Polymer Dynamics and Rheology
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Brownian motion
Harmonic Oscillator
Damped harmonic oscillator
Elastic dumbbell model
Boltzmann superposition principle
Rubber elasticity and viscous drag
Temporary network model (Green & Tobolsky 1946)
Rouse model (1953)
Cox-Merz rule and dynamic viscoelasticity
Reptation
The gel point
The Gaussian Chain

Boltzmann Probability
For a Thermally Equilibrated System

\[ P_B(R) = \exp \left( - \frac{E(R)}{kT} \right) \]

Gaussian Probability
For a Chain of End to End Distance R

\[ P(R) = \left( \frac{3}{2\pi\sigma^2} \right)^{3/2} \exp \left( - \frac{3(R)^2}{2(\sigma)^2} \right) \]

By Comparison The Energy to stretch a Thermally Equilibrated Chain Can be Written

\[ E = kT \frac{3R^2}{2nl^2_k} \]

Assumptions:
-Gaussian Chain
-Thermally Equilibrated
-Small Perturbation of Structure (so it is still Gaussian after the deformation)
Stoke’s Law

\[ F = \nu \zeta \]
\[ \zeta = 6\pi \eta_s R \]
Creep Experiment

\[ \varepsilon_{11} = \sigma_{11}/E \]

\[ d\varepsilon_{12}/dt = \sigma_{12}/\eta \]

\[ \varepsilon_{11} = k \left( 1 - \exp\left(-t/\tau\right) \right) \]

Fig. 6.1. Creep curve of a polymer sample under tension (schematic). The elongation \( \Delta L_z \) induced by a constant force applied at zero time is set up by a superposition of an instantaneous elastic response (dashed line), a retarded anelastic part (dashdot line), and viscous flow (dotted line). An irreversible elongation is retained after an unloading and the completion of the recovery process.

\[ \tau = 1/\omega \quad \text{Cox-Merz Rule} \]
Fig. 6.2. Stress relaxation curve (schematic)
Boltzmann Superposition

Figure 1.11 Storage and loss moduli for a low density polyethylene "Melt I." (These data were measured at several temperatures and shifted along the frequency axis by a "shift factor" $a_T$ to form collapsed curves; see Section 3.5.2). The lines are empirical fits of Eqs. (3-25a) and (3-25b) to the data. (From Laun 1978, reprinted with permission from Steinkopff Publishers.)

Figure 3.9 (a) Loss modulus $G''$ and (b) storage modulus $G'$ versus frequency computed from Eqs. (3-25a) and (3-25b) for the eight modes given in Table 3-1 for Melt I, a polyethylene melt. Summing up over all the modes gives the "envelope" curves shown; these curves are reproduced in Fig. 1-11, where they are seen to represent accurately the linear data for this melt. (From Laun 1978, reprinted with permission from Steinkopff Publishers.)
Stress Relaxation (liquids) \[ E(t) = \frac{\sigma_{11}(t)}{\epsilon_{11}} \]

Creep (solids) \[ J(t) = \frac{\epsilon(t)}{\sigma} \]

Dynamic Measurement \[ E^*(\omega) = \frac{\sigma_{11}(t)}{\epsilon_{11}(t)} \]

\[ \sigma_{11}(t) = \sigma^0_{11} \exp(i\omega t) \]

\[ \epsilon_{11}(t) = \epsilon^0_{11} \exp(-i\delta) \exp(i\omega t) \]

Harmonic Oscillator: \( \delta = 90^\circ \) for all \( \omega \) except \( \omega = 1/\tau \) where \( \delta = 0^\circ \)

Hookean Elastic \( \delta = 0^\circ \)

Newtonian Fluid \( \delta = 90^\circ \)

\[ e^{-iA} = \cos A - i \sin A \]

\[ e^{+iA} = \cos A + i \sin A \]
Fig. 6.3. Time dependence of stress ($\sigma_{zz}$) and strain ($e_{zz}$) in a dynamic-mechanical experiment (schematic)
Brownian Motion

\[ <V(t)> = 0 \]

\[ <V(t_1)V(t_2)> = C_v(t_1 - t_2) \]

\( C_v(t) \) is the velocity correlation function

correlation time, \( \tau_v \)

\[ <V(t_1)V(t_2)> = <V(t)V(0)> = C_v(t) \]

\[ <V^2(t)> = kT/m \quad \text{For short times} \]

For long times \( <V^2(t)> = 0 \)

\[ m \left( \frac{dV}{dt} \right) = -6\pi\eta_s a V \]

\[ V = V_0 \exp(-6\pi\eta_s a \frac{(t_1 - t_2)}{m}) = V_0 \exp\left( -(t_1 - t_2)/\tau_v \right) \]

\[ \tau_v = m/(6\pi\eta_s a) \]
For a sphere of density $\rho$, $m = \left(\frac{4\pi}{3}\right) a^3$, and $\tau_v = \left(\frac{2\pi}{9}\right) a^2/\eta_s$.

The relaxation time, $\tau_v$, is very small for colloidal scale objects such as polymer coils, $O(10^{-10}\text{s})$.

polymer in dilute solution $\quad \tau_v \approx 0$

displacement $\quad \xi(t) = \int_0^t V(t') dt'$

\[
\langle \xi(t)^2 \rangle = \int_0^t dt_1 \int_0^t \langle V(t_1)V(t_2) \rangle dt_2 = 2Dt = \int_0^t dt_1 \int_0^t 2D\delta(t_1-t_2) dt_2
\]

$\langle V(t_1)V(t_2) \rangle = \langle V(t)V(0) \rangle = 2D\delta(t)$
Brownian Motion in a Potential Field:

\[<V> = -(1/\zeta)dU/dx = <dx/dt>\]

\[dx/dt = -(1/\zeta)dU/dx + g(t) \quad \text{Langevin Equation}\]

\[<g(t)> = 0\]

\[<g(t)g(t')> = 2D\delta(t-t')\]
Brownian Motion of a Harmonic Oscillator:

\[ U(x) = \frac{kx^2}{2} \]

\[ \frac{dx}{dt} = -\frac{kx}{\zeta} + g(t) \]

\[ x(t) = \int_{-\infty}^{t} dt' e^{-\frac{k(t-t')}{\zeta}} g(t') \]

\[ \langle x(t)x(0) \rangle = \int_{-\infty}^{t} dt_1 \int_{-\infty}^{0} dt_2 \exp\left[-\frac{k(t-t_1-t_2)}{\zeta}\right] \langle g(t_1)g(t_2) \rangle \]

Using \( \langle g(t)g(t') \rangle = 2D\delta(t-t') \) and \( D = kT/\zeta \),

\[ \langle x(t)x(0) \rangle = \frac{kT \exp(-t/\tau)}{k_{spr}} \]

\[ \tau = \frac{\zeta}{k_{spr}} \]

For \( t \to 0 \), \( \langle x^2 \rangle = \frac{kT}{k_{spr}} \), as predicted by a Boltzman distribution, \( \Psi_{\text{equil}} \propto \exp\left(-\frac{k_{spr}x^2}{2kT}\right) \)
\[ \langle (x(t) - x(0))^2 \rangle = \langle x(t)^2 \rangle + \langle x(0)^2 \rangle - 2 \langle x(t)x(0) \rangle \]

= \[ 2 \langle x^2 \rangle - 2 \langle x(t)x(0) \rangle \]

= \[ 2kT / k_{spr} (1 - \exp(-t/\tau)) \]

For \( t \to 0 \) this yields \( (2kT/\zeta)t = 2Dt \) which is the expected result from the discussion of Brownian motion above.
**General Linear Response Theory:**

$\psi(t)$ as the kind of force that is applied when you strike a bell

$$x(t) = \psi_0 \mu(t)$$

**the primary response function**

$\mu(t)$

describes the response of a material to an infinitely short, pulsed force or field, $\psi(t) = \psi_0 \delta(t)$

$\delta(t)$, has a value of $\infty$ for a given $t$

The integral with respect to time is 1.
Fig. 6.4. Primary response function of a damped harmonic oscillator (a), a perfectly viscous body (b), a Hookean solid (c), and a simple relaxatory system (d)
The response to any force field

\[ x(t) = \int_{-\infty}^{t} \mu(t - t')\psi(t')dt' \]

The latter expression relies on two assumptions:
1) Causality principle, the response is caused by the field or force that the material experienced in the past;
2) Superposition principle, the field or force over time can be described by a sequence of pulses and the response is a summation of the responses to these pulses.
Relationships Between Different Dynamic Measurements:

Creep Measurement:
Following Strobl, p. 200, consider a creep experiment where a stress, $\psi(t)$, is applied to a sample at $t=0$, for $t>0$; $\psi(t) = \psi_0$. The creep, $x(t)$, is given by

$$x(t) = \int_0^t \mu(t-t')\psi_0 \, dt'$$

For this constant stress experiment the displacement, $x(t)$ can be directly normalized by the force, $\psi_0$, to yield the susceptibility, $\alpha(t)$, or the integral of the response function, or the cumulative response function.

$$\frac{x(t)}{\psi_0} = \int_0^t \mu(t-t')dt' = \int_0^t \mu(t'')dt''$$

we can also write that the response function is the derivative of the time dependent susceptibility,

$$\mu(t) = \frac{d\alpha}{dt}(t)$$
Stress Relaxation Measurement:
In the stress relaxation experiment the strain is fixed, $x(t) = x_0$, while the stress relaxes, $\psi(t)$,

$$x_0 = \int_0^t \mu(t - t') \psi(t') dt'$$

It is natural to reduce the stress, $\psi(t)$, by the fixed strain, $x_0$, to yield a time dependent modulus, $a(t) = \psi(t)/x_0$. Then,

$$1 = \int_0^t \mu(t - t') a(t') dt' = \int_0^t \frac{d\alpha}{dt} (t - t') a(t') dt'$$

Fig. 6.2. Stress relaxation curve (schematic)
Boltzmann Superposition Equation:
If the susceptibility is used in the definition of the response function we have,

\[
x(t) = \int_{-\infty}^{t} \mu(t-t')\psi(t')dt' = \int_{-\infty}^{t} \frac{d\alpha}{dt}(t-t')\psi(t')dt'
\]

The latter expression can be reduced using integration by parts;

\[
\int u dv = uv - \int v du
\]

where \(u = \psi(t')\) and \(dv = (da/dt') dt'\), so \(v = a(t')\) and \(du = d\psi(t')\), then,

\[
x(t) = \int_{-\infty}^{t} \alpha(t-t')d\psi(t')
\]

The latter expression indicates that the integral over all time till now of the change in force times the susceptibility yields the response. This equation indicates that the load on a sample can be broken down into differential steps and the response can be obtained by integration of these steps times the susceptibility of the material to loading.
A similar analysis can be made using the definition of the time dependent modulus, \( a(t) \), to describe the corollary of the Boltzmann equation for creep,

\[
\psi(t) = \int_{-\infty}^{t} a(t - t') dx(t')
\]

The force at time \( t \), \( \psi(t) \), is composed of incremental steps of strain, \( dx \), times the time dependent modulus, \( a(t) \).
Dynamic Mechanical Measurements:
In a dynamic mechanical measurement an oscillating force, \( \psi(t) = \psi_0 \exp i \omega t = \psi_0 (\cos \omega t + i \sin \omega t) \), is applied to the sample and the strain response displays a time lag (phase angle difference), \( \delta \), so the strain is written, \( x(t) = x_0 \exp -i\delta \exp i \omega t = x_0 \exp i(\omega t - \delta) \). Using,

\[
x(t) = \int_{0}^{t} \mu(t - t')\psi(t')dt'
\]

and substituting the dynamic expressions,

\[
x_0 \exp \{i(\omega t - \delta)\} = \int_{-\infty}^{t} \mu(t - t')\psi_0 \exp \{i \omega t'\}dt'
\]

The dynamic susceptibility, \( \alpha^*(\omega) \), can be obtained in analogy to the creep experiment, \( \alpha^*(\omega) = \{x_0 \exp -i\delta\}/\psi_0 \). The dynamic susceptibility is related to the primary response function, \( \mu(t) \), by,

\[
\alpha^*(\omega) = \int_{-\infty}^{t} \mu(t - t')\exp \{i \omega (t - t')\}dt' = \int_{0}^{\infty} \mu(t'')\exp \{-i \omega t''\}dt'' = \int_{-\infty}^{\infty} \mu(t'')\exp \{-i \omega t''\}dt''
\]

the latter equality being due to \( \mu = 0 \) below \( t=0 \). Then the complex susceptibility is the Fourier transform of the primary response function, \( \mu(t) \)!
Both loss and storage are based on the primary response function, so it should be possible to express a relationship between the two.

The response function is not defined at $t = \infty$ or at $\omega = 0$. This leads to a singularity where you can’t do the integrals.

Cauchy Integral

$$P\left( \int_{\omega_0}^{\infty} \frac{\alpha''}{\omega - \omega_0} d\omega \right) = \lim_{\phi \to 0} \left[ \int_{\omega_0}^{\infty} \frac{\alpha''}{\omega - \omega_0} d\omega + \int_{\omega_0 + \phi}^{\infty} \frac{\alpha''}{\omega - \omega_0} d\omega \right]$$
\[ P \left( \int_{-\infty}^{\infty} \frac{\alpha''}{\omega - \omega_0} d\omega \right) = \lim_{\phi \to 0} \left[ \int_{-\infty}^{\phi} \frac{\alpha''}{\omega - \omega_0} d\omega + \int_{\omega_0 + \phi}^{\infty} \frac{\alpha''}{\omega - \omega_0} d\omega \right] \]

Then the Kramers-Kronig dispersion relations can be written using the Cauchy integral as,

\[ \alpha'(\omega) = \frac{1}{\pi} P \left[ \int_{-\infty}^{\infty} \frac{\alpha''(\omega)}{\omega - \omega_0} d\omega \right] \]

\[ \alpha''(\omega) = \frac{1}{\pi} P \left[ \int_{-\infty}^{\infty} \frac{\alpha'(\omega)}{\omega - \omega_0} d\omega \right] \]
Power Consumption (Rate of Work) in a Dynamic Measurement:

The power consumption, \((dW/dt)/V\), in a perturbation, \(\psi(t)\), response, \(x(t)\) observation is given by,

\[
\frac{1}{V} \frac{dW}{dt} = \psi \frac{dx}{dt}
\]

\[
\psi(t) = \psi_0 \cos \omega t
\]

\[
dx(t)/dt = -\omega \alpha' \psi_0 \sin \omega t + \omega \alpha'' \psi_0 \cos \omega t
\]

\[
\frac{1}{V} \frac{dW}{dt} = \psi \frac{dx}{dt} = \omega \phi_0^2 \cos(\omega t) \left\{ \alpha'' \cos(\omega t) - \alpha' \sin(\omega t) \right\} = \omega \phi_0^2 \left\{ \alpha'' \cos^2(\omega t) - \frac{\alpha'}{2} \sin(2\omega t) \right\}
\]

\[
\sin(x)\cos(x) = \sin(2x)/2
\]

\(W\) energy = Force \(*\) distance
Dynamic Dielectric Measurements:

\[ D = \varepsilon_0 E + P = \varepsilon_0 \varepsilon E \]

Dielectric Displacement

Parallel Analytic Technique to Dynamic Mechanical
(Most of the math was originally worked out for dielectric relaxation)

Simple types of relaxation can be considered, water molecules for instance.

\[ P = \varepsilon_0 (\varepsilon - 1) E \]
\[ D = \varepsilon_0 \varepsilon E \]

dielectric displacement

\( P \) is the resulting polarization
\( E \) is an applied electric field

\( \varepsilon_0 \) Free Space
\( \varepsilon \) Material
\( \varepsilon_d \) Dynamic material

Creep: a constant field \( E_0 \)

\[ P(t) = \varepsilon_0 (\varepsilon_d - 1) E_0 + \varepsilon_0 \Delta\varepsilon(t) E_0 \]

Instantaneous Response
Time-lag Response

Dynamic:

\[ E(t) = E_0 \exp i\omega t \]
\[ P(t) = \exp i(\omega t - \delta) \]

\[ \varepsilon^*(\omega) = \varepsilon'(\omega) - i \varepsilon''(\omega) = \varepsilon_0 + P_0 (\exp -i\delta)/E_0. \]
Modes of Relaxation

water molecules

\[ P_{or} \approx \{\rho \ p^2 \ E/(3kT)\} \]

Rotational Motion at Equilibrium

p is the dipole moment of the water molecules
electric field, E

A single relaxation mode, \( \tau \) relaxation

100/e % or 36.8% of the molecules have reached the equilibrium state
Single-Time Relaxation Processes:

Creep Measurement

$\sigma_{12}^0$ is applied at time $t = 0$ and the strain $\gamma_{12}(t)$ develops with time

Response

$\Delta J \sigma_{12}^0$, where $\Delta J$ is called the relaxation strength

\[ \frac{d\gamma_{12}(t)}{dt}, \text{ changes with time and reaches 0 when the system is at equilibrium} \]

\[ \gamma_{12}(t) = \Delta J \sigma_{12}^0 \]

a linear decay

\[ \frac{dx}{dt} = -kx/\zeta + g(t) \]

\[ \frac{d\gamma_{12}(t)}{dt} = K (\gamma_{12}(t) - \Delta J \sigma_{12}^0) \quad K = \frac{1}{\tau} \]

\[ \gamma_{12}(t) = \Delta J \sigma_{12}^0 (1 - \exp(-t/\tau)) \]

limiting conditions of $\gamma = 0$ at

$t=0$ or for the $t=\infty$ limit of $\gamma = \Delta J \sigma_{12}^0$

http://mathworld.wolfram.com/First-OrderOrdinaryDifferentialEquation.html
Apply to a dynamic mechanical measurement

\[
\frac{d\gamma_{12}(t)}{dt} = K (\gamma_{12}(t) - \Delta J \sigma_{12}^0)
\]

\[
\gamma_{12}(t) = \Delta J \sigma_{12}^0 \left(1 - \exp\left(-\frac{t}{\tau}\right)\right)
\]

\[
\Delta J \sigma_{12}^0, \quad \Delta J \sigma_{12}(t), \quad \sigma_{12}(t) = \sigma_{12}^0 \exp(i\omega t)
\]

\[
\frac{d\gamma_{12}(t)}{dt} = (-1/\tau) (\gamma_{12}(t) - \Delta J \sigma_{12}^0 \exp(i\omega t))
\]

\[
\gamma_{12}(t) = \sigma_{12}^0 J^*(\omega) \exp(i\omega t)
\]

\[
\frac{d\gamma_{12}(t)}{dt} = i\omega \sigma_{12}^0 J^*(\omega) \exp(i\omega t)
\]

\[
J^*(\omega) = \frac{\Delta J}{1 + i\omega \tau}
\]

Single mode
Debye Relaxation
Multiply by \(\frac{(i\omega \tau - 1)}{(i\omega \tau - 1)}\)

\[
J^*(\omega) = J^* - iJ'' = \frac{\Delta J}{1 + \omega^2 \tau^2} - i \frac{\Delta J \omega \tau}{1 + \omega^2 \tau^2}
\]
Single mode
Debye Relaxation

\[ J^*(\omega) = J' - iJ'' = \Delta J \frac{1}{1 + \omega^2 \tau^2} - i \Delta J \frac{\omega \tau}{1 + \omega^2 \tau^2} \]

\[ \Delta J \omega \tau / (1 + \omega^2 \tau^2) = \Delta J / \{ (1/\omega \tau) + \omega \tau \} = \Delta J / \{ 10^{\log \omega \tau} + 10^{\log \omega \tau} \} \]

Symmetric on a log-log plot

![Graphs showing the real and imaginary parts of dynamic compliance](image)

**Fig. 6.5.** Real part (left) and imaginary part (right) of the dynamic compliance associated with a mechanical Debye process
Relationship between the Loss and Storage Compliance for a Debye-Process:

\[ J^*(\omega) = J' - iJ'' = \frac{\Delta J}{1 + \omega^2 \tau^2} - i \frac{\Delta J \omega \tau}{1 + \omega^2 \tau^2} \]

\[ \Delta J \omega \tau / (1 + \omega^2 \tau^2) = \Delta J / \{ (1/\omega \tau) + \omega \tau \} = \Delta J / \{ 10^{\log_{10}\tau} + 10^{\log_{10}\tau} \} \]

\[ \int_{-\infty}^{\infty} J''' \, d \log(\omega \tau) = \frac{\pi}{2 \ln 10} \Delta J \]

"impossible to have a loss compliance without a corresponding (in frequency) change in the storage compliance"
Single mode
Debye Relaxation

The total width at half-height is 1.2 decades.
lower limit for a relaxation process

More complex processes have a broader peak

harmonic oscillator is single valued
a damped harmonic oscillator

Shows a broader peak but much narrower than a Debye relaxation

The width of the loss peak indicates the difference
between a vibration and a relaxation process

Oscillating system displays a moment of inertia
Relaxing system only dissipates energy
Equation for a circle in $J'$-$J''$ space

$$
(x-x_0)^2 + (y-y_0)^2 = K^2
$$

$$
J^* (\omega) = J' - iJ'' = \frac{\Delta J}{1 + \omega^2 \tau^2} - i \frac{\Delta J \omega \tau}{1 + \omega^2 \tau^2}
$$

$$
\left( J' - \frac{\Delta J}{2} \right)^2 + J''^2 = \left( \frac{\Delta J}{2} \left( 1 - \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \right) \right)^2 + \left( \frac{\Delta J \omega \tau}{1 + \omega^2 \tau^2} \right)^2 = \frac{\Delta J^2}{4} \left\{ \frac{1 + 2 \omega^2 \tau^2 + \omega^4 \tau^4}{(1 + \omega^2 \tau^2)^2} \right\}
$$

$$
= \frac{\Delta J^2}{4} \frac{(1 + \omega^2 \tau^2)^2}{(1 + \omega^2 \tau^2)^2} = \frac{\Delta J^2}{4}
$$

**Fig. 6.6.** Cole–Cole plots of dielectric data obtained for a dipole carrying a rod-like molecule of low molar mass *(left)* and a polysiloxane with these molecules attached as side-groups *(right)* [67]
Cole-Cole Plot:

\[
\left( \varepsilon' - \left( \varepsilon_u + \frac{\Delta \varepsilon}{2} \right) \right)^2 + (\varepsilon'')^2 = \frac{\Delta \varepsilon^2}{4}
\]

Fig. 6.6. Cole–Cole plots of dielectric data obtained for a dipole carrying a rod-like molecule of low molar mass (left) and a polysiloxane with these molecules attached as side-groups (right) [67]

The left curve is for a rod molecule with a strong dipole moment that displays a simple Debye-process relaxation. The instantaneous polarization, \( \varepsilon_u \), is about \( \varepsilon_u = 3.73 \) which is determined at the left of the plot (\( \omega \to \infty \) limit). The right intercept, \( \varepsilon' = \varepsilon_u + \Delta \varepsilon \), is at about 5.06 so \( \Delta \varepsilon = 1.33 \). The peak occurs at about \( \varepsilon'' = \Delta \varepsilon/2 = 0.67 \) for \( \varepsilon' = \varepsilon_u + \Delta \varepsilon/2 = 4.40 \).

The right curve is for the same rod-like chemical group attached as a side-group to a polymer chain. For the Debye-process (left curve) we had \( \varepsilon'(\omega \tau) = \varepsilon_u + \Delta \varepsilon/(1 + i \omega \tau) = \varepsilon_u + \Delta \varepsilon (1 - \omega \tau)/(1 + (\omega \tau)^2) \cdot i \omega \tau \Delta \varepsilon/(1 + (\omega \tau)^2) \). A comparison between the simple single-valued relaxation time, Debye-process of the left curve and the deviatory process of the right curve include:

1) Shift of \( \varepsilon_u \) from 3.73 to about 3.89 (larger instantaneous polarization)
2) Shift of \( \Delta \varepsilon \) from 1.33 to 1.71 (larger relaxation strength, \( \Delta \varepsilon \))
3) The center of the relaxation circle occurs at \( \varepsilon' = 4.75 \) which remains close to \( \varepsilon' = \varepsilon_u + \Delta \varepsilon/2 \).
4) Peak value is lower than \( \varepsilon'' = \Delta \varepsilon/2, \varepsilon''_{peak} = 0.69 \) (compare to the expected value of 0.86).

Deviations from the Debye-process in the right curve can be modeled by a Cole-Cole Function that includes a scaling parameter, \( \beta, \varepsilon'(\omega \tau) = \varepsilon_u + \Delta \varepsilon/(1 + i \omega \tau)^\beta \), where \( \beta = 0 \) for a Debye-process. Expansion of this equation yields a coupling between the imaginary and real relaxation terms, \( \varepsilon'(\omega \tau) = \varepsilon_u + \Delta \varepsilon(1 - i \omega \tau)^\beta/(1 + \omega^2 \tau^2)^\beta \).
Relaxation Spectra:

\[ J^*(\omega) = \Delta J \sigma_{12}(t) \]

\[ \sigma_{12}(t) = \sigma_{12}^0 \exp(i\omega t) \]

\[ \frac{d\gamma_{12}(t)}{dt} = \frac{-\gamma(t)}{\tau} + \Delta J \sigma_0 \]

\[ \gamma_{12}(t) = \sigma_{12}^0 J^*(\omega) \exp(i\omega t) \]

By substitution of this expression into the differential equation and solving for the dynamic compliance, \( J^*(\omega) \),

\[ J^*(\omega) = \frac{\Delta J}{1 + i\omega\tau} \]

\[ J^*(\omega) = J' - iJ'' = \frac{\Delta J}{1 + \omega^2\tau^2} - i \frac{\Delta J\omega\tau}{1 + \omega^2\tau^2} \]

A linear sum of Debye-processes is the simplest description of a series of relaxation processes each with a strength of relaxation, \( \Delta J_l \) and a time constant \( \tau_l \),

\[ J^*(\omega) = J_u + \sum_l \frac{\Delta J_l}{1 + i\omega\tau_l} \]

\[ J^*(\omega) = J_u + \int \frac{L_j(\log \tau)}{1 + i\omega\tau} d(\log \tau) \]

\( L_j(\log \tau) \) is called the retardation time spectrum.
For a creep measurement, the strain with time is given by $\gamma_{12}(t) = \Delta J \sigma_{12}^0 (1-\exp(-t/\tau))$. The retardation time spectrum, $L_J(log\tau)$ can be used to describe the creep of a complex material with a relaxation spectrum,

$$J(t) = J_0 \Theta(t) + \int \left\{ 1 - \exp \left( -\frac{t}{\tau} \right) \right\} L_J(log\tau) d(log\tau)$$

where $\Theta(t)$ is 1 for $t>0$ and 0 for $t<0$. 

J*(ω) = J_u + ΔJ/(1 + iωτ))

G*(ω) = 1/J*(ω)

substituting $J_r = J_u + ΔJ \quad \tau = J_u/J_r$, $G_u = 1/J_u$, $G_r = 1/J_r$, and $ΔG = G_u - G_r$

$G^*(ω) = G_u + ΔG/(1 + iωτ)$

$G^*(ω) = G_u - \int \frac{H_G(log\hat{τ})}{1+iω\hat{τ}} d(log\hat{τ})$

$G(t) = G_u \Theta(t) + \int \left\{ \exp \left( \frac{-t}{\hat{τ}} \right) \right\} H_G(log\hat{τ}) d(log\hat{τ})$

$H_G(log\hat{τ})$ is called the relaxation time spectrum for the material.
Boltzmann Superposition

Figure 1.11 Storage and loss moduli for a low density polyethylene "Melt I." (These data were measured at several temperatures and shifted along the frequency axis by a "shift factor" $a_T$ to form collapsed curves; see Section 3.5.2). The lines are empirical fits of Eqs. (3-25a) and (3-25b) to the data. (From Laun 1978, reprinted with permission from Steinkopff Publishers.)

Figure 3.9 (a) Loss modulus $G''$ and (b) storage modulus $G'$ versus frequency computed from Eqs. (3-25a) and (3-25b) for the eight modes given in Table 3-1 for Melt I, a polyethylene melt. Summing up over all the modes gives the "envelope" curves shown; these curves are reproduced in Fig. 1-11, where they are seen to represent accurately the linear data for this melt. (From Laun 1978, reprinted with permission from Steinkopff Publishers.)
Newtonian fluid there would be no storage shear modulus, $G'$.

**Fig. 6.16.** Storage shear moduli measured for a series of fractions of PS with different molar masses in the range $M = 8.9 \times 10^3$ to $5.81 \times 10^5$ g mol$^{-1}$. The dashed line in the upper right corner indicates the slope corresponding to the power law Eq. (8.82) derived for the Rouse model of the glass transition. Data from Onogi et al. [74]

Following the plateau regime a second power law regime is observed in the log-log plot of figure 5.15. The slope in this regime is 2 for a frequency plot and $-2$ for a time plot, $G'(\omega) = K_\eta \omega^2$ or $E(t) = K_\eta t^{-2}$. 

Rouse Dynamics

$G''(\omega) \propto (\eta_0\omega)^{1/2}$
\[ \frac{dJ'}{dt} = \frac{d\gamma_{12}(t)}{dt} \left( \frac{1}{\sigma_{12}} \right) = \frac{1}{\eta} \]

**Fig. 6.12.** General shape of the complete creep curve of PS, as suggested by the appearance of the different parts shown in Fig. 6.11
For a Newtonian fluid, \( \sigma_{xy} = \eta_0 \, d\gamma_{xy}/dt \). If a Newtonian fluid is measured in a dynamic compliance experiment, where, \( \sigma_{xy} = \sigma_{xy}^0 \exp(i\omega t) \) and \( \gamma = J^*\sigma_{xy}^0 \exp(i\omega t) \). Taking the derivative of the strain and inserting into Newton’s law of viscosity yields,

\[
J^* = -i/(\eta_0 \omega)
\]

The Newtonian fluid differs from a polymeric melt in that the Newtonian fluid does not display a recoverable shear compliance, \( J_c^0 \), associated with elasticity of the melt. At the zero-shear rate limit the dynamic compliance for a polymeric fluid is given by,

\[
J^*(\omega\rightarrow0) = J_c^0 - i/(\eta_0 \omega)
\]

Then, the recoverable shear compliance is the real part of the zero shear rate compliance, \( J' \), and the zero-shear rate viscosity is related to the imaginary part of the zero shear rate compliance, \( J'' \).
By taking the inverse of $J^*$ we can obtain $G^*$ as.

$$G^*(\omega \rightarrow 0) = J_e^0 (\omega \eta_0)^2 + i (\omega \eta_0)$$

Then we have well defined power-laws in frequency for $G^*$ and $J^*$ at the zero shear rate limit (low frequency regime) and the recoverable shear compliance and zero shear rate viscosity are the primary parameters of importance. The $\omega^2$ dependence is shown in the first plot of this chapter ($G'$ versus $\omega$ in figure 5.15).
Fig. 9.3  
Master curve at 25°C from oscillatory shear data at six temperatures for a 1,4-polybutadiene sample with $M_w = 130,000$ g mol$^{-1}$. Data from W. W. Graessley, L. J. Felters and R. H. Colby, Macromolecules 20, 2226 (1987).
\[ \psi(t) = \int_{-\infty}^{t} a(t - t') dx(t') \]

and the viscosity, \( \eta \), is the stress, \( \psi(t) \), divided by the strain rate, \( \frac{de}{dt} \), so the zero shear rate viscosity, \( \eta_0 \), (at infinite time, \( t = \infty \)) in a shear experiment where there is no strain before time \( t=0 \), is given by,

\[ \eta_0 = \int_{0}^{\infty} G(t) dt \]
The time dependent modulus, \( a(t) \) or here \( G(t) \), is related to the primary response function by:

\[
\mu(t) = \frac{dG(t)}{dt}
\]

\( J_e^0 \) can also be related to the time dependent modulus and the primary response function by considering a dynamic mechanical experiment where \( e(t) = e_0 \exp(i\omega t) \) and \( \sigma(t) = G^* e(t) \). Using the above equation for the Boltzmann superposition principle:

\[
\sigma(t) = \int_{-\infty}^{t} G(t - t') \dot{e}(t') dt'
\]

taking the derivative of the strain, \( \frac{de}{dt} = i\omega \exp(i\omega t) \) and substituting \( t'' = t - t' \),

\[
G^* = \int_{t''=0}^{\infty} G(t'') i\omega e^{-i\omega t''} dt''
\]
For $\omega \Rightarrow 0$, the exponential can be expanded, $\exp(-iA) = 1 + A + \ldots$, so,

$$G'(\omega \Rightarrow 0) = \omega^2 \int_{t=0}^{\infty} tG(i)dt$$

$$G''(\omega \Rightarrow 0) = \omega \int_{t=0}^{\infty} G(t)dt$$

The first expression can be coupled with the previous expression for $G'$, $G' = J_0^0 (\omega\eta_0)^2$, to yield a description of $J_0^0$,

$$J_0^0 \eta_0^2 = \int_{0}^{\infty} tG(t)dt$$
The ratios of the two integrals that define $J_c^0$ and $\eta_0$, yields a time,

$$\bar{\tau} = \frac{\int_0^\infty tG(t)dt}{\int_0^\infty G(t)dt} = J_c^0\eta_0$$

This time is called the mean viscoelastic relaxation time. For non-entangled melts (below $M_c$) this time is proportional to the molecular weight squared. For entangled melts it is proportional to the molecular weight to the 3.4 power. This is because for entangled melts $J_c^0$ is constant (plateau) and the time is proportional to the viscosity that increases with a 3.4 power experimentally. Below the entanglement molecular weight both $J_c^0$ and the zero shear rate viscosity are proportional to $M$ (as will be discussed later).
\[ \eta(\dot{\gamma}) = \frac{\sigma_{xx}}{\gamma} \]

\[ \Psi_1(\dot{\gamma}) = \frac{(\sigma_{xx} - \sigma_{zz})}{(\dot{\gamma})^2} \]

\[ \Psi_2(\dot{\gamma}) = \frac{(\sigma_{yy} - \sigma_{zz})}{(\dot{\gamma})^2} \]

**Fig. 9.17.** PE under steady state shear flow at 150 °C: Strain rate dependencies of the viscosity \( \eta \), the primary normal stress coefficient \( \Psi_1 \) and the recoverable shear strain \( \gamma_e \). The dotted line represents Eq. (9.157). Results obtained by Laun [116]
Figure 7.15 shows the recoverable shear strain, $\gamma_e$, that is proportional to the recoverable shear compliance, $J_e = \gamma_e/\sigma_{zz}$. At low strain rates the recoverable shear strain is just linear in the rate of strain as indicated by the dashed line. The linear behavior occurs in the regime where the viscosity and first normal stress coefficient are constant. In fact, the dashed line follows a linear function of the viscosity and first normal stress coefficient,

$$\gamma_e(\gamma'\rightarrow0) = \frac{\Psi_1(\gamma'\rightarrow0)}{2\eta(\gamma'\rightarrow0)} \quad \gamma' = \frac{\sigma_{xx} - \sigma_{zz}}{2\sigma_{zx}}$$

then,

$$J_e^0 = \frac{\gamma_e(\gamma'\rightarrow0)}{\sigma_{zx}} = \frac{\Psi_{1,0}}{2\eta_0^2}$$

At low shear rates there remain only two independent parameters that describe polymeric flow.
Fig. 9.3
Master curve at 25°C from oscillatory shear data at six temperatures for a 1,4-polybutadiene sample with \( M_w = 130,000 \text{ g mol}^{-1} \). Data from R. H. Colby, L. J. Fetters and W. W. Graessley, *Macromolecules* 20, 2226 (1987).
Lodge Liquid and Transient Network Model

\[
\sigma(t) = - \int_{t'=-\infty}^{t} G(t - t') \frac{dB(t, t')}{dt'} dt'
\]

\[
B(t, t') = \begin{pmatrix}
1 + (\gamma(t) - \gamma(t'))^2 & 0 & \gamma(t) - \gamma(t') \\
0 & 1 & 0 \\
\gamma(t) - \gamma(t') & 0 & 1
\end{pmatrix}
\]

\[
\sigma_{xx}(t) = \int_{t'=-\infty}^{t} G(t - t') \frac{d\gamma}{dt'} dt'
\]

\[
(\sigma_{xx} - \sigma_{zz})(t) = 2 \int_{t'=-\infty}^{t} G(t - t')(\gamma(t) - \gamma(t')) \frac{d\gamma}{dt'} dt'
\]

\[
\sigma_{yy} - \sigma_{zz} = 0
\]

Simple Shear Finger Tensor

Simple Shear Stress

First Normal Stress

Second Normal Stress
For a Hookean Elastic

\[ G = \text{const} \]

\[
\sigma_{xx}(t) = G\gamma(t),
\]

\[
(\sigma_{xx} - \sigma_{zz})(t) = 2G \int_{t' = 0}^{t} (\gamma(t) - \gamma(t')) \frac{d\gamma}{dt'} dt'
\]

\[ = G\gamma^2(t). \]
For Newtonian Fluid

\[ G(t - t') = \eta \delta(t - t') \]

\[ \sigma_{zz}(t) = \eta \frac{d\gamma}{dt} \]

\[ (\sigma_{xx} - \sigma_{zz})(t) = 0 \]
Fig. 9.17. PE under steady state shear flow at 150°C: Strain rate dependencies of the viscosity $\eta$, the primary normal stress coefficient $\Psi_1$ and the recoverable shear strain $\gamma_e$. The dotted line represents Eq. (9.157). Results obtained by Laun [116]
Dumbbell Model

\[ \frac{dx}{dt} = -(dU/dx)/Z + g(t) = -kx/Z + g(t) \]

\[ x(t) = \int_{-\infty}^{t} dt' \exp \left( \frac{-k(t-t')}{\xi} \right) g(t) \]

Fig. 8.4. Time dependence of the amplitude $Z_m$ of a Rouse mode (schematic)

\[ <x(t_1)x(0)> = kT \exp(-t/t)/k \]
Dilute Solution Chain
Dynamics of the chain
Rouse Motion

Beads 0 and N are special
For Beads 1 to N-1
\[
\frac{dR_i}{dt} = -\frac{k_{spr}}{\xi} \left( R_{i+1} + R_{i-1} - 2R_i \right) + g_i(t)
\]
For Bead 0 use \( R_{-1} = R_0 \) and for bead N \( R_{N+1} = R_N \)
This is called a closure relationship
Dilute Solution Chain

Dynamics of the chain

Rouse Motion

The Rouse unit size is arbitrary so we can make it very small and:

\[
\frac{dR_i}{dt} = -\frac{k_{spr}}{\xi} \left(R_{i+1} + R_{i-1} - 2R_i\right) + g_i(t)
\]

With \(dR/dt = 0\) at \(i = 0\) and \(N\)

\[
\frac{d^2 R}{dt^2} = \frac{-k_{spr}}{\xi} \frac{d^2 R}{di^2} + g_i(t)
\]

Reflects the curvature of \(R\) in \(i\),

it describes modes of vibration like on a guitar string
x, y, z decouple (are equivalent) so you can just deal with z

\[ \zeta_R \frac{dz_i}{dt} = b_R (z_{i+1} - z_i) + b_R (z_{i-1} - z_i) \]

For a chain of infinite molecular weight there are wave solutions to this series of differential equations

\[ z_i \sim \exp \left( -\frac{t}{\tau} \right) \exp(i \delta) \quad \text{Phase shift between adjacent beads} \]

Use the proposed solution in the differential equation results in:

\[ \tau^{-1} = \frac{b_R}{\zeta_R} (2 - 2 \cos \delta) = \frac{4b_R}{\zeta_R} \sin^2 \frac{\delta}{2} \]
For $N_R = 10$.

Fig. 8.2. Relaxation rates of Rouse modes as a function of the phase shift $\delta$. Marks on the inside of the abscissa show the mode positions for a cyclic chain with $N_R = 10$ beads, the marks on the outside give the modes of a linear chain with the same length. The lowest order Rouse modes of the two chains with relaxation rates $\tau_R^{-1}$ are especially indicated by a filled square and a filled circle.

Cyclic Boundary Conditions:

$$z_l = z_{l+N_R}$$

$$N_R \delta = m2\pi$$

$N_R$ values of phase shift

$$\delta_m = \frac{2\pi}{N_R} m; \quad m = -\left(\frac{N_R}{2} - 1\right), \ldots, \frac{N_R}{2}$$

$$\tau^{-1} = \frac{b_R}{\zeta_R} (2 - 2\cos\delta) = \frac{4b_R}{\zeta_R} \sin^2 \frac{\delta}{2}$$
For $N_R = 10$

$$\tau^{-1} = \frac{b_R}{\zeta_R} (2 - 2 \cos \delta) = \frac{4b_R}{\zeta_R} \sin^2 \frac{\delta}{2}$$

**Free End Boundary Conditions:**

$$z_l - z_0 = z_{N_R - 1} - z_{N_R - 2} = 0$$

$$\frac{dz}{dl}(l = 0) = \frac{dz}{dl}(l = N_R - 1) = 0$$

$$(N_R - 1)\delta = m\pi$$

$N_R$ values of phase shift

$N_R$ Rouse Modes of order “m”

$$\delta_m = \frac{\pi}{(N_R - 1)} m; \quad m = 0, 1, 2, \ldots, (N_R - 1)$$
Lowest order relaxation time dominates the response

\[ \tau_R = \frac{1}{3\pi^2} \frac{\left( \frac{\zeta_R}{a_R^2} \right)}{kT} R_0^4 \]

This assumes that \( \left( \frac{\zeta_R}{a_R^2} \right) \)

is constant, friction coefficient is proportional to number of monomer units in a Rouse segment

This is the basic assumption of the Rouse model,

\[ \zeta_R \sim a_R^2 \sim \frac{N}{N_R} = n_R \]
Lowest order relaxation time dominates the response

\[ \tau_R = \frac{1}{3\pi^2} \left( \frac{\zeta_R}{\alpha_R^2} \right) R_0^4 \]

Since \[ R_0^2 = a_0^2 N \]

\[ \tau_R \sim \frac{N^2}{kT} \]
The amplitude of the Rouse modes is given by:

\[ \langle Z_m^2 \rangle = \frac{2}{3\pi^2} \frac{R_0^2}{m^2} \]

The amplitude is independent of temperature because the free energy of a mode is proportional to kT and the modes are distributed by Boltzmann statistics

\[ p(Z_m) = \exp \left( -\frac{\langle F \rangle}{kT} \right) \]

90% of the total mean-square end to end distance of the chain originates from the lowest order Rouse-modes so the chain can be often represented as an elastic dumbbell.
Rouse dynamics (like a dumbbell response)

\[ \frac{dx}{dt} = - \frac{dU}{dx} \frac{dx}{\zeta} + g(t) = - \frac{k_{spr} x}{\zeta} + g(t) \]

\[ x(t) = \int_{-\infty}^{t} \exp \left( - \frac{t-t'}{\tau} \right) g(t') \]

\[ \tau = \frac{\zeta}{k_{spr}} \]

\[ \tau_R = \frac{\zeta_R}{4b_R \sin^2 \frac{\delta}{2}} \]

\[ \delta = \frac{\pi}{N_R - 1} m, \ m=0,1,2,...,N_R - 1 \]
Rouse dynamics (like a dumbell response)

\[ \langle g(t_1) g(t_2) \rangle = 2D \delta(t) \]  where \( t = t_1 - t_2 \)  and \( \delta(\ ) \) is the delta function whose integral is 1

Also,

\[ D = \frac{kT}{\zeta} \]

\[ \langle x(t) x(0) \rangle = \frac{kT \exp\left(-\frac{t}{\tau}\right)}{k_{spr}} \]  \[ \tau = \frac{\zeta}{k_{spr}} \]  For \( t \rightarrow 0 \),

\[ \langle x^2 \rangle = \frac{kT}{k_{spr}} \]
Predictions of Rouse Model

\[ G(t) \sim t^{-\frac{1}{2}} \]

\[ G'(\omega) \sim (\omega \eta_0)^{\frac{1}{2}} \]

\[ \eta_0 = kT \rho_p \tau_R \frac{\pi^2}{12} \sim N \]

Fig. 8.6. Time-dependent shear modulus of PVC. Master curve set up for \( T_g = 65^\circ C \) as the reference temperature. The dashed line indicates the slope predicted by the Rouse model. Data from Eisele [101]
Newtonian Flow  Entanglement Reptation  Rouse Behavior

Fig. 9.3
Dilute Solution Chain

Dynamics of the chain

Rouse Motion

Predicts that the viscosity will follow $N$ which is true for low molecular weights in the melt and for fully draining polymers in solution

Rouse model predicts

Relaxation time follows $N^2$ (actually follows $N^{3/df}$)
Diffusion constant follows $1/N$ (zeroth order mode is translation of the molecule) (actually follows $N^{-1/df}$)

Both failings are due to hydrodynamic interactions (incomplete draining of coil)
Dilute Solution Chain Dynamics of the chain

Rouse Motion

Predicts that the viscosity will follow $N^2$ which is true for low molecular weights in the melt and for fully draining polymers in solution.

Rouse model predicts
Relaxation time follows $N^2$ (actually follows $N^3/df$)
Hierarchy of Entangled Melts

Chain dynamics in the melt can be described by a small set of "physically motivated, material-specific parameters"

- Tube Diameter $d_T$
- Kuhn Length $l_K$
- Packing Length $p$

Parameters $\lambda = k_B T / 6 \pi \eta R$, $\zeta$

Quasi-elastic neutron scattering data demonstrating the existence of the tube

Unconstrained motion ⇒ $S(q)$ goes to 0 at very long times

Each curve is for a different $q = 1/$size

At small size there are less constraints (within the tube)

At large sizes there is substantial constraint (the tube)

By extrapolation to high times a size for the tube can be obtained $d_T$
There are two regimes of hierarchy in time dependence
Small-scale unconstrained Rouse behavior
Large-scale tube behavior

We say that the tube follows a “primitive path”
This path can “relax” in time = Tube relaxation or Tube Renewal

Without tube renewal the Reptation model predicts that viscosity follows $N^3$ (observed is $N^{3.4}$)
Without tube renewal the Reptation model predicts that viscosity follows $N^3$ (observed is $N^{3.4}$).
Reptation predicts that the diffusion coefficient will follow $N^2$ (Experimentally it follows $N^2$).
Reptation has some experimental verification.
Where it is not verified we understand that tube renewal is the main issue.

(Rouse Model predicts $D \sim 1/N$)
Reptation of DNA in a concentrated solution

Fig. 6.13. Series of images of a fluorescently stained DNA chain embedded in a concentrated solution of unstained chains: Initial conformation (left); partial stretching by a rapid move of the bead at one end (second from the left); chain recoil by a reptative motion in the tube (subsequent pictures to the right). Reprinted with permission from T. Perkins, D. E. Smith and S. Chu. Science, 264:819, 1994. Copyright (1994) American Association for the Advancement of Science
Simulation of the tube

Fig. 3. Result of the primitive-path analysis of a melt of 200 chains of $N + 1 = 350$ beads. We show the primitive path of one chain (red) together with all of those it is entangled with (blue). The primitive paths of all other chains in the system are shown as thin lines.
Fig. 3. A representative amorphous polymer sample and the corresponding network of primitive paths.
Plateau Modulus

Not Dependent on N, Depends on T and concentration

\[ G_0 = \frac{4\rho RT}{5M_c} = \frac{4RT}{5p^3} \]

Fig. 5.15. Storage shear moduli measured for a series of fractions of PS with different molecular weights in the range \( M = 8.9 \cdot 10^3 \) to \( M = 5.81 \cdot 10^5 \). The dashed line in the upper right corner indicates the slope corresponding to the power law Eq. (6.81) derived for the Rouse-model of the glass-transition. Data from Onogi et al.[54]
Kuhn Length- conformations of chains  $<R^2> = l_k L$

Packing Length- length were polymers interpenetrate  $p = 1/(\rho_{\text{chain}} <R^2>)$
where $\rho_{\text{chain}}$ is the number density of monomers
Fig. 2. Dimensionless plateau moduli $G_0 l_k^3 / k_B T$ as a function of the dimensionless ratio $l_k / p$ of Kuhn length $l_k$ and packing length $p$. The figure contains (i) experimentally measured plateau moduli for polymer melts (25) (+; colors mark different groups of polymers as indicated) and semidilute solutions (26–28) (∗); (ii) plateau moduli inferred from the normal tensions measured in computer simulation of bead-spring melts (35, 36) (○) and a semi-atomistic polycarbonate melt (37) (◇) under an elongational strain; and (iii) predictions of the tube model Eq. 1 based on the results of our primitive-path analysis for bead-spring melts (■), bead-spring semidilute solutions (●), and the semi-atomistic polycarbonate melt (◇). The line indicates the best fit to the experimental data for polymer melts by Fetters et al. (24). Errors for all the simulation data are smaller than the symbol size.

this implies that $d_T \sim p$
Fig. 1. Schematic representation of dual slip-links. (a) Chains coupled by virtual links. (b) Dual slip-links. (c) Real space representation of the corresponding network of primitive paths.
McLeish/Milner/Read/Larsen Hierarchical Relaxation Model
