Dilute Solution Chain
Dynamics of the chain

For Viscous Motion (a relaxatory system)
\[ m \left( \frac{dV}{dt} \right) = -6\pi \eta a V \quad F = ma = \zeta V \]
\[ V = V_0 \exp\left(-6\pi \eta a (t_1 - t_2)/m\right) = V_0 \exp\left(-t_1 - t_2)/\tau_v\right) \quad \text{Integrate} \]

Position is the integral of velocity dt
\[ x(t) = \int_{-\infty}^{t} dt' \exp\left(-k_{spr} \left(t - t'\right)/\xi\right) g(t') \]

The exponential term is the “response function”
response to a pulse perturbation
\( g(t) \) is random \( \pm \) pulses due to \( kT \)

Fig. 5.4. Primary response function of a damped harmonic oscillator \( (a) \), a perfectly viscous body \( (b) \), a Hookean solid \( (c) \), a simple relaxatory system \( (d) \)
Simple exponential relaxor

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

For Brownian motion of a harmonic bead in a solvent this response function can be used to calculate the time correlation function \( <x(t)x(0)> \) for DLS for instance.

\[ <x(t)x(0)> = \int_{-\infty}^{t} dt_1 \int_{-\infty}^{0} dt_2 \exp\left[-k_{spr} (t_1 - t_2 - t)/\xi\right] <g(t_1)g(t_2)> \]

\[ <g(t_1)g(t_2)> = \frac{2kT}{\xi} \delta(t_1 - t_2) \]

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

\( \tau \) is a relaxation time.

\[ \tau = \frac{\xi}{k_{spr}} \]
Draining vs Non-Draining
Rouse vs Zimm

Consider Diffusion of a Chain

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

For Non-Draining
\[ G'(\omega) \approx \frac{\phi k T}{b^3 N} \frac{\left(\omega \tau_R\right)^2}{\sqrt{1 + (\omega \tau_R)^2}} \left[ \frac{\sqrt{1 + (\omega \tau_R)^2} + 1}{\sqrt{1 + (\omega \tau_R)^2} + 1} \right] \quad \text{for } \omega < 1/\tau_0. \quad (8.49) \]

\[ G''(\omega) \approx \frac{\phi k T}{b^3 N} \omega \tau_R \sqrt{1 + (\omega \tau_R)^2 + 1} \quad \text{for } \omega < 1/\tau_0. \quad (8.50) \]

\[ G'(\omega) \approx G''(\omega) \sim \omega^{1/2} \quad \text{for } 1/\tau_R \ll \omega \ll 1/\tau_0. \quad (8.51) \]

Fig. 8.5
Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus \( G' \) and filled symbols are the loss modulus \( G'' \). Squares have \( c = 0.5 \text{ g L}^{-1} \), triangles have \( c = 1.0 \text{ g L}^{-1} \), and circles have \( c = 2.0 \text{ g L}^{-1} \). The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* 94, 4581 (1991).
Dilute Solution Chain

Dynamics of the chain

Rouse Motion

\[ E = \frac{k_{spr}}{2} \sum_{i=1}^{N} (R_i - R_{i-1})^2 \]

\[ \frac{dR_i}{dt} = -\frac{dE/dR_i}{\xi} + g_i(t) \]

\[ \xi = 6\pi\eta_{\text{solvent}}a \]

Beads 0 and N are special

For Beads 1 to N-1

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

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

\[ \frac{dR_i}{dt} = -\frac{k_{spr}}{\xi} (R_{i+1} + R_{i-1} - 2R_i) + \dot{g}_i(t) \]

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

\[ \frac{dR}{dt} = -\frac{k_{spr}}{\xi} \frac{d^2 R}{dt^2} + \dot{g}_i(t) \]

With \( \frac{dR}{dt} = 0 \) at \( i = 0 \) and \( N \)

\[ \frac{d^2 R}{di^2} \]

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

it describes modes of vibration like on a guitar string
Dilute Solution Chain
Dynamics of the chain
Rouse Motion

\[ \frac{d^2 R}{dt^2} \]

Describes modes of vibration like on a guitar string

For the “p’ th” mode (0’ th mode is the whole chain (string))

\[ k_{spr,p} = \frac{2p^2 \pi^2 k_{spr}}{N} = \frac{6\pi^2 kT}{Nb^2} p^2 \]

\[ \xi_p = 2N\xi \quad \xi_0 = N\xi \]

\[ \tau_p = \frac{\xi_p}{k_{spr,p}} = \frac{2N^2 b^2 \xi}{3\pi^2 p^2 kT} \]
x, y, z decouple (are equivalent) so you can just deal with z

\[ \zeta_R \frac{dz_l}{dt} = b_R (z_{l+1} - z_l) + b_R (z_{l-1} - z_l) \]

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

\[ z_l \sim \exp \left( -\frac{t}{\tau} \right) \exp(i\delta) \]

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

\[ \tau^{-1} = \frac{b_R}{\zeta_R} \left( 2 - 2 \cos \delta \right) = \frac{4b_R}{\zeta_R} \sin^2 \frac{\delta}{2} \]

Cyclic Boundary Conditions:

\[ z_l = z_{l+N_R} \]

\[ N_R \delta = m2\pi \]

$N_R$ values of phase shift

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

$$z_1 - z_0 = z_{N_R-1} - z_{N_R-2} = 0$$

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

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

$N_R$ 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

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

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,

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

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

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 dumbell response)

\[
\begin{align*}
\frac{dx}{dt} &= -\left(\frac{dU}{dx}\right)\frac{\zeta}{\zeta} + g(t) = -\frac{k_{spr}x}{\zeta} + g(t) \\
\tau &= \frac{\zeta}{k_{spr}} \\
x(t) &= \int_{-\infty}^{t} dt' \exp\left(-\frac{t-t'}{\tau}\right)g(t') \\
\tau_R &= \frac{\zeta_R}{4b_R \sin^2 \frac{\delta}{2}} \\
\delta &= \frac{\pi}{N_R - 1} m, \quad m=0,1,2,\ldots,N_R-1
\end{align*}
\]
Rouse dynamics (like a dumbell response)

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

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

\[ \langle x(t)x(0) \rangle = \frac{kT \exp\left(-\frac{t}{\tau}\right)}{k_{spr}} \quad \tau = \frac{\zeta}{k_{spr}} \quad \text{For } t \to 0, \quad \langle x^2 \rangle = \frac{kT}{k_{spr}} \]
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. 6.6. Time dependent shear modulus of PVC. Master curve set up for \( T_g = 65^\circ\text{C} \) as the reference temperature. The dotted line indicates the slope predicted by the Rouse model. Data from Eisele [66]
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 $N$ 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 $N^3/df$)