molecular model which we employ
limits the structural details which may be deduced by means of the theory
from experimental data relating to irreversible processes. Further ad-
vances in the theory should be directed toward the development of methods
for treating molecular interaction and toward the exploration of the proper-
ties of more detailed molecular models.

GENERALIZED MACROMOLECULAR BROWNIAN MOTION

We shall adopt the general feature of the pearl necklace model to de-
scribe the hydrodynamic behavior of a macromolecule in solution in a sol-
vent of low molecular weight. The molecule is regarded as an array of n
identical structural units, attached to a rigid or flexible framework, and
immersed in a structureless fluid continuum, which is supposed to possess
the viscosity coefficient, refractive index, and dielectric constant of the
solvent in bulk. Each structural unit of the molecule is assumed to exert
a hydrodynamic force on the solvent which is proportional to its velocity
relative to the local particle velocity of the fluid, with a friction constant
ζ, in accordance with the theory of Brownian motion. Due to structural
restraints, fixed bond angles, bond lengths, etc., the molecule will in general
possess a number of degrees of freedom, ν, which is less than $3n$. Three of
its degrees of freedom will be translational, associated with the coordinates
specifying the position of its center of mass, three will be rotational, as-
sociated with coordinates specifying its orientation relative to an external
frame of reference, and ν-6 will be internal degrees of freedom associated
with coordinates specifying the configuration of the n structural units rela-
tive to each other. In the case of rigid molecules, such as the globular pro-
teins, the significant degrees of freedom are the six degrees of translational
and rotational freedom. In the case of flexible molecules, such as the high
polymers, there are additional degrees of freedom describing internal con-
figuration, specified, for example, by the angles between the planes de-
termined by successive pairs of bonds of the skeletal chain of the polymer
molecule. In general, because of the small amplitude of the motion as-
sociated with them, we can ignore the influence of vibrational degrees of
freedom on the hydrodynamic behavior of solutions of macromolecules.
We shall refer to the ν-dimensional molecular configuration space as m-
space, a point in which will be specified by a conveniently selected set of
generalized coordinates, $q^1 \ldots q^\nu$. The m-space is a sub-space of the com-
plete $3n$-dimensional configuration space of the n structural elements,
which will be referred to as e-space. If $\mathbf{R}$ is the $3n$-dimensional vector
specifying the position of the n structural elements in e-space, we may span
m-space by the following set of covariant vectors, $\mathbf{a}_\alpha$:

$$\mathbf{a}_\alpha = \sum_{l=1}^{n} (\partial \mathbf{R}^l / \partial q^\alpha)$$

$$\mathbf{R} = \sum_{l=1}^{n} \mathbf{R}^l \tag{1}$$

where $\mathbf{R}^l$ is the projection of $\mathbf{R}$ on the 3-dimensional space of element l, and the derivatives are to be taken at constant values of all other q^β and subject to the structural restraints characteristic of the molecule. The metric tensor of the m-space is given by:

$$g_{\alpha\beta} = \sum_{l=1}^{n} \frac{\partial \mathbf{R}^l}{\partial q^\alpha} \cdot \frac{\partial \mathbf{R}^l}{\partial q^\beta}$$

$$\mathbf{a}^\alpha = \sum_\beta g^{\alpha\beta} \mathbf{a}_\beta$$

$$g^{\alpha\beta} = \frac{|g|_{\alpha\beta}}{g}; \qquad g = |g_{\alpha\beta}| \tag{2}$$

where $\mathbf{a}^\alpha$ is the contravariant vector reciprocal to $\mathbf{a}_\alpha$ and $|g|_{\alpha\beta}$ is the appropriate minor of the determinant. The explicit determination of the elements $g_{\alpha\beta}$ of the metric tensor depends upon a knowledge of the structural details of the molecule.

The probability density $f(q,t)$ of the ensemble describing the statistical mechanical behavior of the system, macromolecule-solvent, determines the observed value of a function $\varphi(q)$ of the coordinates q as the average value:

$$\bar{\varphi}(t) = \int \dots \int \sqrt{g} \; \varphi(q) f(q,t) \prod_\alpha dq^\alpha \tag{3}$$

where the integration extends over all of m-space. In the canonical ensemble appropriate for thermodynamic equilibrium, the probability density $f(q,t)$ reduces to:

$$f^0(q) = e^{\beta[A_0 - W_0(q)]} \tag{4}$$

$$\beta = 1/kT$$

where A_0 is the configurational free energy of the molecule and $W_0(q)$ the potential of average force associated with its internal degrees of freedom. For systems departing from equilibrium, the probability density, $f(q,t)$, is determined by the generalized diffusion equation:

$$\sum_{\substack{\alpha,\beta \\ =1}}^{\nu} \frac{1}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial q^\beta} \left(D^{\alpha\beta} \frac{\partial f}{\partial q^\alpha} + \frac{D^{\alpha\beta}}{kT} \frac{\partial W_0}{\partial q^\alpha} f \right) - \frac{\partial f}{\partial t} =$$

$$\sum_{\substack{\alpha,\beta \\ =1}}^{\nu} \frac{1}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial q^\beta} \left(\frac{D^{\alpha\beta}}{kT} X_\alpha f + g^{\alpha\beta} v_\alpha^0 f \right); \quad \int \dots \int \sqrt{g} f(q,t) \prod_\alpha dq^\alpha = 1 \tag{5}$$

where the X_α are the covariant components of external force, for example, external electric, magnetic, or gravitational fields, and the v_α^0 are the covari-

ant components of the hydrodynamic particle velocity of the solvent, un-
perturbed by the presence of the macromolecule. The quantities $D^{\alpha\beta}$ are
the contravariant components of the diffusion tensor in m-space, given by:

$$D^{\alpha\beta} = kT[(g^{\alpha\beta}/\zeta) + T^{\alpha\beta}]; \qquad T^{\alpha\beta} = \sum_{\substack{l \pm s \\ =1}}^{n} T_{ls}^{\alpha\beta}$$

$$T_{ls}^{\alpha\beta} = \frac{1}{8\pi\eta_0 R_{ls}} \sum_{\substack{\sigma,\tau \\ =1}}^{\nu} g^{\alpha\sigma} g^{\beta\tau} \left[\frac{\partial \mathbf{R}_l}{\partial q_\sigma} \cdot \frac{\partial \mathbf{R}_s}{\partial q_\tau} + \frac{1}{R_{ls}^2} \left(\mathbf{R}_{ls} \cdot \frac{\partial \mathbf{R}_l}{\partial q^\sigma} \right) \left(\mathbf{R}_{ls} \cdot \frac{\partial \mathbf{R}_s}{\partial q^\tau} \right) \right] \quad (6)$$

where the $T^{\alpha\beta}$ are the contravariant components of the Oseen hydrody-
namic interaction tensor, η_0 is the viscosity coefficient of the solvent, and
ζ is the friction constant associated with the motion of an isolated struc-
tural unit of the molecule in the solvent. The vectors $\mathbf{R}_l$ and $\mathbf{R}_s$ specify
the positions of the structural units l and s in a common 3-dimensional space
and R_{ls} is the distance between them in the specified configuration.

The determination of the general elements $D^{\alpha\beta}$ of the diffusion tensor
requires detailed knowledge of the molecular structure. However, the
translational components, associated with coordinates q^1, q^2, q^3, specifying
the position of the center of mass in an external rectangular coordinate
system, may be expressed in general form, by virtue of the relations:

$$g_{\alpha\beta} = n\delta_{\alpha\beta}$$

$$g^{\alpha\beta} = \frac{\delta_{\alpha\beta}}{n}; \qquad \alpha = 1, 2, 3; \beta = 1, \ldots, \nu \qquad (7)$$

Equations (6) and (7) lead to the simple result:

$$D^{\alpha\beta} = kT \left[\frac{\delta_{\alpha\beta}}{n\zeta} + \frac{1}{8\pi n^2 \eta_0} \sum_{\substack{l \pm s \\ =1}}^{n} \left(\frac{\delta_{\alpha\beta}}{R_{ls}} + \frac{X_{ls}^\alpha X_{ls}^\beta}{R_{ls}^3} \right) \right] \quad \alpha, \beta = 1, 2, 3 \quad (8)$$

where X_{ls}^α is the component of the distance between units l and s along the
rectangular axis α of the coordinate system to which the position of the
center of mass is referred. The mean translational diffusion constant, $\bar{D}$,
is equal to one-third of the trace of $D^{\alpha\beta}$, averaged over the internal coor-
dinates:

$$\bar{D} = kT \left[\frac{1}{n\zeta} + \frac{1}{6\pi n^2 \eta_0} \sum_{\substack{l,s \\ =1}}^{n} \overline{\left(\frac{1}{R_{ls}} \right)} \right] \qquad (9)$$

The sedimentation constant, s, is then given by:

$$s = \frac{M}{nN} \left[\frac{1}{\zeta} + \frac{1}{6\pi n \eta_0} \sum_{\substack{l,s \\ =1}}^{n} \overline{\left(\frac{1}{R_{ls}} \right)} \right] \qquad (10)$$

where M is the molecular weight and N is Avogadro's number. For the
randomly coiled polymer molecule, consisting of n statistical units of length
b, we have:

$$\bar{D} = \frac{kT}{n\zeta} \left(1 + \frac{8}{3} \lambda_0 n^{1/3} \right)$$

$$s = \frac{M_0}{N\zeta} \left(1 + \frac{8}{3} \lambda_0 n^{1/3} \right)$$

$$\lambda_0 = \zeta / \sqrt{6\pi^3} \eta_0 b \tag{11}$$

where M_0 is the molecular weight of the statistical unit. This result agrees with that obtained by Kirkwood and Riseman[4] by a less rigorous method. Except in sedimentation processes, the translational coordinates are redundant, since $f(q,t)$ is independent of them, and equations (3) and (5) are valid in the space of the internal coordinates of the molecule with ν equal to the total number of degrees of freedom less three, with $f(q,t)$ normalized to unity in the internal space alone.

We shall now investigate the solution of equation (5) by the methods of perturbation theory. We first transform equation (5) in the following manner:

$$f(q,t) = e^{\beta[A_0 - W_0]/2} \rho(q,t)$$

$$L\rho - (\partial\rho/\partial t) = -Q\rho$$

$$L = \sum_{\alpha,\beta} \frac{1}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial q^\alpha} \left(D^{\alpha\beta} \frac{\partial}{\partial q^\beta} \right) + U \tag{12}$$

$$U = \frac{1}{2kT} \sum_{\alpha,\beta} \frac{1}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial q^\alpha} \left(D^{\alpha\beta} \frac{\partial W_0}{\partial q^\beta} \right) - \frac{1}{(2kT)^2} \sum_{\alpha,\beta} D^{\alpha\beta} \frac{\partial W_0}{\partial q^\alpha} \frac{\partial W_0}{\partial q^\beta}$$

$$Q(q,t) = -e^{-\beta[A_0 - W_0]/2} \sum_{\alpha,\beta} \frac{1}{\sqrt{g}} \frac{\partial \sqrt{g}}{\partial q^\beta} \left\{ \left[\frac{D^{\alpha\beta}}{kT} X_\alpha + g^{\alpha\beta} v_\alpha^0 \right] e^{\beta[A_0 - W_0]/2}(\ ) \right\}$$

The differential operator L is self-adjoint, and therefore possesses a complete orthonormal set of eigenfunctions ψ_λ:

$$L\psi_\lambda + \lambda\psi_\lambda = 0 \tag{13}$$

with negative eigenvalues, $-\lambda$, subject to the boundary conditions of single-valuedness and integrability in m-space. We now suppose that the operator Q may be expanded in powers of a parameter γ, for example, the rate shear of the velocity field v^0 in the solvent, or the strength of an externally applied electric field:

$$Q = \gamma Q^{(1)} + \gamma^2 Q^{(2)} + \cdots \tag{14}$$

We further suppose that the function ρ may be similarly expanded:

$$\rho(q,t) = f^{0\,1/2} + \sum_{s=1}^{\infty} \rho^{(s)} \gamma^s$$

$$f^{0\,1/2} = e^{\beta[A_0 - W_0]/2} \tag{15}$$

where the first term corresponds to thermodynamic equilibrium and the remaining terms describe the departure of the distribution function from its equilibrium value as a result of the perturbation Q, given by equation (14). Equation (12), (14), and (15) then yield the following system of inhomogeneous differential equations for the functions $\rho^{(s)}$

$$L\rho^{(1)} - (\partial\rho^{(1)}/\partial t) = -Q^{(1)}f^0{}^{1/2}$$

$$L\rho^{(2)} - (\partial\rho^{(2)}/\partial t) = -Q^{(1)}\rho^{(1)} - Q^{(2)}f^0{}^{1/2}$$

$$L\rho^{(s)} - (\partial\rho^{(s)}/\partial t) = -Q^{(1)}\rho^{(s-1)} - Q^{(2)}\rho^{s-2} + \ldots \tag{15}$$

The function $\rho^{(1)}(q,t)$ may be expanded in the eigenfunctions $\psi_\lambda(q)$ of the operator L in the form:

$$\rho^{(1)}(q,t) = \int_{-\infty}^{+\infty} G^{(1)}(q,\omega)e^{i\omega t}d\omega$$

$$G^{(1)}(q,\omega) = \sum_\lambda \frac{B_\lambda^{(1)}(\omega)}{\lambda + i\omega}\,\psi_\lambda(q)$$

$$B_\lambda^{(1)} = (1/2\pi)\int_{-0}^{+\infty}(Q^{(1)}f^0{}^{1/2})_\lambda e^{-i\omega t}dt$$

$$(Q^{(1)}f^{0 1/2})_\lambda = \int\ldots\int \sqrt{g}\psi_\lambda^*(q)Q^{(1)}f^{0 1/2}\prod_\alpha dq^\alpha \tag{16}$$

Carrying the perturbation calculation to the second order, we obtain for the function $\rho^{(2)}(q,t)$:

$$\rho^{(2)}(q,t) = \int_{-\infty}^{+\infty} G^{(2)}(q,\omega)e^{i\omega t}\,d\omega$$

$$G^{(2)}(q,\omega) = \sum_\lambda \frac{G_\lambda^{(2)}(\omega)}{\lambda + i\omega}\,\psi_\lambda(q)$$

$$G_\lambda^{(2)}(\omega) = \sum_{\lambda'}\int_{-\infty}^{+\infty}\frac{K_{\lambda\lambda'}^{(1)}(\omega - \omega')B_\lambda^{(1)}(\omega')}{\lambda' + i\omega'}\,d\omega' + B_\lambda^{(2)}(\omega)$$

$$K_{\lambda\lambda'}^{(1)}(\omega) = (1/2\pi)\int_{-\infty}^{+\infty}Q_{\lambda\lambda'}^{(1)}\,e^{-i\omega t}\,dt$$

$$Q_{\lambda\lambda'}^{(1)} = \int\ldots\int\sqrt{g}\psi_\lambda^*Q^{(1)}\psi_{\lambda'}\prod_\alpha dq^\alpha$$

$$B_\lambda^{(2)} = (1/2\pi)\int_{-\infty}^{+\infty}(Q^{(2)}f^{0 1/2})_\lambda e^{-i\omega t}\,dt \tag{17}$$

Perturbations of higher order may be obtained by similar methods. Mean values of functions $\varphi(q)$, equation (3), may now be expanded in the form:

$$\bar\varphi(t) = \bar\varphi^0 + \gamma\bar\varphi^{(1)} + \gamma^2\bar\varphi^{(2)} + \ldots$$

$$\bar\varphi^0 = \int\ldots\int\sqrt{g}\varphi e^{\beta[A_0 - W_0]}\prod_\alpha dq^\alpha$$

$$\bar\varphi^{(1)} = \int\ldots\int\sqrt{g}\varphi e^{\beta[A_0 - W_0]/2}\rho^{(1)}\prod_\alpha dq^\alpha$$

$$\bar\varphi^{(2)} = \int\ldots\int\sqrt{g}\varphi e^{\beta[A_0 - W_0]/2}\rho^{(2)}\prod_\alpha dq^\alpha \tag{18}$$

where $\bar{\varphi}^0$ corresponds to thermodynamic equilibrium. The techniques useful in determining the eigenfunctions ψ_λ and eigenvalues $-\lambda$ of the operator L are identical with those employed in the solution of the Schrödinger equation in quantum mechanics. The reciprocals of the λ-spectrum constitute the relaxation time spectrum, $\tau = 1/\lambda$, of the system, a set of real positive number, determined by the diffusion tensor $D^{\alpha\beta}$.

VISCO-ELASTIC PARAMETERS

The visco-elastic properties of solutions of macromolecules are determined by the hydrodynamic forces, $-\mathbf{F}_l$, which the structural units of the molecule exert on the solvent. These forces produce perturbations in the velocity field of the solvent, which may manifest themselves not only in an increment in the viscosity coefficient but also by imparting a rigidity to the solution for time dependent rates of strain. The intrinsic viscosity $[\eta]$ of the solution is related to the hydrodynamic forces $\mathbf{F}_l$, exerted by the fluid on the structural elements according to the following relation:[4]

$$[\eta] = N\Phi/100M\eta_0$$

$$\Phi = -\frac{1}{\dot{\epsilon}^2} \sum_{l=1}^{n} \overline{\mathbf{F}_l \cdot \mathbf{V}_l^0} \tag{19}$$

where $\dot{\epsilon}$ is the magnitude of the rate of shear, and $\mathbf{V}_l^0$ is the unperturbed velocity of the solvent at the point of location of structural element l relative to the velocity of the center of gravity of the molecule. For a simple alternating shear of frequency $\omega/2\pi$, in direction $\mathbf{e}_x$ propagated in the direction $\mathbf{e}_y$, we may write:

$$\mathbf{V}_l^0 = \dot{\epsilon}(\mathbf{R}_{ol} \cdot \mathbf{e}_y)\mathbf{e}_x e^{i\omega t} \tag{20}$$

where $\mathbf{R}_{ol}$ is the position of element l relative to the molecular center of mass. According to the Oseen method, as employed by Burgers[1] and by Kirkwood and Riseman,[4] the forces $\mathbf{F}_l$, regarded as vectors in the common 3-space of all structural elements, have been shown to satisfy the following set of linear equations:

$$\mathbf{F}_l + \zeta \sum_{s=1}^{n} \mathbf{T}_{ls} \cdot \mathbf{F}_s = \zeta(\mathbf{V}_l^0 - \mathbf{U}_l)$$

$$\mathbf{T}_{ls} = \frac{1}{8\pi\eta_0 \mathbf{R}_{ls}} \left(1 + \frac{\mathbf{R}_{ls}\mathbf{R}_{ls}}{R_{ls}^2}\right) \tag{21}$$

where $\mathbf{R}_{ls}$ is the vector distance between elements l and s, 1 is unit tensor, $\mathbf{U}_l$ is the velocity of element l, and ζ is the friction constant of a single element. The velocities $\mathbf{U}_l$ are determined by balancing the components of the hydrodynamic force in m-space by the corresponding components of the diffusion forces, according to the theory of Brownian motion, to obtain:

$$\mathbf{U}_l = \sum_{\alpha} v^{0\alpha} \frac{\partial \mathbf{R}_{ol}}{\partial q^\alpha} - \sum_{\alpha,\beta} D^{\alpha\beta} \frac{\partial \log f}{\partial q^\beta} \frac{\partial \mathbf{R}_{ol}}{\partial q^\alpha} \tag{22}$$

where f is the probability density in m-space, which satisfies equation (3). For alternating shearing strain f exhibits, according to equations (12), (15), and (16), a lag in phase relative to the rate of shear in the solvent. As a consequence, the function Φ possesses both real and imaginary parts, and thus $[\eta]$ also possesses both real and imaginary parts:

$$[\eta] = [\eta'] - i[\eta'']$$

$$[\mu] = \lim_{c \to 0} \mu/c = \omega\eta_0[\eta''] \qquad (23)$$

where the real part $[\eta']$ is the observed intrinsic viscosity, and the imaginary part determines the intrinsic rigidity $[\mu]$, experimentally observed by Mason and Baker[3] and their collaborators. A detailed application of the theory which has been outlined here to the rectilinear pearl necklace molecule has been carried out by Kirkwood and Auer.[5] For a molecule composed of a set of hydrodynamically resisting elements spaced at equal intervals b on a straight line segment of length L, they obtain:

$$[\eta'] = \frac{\pi N b L^2}{9000 M_0 \log (L/b)} \left(1 + \frac{3}{1 + \omega^2\tau^2}\right)$$

$$[\mu] = \frac{6NkT}{1000M} \frac{\omega^2\tau^2}{1 + \omega^2\tau^2}$$

$$\tau = \pi\eta_0 L^3/18kT \log (L/b) \qquad (24)$$

For stationary viscous flow, $\omega = 0$, the rigidity of the solution vanishes and $[\eta']$ becomes equal to the asymptotic form of Simha's formula[6] for the prolate ellipsoid of eccentricity approaching unity.

BIREFRINGENCE

When macromolecules dissolved in optically isotropic solvents are subjected to external torques, hydrodynamic, electric, or magnetic, their solutions become birefringent. This phenomenon is known as flow birefringence when the torque is hydrodynamic and as the Kerr effect when the torque is produced by an external electric field. In this section, we shall briefly describe the phenomenon of macromolecular birefringence in terms of the general theory.

We suppose each structural unit of the molecule to possess a polarizability tensor increment α_l, dependent on the coordinates q_α, in excess of the polarizability of the solvent which it displaces. The average polarizability tensor $\bar{\alpha}$ of the entire molecule is then given by equation (3) in the form:

$$\alpha = \sum_{l=1}^{n} \alpha_l$$

$$\bar{\alpha} = \int \ldots \int \sqrt{g}\,\alpha f(q,t) \prod_\alpha dq^\alpha \qquad (25)$$

In flow birefringence produced by a simple shear or in the Kerr effect produced by a homogeneous electric field, $\bar{\alpha}$ is uniaxial. If we denote by the

unit vector $\mathbf{e}_x$ the direction of the streamlines of the solvent velocity field in the first instance or the direction of the electric field in the second, the birefringence, $n_1 - n_2$, equal to the difference of the principal refractive indices in the x,y plane, is given by:

$$n_1 - n_2 = \frac{4\pi}{3} \left(\frac{n_0^2 + 2}{3}\right)^2 c \left[(\bar{\alpha}_{xx} - \bar{\alpha}_{yy})^2 + 4\bar{\alpha}_{xy}^2\right]^{1/2} \qquad (26)$$

where n_0 is the refractive index of the solvent, c is the number of macromolecules in unit volume, and $\bar{\alpha}_{xx}$, $\bar{\alpha}_{yy}$, $\bar{\alpha}_{xy}$ are the appropriate components of the mean polarizability tensor. The tangent of the extinction angle χ between $\mathbf{e}_x$ and the principal axis $\mathbf{e}_2$ of the dielectric constant tensor in the x-y plane is related to $\bar{\alpha}_{xx}$, $\bar{\alpha}_{yy}$, and $\bar{\alpha}_{xy}$ in the following manner:

$$\tan \chi = \frac{[(\bar{\alpha}_{xx} - \bar{\alpha}_{yy})^2 + 4\bar{\alpha}_{xy}^2]^{1/2} + \bar{\alpha}_{xx} - \bar{\alpha}_{yy}}{2\bar{\alpha}_{xy}}$$

$$= 1 + \frac{\bar{\alpha}_{xx} - \bar{\alpha}_{yy}}{2\bar{\alpha}_{xy}} + \ldots$$

$$\chi = \frac{\pi}{4} + \frac{\bar{\alpha}_{xx} - \bar{\alpha}_{yy}}{2\bar{\alpha}_{xy}} + \ldots \qquad (27)$$

We consider first the case of flow birefringence produced by a constant rate of shear in the solvent, corresponding to the velocity field of equation (20) with ω equal to zero. We set the perturbation parameter γ of equation (14) equal to the rate of shear $\dot{\epsilon}$, and obtain from the last of equation (12):

$$Q = \dot{\epsilon} Q^{(1)}$$

$$Q^{(1)} = -e^{-\beta[A_0 - W_0]/2} \sum_{\alpha,\beta} \frac{1}{\sqrt{g}} \frac{\partial}{\partial q^\beta} \frac{\sqrt{g}}{} \left[g^{\alpha\beta}(\mathbf{R}_{ol} \cdot \mathbf{e}_y)\left(\mathbf{e}_x \cdot \frac{\partial \mathbf{R}_{ol}}{\partial q^\alpha}\right) f^{0\,1/2}\,(\,)\right]$$

$$(28)$$

For the stationary case, the distribution functions $\rho^{(1)}$ and $\rho^{(2)}$ of equations (16) and (17) reduce to:

$$\rho^{(1)}(q) = \sum_\lambda \frac{(Q^{(1)} f^{0\,1/2})_\lambda}{\lambda} \psi_\lambda(q)$$

$$\rho^{(2)}(q) = \sum_{\lambda,\lambda'} \frac{Q^{(1)}_{\lambda\lambda'}(Q^{(1)} f^{0\,1/2})_{\lambda'}}{\lambda\lambda'} \psi_\lambda(q) \qquad (29)$$

With these distribution functions, we obtain from equations (18) and (25):

$$\bar{\alpha}_{xy} = \dot{\epsilon} \sum_\lambda \frac{(\alpha_{xy} f^{0\,1/2})_\lambda (Q^{(1)} f^{0\,1/2})_\lambda}{\lambda} + \ldots$$

$$\bar{\alpha}_{xx} - \bar{\alpha}_{yy} = \dot{\epsilon}^2 \sum_{\lambda,\lambda'} \frac{[(\alpha_{xx} - \alpha_{yy})f^{0\,1/2}]_\lambda Q^{(1)}_{\lambda\lambda'}(Q^{(1)} f^{0\,1/2})_{\lambda'}}{\lambda\lambda'} \qquad (30)$$

The mean values of equation (30), when substituted in equations (26) and (27), yield the desired expansions of the birefringence and extinction angle in powers of the rate of shear, as sums over the relaxation time spectrum of the molecule.

Birefringence due to the Kerr effect produced by an alternating electric field of frequency ω, with direction e_z may be treated in the following manner. The internal electric field E', acting on the macromolecule in a nonpolar solvent is:

$$E' = \frac{\epsilon_0 + 2}{3} E$$

$$E = E_0 e_z \cos \omega t \qquad\qquad (31)$$

where E_0 is the amplitude of the external field and ϵ_0 is the dielectric constant of the solvent. The applied field produces generalized torques X_α in m-space which may be derived from a potential, V:

$$V = -\frac{\epsilon_0 + 2}{3} \mathbf{\mu} \cdot e_z E_0 \cos \omega t - \frac{1}{2}\left(\frac{\epsilon_0 + 2}{3}\right)^2 (e_z \cdot \alpha \cdot e_z) E^2 \cos^2 \omega t$$

$$X_\alpha = -\frac{\partial V}{\partial q^\alpha} \qquad\qquad (32)$$

where $\mathbf{\mu}$ is the electric dipole moment of the molecule, equal to the sum of the dipole moments $\mathbf{\mu}_i$ of its structural units, and α is again the polarizability tensor. Setting the perturbation parameter of equation (14) equal to the amplitude, E_0, of the electric field, we obtain from equations (12) and (32) the following perturbation operator:

$$Q = Q^{(1)} E_0 + Q^{(2)} E_0^2$$

$$Q^{(1)} = -\frac{e^{-\beta[A_0 - W_0]/2}}{kT}\frac{\epsilon_0 + 2}{3}\sum_{\alpha,\beta}\frac{1}{\sqrt{g}}\frac{\partial \sqrt{g}}{\partial q^\beta}\left[D^{\alpha\beta}\frac{\partial \mathbf{\mu}\cdot e_z}{\partial q^\alpha} f^{0\,1/2}\,(\ )\right]$$

$$Q^{(2)} = -\frac{e^{-\beta[A_0 - W_0]/2}}{2kT}\left(\frac{\epsilon_0 + 2}{3}\right)^2\sum_{\alpha,\beta}\frac{1}{\sqrt{g}}\frac{\partial \sqrt{g}}{\partial q^\beta}\left[D^{\alpha\beta}\frac{\partial e_z\cdot\alpha\cdot e_z}{\partial q^\alpha} f^{0\,1/2}\,(\ )\right]$$

$$\qquad\qquad (33)$$

Equations (17), (18), and (33) lead to the appropriate mean values of $\bar{\alpha}_{xx}$, $\bar{\alpha}_{yy}$, and $\bar{\alpha}_{xy}$, and these in turn yield the birefringence and extinction angle when substituted in equations (26) and (27). The rather cumbersome resulting expressions will not be displayed here. The birefringence is proportional to the square of the amplitude of the applied field and the extinction angle is found to be $\pi/2$, since $\bar{\alpha}_{xy}$ vanishes by symmetry for all field strengths. Thus the two principal axes of the dielectric constant

tensor remain parallel and perpendicular to the direction of the applied field. The relaxation of the Kerr effects arising from $Q^{(1)}$ and $Q^{(2)}$, the contributions of the permanent and induced electric moments, exhibit entirely different frequency dependence, with the induced component the only surviving one at very high frequencies.

DIELECTRIC POLARIZATION AND DISPERSION

We shall briefly review the application of the general theory to the analysis of dielectric polarization and dispersion of solutions of polar macromolecules. The principal results of the previous treatment of the problem, with special reference to polar polymers, by Kirkwood and Fuoss[7] will be shown to be a consequence of the general theory of irreversible processes.

We shall suppose the solution to be polarized by a homogeneous alternating electric field of frequency $\omega/2\pi$ acting in the e_x direction, equal to the real part of the complex field E:

$$E = e_x E_0 e^{i\omega t} \qquad (34)$$

The internal field E' acting on a macromolecule will be approximated by the Lorentz field in the case of nonpolar solvents and by the Onsager field in the case of polar solvents.

$$E' = E_0' e_x e^{i\omega}$$

$$E_0'/E_0 = \frac{\epsilon_0 + 2}{3}; \quad \text{nonpolar solvent}$$

$$E_0'/E_0 = \frac{3\epsilon_0}{2\epsilon_0 + 2}; \quad \text{polar solvent} \qquad (35)$$

where ϵ_0 is the real dielectric constant of the solvent, which will be assumed to have negligible dispersion at frequency ω.

The complex dielectric constant increment, Δ, per molecule is defined by the relation:

$$\Delta = \lim_{:\to 0} (d\epsilon/dc)$$

$$\epsilon = \epsilon' - i\epsilon'' \qquad (36)$$

$$\Delta = \Delta' - i\Delta''$$

where ϵ is the complex dielectric constant of the solution and c is the number of macromolecules in unit volume. If we ignore the optical contribution to its polarization and also assume that the polarization of the solvent displaced by a macromolecule is negligible, the dielectric increment Δ is related to the average component of the macromolecular dipole moment $\overline{\mu \cdot e_x}$ in the direction of the applied field in the following manner:

$$\Delta = \sigma \mu_x^{(1)}$$

$$\overline{\mathbf{u} \cdot \mathbf{e}_x} = \mu_x^{(1)} E_0' e^{i\omega t} + O(E_0^{12})$$

$$\sigma = 4\pi \left(\frac{\epsilon_0 + 2}{3}\right)^2; \quad \text{nonpolar solvent}$$

$$\sigma = \frac{12\pi\epsilon_0^2}{2\epsilon_0^2 + 1}; \quad \text{polar solvent} \qquad (37)$$

The appropriate perturbation function, adequate for the calculation of $\mu_x^{(1)}$ is obtained from equations (12) and (14) by setting the parameter γ equal to the amplitude E_0' of the internal field.

$$Q = Q^{(1)} E_0'$$

$$X_\alpha = \frac{\partial(\mathbf{u} \cdot \mathbf{e}_x)}{\partial q^\alpha} E_0' e^{i\omega t}$$

$$Q^{(1)} = -\frac{1}{f^{0\,1/2} kT} \sum_{\alpha,\beta} \frac{1}{\sqrt{g}} \frac{\partial\sqrt{g}}{\partial q^\beta} \left[D^{\alpha\beta} \frac{\partial(\mathbf{u} \cdot \mathbf{e}_x)}{\partial q^\alpha} f^{0\,1/2} (\ ) \right]$$

$$Q^{(1)} f^{0\,1/2} = -\frac{1}{kT} L[f^{0\,1/2}(\mathbf{u} \cdot \mathbf{e}_x)] e^{i\omega t} \qquad (38)$$

We then obtain from equations (16), (18), and (27):

$$\mu_x^{(1)} = \frac{1}{kT} \sum_\lambda \frac{\lambda(\tilde{\mathbf{u}} \cdot \mathbf{e}_x)_\lambda^*(\tilde{\mathbf{u}} \cdot \mathbf{e}_x)_\lambda}{\lambda + iw}$$

$$= \frac{1}{3kT} \sum_\lambda \frac{\tilde{\mathbf{u}}_\lambda^* \cdot \tilde{\mathbf{u}}_\lambda}{1 + i\omega\tau_\lambda}$$

$$\tilde{\mathbf{u}} = f^{0\,1/2} \mathbf{u} \qquad \tau_\lambda = 1/\lambda$$

$$\sum \tilde{\mathbf{u}}_\lambda^* \cdot \tilde{\mathbf{u}}_\lambda = \int \ldots \int \sqrt{g}\, f^0(q) \mu^2 \prod_\alpha dq^\alpha = \overline{\mu^2}^0 \qquad (39)$$

where $\overline{\mu^2}^0$ is the mean square electric moment of the macromolecule in the absence of the external field. The real and complex parts of the dielectric constant increment, Δ, are then given by:

$$\Delta' = \frac{\sigma}{3kT} \sum_\lambda \frac{\tilde{\mathbf{u}}_\lambda^* \cdot \tilde{\mathbf{u}}_\lambda}{1 + \omega^2\tau_\lambda^2}$$

$$\Delta'' = \frac{\sigma}{3kT} \sum_\lambda \frac{\omega\tau \tilde{\mathbf{u}}_\lambda^* \cdot \tilde{\mathbf{u}}_\lambda}{1 + \omega^2\tau_\lambda^2} \qquad (40)$$

Equation (40) generalizes the results of the earlier treatment of Kirkwood and Fuoss and presents them as a consequence of the general theory.

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Synopsis

The general theory of irreversible processes in solutions of macromolecules, previously formulated by the author, is reviewed. The theory is based upon the Oseen method for determining the perturbation in the hydrodynamic flow pattern produced by the frictional forces exerted by the macromolecule on the solvent, and on a generalized theory of Brownian motion in molecular configuration space. Applications of theory to viscoelastic behavior, flow birefringence, and the Kerr effect, and to dielectric dispersion are presented in outline.

Résumé

La théorie de procès irréversibles dans les solutions de macromolécules, plus tôt présentée par l'auteur, est résumée. Elle est fondée sur la méthode d'Oseen pour la détermination des variations de l'écoulement hydrodynamique causées par des forces de friction, qui sont exercées sur le dissolvant par la macromolécule, ainsi que sur une théorie généralisée du mouvement brownien dans l'espace de la configuration moléculaire.

Les applications de la théorie à la visco-elasticité, à la biréfrigence d'écoulement et l'effet Kerr ainsi qu'à la dispersion diélectrique ont été ébauchées.

Zusammenfassung

Die vom Verfasser früher aufgestellte Theorie irreversibler Processe in Lösungen von Makromolekeln wird revidiert. Die Theorie gründet sich auf Oseens Methode zur Bestimmung der Störungen im Verlaufe der hydrodynamischen Strömung, welche durch von der Makromolekel auf das Lösungsmittel ausgeübte Reibungskräfte verursacht sind, sowie auf eine von allgemeinste Theorie der Brownschen Bewegung im Raume molekularer Anordnung.

Anwendungen der Theorie auf visco-elastisches Verhalten, Strömungsdoppelbrechung und Kerreffect sowie dielektrische Dispersion werden in Umrissen vorgelegt.

Discussion

Professor W. Kuhn (*Basel*): For some years we have been particularly interested in the irreversible processes connected with the orientation of geometrically anisotropic particles and with the orientation and deformation of chain molecules in streaming solutions. (W. Kuhn and H. Kuhn, *Helv. Chim. Acta*, **37,** 97 (1944); **38,** 1533 (1945); **39,** 71 (1946).)

In the case of very elongated particles in a streaming solution a *partial orientation* of the long axis is taking place, an orientation which gives rise to angular diffusion of the particle axis which is analogous to the ordinary diffusion of particles in a liquid in which a concentration gradient exists. Taking this irreversible (angular) diffusion process into account increases the heat developed per unit time and volume by a factor of 2.

That is, the intrinsic viscosity is twice as high (compared with the case in which only the hydrodynamic effects with neglect of the Brownian movement are taken into account) if the orientation of the particle axis by the field of flow and the irreversible diffusion processes competing with the orienting influences are taken into account. This factor 2 is of interest. It disappears in the case of very high velocity gradients where Brownian movement becomes negligible, a circumstance which explains the decrease of viscosity with increasing rate of shear in very dilute solutions of geometrically anisotropic particles.

For less elongated particles, the factor is smaller than 2 and becomes equal to 1 in the case of spheres. The factor 2 is therefore characteristic for small rate of shear and for very elongated particles. It would be interesting to know whether 2 is a general maximum value of the factor by which the heat development per unit of time is increased, taking the Brownian movement into account, above the value which would occur if the effects of the Brownian movement were neglected. The general theory developed by Dr. Kirkwood might give an answer to this question.

Professor J. G. Kirkwood (*Yale*): Dr. Kuhn was the first to point out that the hydrodynamic torque on a macromolecule is not zero but equal to the rotatory diffusion torque, and to show that the intrinsic viscosity is significantly affected by the gradient of the orientational distribution function. This was also recognized by Simha (*J. Phys. Chem.*, 44, 25 (1940)). However, both Simha and Kirkwood and Auer (*J. Chem. Phys.*, 3, 281 (1951)) find that the intrinsic viscosity of extremely elongated molecules is four times the value obtained with the neglect of rotatory Brownian motion, whereas Dr. Kuhn finds a factor of two. I do not know the reason for this discrepancy.