Dilute Solution Chain
Dynamics of the chain

For Viscous Motion (a relaxatory system)

$m\,(dV/dt) = -6\pi\eta_s a\,V$ $\qquad F = ma = \zeta V$

$V = V_0\exp(-6\pi\eta_s a\,(t_1 - t_2)/m) = V_0\exp(-(t_1 - t_2)/\tau_V)$ Integrate

Position is the integral of velocity dt

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

The exponential term is the "response function"
response to a pulse perturbation
***g*(t) is random ± pulses due to kT**

5.1 Response Functions 199

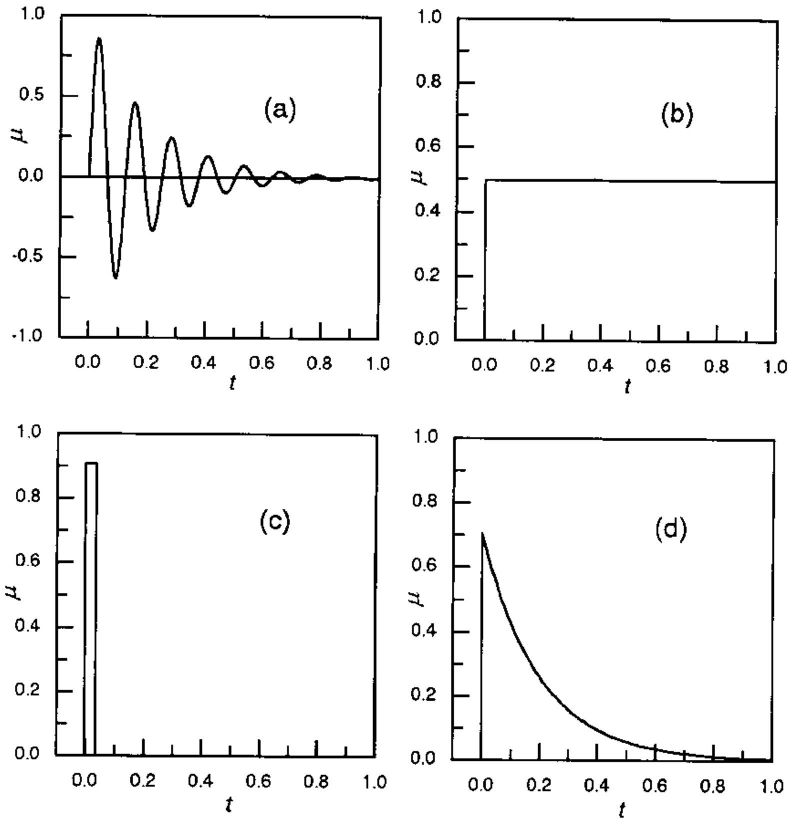
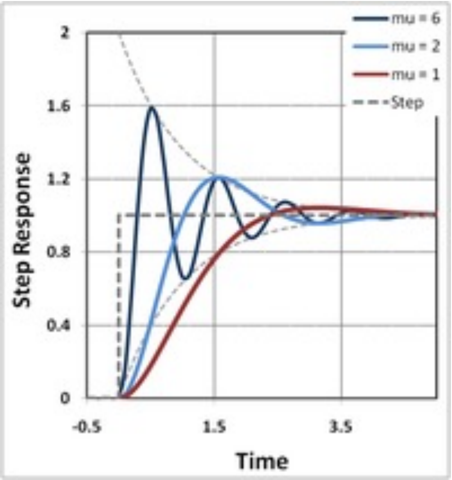


Fig. 5.4. Primary response function of a damped harmonic oscillator (a), a perfectly viscous body (b), a Hookean solid (c), a simple relaxatory system (d)

Dilute Solution Chain
Dynamics of the chain

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



Simple exponential relaxor

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

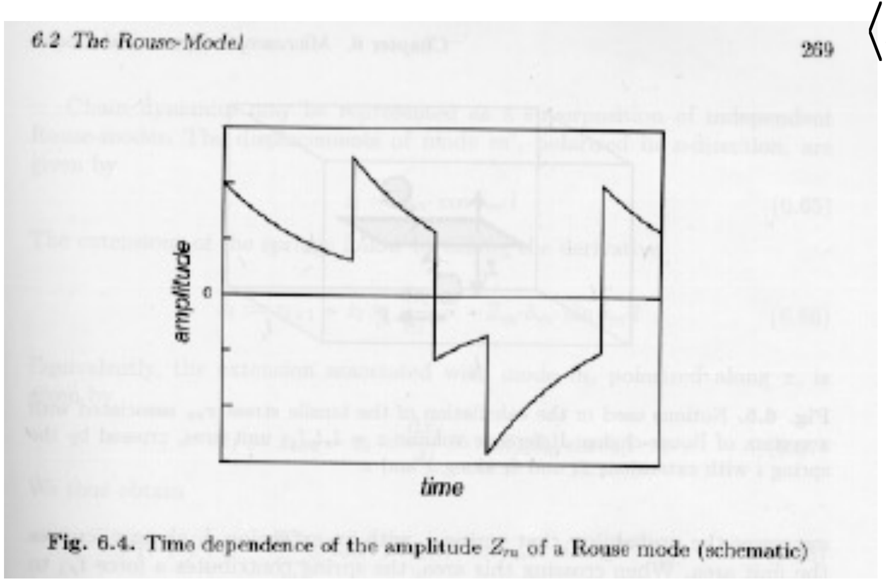

6.2 The Rouse Model 269

Fig. 6.4. Time dependence of the amplitude $Z_{\tau n}$ of a Rouse mode (schematic)

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

$$\langle g(t_1)g(t_2)\rangle = \frac{2kT}{\xi}\partial(t_1-t_2)$$

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

τ is a relaxation time.

$$\tau = \frac{\xi}{k_{spr}}$$

Draining vs Non-Draining
Rouse vs Zimm

Consider Diffusion of a Chain

$D = kT/\zeta$

For Non-Draining

$$G'(\omega) \approx \frac{\phi kT}{b^3 N} \frac{(\omega\tau_{\mathrm{R}})^2}{\sqrt{[1+(\omega\tau_{\mathrm{R}})^2]\left[\sqrt{1+(\omega\tau_{\mathrm{R}})^2}+1\right]}} \quad \text{for } \omega < 1/\tau_0, \tag{8.49}$$

$$G''(\omega) \approx \frac{\phi kT}{b^3 N} \omega\tau_{\mathrm{R}} \sqrt{\frac{\sqrt{1+(\omega\tau_{\mathrm{R}})^2}+1}{1+(\omega\tau_{\mathrm{R}})^2}} \quad \text{for } \omega < 1/\tau_0. \tag{8.50}$$

$$G'(\omega) \cong G''(\omega) \sim \omega^{1/2} \quad \text{for } 1/\tau_{\mathrm{R}} \ll \omega \ll 1/\tau_0. \tag{8.51}$$

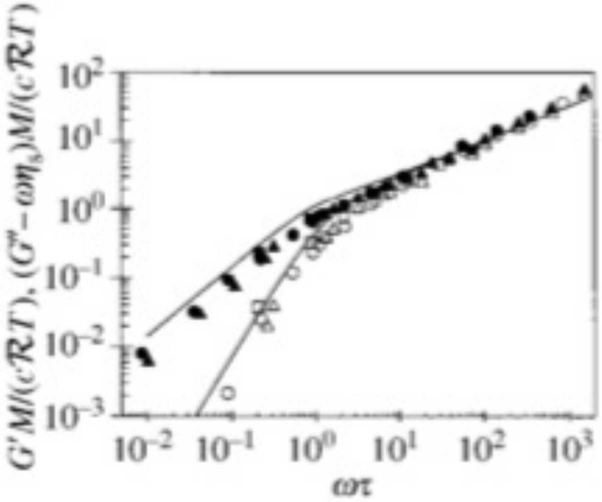


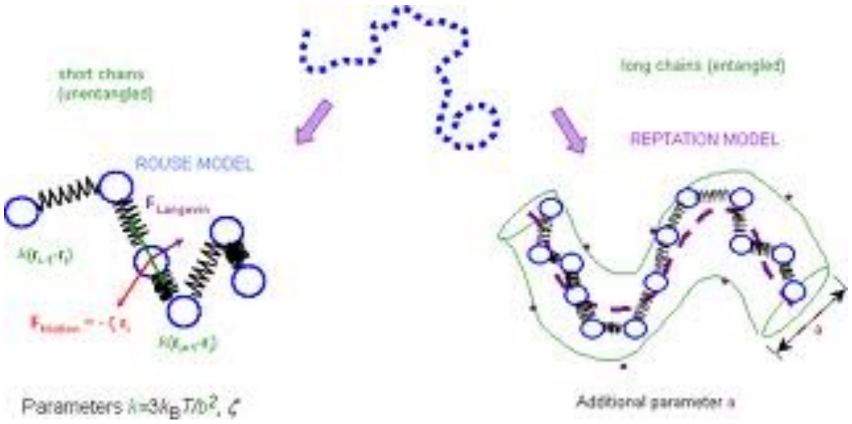
Fig. 8.5

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 $c = 0.5\,\mathrm{g\,L^{-1}}$, triangles have $c = 1.0\,\mathrm{g\,L^{-1}}$, and circles have $c = 2.0\,\mathrm{g\,L^{-1}}$. 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



$$E = \frac{k_{spr}}{2} \sum_{i=1}^{N} \left(R_i - R_{i-1} \right)^2$$

$$\frac{dR_i}{dt} = \frac{-\left(dE/dR_i \right)}{\xi} + g_i(t)$$

$$\xi = 6\pi\eta_{solvent} a$$

Beads 0 and N are special

For Beads 1 to N-1

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

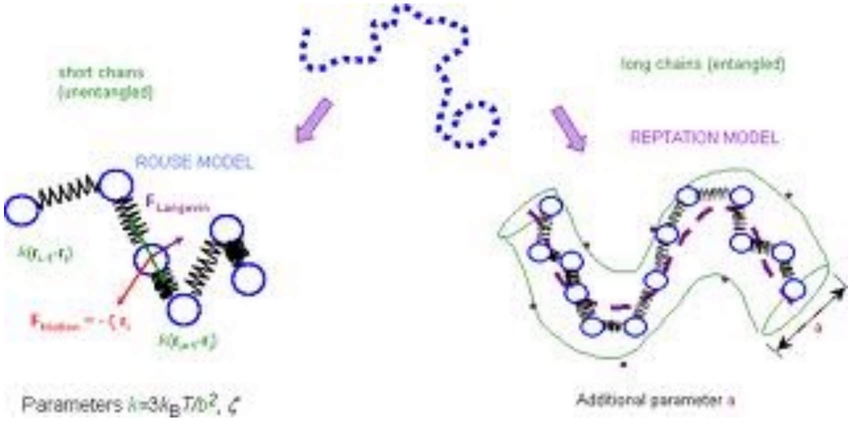
For Bead 0 use $R_{-1} = R_0$ and for bead N $R_{N+1} = R_N$

This is called a closure relationship

Dilute Solution Chain

Dynamics of the chain

Rouse Motion



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

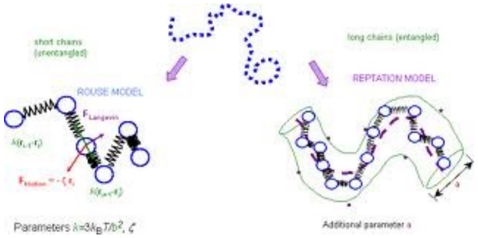
The Rouse unit size is arbitrary so we can make it very small and:

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

With dR/dt = 0 at i = 0 and N

$$\frac{d^2R}{di^2}$$

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

$$\frac{d^2 R}{di^2}$$ Describes modes of vibration like on a guitar string

For the "p' th" mode (0' th mode is the whole chain (string))

$$k_{spr,p} = \frac{2p^2\pi^2 k_{spr}}{N} = \frac{6\pi^2 kT}{Nb^2} p^2 \qquad \xi_p = 2N\xi \qquad \xi_0 = N\xi$$

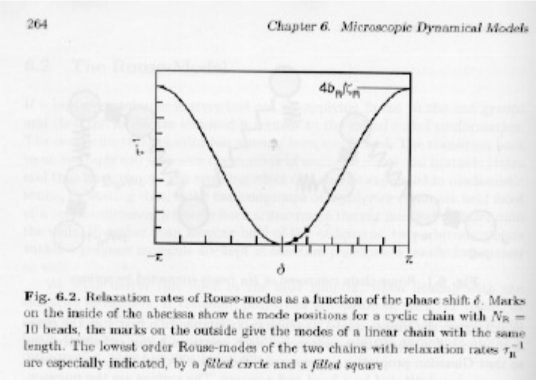
$$\tau_p = \frac{\xi_p}{k_{spr,p}} = \frac{2N^2 b^2 \xi}{3\pi^2 p^2 kT}$$

x, y, z decouple (are equivalent) so you can just deal with z

$$\varsigma_R \frac{dz_l}{dt} = b_R(z_{l+1} - z_l) + b_R(z_{l-1} - z_l)$$

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

$$z_l \sim \exp\left(-\frac{t}{\tau}\right)\exp(il\delta)$$



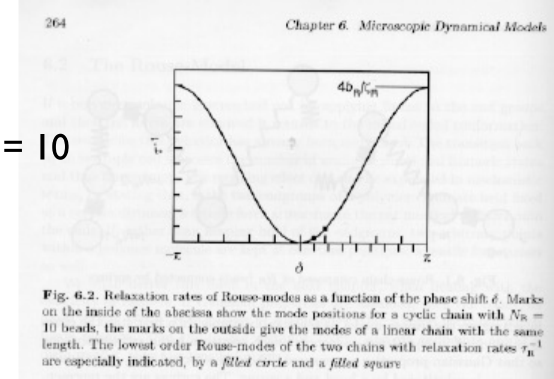
264

Chapter 6. Microscopic Dynamical Models

Fig. 6.2. Relaxation rates of Rouse-modes as a function of the phase shift δ. 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 τ_R^{-1} are especially indicated, by a *filled circle* and a *filled square*

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

For N_R = 10



264 *Chapter 6. Microscopic Dynamical Models*

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

Cyclic Boundary Conditions:

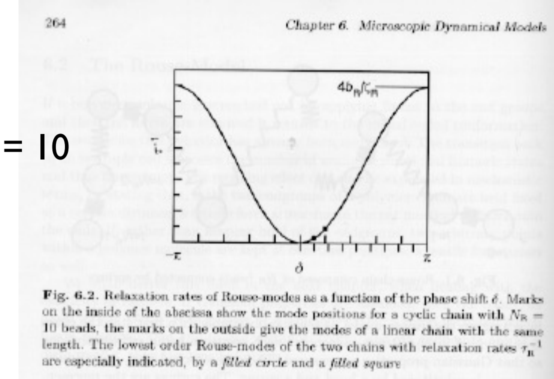
$$z_l = z_{l+N_R}$$

$$N_R\delta = m2\pi$$

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 $N_R = 10$


264 Chapter 6. *Microscopic Dynamical Models*

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

Free End Boundary Conditions:

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

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

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

N_R values of phase shift

N_R Rouse Modes of order "m"

$$\delta_m = \frac{\pi}{\left(N_R - 1\right)}m; \quad m = 0,1,2,\ldots,\left(N_R - 1\right)$$

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

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

Since $R_0^2 = a_0^2 N$

$$\tau_R \sim \frac{N^2}{kT}$$

The amplitude of the Rouse modes is given by:

$$\left\langle Z_m^2 \right\rangle = \frac{2}{3\pi^2} \frac{R_0^2}{m^2}$$

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

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

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

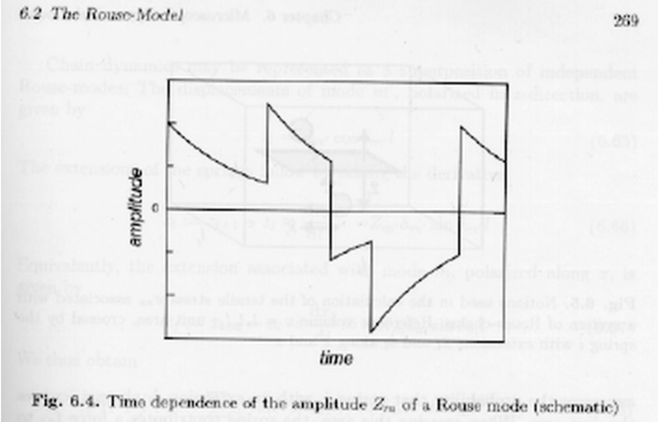


Fig. 6.4. Time dependence of the amplitude Z_{rn} of a Rouse mode (schematic)

Rouse dynamics (like a dumbell response)

Dumbbell

$$\frac{dx}{dt} = -\frac{\left(\frac{dU}{dx}\right)}{\zeta} + g(t) = -\frac{k_{spr}x}{\zeta} + g(t)$$

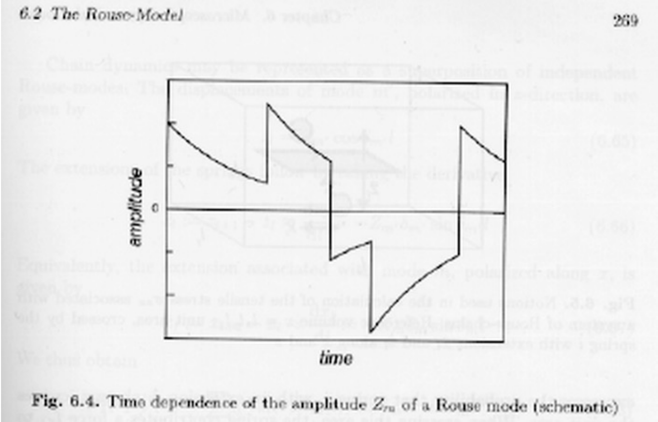
$$x(t) = \int_{-\infty}^{t} dt' \exp\left(-\frac{t-t'}{\tau}\right) g(t)$$

$$\tau = \frac{\zeta}{k_{spr}}$$

Rouse

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

$$\delta = \frac{\pi}{N_R - 1} m \ , \quad \text{m=0,1,2,...,N}_\text{R}\text{-1}$$



6.2 The Rouse-Model 269

Fig. 6.4. Time dependence of the amplitude Z_{ru} of a Rouse mode (schematic)

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, $D = \dfrac{kT}{\zeta}$

$\langle x(t) x(0) \rangle = \dfrac{kT \exp\left(-\dfrac{t}{\tau}\right)}{k_{spr}}$ $\tau = \dfrac{\zeta}{k_{spr}}$ For t => 0, $\langle x^2 \rangle = \dfrac{kT}{k_{spr}}$

Predictions of Rouse Model

6.2 The Rouse-Model 273

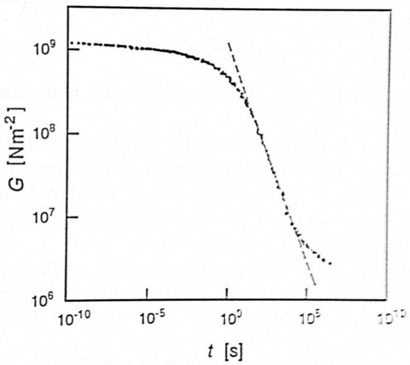
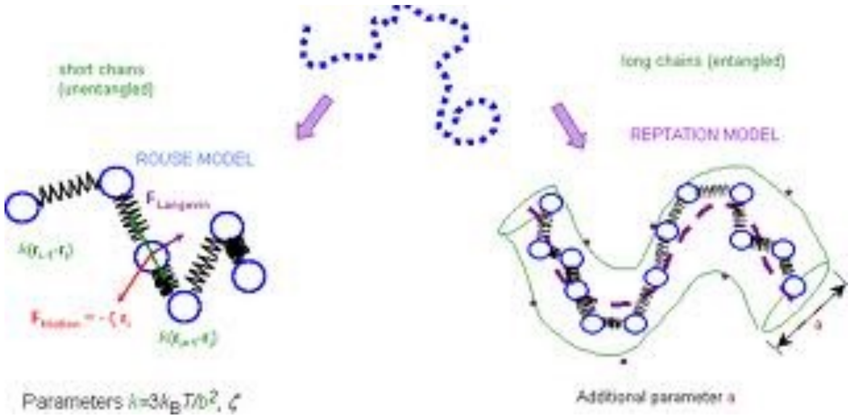


Fig. 6.6. Time dependent shear modulus of PVC. Master curve set up for T_g = 65 °C as the reference temperature. The *dashed line* indicates the slope predicted by the Rouse-model. Data from Eisele [66]

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

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

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



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

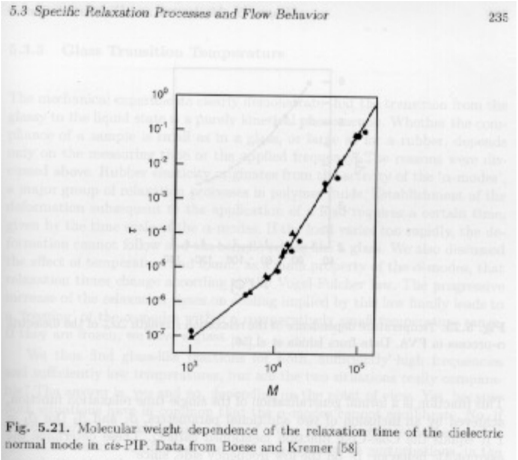


Fig. 5.21. Molecular weight dependence of the relaxation time of the dielectric normal mode in *cis*-PIP. Data from Boese and Kremer [58]

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

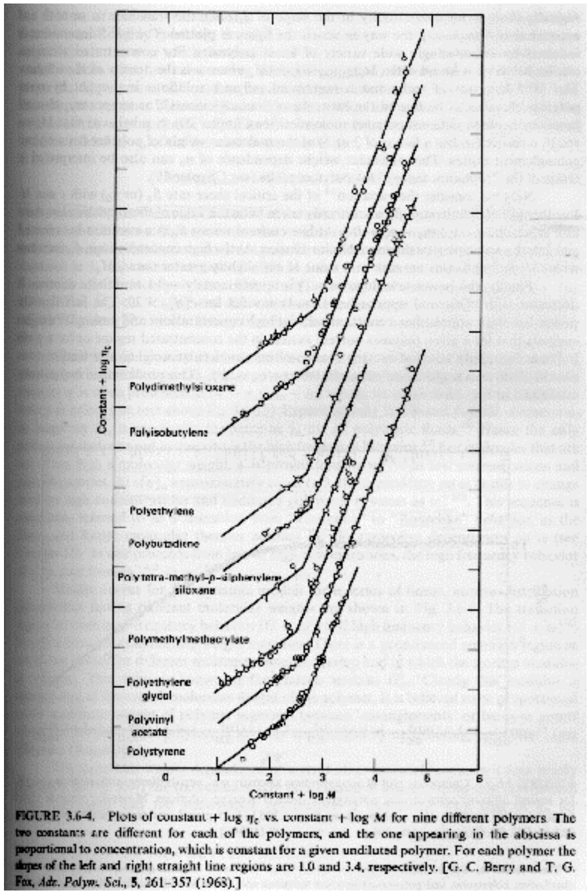


FIGURE 3.6-4. Plots of constant + log η_c vs. constant + log M for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, 5, 261–357 (1968).]

Rouse model predicts
Relaxation time follows N^2 (actually follows N^3/df)