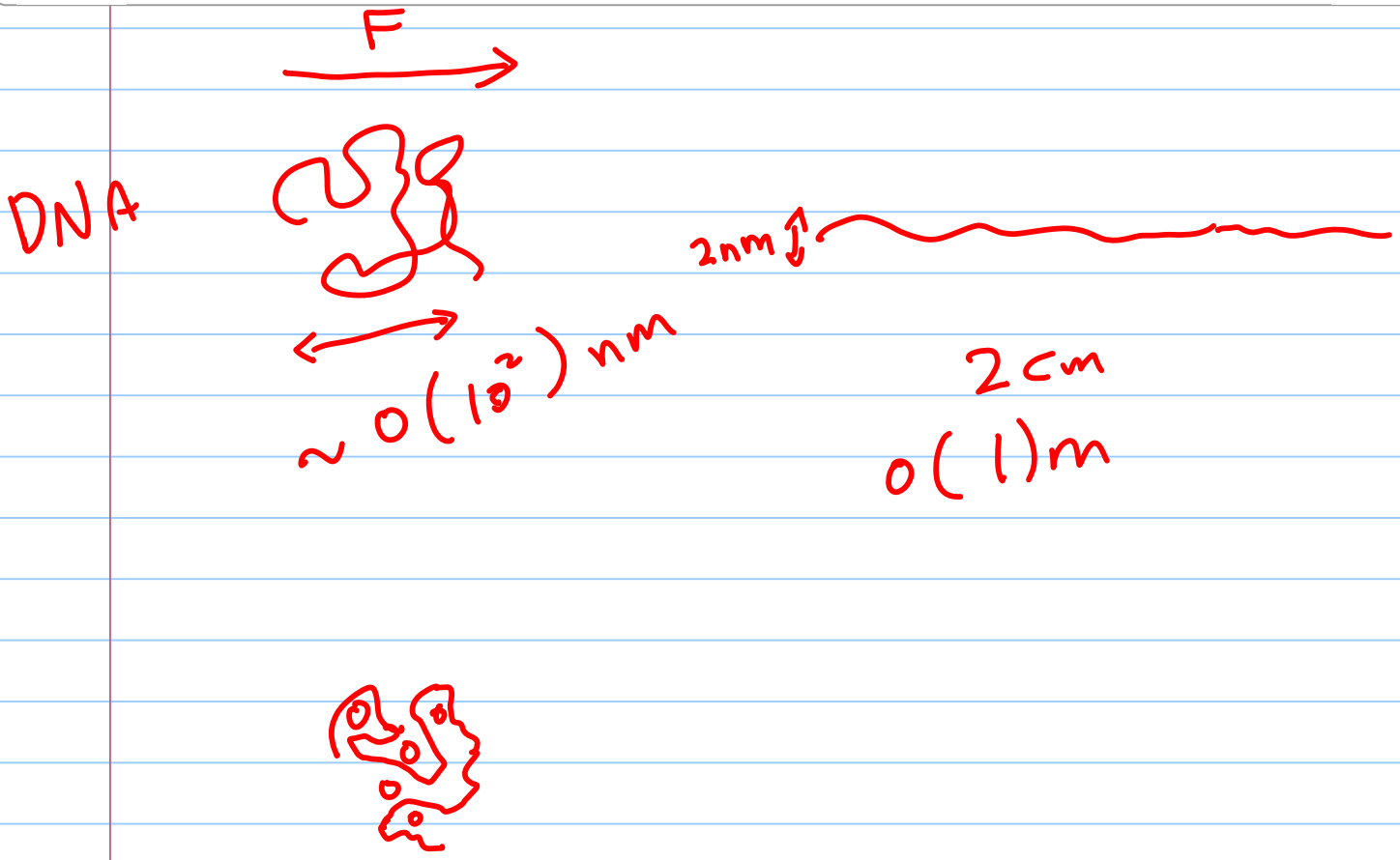
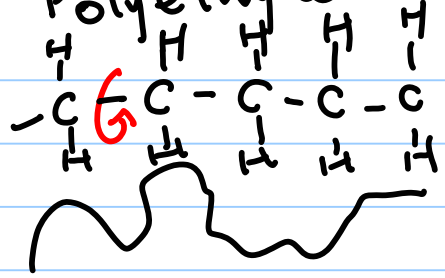
Note Title 10/14/2009



Polyethylene (PE)

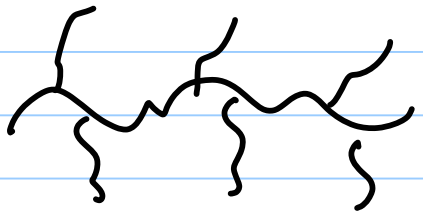


plastic bags

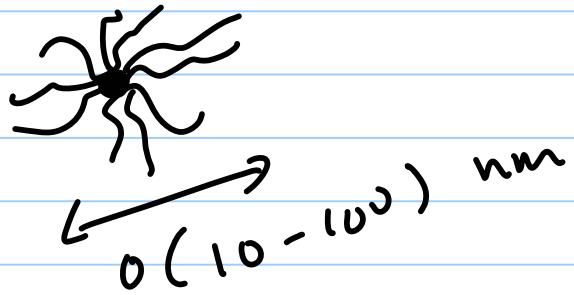
linear low MW PE.

bullet-proof vests

high MW PE

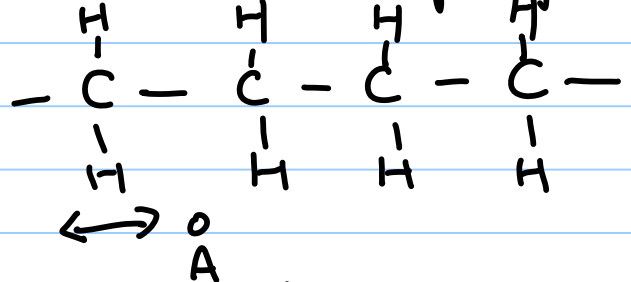


branched polymers



Star polymers.

PE is a homopolymer.

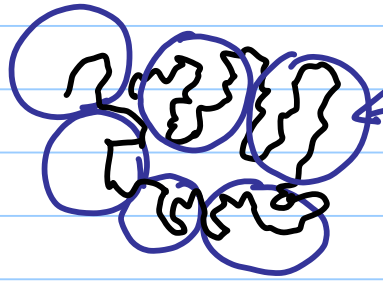


DNA is a heteropolymer

-A-G-T-C-C-T-A-A-

To understand the physical properties of polymers, we do not need to understand polymer chemistry on the atomic level. Instead, we can use statistics and statistical mechanics to derive macroscopic properties

$-C-C-C-C-C$

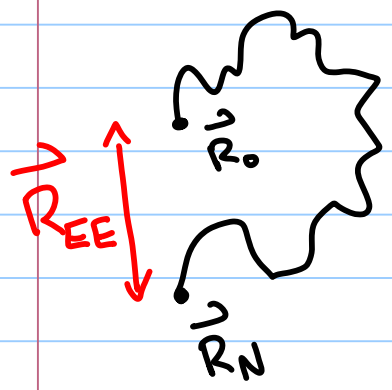


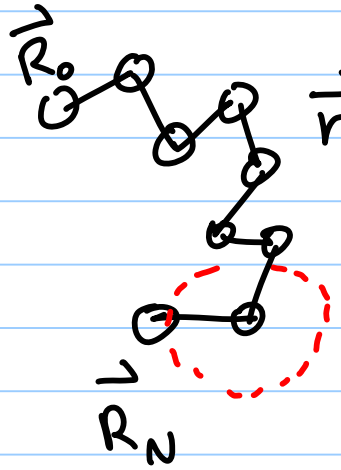
blob chain

Conformation of a polymer depends on its flexibility and temperature.

Entropy - polymers can have more configurations in coiled state then in stretched state

$S = k \ln \Omega$





$$\vec{r}_n = \vec{R}_n - \vec{R}_{n-1}$$

$$n = 0 \;..\; N$$

$$\langle \vec{r}_n \cdot \vec{r}_m \rangle = b\,\delta_{nm}$$

$$\psi(\vec{r}) = \frac{1}{4\pi b^2}\,\delta(|r| - b)$$

$$\int \psi(\vec{r})\, d\vec{r} = 1$$

$$\vec{R}_{EE} = \vec{R}_N - \vec{R}_0 = \sum_{n=0}^{N} \vec{r}_n$$

$$\langle \vec{r} \rangle = \int \vec{r}\, \psi(\vec{r})\, d\vec{r} = 0$$

$$\Rightarrow \langle \vec{R}_{EE} \rangle = 0$$

$$\langle \vec{R}_{EE}^{\,2} \rangle = \langle (\vec{R}_N - \vec{R}_0)^2 \rangle$$

$$= \sum_{n,m=1}^{N} \langle \vec{r}_n \cdot \vec{r}_m \rangle$$

$$= \sum_{n=1}^{N} \langle \vec{r}_n^{\,2} \rangle + 2 \sum_{n>m} \langle \vec{r}_n \cdot \vec{r}_m \rangle$$

($\langle \vec{r}_n \cdot \vec{r}_m \rangle \to 0$)

$$= N b^2$$

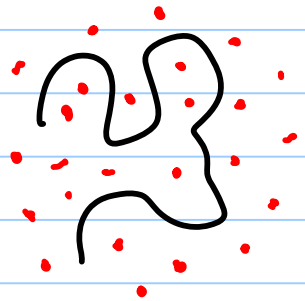
$$\sqrt{\langle \vec{R}_{EE}^{\,2} \rangle} = \sqrt{N}\, b$$

freely-jointed chain

"ideal" chain.

non-ideal interactions:

- self-avoiding repulsions
- electrostatic interactions
- polymer-solvent interaction



Solvent-polymer favorable

$\Rightarrow$ effective polymer-polymer repulsion

polymer-polymer favorable

$\Rightarrow$ effective polymer attraction

Free solution

Ideal: $\langle R_{EE}^2 \rangle^{1/2} \sim N^{1/2} b$

Self-avoiding: $\langle R_{EE} \rangle^{1/2} \sim N^{3/5} b$

good solvent

poor solvent : $\langle R_{EE} \rangle^{1/2} \sim N^{1/3} b$

$(N >> 1.)$

b = statistical length

length where we can treat each blob as statistically unconnected segments.

PE : $b \approx 2$ nm.

ds DNA : $b \approx 100$ nm.

Size of polymers in confinement

Ideal : 3D $\langle R_{EE}^2 \rangle^{1/2} \sim N^{1/2} b$.

2D $\langle R_{EE}^2 \rangle^{1/2} \sim N^{1/2} b$

1D $\langle R_{EE}^2 \rangle^{1/2} \sim N b$

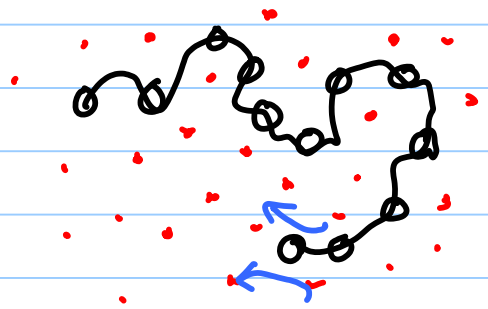
Self-avoiding : 3D : $\langle R_{EE}^2 \rangle^{1/2} \sim N^{3/5} b$.

2D : $\langle R_{EE}^2 \rangle^{1/2} \sim N^{3/4} b$.

1D : $\langle R_{EE}^2 \rangle^{1/2} \sim N b$.

Polymer dynamics

Dilute polymer solns. (ideal coil)



polymer thermal motion

polymer - solvent interaction.

solvent movement that affects polymer motion

(hydrodynamic interaction)

treat polymer beads as Brownian particles.

Expt show that the dynamic behavior of polymers on scale $> b$ is generally independent of local monomer structure

Use solvent as a continuum fluid that exerts a "fluctuating force" & "friction" on the polymer segments

→ Langevin Eqn. for the N polymer segments

→ N - coupled Equations of Motion

Langevin Eqn.

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

$\frac{d\vec{v}_\alpha}{dt}$: acceleration

$\vec{F}_\alpha$: total force exerted on segment α

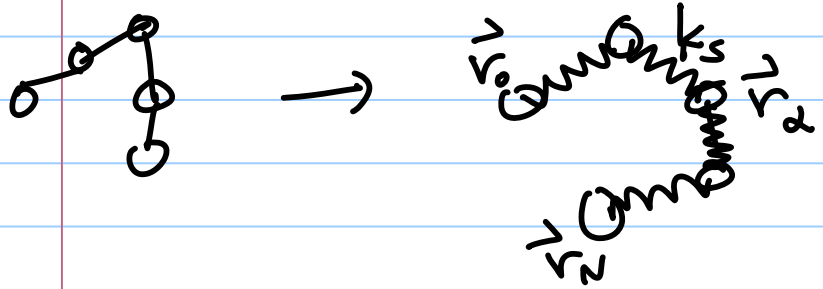
$\Rightarrow$ Overdamped limit

polymer is diffusive

$\rightarrow \emptyset$

$\vec{F}_\alpha$: multiple origin

(1) Connectivity — intramolecular force.



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

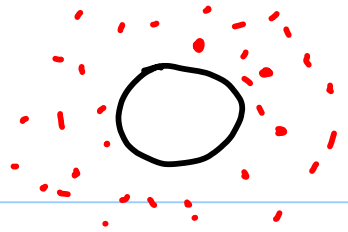
$$+ \sum_{\alpha > \gamma = 1}^{N} U^{\text{exc. vol.}}(r_{\alpha\gamma})$$

$\emptyset$ for ideal chains.

$$\vec{F}_\alpha^{\text{intra}} = -\frac{\partial U}{\partial \vec{r}_\alpha} = \text{linear Hooke's law}$$

(2) local forces between polymer segments & solvent

Brownian fluctuations:



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

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

in one coord.

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

ζ = friction coefficient of polymer segment

$$= 6\pi \eta_{solvent} \frac{b}{2}$$

Einstein - Stokes relation

$\eta_{solvent}$ ↑ solvent viscosity

Diffusivity of one polymer segment

$$D = \frac{kT}{\zeta}.$$

(3) Hydrodynamic Interactions

purely dynamic solvent-induced forces between N connected polymer segments.

"long range" — couple all segments

General problems — All 3 types of forces are important ⇒ very complex even in the Brownian regime.

2 Classical models

I. "Rouse model" --- ignores hydrodynamics

assumes (1) ideal solvent

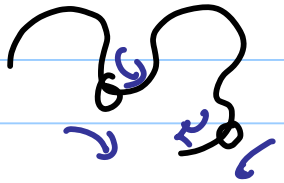
(2) No HI.

turns out (2) is never valid.

Fails for dilute soln. But it correctly contains several physical aspects and it's surprisingly good for dense polymer melts of "short, unentangled chains"

II. "Zimm" model → Rouse model + approx. inclusion of hydrodynamics

time-configuration dependent.



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

I). Rouse model.

N segments → N coupled EOM

$$M \frac{d\vec{v}_\alpha}{dt} = \vec{F}_\alpha(t) \qquad \alpha = 1 \ldots N$$

($M \frac{d\vec{v}_\alpha}{dt} \to 0$)

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

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

$\alpha = 1, N$ only 1 spring.

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

⇒ N linear coupled eqns w/ const. coefs.

↳ 1st order stochastic differential eqn.

↳ N coupled oscillators → Normal mode analysis.

Introduces "normal coordinates"

Collective quantities. "phonons"

Dynamics of each mode is independent.

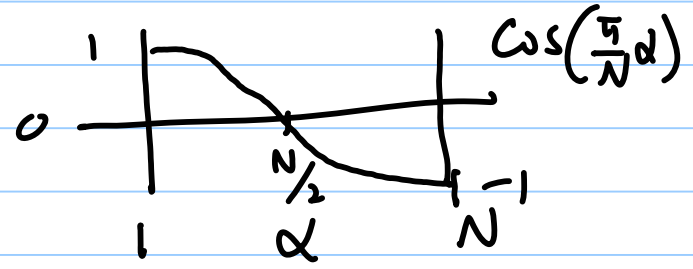
$$\vec{X}_p(t) \equiv \frac{1}{N} \sum_{\alpha=1}^{N} \cos\left(\frac{p\pi\alpha}{N}\right) \vec{r}_\alpha(t)$$

↑ normal mode index $p = 0, \ldots N-1$ — Cosine transform

$$\langle \vec{X}_p(t)\, \vec{X}_q(t) \rangle = 0 \quad \text{if } p \neq q.$$

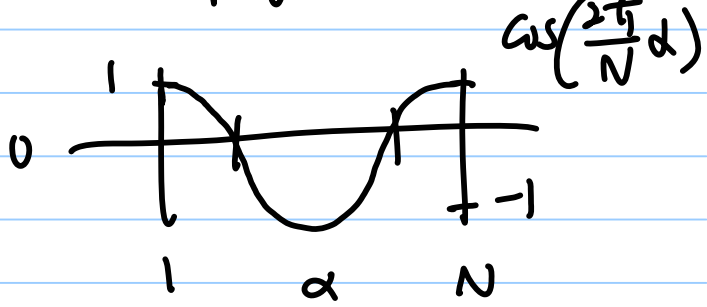
"Rouse modes" $\approx$ "standing waves" along chain backbone.

1st mode : $p=1$



sensitive to the reorientation of the whole polymer.

2nd mode : $p=2$



divide chain into two halves & probe reorientation of these 2 halves.

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

Cosine transform.

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

inversion

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

0^{th} mode = center of mass of chain.

① Internal mode displacements.

$$C_{pp'}(t) \equiv \langle \vec{X}_{p'}(0) \cdot \vec{X}_p(t) \rangle.$$

Cosine transform the N-EOM.

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

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

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

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

use Eqn. (1), (2), (3) to find D,

$\langle \delta R_{cm}^2(t) \rangle$

$\langle \delta \vec{r}_\alpha(t) \rangle$.

① internal mode displacement

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

multiply (1) by $\vec{x}_{p'}(0)$ and take $\langle \cdots \rangle$

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

$$\langle \delta \vec{f}_p(t) \cdot \vec{x}_{p'}(0) \rangle \to 0.$$

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

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

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

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

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

τ_R = Rouse relaxation time.

= longest internal mode relaxation time

i) $\tau_R \propto N^2 J/T$.

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

② Center-of-mass motion.

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

into Eqn. (1) $\langle \vec{x}_0(t)\,\vec{x}_0(0)\rangle = \langle \vec{x}_0^{\,2}\rangle e^{-t/\tau_p}\Big|_{p=0}$.

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

Since CoM diffusion is unbounded over macroscopic distances $\tau_p \to \infty$ as $p \to 0$.

What we want for CoM is

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

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

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

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

Eqn (2) $\Rightarrow$

$$= \frac{6k_BTt}{J_{p=0}} = \frac{6k_BTt}{NJ_0}$$

$$\langle (\vec{x}_0(t) - \vec{x}_0(0))^2 \rangle = \boxed{\frac{6 k_B T}{N \zeta_0}} t = 6 D t$$

$$\boxed{D \sim \frac{1}{N}}$$

total friction on a polymer is simply the sum of independent contributions.

Rouse model

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

expt - dynamic light scattering

fluorescent microscopy of DNA

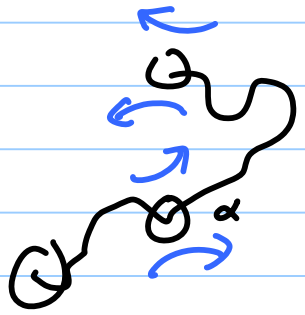
find $D \propto \frac{1}{N}$. in bulk soln.

$\tau_p \propto \frac{1}{p^2}$.

However, in confined systems such as micro- & nano-channels. where channel size $\ll \langle \vec{R}_{ee}^{\,2} \rangle^{1/2}$, Rouse

model works!

II. Zimm model



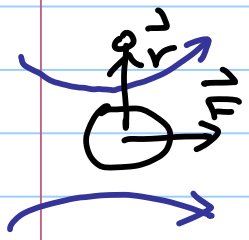
$$\vec{V}_\alpha = \sum_{\gamma=1}^{N} \vec{H}_{\alpha\gamma} \cdot \vec{F}_\alpha$$

$\vec{H}_{\alpha\gamma}$: hydrodynamic interaction between α & γ

The "Oseen" tensor

The HI must induce spatially "long range" coupling of forces exerted on polymer segments by solvent.

low Re-flow around a sphere



$$\underset{\approx}{H}(\vec{r}) = \frac{1}{8\pi\eta_s r}\left(\underset{\approx}{I} + \frac{\vec{r}\,\vec{r}}{r^2}\right)$$

$\longrightarrow$ modified Langevin Eqn.

$$\zeta \frac{\partial}{\partial t}\vec{r}_\alpha(t) \approx \sum_{\alpha=1}^{N} \langle H_{\alpha,\gamma} \rangle \left[\vec{F}_\gamma + \delta\vec{F}_\gamma(t)\right]$$

$\vec{F}_\gamma$: elastic

$\langle H_{\alpha,\gamma} \rangle$: pre-averaging HI approx. averaged over all equilibrium conformations $\{r_\alpha\}$

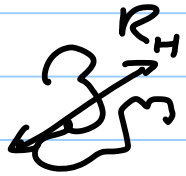
$$\langle H_{\alpha\gamma} \rangle \propto \frac{1}{\sqrt{|\alpha-\gamma|}}$$ --- very long range

vs. Rouse $\langle H_{\alpha\gamma} \rangle \sim \delta_{\alpha\gamma}$

Zimm eqns:

still linear → concept of Rouse modes still applies but w/ HI.

Result: $D_{chain} \propto \frac{k_B T}{R_H \eta_s}$



$R_H \equiv$ hydrodynamic radius.

$$\propto \langle R_{EE}^2 \rangle^{1/2} \sim N^{1/2}$$

Zimm: $D_{chain} \sim N^{-1/2}$ ← good in bulk soln.

Rouse: $D_{chain} \sim N^{-1}$ ← good in confined soln.

In bulk soln, the friction coef. of a polymer coil depends on the coil size.