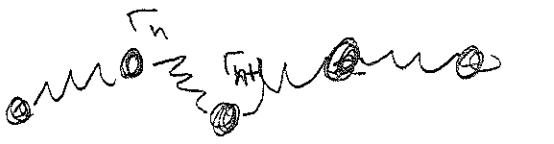
Lecture 11 Polymer dynamics

The Rouse model

P.E. Rouse 1953



ideal chain

Springs with $F_{n,n+1} = \frac{3T}{2}\frac{(r_{n+1}-r_n)^2}{a^2}$, $F_{el} = \sum_n F_{n,n+1}$

force $\varphi_n = -\frac{\partial F_{el}}{\partial r_n} = \frac{3T}{a^2}\left[(r_{n+1}-r_n)+(r_{n-1}-r_n)\right]$

- local response and mobility

$$\frac{\partial r_n}{\partial t} = \mu\,\varphi_n \equiv \frac{3T\mu}{a^2}\frac{\partial^2 r}{\partial n^2}$$

eigenmodes $r_{np}(t) = a_p \cos\frac{\pi p n}{N} e^{-t/\tau_p}$ (free boundary conditions $\left.\frac{\partial r_n}{\partial n}\right|_{0,N} = 0$)

relaxation time $\tau_p = \frac{a^2}{3\pi^2 T\mu}\left(\frac{N}{p}\right)^2$.

The longest relaxation time $\propto N^2$

- If external forces:

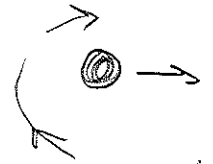
$$\frac{\partial r_n}{\partial t} = \mu\left[f_{en} + \frac{3T}{a^2}\frac{\partial^2 r}{\partial n^2}\right]$$. If all f_n are equal

then $\frac{\partial r_n}{\partial t} = V = \underbrace{\frac{\mu}{N}}_{\mu_{chain}} \underbrace{N f_{en}}_{f_{tot}} \Rightarrow \mu_{chain} \sim \frac{1}{N}$

Internal barriers are not important for the motion as a whole (first Rouse modes)

Problem 1 Find time evolution of some point of the chain $\langle [r(m,0) - r(m,t)]^2 \rangle_{th} = ?$

Back-flow effects



when monomer moves then velocity field is strongly distorted $\sim \frac{1}{r}$ => mobility is nonlocal

Kirkwood Riseman approximation (1948)

$\vec{v} = \mu_{chain} \vec{f}_{tot}$, Einstein relation =>

$D = \mu_{chain} T$

$$D = \frac{1}{3} \int_{t_1}^{\infty} \langle \vec{V}(t_1) \cdot \vec{V}(t_2) \rangle dt_2$$

$$V(t) = \frac{1}{N} \sum_n v_n = \frac{1}{N} \int c(r,t)\, v(r,t)\, dr$$

$V(t)$: center of mass velocity; $c(r,t)$: concentration; $v(r,t)$: local velocity

$$\Downarrow$$

$$D = \frac{1}{3} N^{-2} \int \langle c(r_1,t_1)\, c(r_2,t_2)\, v(r_1,t_1)\, v(r_2,t_2) \rangle dr_1 dr_2 dt_2$$

- Assumptions: 1) $\langle cc\, vv \rangle = \langle cc \rangle \langle vv \rangle$

2) $\langle c(r_1,t_1)\, c(r_2,t_2) \rangle = \frac{N}{Volume}\, g(r_1 - r_2)$

(all time dependence is in the velocity corr. function)

3) $\langle vv \rangle$ is calculated for a pure solvent (no effect of the polymer) =>

$$\left.\begin{aligned} &\frac{\partial}{\partial t}(\rho v_q) + \eta_s q^2 v_q = 0 \\ &\vec{q} \cdot \vec{v}_q = 0 \end{aligned}\right\} \text{Navier-Stokes (Eq.)}$$

η_s - viscosity

ρ - density

Thus $\langle U_{-q}(0)\, U_q(t)\rangle = \langle U_{-q}(0) U_q(0)\rangle \exp\left(-\frac{\eta_s q^2 t}{9}\right)$

$\frac{1}{2}\rho\langle U_{-q}(0)\, U_q(0)\rangle = \frac{T}{2}$ => in real space

$$\frac{1}{T}\int_0^\infty \langle U_\alpha(0,0)\, U_\beta(r,t)\rangle dt = \frac{1}{8\pi\eta_s r}\left[\delta_{\alpha\beta} + \frac{r_\alpha r_\beta}{r^2}\right]$$

$$\Downarrow$$

$$D = \frac{1}{N}\int d^3r\, g(r)\, \frac{T}{6\pi\eta_s r}$$

g has a scaling form

$$g(r) = \frac{N}{R_F^3}\,\tilde{g}\left(\frac{r}{R_F}\right) \Rightarrow$$

$$D = \frac{T}{6\pi\eta_s R_F}\int dx\, \tilde{g}(x)\, x \sim \frac{T}{6\pi\eta_s R_F} \Rightarrow$$

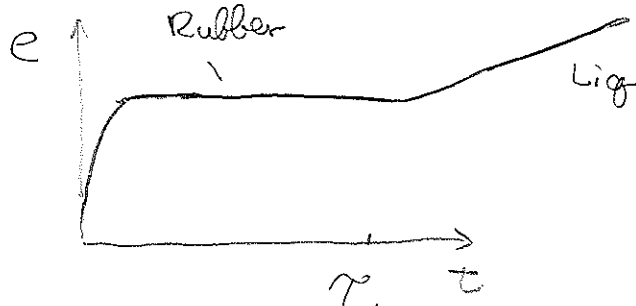
$$\mu_{tot} = \frac{D}{T} \sim (6\pi\eta_s R)^{-1} \sim N^{-\nu}$$

- Thus mobility is of the order of mobility of the solid sphere with radius R_F

Friction is reduced with respect to the Rouse model

Entanglement

If we apply a stress σ, then the strain $e(t)$ as a function of time



τ_t – relaxation time

for $t \ll \tau_t$ $\quad e \approx \frac{\sigma}{E}$ – elastic modulus

for $t \gg \tau_t$ $\quad e \sim \frac{t}{\eta}\sigma \Rightarrow$

viscosity $\eta = E\tau_t$

Very viscous liquid (Maxwell)

Shear modulus $\mu(\omega) \sim \frac{\mu}{1 + \frac{i}{\omega\tau_t}}$

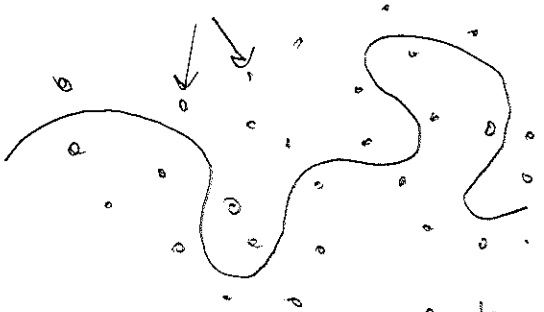
Solid at high frequencies, liquid at low

For long chains elastic modulus is independent on chain length and is measure of number of entanglement points $E \sim \frac{cT}{N_e}$

Reptation

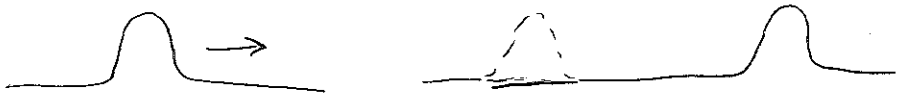
de Gennes (1971)

We consider motion of the single chain surrounded by obstacles in the network



Chain cannot cross obstacles

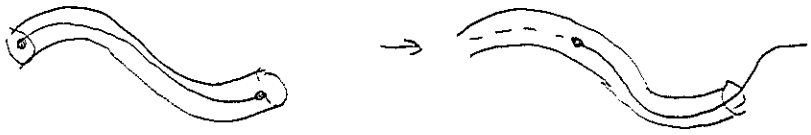
- It can move in between - reptation



It is useful to view it as a motion in a tube

S. Edwards

When chain moves it leaves some part and creates new parts of the tube



relaxation time τ_t is the time to change the tube

Consider chain with N monomers in the infinitely long tube. For motion along the tube $v = \mu_{tube} f$. Friction ~ length (no backflow effects) $\Rightarrow \mu_{tube} = \frac{\mu_1}{N} \Rightarrow$

Diffusion coefficient $D_{tube} = \frac{\mu_1 T}{N} = \frac{D_1}{N}$

to change the tube the chains must diffuse $L \sim N \Rightarrow$

$$\tau_t \simeq \frac{L^2}{D_{tube}} \cong \frac{N L^2}{D_1} \sim \underline{\tau_1 N^3}$$

Thus the relaxation time $\propto L^3 \propto N^3$

In the experiment $\sim N^{3,3}$

although along the tube chain moved by $L \sim N a$

but in real space it corresponds to $R_0 \sim N^{1/2} a \Rightarrow$

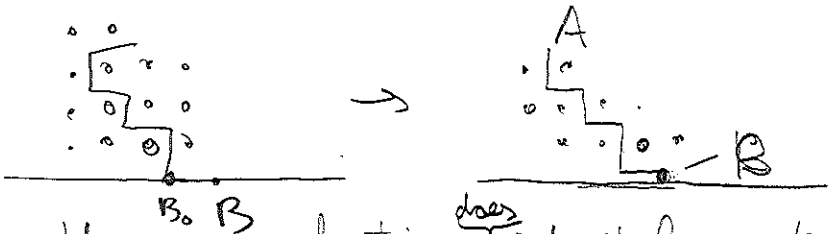
(Note that in a dense solution chains are ideal! Flory)

Diffusion coefficient in real space

$$D_{rep} \simeq \frac{R_0^2}{\tau_t} = D_1 N^{-2}$$

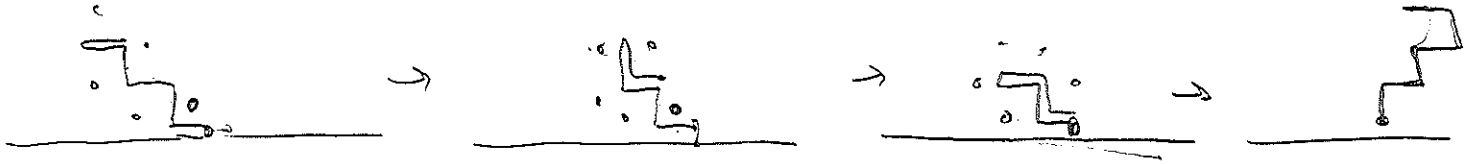
Reptation of a branched chain

de Gennes (1975)



How much time does it take to move the side group?

One end B is fixed. The only way is to retrace A along the chain to B



The probability of retracing $\sim \frac{n_0^{(N)}}{n_{N_s}}$

where n_0 - number of paths topologically equivalent to 

$n_N \sim z^{N_s}$ very rough $n_0 \sim z^{\frac{N_s}{2}}$

(twice less steps - excluding branching) $\Rightarrow$

$P \sim e^{-\alpha N_s}$ and relaxation time for reptation $\sim \exp \alpha N_s$