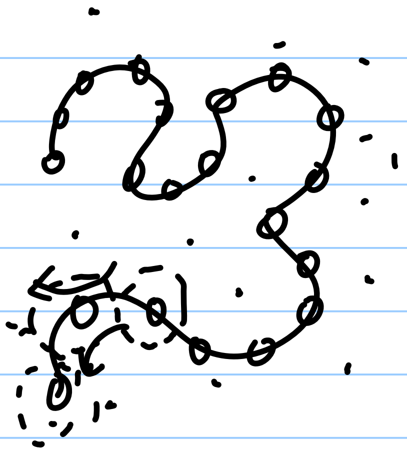
Polymer dynamics Week 7.

Dilute solns : polymer as ideal coil



- polymer thermal motion
- polymor solvent interaction
- solvent movement affect polymer motion (hydrodynamic Interaction)

treat polymer beads as Browdan particles

Exp't shows that the dynamics of polymers on scale > blob size is generally independent of local monomer structure. (blob is the segment correlation length)

polymer ≃ chain of blobs.

Solvent : consider as a continuum fluid
- exert fluctuating force & friction on polymer beads

EOM polymer : Langevin Eqn. for the N polymer blobs

$\Rightarrow$ N - coupled EOM

Langevin Equ.

$$M \frac{d\vec{V}_\alpha}{dt} = \vec{F}_\alpha$$

α = particle α

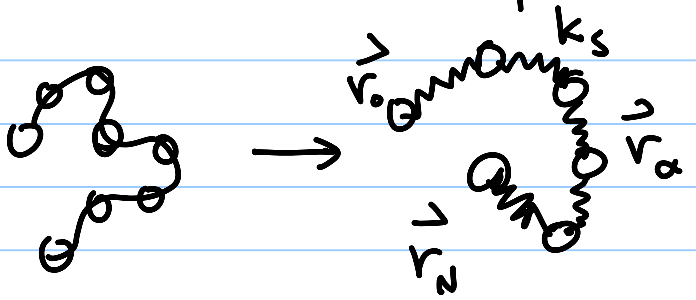
↗ acceleration

↑ total force on α

Consider over damped in solvent
polymer is purely diffusive : $\frac{d\vec{V}_\alpha}{dt} \to 0$

$\vec{F}_\alpha$ has multiple components.

(1) connectivity



$$U_{\text{intrapolymer}}(\{\vec{r}_\alpha\}) = \frac{1}{2} k_s \sum_{\alpha=1}^{N-1} (\vec{r}_\alpha - \vec{r}_{\alpha+1})^2$$

$$+ \sum_{\alpha>\gamma=1}^{N} \cancel{U}^{\text{exc.vol.}}$$

↙ 0 for ideal chains

$$\vec{F}_\alpha^{\,\text{intra}} = -\frac{\partial U}{\partial \vec{r}_\alpha}$$

linear Hooke's law

(2) local forces between polymer segments & solvent

$$\vec{F}_\alpha^{fric} = -\zeta \left(\vec{V}_\alpha - \underbrace{\vec{V}_{fluid}(\alpha)}_{0} \right)$$

$$= -\zeta \vec{V}_\alpha$$

(3) Brownian fluctuations (thermal)

$\delta \vec{f}_\alpha(t)$ = fluctuating random force on α (Gaussian)

$$\langle \delta \vec{f}_\alpha(t) \rangle = 0$$

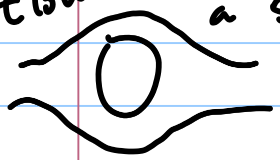
in one coordinate $\langle \delta \vec{f}_\alpha(t') \, \delta \vec{f}_\beta(t') \rangle = 2kT \zeta \, \delta_{\alpha\beta} \, \delta_{tt'}$

" fluctuation - dissipation theorem).

ζ = friction coef. of blob = $6\pi \eta_{solvent} \frac{b}{2}$

$b \equiv$ blob size

flow around a sphere



(Einstein - Stokes Reletion)

$D = \frac{kT}{\zeta}$ Diffusivity of a blob

(4) Hydrodynamic Interactions

purely solvent mediated force between N-connected polymer segments

"long range" $\sim \frac{1}{r}$ Couple all segments

depends on the instanteneous configuration of polymer.

Generally, accounting all 4 effects are important. Very complex even for ideal coil

2 Classical models

I. Rouse model (1950s).

--- ignores hydrodynamics

assumes (i) ideal solvent

(ii) No HI

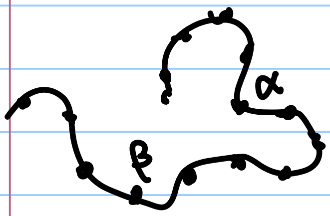
- turn out that (ii) is never valid for polymers in soln.
- Has several importent physical aspects.

- Surprising good for dense polymer melts of "short, unentangled chains"

II Zimm model (1960s)

Rouse model + approx. inclusion of HI.

preaverages HI. $R_g \sim N^{1/2}$

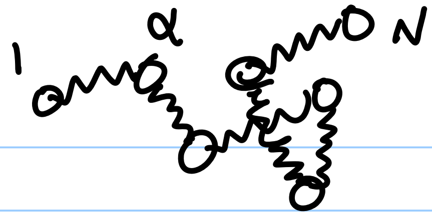


$$V_\alpha(t) = H_{\alpha\beta}(t)\, V_\beta(t)$$

velocity of α

preaveraged HI tensor

Rouse model



N segments → N coupled EOM.

$$M \cancelto{0}{\frac{d\vec{V}_\alpha}{dt}} = \vec{F}_\alpha(t) \qquad \alpha = 1..N$$

$\alpha = 2, 3, \ldots N-1$

$$0 = -k_s(2\vec{r}_\alpha - \vec{r}_{\alpha+1} - \vec{r}_{\alpha-1}) - \zeta \vec{V}_\alpha(t) + \delta\vec{f}_\alpha(t)$$

$\alpha = 1, N$

$$\begin{cases} 0 = -k_s(\vec{r}_1 - \vec{r}_2) - \zeta \vec{V}_1(t) + \delta\vec{f}_1(t) \\ 0 = -k_s(\vec{r}_{N-1} - \vec{r}_N) - \zeta \vec{V}_N(t) + \delta\vec{f}_N(t) \end{cases}$$

⇒ a system of N linear coupled eqns w/ const. coefs.

→ 1st order stochastic differential eqns.

N- coupled oscillators ⇒ Normal mode analysis

"Normal coordinates" "Phonons"

Collective quantities

Dynamics of each mode is independent (orthogonal)

mode $\left\{ \begin{array}{l} \vec{X}_p \equiv \frac{1}{N} \sum_{\alpha=1}^{N} \cos\left(\frac{p\pi\alpha}{N}\right) \vec{r}_\alpha(t) \\ \uparrow \\ \text{mode index} \\ p = 0, \dots\dots N-1 \\ \langle \vec{X}_p(t)\, \vec{X}_q(t) \rangle = 0 \end{array} \right.$

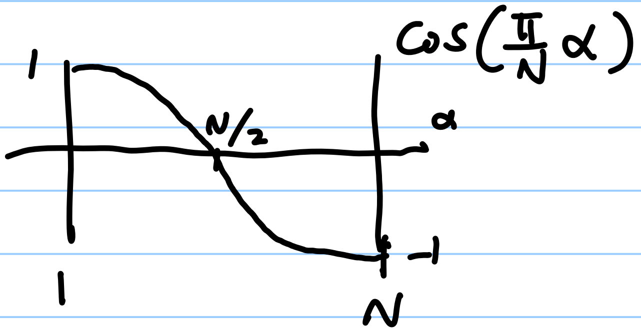
Cosine transform

if $p \neq q$.

Rouse modes ≃ "standing waves" along chain backbone

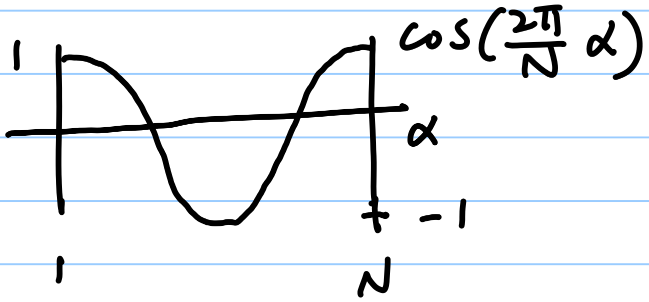
$p=0$: Center of mass motion

$p=1$:



Sensitive to the orientation of whole polymer

$p=2$:



divides chain into two halves & probe the orientation of 2 halves

As $p \uparrow$, modes further decompose chain into smaller units. Smallest unit = length of segment

Cosine transform can be inverted

$$\vec{X}_p = \frac{1}{N}\sum_{\alpha=1}^{N} \vec{r}_\alpha(t)\cos\left(\frac{p\pi}{N}\alpha\right)$$

$$\vec{r}_\alpha = \vec{X}_0(t) + 2\sum_{p=1}^{N-1}\cos\left(\frac{p\pi}{N}\alpha\right)\vec{X}_p(t)$$

① Internal mode displacements

$$C_{pp'}(t) \equiv \left\langle \vec{X}_{p'}(0)\,\vec{X}_p(t)\right\rangle$$

Cosine transform of N-EOM

Eqn. (1) $$\zeta_p \frac{\partial}{\partial t}\vec{X}_p(t) = -k_p\vec{X}_p(t) + \delta\vec{f}_p(t).$$

Eqn. (2) $$\begin{cases} \zeta_p = \begin{cases} 2N\zeta & , \ p>0 \\ N\zeta & , \ p=0. \end{cases} \\ k_p = \text{spring const. of mode } p = 2\pi^2 k_s \frac{p^2}{N} \end{cases}$$

$$k_s = \frac{3kT}{b^2} \Rightarrow \boxed{k_p = \frac{6\pi^2}{Nb^2}kT\,p^2}$$

Eq. (3)
$$\begin{cases} \langle \delta \vec{f}_p(t) \rangle = 0 \\ \langle \delta \vec{f}_p(0) \cdot \delta \vec{f}_{p'}(t) \rangle = 6 \delta_t \, \delta_{p,p'} k_B T \zeta_p \end{cases}$$

use Equs. (1), (2), & (3) to find

D_{CoM}, $\langle \delta R_{CM}^2 \rangle$, $\langle \delta \vec{r}_\alpha(t) \rangle$

(i) $$C_{pp'} = \langle \vec{x}_{p'}(0) \cdot \vec{x}_p(t) \rangle$$

Take Eqn. (1) & multiply by $\vec{x}_{p'}(0)$ then $\langle " \rangle$

$$\Rightarrow \zeta_p \frac{\partial}{\partial t} \langle \vec{x}_{p'}(0) \vec{x}_p(t) \rangle = - k_p \langle \vec{x}_{p'}(0) \vec{x}_p(t) \rangle + \underbrace{\langle \delta \vec{f}_p(t) \cdot \vec{x}_{p'}(0) \rangle}_{0.}$$

$$\Rightarrow \zeta_p \frac{\partial}{\partial t} C_{pp'}(t) = - k_p C_{pp'}(t)$$

$$\Rightarrow C_{pp'}(t) = C_{pp'}(0) \, e^{-\frac{k_p}{\zeta_p} t}$$

$$\begin{cases} C_{pp}(0) = \langle \vec{x}_p(0)^2 \rangle = \dfrac{3 k_B T}{k_p}. & \text{for } p = p' \\ C_{pp'}(0) = 0 & \text{if } p \neq p' \end{cases}$$

$$C_{pp'}(t) = \delta_{p,p'} \frac{3k_BT}{k_p} e^{-t/\tau_p}$$

$$\tau_p \equiv \frac{\zeta_p}{k_p} = \underbrace{\left(\frac{\zeta N^2 b^2}{3\pi^2 k_B T}\right)}_{}\frac{1}{p^2}$$ (Rouse relaxation time of mode p)

τ_R = longest relaxation time of internal modes.

(i) $\tau_R \propto \frac{N^2 \zeta}{T}$

(ii) $\tau_p \propto \frac{1}{p^2}$ ⇒ faster relaxation as cooperative length scale decreases.

② Center-of-mass motion

$$\vec{X}_{p=0}(t) = \frac{1}{N}\sum_{\alpha=1}^{N} \vec{r}_\alpha(t).$$

sub. into Equ. (1)

$$\langle \vec{X}_0(t)\vec{X}_0(0)\rangle = \langle \vec{X}_0^{\,2}\rangle e^{-t/\tau_p}\Big|_{p=0.}$$

$$\langle \vec{X}_0^{\,2}\rangle = \frac{3k_BT}{k_p} \to \infty \quad \text{as } p \to 0.$$

COM diffusion is unbounded over macroscopic distances $\tau_p \to \infty$ as $p \to 0$

$$\langle (\vec{x}_0(t) - \vec{x}_0(0))^2 \rangle$$

$$= 2 \left[\langle \vec{x}_0(0) \rangle^2 - \langle \vec{x}_0(0) \cdot \vec{x}_0(t) \rangle \right]$$

$$= 2 \underbrace{\langle \vec{x}_0^{\,2}(0) \rangle}_{\to \infty} \left[1 - \underbrace{e^{-t/\tau_p} \Big|_{p \to 0}}_{\to 0} \right].$$

Eqn. 2. ↳

$$= \frac{6 k_B T t}{\zeta_{p=0}} = \frac{6 \boxed{k_B T} t}{\boxed{N \zeta_0}}$$

← friction of a segment.

CoM diffusion coef.

$$\langle \Delta r^2 \rangle = 6 D t \qquad D_{CoM} = \frac{k_B T}{\boxed{N \zeta_0}}$$

← friction of polymer

$$\zeta_{polymer} = N \zeta_0$$

total friction on a polymer is the sum of individual contributions.

Summary of Rouse model

- relaxation time of mode $p \sim \frac{1}{p^2}$
- $D_{polymer} \sim \frac{1}{N}$

Expt's of DNA in free soln.
show $D \sim \frac{1}{N^{0.6}}$

$$\tau_p \not\propto \frac{1}{p^2}.$$

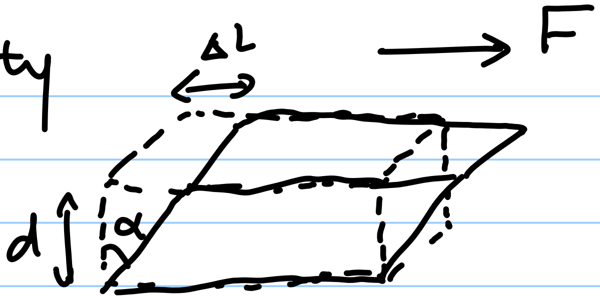
Rouse model fails of polymers in soln.
– neglects HI

When HI is not important in Expt's
(melt, confined DNA, narrow slit or channel)
Rouse model works

Dilute solns : need to account for
HI.

Sidetrack

Viscoelasticity



defimation is characterized by ΔL.

Shear stress $S = \frac{F}{A}$ A = area that F acts on

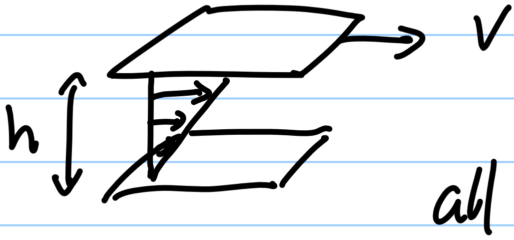
Strain $\gamma = \tan\alpha = \frac{\Delta L}{d}$

① For ideal elestic solid, all mechanical energy is stored, no dissipation

$$S = G \cdot \gamma$$

↑ shear modulus

② For ideal fluid



$\dot{\gamma} = \frac{v}{h} = \frac{\partial v_x}{\partial y} =$ shear rate

all mechanical energy is dissipated by moving fluid

$$S = \frac{F_x}{A} = \eta\,\dot{\gamma}$$

↑ viscosity of fluid

Viscoelasticity : How "solid-like" or "fluid-like" is the matenal as a fcn. of time?

timescale ⟷ "frequency" of probe

$$\omega = \frac{2\pi}{t}$$

Define instantaneous stress $S(t;\dot{\gamma})$

Define transient viscosity $\eta^{+}(t,\dot{\gamma}) = \frac{S(t;\dot{\gamma})}{\dot{\gamma}}$

⇒ info. about structure changes in complex fluid.

For "linear" viscoelastic regime, we can characterize the dynamic response by the "stress relaxation time" $G(t)$

memory of deformation.

$$S(t) = \int_{-\infty}^{t} G(t-t')\,\dot{\gamma}(t')\,dt'$$

↖ begin of exp't.

$G(t-t') \equiv$ non-instantaneous rxn. of molecules due to external perturbation

Fluid: $G(t) \to 0 \qquad t \to \infty$

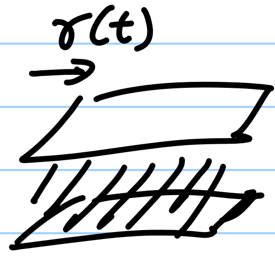
Solid: $G(t) \neq 0 \qquad t \to \infty$

e.g. (i) sudden application of strain (impulse)

$$\dot{\gamma}(t) = \gamma\,\delta(t) \qquad \text{impulse @ } t=0.$$

$$\Rightarrow S = \gamma\, G(t)$$

(ii) Oscillatory shear @ freq ω



dimensionless strain amplitude

$$= \gamma(t) = \underset{\substack{\nearrow \\ \text{max plate displacement}}}{\gamma_0} \sin(\omega t)$$

linear regime $\gamma_0 <<< 1$

Stress can in-phase and out-of phase to oscillatory shear

$$S(t) \equiv \gamma_0 \left[\underset{\substack{\nearrow \\ \text{Storage modulus} \\ \text{(elastic)}}}{G'(\omega)} \sin(\omega t) + \underset{\substack{\nearrow \\ \text{loss modulus} \\ \text{(viscous)}}}{G''(\omega)} \cos(\omega t) \right].$$

G' & G'' carry the same info. as $G(t)$

can show $$G''(\omega) = \omega \int_0^\infty dt \cos(\omega t)\, G(t)$$

$$G'(\omega) = \omega \int_0^\infty dt \sin(\omega t)\, G(t)$$

shear viscosity $$\eta = \lim_{t\to\infty} \frac{S(t)}{\dot{\gamma}(t)} \xrightarrow{\text{can show}} \lim_{\omega\to 0} \frac{G''(\omega)}{\omega}$$

$$\Downarrow$$

$$\lim_{\omega\to 0} \eta(\omega) = \int_0^\infty dt\, G(t)$$

Example : "Maxwell fluid" (1867)

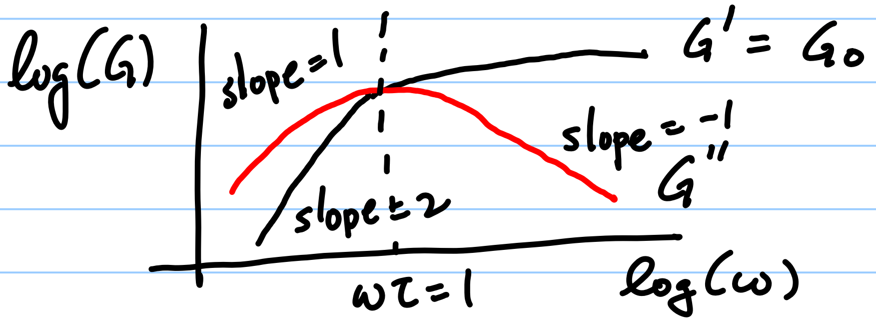
Simplest model of viscoelastic fluid

Only 1 relaxation time for stress relaxation

$$\Rightarrow \quad G = G_0 e^{-t/\tau}$$ $\tau =$ stress relax time.

$$G'(\omega) = \omega \int_0^\infty dt \sin(\omega t) G(t) = G_0 \frac{(\omega\tau)^2}{1+(\omega\tau)^2}$$

$$G''(\omega) = \omega \int_0^\infty dt \cos(\omega t) G(t) = G_0 \frac{(\omega\tau)}{1+(\omega\tau)^2}$$



$$\eta = \lim_{\omega \to 0} \frac{1}{\omega} G''(\omega) = G_0 \tau$$ ← Maxwell Eqn.

Small molecules : simple fluid , little complex structure

H_2O @ 25°C $\eta = 10^{-2}$

$G_0 = 10^{11}$ Pa.

$\tau \approx 10^{-13}$ s

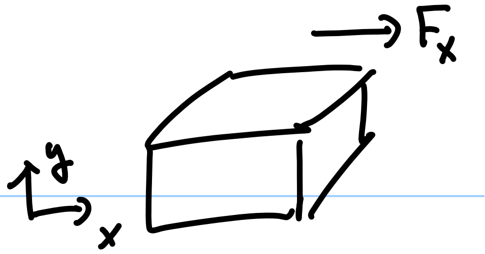
Complex fluid - polymers or dence colloids

much "softer"

G_0 much less

τ much longer

Polymer stress relaxation



stress comes from chein connectivity.

Shear stress & total viscosity

$$\eta = \frac{\sigma_{x,y}}{\gamma}.$$

F_x on A_y

$$\underset{\approx}{S} = \begin{bmatrix} \sigma_{xx} & \overset{\downarrow}{\sigma_{xy}} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix}$$

$$\eta = \eta_{solvent} + \int_0^\infty \overset{\text{polymer}}{G(t)}\, dt.$$

2nd Green-Kubo Theorem

$$G(t) = \frac{1}{k_B T} \rho_p \langle J_{xy}(0) J_{xy}(t) \rangle$$

#/volume

$$J_{xy}(t) = \sum_{\alpha=1}^{N} x_\alpha(t)\, F_\alpha^y(t)$$

x-displacement of segment α

y-component of spring force on segment α

Rouse model ⇒

$$F_\alpha^y(t) = -k_s[2y_\alpha(t) - y_{\alpha+1}(t) - y_{\alpha-1}(t)]$$

$$\approx -k_s \frac{\partial^2 y}{\partial \alpha^2}$$

ideal coil

$$\Rightarrow k_s = \frac{3k_B T}{\sigma^2}$$

$\beta = \frac{1}{k_B T}$

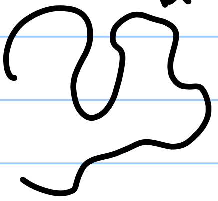
$$\frac{G(t)}{\rho \beta} = \sum_{\alpha=1}^{N} \sum_{\gamma=1}^{N} \langle x_\alpha(0) F_\alpha^y(0) \, x_\gamma(t) F_\gamma^y(t) \rangle$$

by linearity & EOM

$$= \sum_{\alpha=1}^{N} \sum_{\gamma=1}^{N} \underbrace{\langle x_\alpha(0) x_\gamma(t) \rangle}_{} \underbrace{\langle F_\alpha^y(0) F_\gamma^y(t) \rangle}_{}$$

Physically ; $G(t)$ probes (i) segmental displacement

(ii) dynamics of local Curvature of chain backbone



$$\kappa = \frac{\partial^2 \vec{r}_\alpha}{\partial \alpha^2}$$

Switch to normal mode

$$y_\alpha(t) = Y_0(t) + 2 \sum_{p=1}^{N-1} \cos\left(\frac{p\pi}{N}\alpha\right) y_p(t)$$

$$\rightarrow Y_0(t) + \underbrace{2 \int dp \cos\left(\frac{p\pi}{N}\alpha\right) y_p(t)}$$

$$\frac{F}{k_s} \sim \frac{\partial^2}{\partial \alpha^2} y_\alpha(t) \Rightarrow -2 \int dp \left(\frac{p\pi}{N}\right)^2 \cos\left(\frac{p\pi}{N}\alpha\right) y_p(t)$$

need $\left. \langle x_p(t) x_{p'}(0) \rangle \ \& \ \langle y_p(t) y_{p'}(0) \rangle \right\} \delta_{p,p'}$

Some manipulation

$$\Rightarrow G^{\text{polymer}}(t) \propto \frac{k_s^2 \beta \rho}{N^3} \sum_{p=1}^{N} p^4 \, C_{pp}^2(t)$$

$$C_{pp}(t) = \langle \vec{x}_p(0)\vec{x}_p(t)\rangle = \frac{3k_BT}{k_p} e^{-t/\tau_p}$$

$$= \frac{N\sigma^2}{2\pi^2}\frac{1}{p^2} e^{-tp^2/\tau_R}$$

Classic result

$$\boxed{\overset{\text{polymer}}{G}(t) = \frac{k_BT}{N}\rho_{seg}\sum_{p=1}^{N} e^{-2tp^2/\tau_R}}$$

short time : $G(t=0) = \rho_{seg} k_B T$.

$$\tau_R = \frac{\zeta}{3\pi^2}\frac{Nb^2}{k_BT}.$$

Make 5 predictions

(i) short time $(t \ll \tau_R)$

many modes to stress relaxation

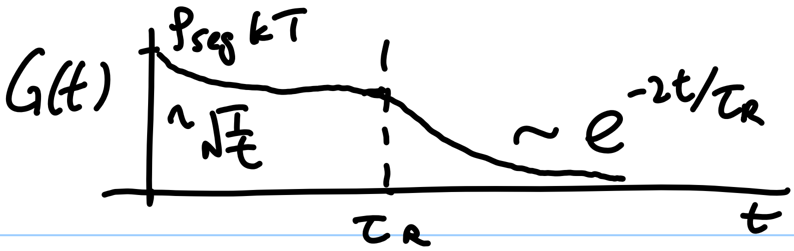
$$\Rightarrow \quad G(t) \propto \frac{k_BT}{N}\rho_{seg}\sqrt{\frac{\tau_R}{t}}$$

$\Sigma \to \int$

$$\propto \frac{1}{\sqrt{t}} \quad \rho_{seg}\sqrt{kT\zeta b^2} \sim N^0$$

(ii) long time $(t > \tau_R)$ p=1 dominate

$$G(t) \simeq \frac{kT\rho_{seg}}{N} e^{-2t/\tau_R}$$



(iii) viscosity of polymer

$$\eta_{poly} = \int_0^\infty dt \; G(t) = \frac{\rho_{seg}}{N} k_B T \sum_{p=1}^{N} \frac{\tau_R}{2p^2}$$

dominant contribution from low p $\qquad \propto N \rho_{seg} \zeta b^2$.

(iv) COM diffusion : $\quad D = \frac{k_B T}{N \zeta}$.

(v) oscillatory expt

$$G'(\omega) = \omega \int_0^\infty dt \, \sin(\omega t) G(t) \qquad \tau_p = \frac{\tau_R}{2p^2}$$

$$= \rho_{seg} k_B T \sum_{p=1}^{N} \frac{(\omega \tau_p)^2}{1 + (\omega \tau_p)^2}$$

$$G''(\omega) = \rho_{seg} k_B T \sum_{p=1}^{N} \frac{(\omega \tau_p)}{1 + (\omega \tau_p)^2}$$

low ω, long time $\qquad G'(\omega) \propto (\omega \tau_R)^2$

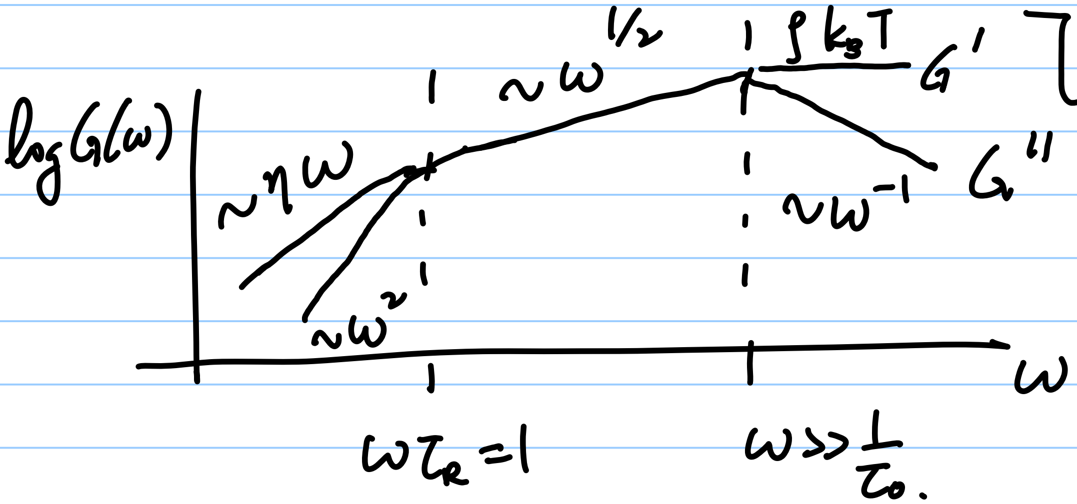
$$G''(\omega) \propto (\omega \tau_R)$$

hi ω, short time $\Sigma \to \int dp$

$$G'(\omega) \sim G''(\omega) \propto \frac{1}{N}\sqrt{\omega\tau_R}$$

$$\propto \sqrt{\omega\tau_0}$$

$$\boxed{\tau_R = \tau_0 N^2.}$$



Rouse model works for melt of short, unentangled chains.