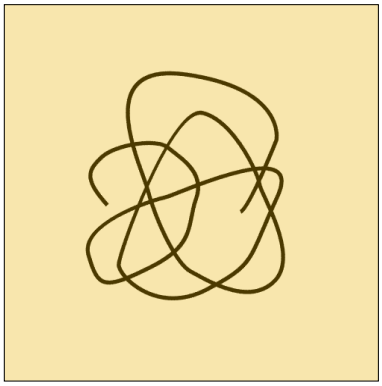
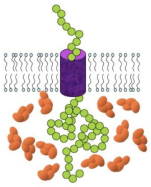
Polymer dynamics

Jasper van der Gucht

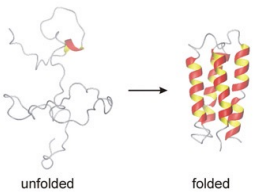


1

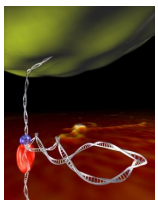
Rate of biological processes



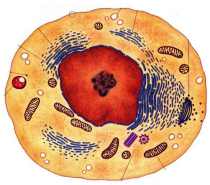
DNA translocation



Protein folding



DNA internal dynamics: gene transcription



Intracellular diffusion

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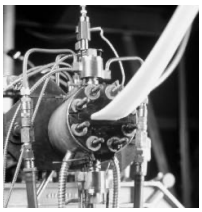
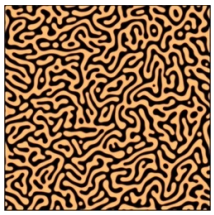
Rheology, mixing, phase separation, processing

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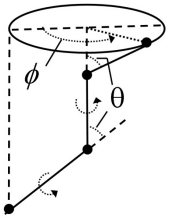
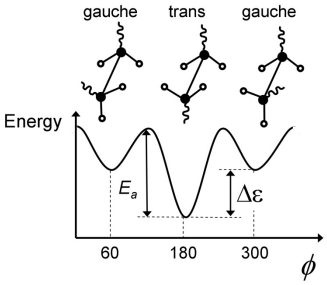
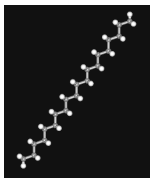
Polymer conformations

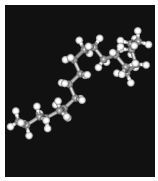




-Hindered rotation

- Energy barrier Ea, and $\Delta\varepsilon$ depend on side groups


Large $\Delta\varepsilon$


Small $\Delta\varepsilon$

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Program

1. Average properties: Gaussian chain
2. The Langevin equation
3. Unentangled polymers: Rouse and Zimm models
4. Entangled polymers: reptation & tube model

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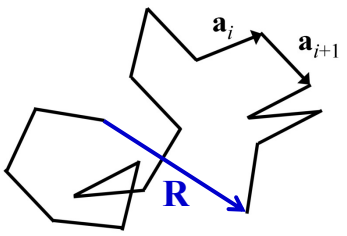
The freely-jointed chain model



-Every bond can take any direction, independent of other bonds

- Length of each bond: a

End-to-end vector: $\mathbf{R} = \sum_i \mathbf{a}_i$

Average: $\langle \mathbf{R} \rangle = 0$

Mean-square: $\langle \mathbf{R}^2 \rangle = N a_0^{\,2}$

Ideal chain: $R_0 = N^{1/2} a_0$

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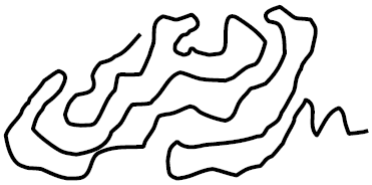
Real chains: interactions between monomers

Ideal chain (random walk) can intersect itself

$$R \sim N^{1/2}$$



Real chain cannot intersect itself: self-avoiding walk; chain is swollen

Numerical simulation (3D): $R \sim N^{\nu}$

ν=0.588

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Effect of interactions

Good solvent

$\beta_{\text{mon}} > 0$

$\chi < \frac{1}{2}$

$\bar{R} \approx N^{3/5} b^{2/5} \beta_{\text{mon}}^{1/5}$

Swollen chain

Theta solvent

$\beta_{\text{mon}} = 0$

$\chi = \frac{1}{2}$

$\bar{R} = N^{1/2} b$

Ideal chain

Poor solvent

$\beta_{\text{mon}} < 0$

$\chi > \frac{1}{2}$

$\bar{R} \sim N^{1/3}$

Collapsed chain

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Most of polymer conformation are self-similar (fractal)

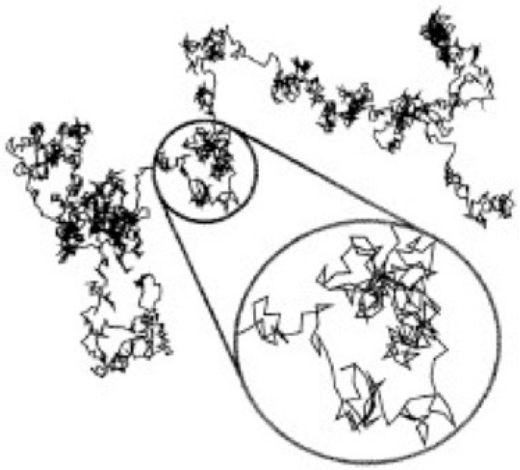

Fig. 1.14 Fractal structure of an ideal chain with fractal dimension $D = 2$
Obtained by computer simulation.

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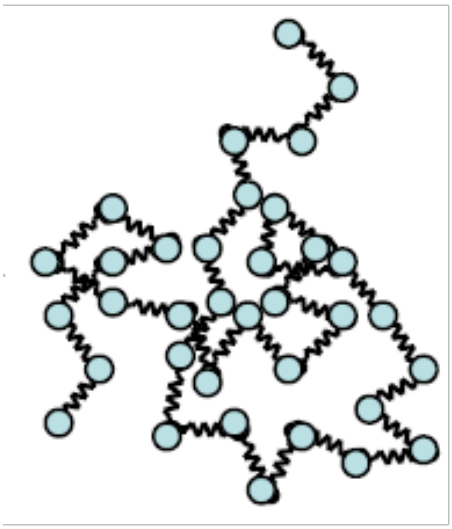

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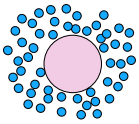
Dynamics: the Langevin equation



Equation of motion of the particle (Langevin equation):

$$m\vec{a} = \vec{f}_{ext} - \zeta\vec{v} + \vec{f}^{R}$$

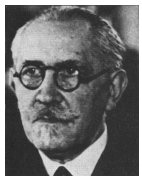
'noise' (collisions with solvent molecules)

inertia — applied force — friction

Friction force $\vec{f}_{fric} = \zeta\vec{v}$

Friction coefficient: $\zeta = 6\pi\eta R$

George Stokes
(1819-1903)



Paul Langevin
(1872-1946)

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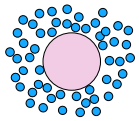
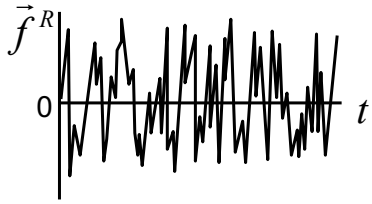
Properties of the random force: Fluctuation-dissipation theorem



Random force is due to collisions with solvent molecules



$$\left\langle \vec{f}^{R}(t) \right\rangle = 0$$

$$\left\langle \vec{f}^{R}(t) \cdot \vec{f}^{R}(t') \right\rangle = C\delta(t - t')$$

very rapid fluctuations
(no correlations for $t \neq t'$)

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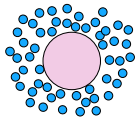
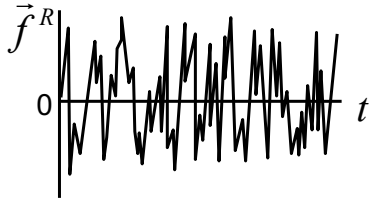
Properties of the random force: Fluctuation-dissipation theorem



Random force is due to collisions with solvent molecules



$$\left\langle \vec{f}^R(t) \right\rangle = 0$$

$$\left\langle \vec{f}^R(t) \cdot \vec{f}^R(t') \right\rangle = 6kT\zeta\delta(t-t')$$

fluctuation - dissipation

very rapid fluctuations
(no correlations for $t \neq t'$)

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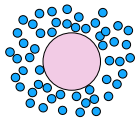
Freely moving particle, overdamped dynamics



$$\zeta \frac{d\vec{r}(t)}{dt} = \vec{f}^R(t)$$

Solution:

$$\vec{r}(t) = \vec{r}_0 + \frac{1}{\zeta}\int_0^t \vec{f}^R(t')dt'$$

Mean displacement: $\left\langle \vec{r}(t) - \vec{r}_0 \right\rangle = \frac{1}{\zeta}\int_0^t \left\langle \vec{f}^R(t') \right\rangle dt' = 0$

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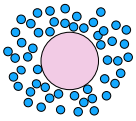
Freely moving particle (no external field)



$$\zeta \frac{d\vec{r}(t)}{dt} = \vec{f}^{R}(t)$$

Solution:

$$\vec{r}(t) = \vec{r}_0 + \frac{1}{\zeta}\int_0^t \vec{f}^{R}(t')dt'$$

Mean square displacement:

$$\left\langle (\vec{r}(t) - \vec{r}_0)^2 \right\rangle = \left\langle \left(\frac{1}{\zeta}\int_0^t \vec{f}^{R}(t')dt' \right) \cdot \left(\frac{1}{\zeta}\int_0^t \vec{f}^{R}(t'')dt'' \right) \right\rangle$$

$$= \frac{1}{\zeta^2}\int_0^t\int_0^t \underbrace{\left\langle \vec{f}^{R}(t') \cdot \vec{f}^{R}(t'') \right\rangle}_{6kT\zeta\delta(t'-t'')} dt'\,dt'' = \frac{6kT\zeta}{\zeta^2}t$$

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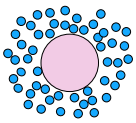
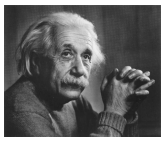
Freely moving particle



$$\left\langle (\vec{r}(t) - \vec{r}_0)^2 \right\rangle = \frac{6kT}{\zeta}t$$

Stokes-Einstein:

$$\left\langle (\vec{r}(t) - \vec{r}_0)^2 \right\rangle = 6Dt \longrightarrow D = \frac{kT}{\zeta}$$



Albert Einstein
(1879-1955)

Time for particle to diffuse distance comparable to its own size:

$$\tau \cong \frac{R^2}{D} \cong \frac{R^2\zeta}{kT}$$

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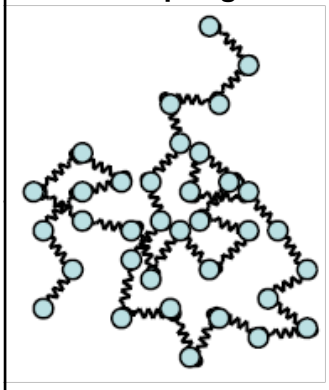
Rouse model for polymer chain

Bead-spring model



N beads connected by springs, each of root-mean-square size a

friction coefficient of one bead: ζ_0

spring constant: $\dfrac{3kT}{a^2}$

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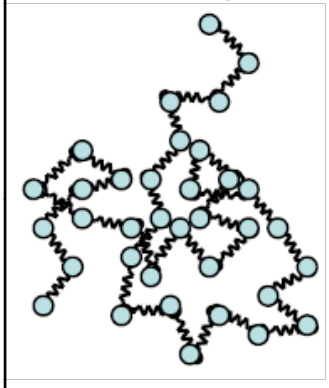
Rouse model for polymer chain

Bead-spring model



Friction of one monomer: ζ_0

Friction of whole chain: $\zeta_R = N\zeta_0$

Diffusion coefficient: $D_R = \dfrac{kT}{\zeta_R} = \dfrac{kT}{N\zeta_0}$

Whole-chain relaxation time:

$$\tau_R \cong \frac{R_0^2}{D_R} \cong \frac{\zeta_0 a^2 N^2}{kT}$$

(ideal chains)

$R_0 = N^{1/2} a_0$

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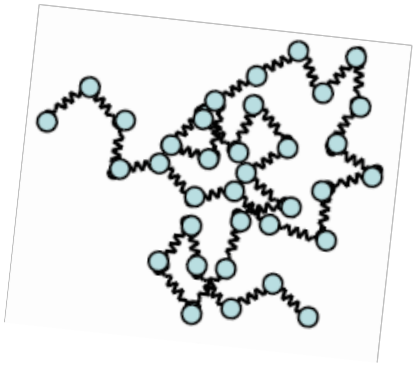
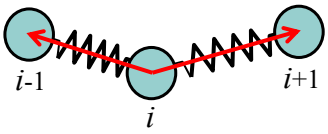
Internal modes: force between monomers



N beads connected by springs, each of root-mean-square size a

friction coefficient of one bead: ζ_0

spring constant: $\dfrac{3kT}{a^2}$



Equation of motion for monomer i:

$$\zeta_i \frac{d\vec{r}_i}{dt} = \vec{f}_i^{\,R} + \frac{3kT}{a^2}\left[(\vec{r}_{i+1} - \vec{r}_i) + (\vec{r}_{i-1} - \vec{r}_i)\right]$$

for $i=1,2,\ldots, N$

Prince E. Rouse, 1953

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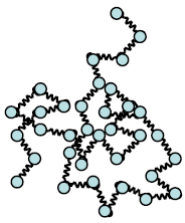
Langevin equation for a Rouse chain



We obtain N coupled stochastic differential equations:

$$\zeta_0 \frac{d}{dt}\begin{pmatrix}\vec{r}_1\\ \vec{r}_2\\ \vec{r}_3\\ \\ \vec{r}_N\end{pmatrix} = \begin{pmatrix}\vec{f}_1^{\,R}\\ \vec{f}_2^{\,R}\\ \vec{f}_3^{\,R}\\ \\ \vec{f}_N^{\,R}\end{pmatrix} - \frac{3kT}{a^2}\begin{pmatrix}1 & -1 & & & \\ 1 & -2 & 1 & & \\ & 1 & -2 & 1 & \\ & & \ddots & \ddots & \ddots \\ & & & 1 & -1\end{pmatrix}\cdot\begin{pmatrix}\vec{r}_1\\ \vec{r}_2\\ \vec{r}_3\\ \\ \vec{r}_N\end{pmatrix}$$

Can be solved by normal mode analysis (exercise)

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Solution of the Rouse model: normal modes

$$r_n(t) = X_0(t) + 2\sum_{p=1}^{N} X_p(t)\cos\left(\frac{p\pi n}{N}\right)$$

$$\left\langle X_p(0)X_q(t)\right\rangle = \delta_{pq}\left\langle X_p^2\right\rangle e^{-t/\tau_p}$$

$$\left\langle X_p^2\right\rangle = \frac{Na^2}{6\pi^2 p^2}$$

$$\tau_p = \frac{\zeta_0 a^2}{3\pi^2 kT}\left(\frac{N}{p}\right)^2$$

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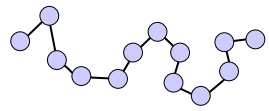
Spectrum of relaxation times



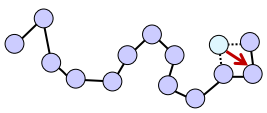
Spectrum of relaxation times:

$$\tau_p = \frac{\zeta_0 a^2}{3\pi^2 kT}\left(\frac{N}{p}\right)^2 \qquad (p = 1,2,\ldots N)$$

Shortest relaxation time ($p = N$):

$$\tau_0 = \frac{\zeta_0 a^2}{3\pi^2 kT}$$

Relaxation time of a monomer:



$$\tau_0 \cong \frac{a^2}{D_{mon}} \cong \frac{\zeta_0 a^2}{kT}$$

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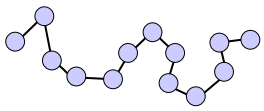
The spectrum of a Rouse chain

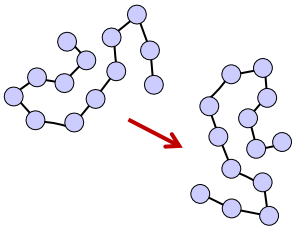


Spectrum of relaxation times:

$$\tau_p = \frac{\zeta_0 a^2}{3\pi^2 kT}\left(\frac{N}{p}\right)^2 \qquad (p = 1,2,\ldots N)$$

Longest relaxation time ($p = 1$):

$$\tau_R = \frac{\zeta_0 a^2 N^2}{3\pi^2 kT} = \tau_0 N^2$$



Time needed for whole chain to diffuse a distance comparable to its size

$$\tau_R \cong \frac{R_0^2}{D_R} \cong \frac{\zeta_0 a^2 N^2}{kT}$$

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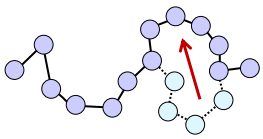
The spectrum of a Rouse chain



Spectrum of relaxation times:

$$\tau_p = \frac{\zeta_0 a^2}{3\pi^2 kT}\left(\frac{N}{p}\right)^2 \qquad (p = 1,2,\ldots N)$$

Mode p corresponds to collective motion of N/p monomers

$$\tau_p = \tau_0\left(\frac{N}{p}\right)^2$$

Movements that involve more monomers are slower

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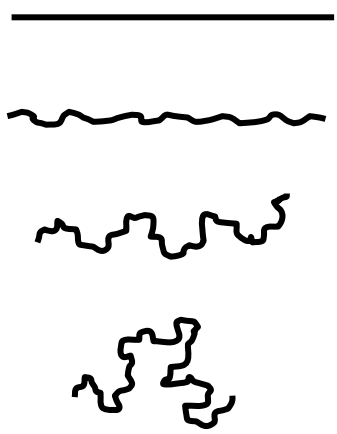
Relaxation of a stretched Rouse chain



Increasing time:
lower mode numbers

$$\tau_0 = \frac{\zeta_0 a^2}{3\pi^2 kT} \cong 10^{-10}\ \text{s}$$

$$\tau_R = \tau_0 N^2 \cong 10^{-4}\ \text{s}$$

for $N = 1000$

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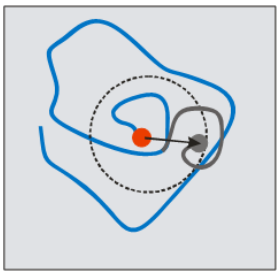
Motion of monomers



How long does it take for a specific monomer to move a given distance ?

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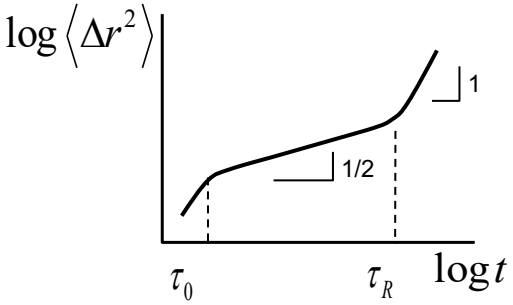
Solution of Rouse model

$$\left\langle \left(r_n(t) - r_n(0)\right)^2 \right\rangle = \frac{6kT}{N\zeta} t + \frac{4Na^2}{\pi^2} \sum_{p=1}^{N} \frac{1}{p^2} \cos^2\left(\frac{\pi p n}{N}\right)\left[1 - e^{-t/\tau_p}\right]$$



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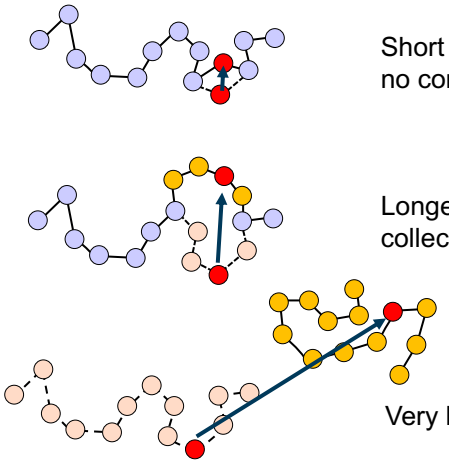
Motion of monomers



Short times / small distances: free motion, no constraints from other monomers

Longer times : larger displacements require collective motion of multiple monomers

Very long times : whole chain has to move

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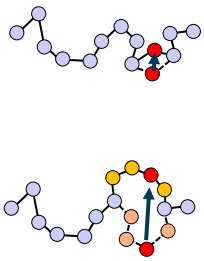
Motion of monomers



$t < \tau_0$: free monomer diffusion:

$$\left\langle \Delta r^2 \right\rangle \cong \frac{kT}{\zeta_0} t$$

$t \approx \tau_p$: N/p monomers are moving together

$$\left\langle \Delta r^2 \left(\tau_p \right) \right\rangle \cong a^2 \frac{N}{p}$$

$$\tau_p = \tau_0 \left(\frac{N}{p} \right)^2 \rightarrow \; p = N \left(\frac{\tau_0}{\tau_p} \right)^{1/2}$$

$$\longrightarrow \; \left\langle \Delta r^2 (t) \right\rangle \cong a^2 \left(\frac{t}{\tau_0} \right)^{1/2}$$

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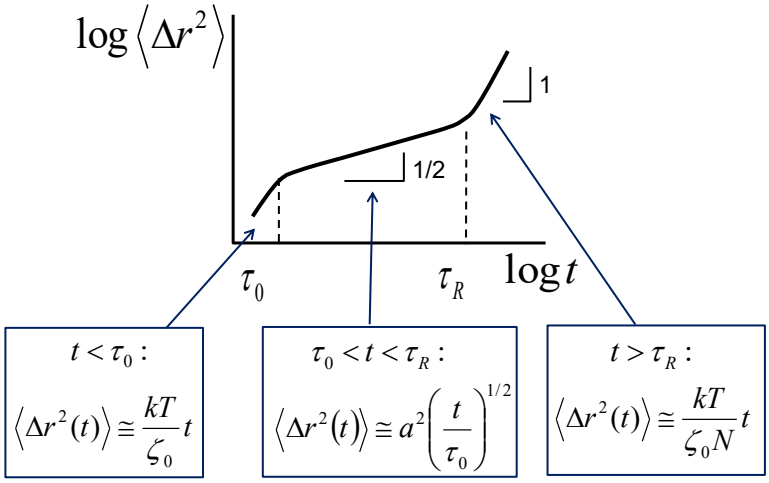
Motion of monomers



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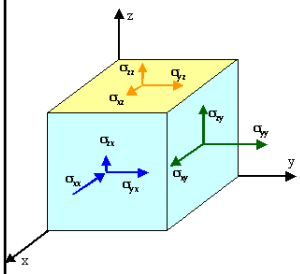
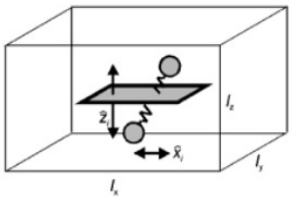
Visco-elasticity: stress tensor





Stress tensor (see e.g. Doi & Edwards):

$$\sigma_{\alpha\beta} = \frac{c}{N}\sum_{n=1}^{N}\langle R_{n\alpha}F_{n\beta}\rangle$$

$$= \frac{c}{N}\frac{3kT}{a^2}\sum_{n=1}^{N}\langle\frac{\partial r_{n\alpha}}{\partial n}\frac{\partial r_{n\beta}}{\partial n}\rangle$$

Stress relaxation modulus: $G(t) = \frac{V}{kT}\langle\sigma_{xy}(0)\sigma_{xy}(t)\rangle$

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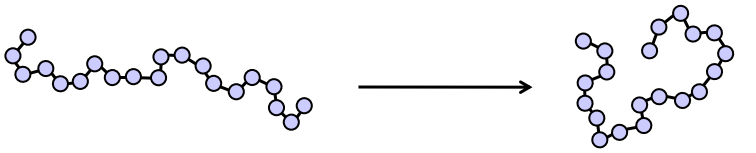
Solution of the Rouse model: relaxation modulus



Deformed chain:
carries internal stress

Relaxed chain

Rouse result:

$$G(t) = \frac{kT}{V}\sum_{p=1}^{N}\left[\frac{\langle X_p(0)X_p(t)\rangle}{\langle X_p^2\rangle}\right]^2$$

$$= \frac{ckT}{N}\sum_{p=1}^{N}\exp\left(-\frac{2t}{\tau_p}\right)$$

with $\tau_p = \frac{\zeta_0 a^2}{3\pi^2 kT}\left(\frac{N}{p}\right)^2$

c : monomer concentration

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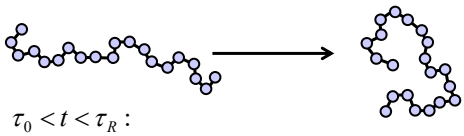
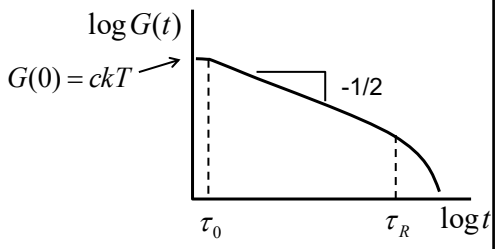
Relaxation modulus



$\tau_0 < t < \tau_R$:

$$G(t) = \frac{ckT}{N}\sum_{p=1}^{N}\exp\left(-\frac{2t}{\tau_p}\right)$$

$$= \frac{ckT}{N}\sum_{p=1}^{N}\exp\left(-\frac{2p^2 t}{\tau_0 N^2}\right)$$



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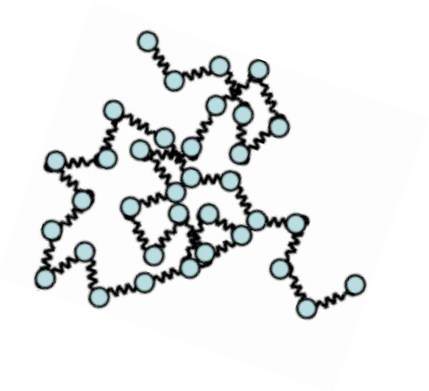
Does Rouse theory agree with experiment?



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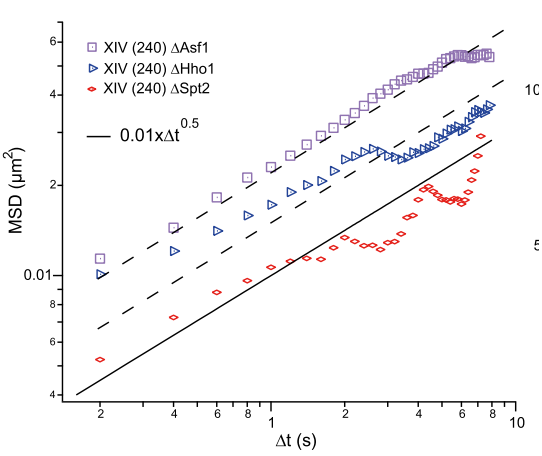
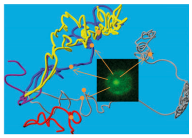
Chromosome dynamics in living yeast cells





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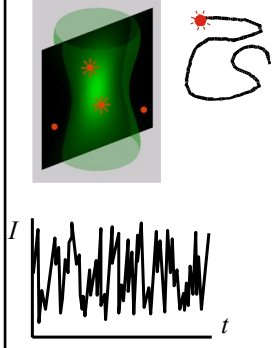
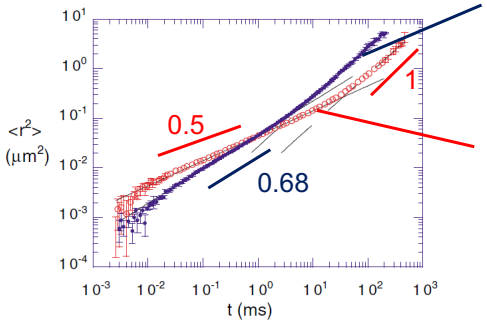
Experiment: monomer motion

Track specifically labeled DNA with fluorescence correlation spectroscopy



Rouse: $\left\langle \Delta r^2(t) \right\rangle \sim t^{1/2}$



single-stranded DNA

double-stranded DNA

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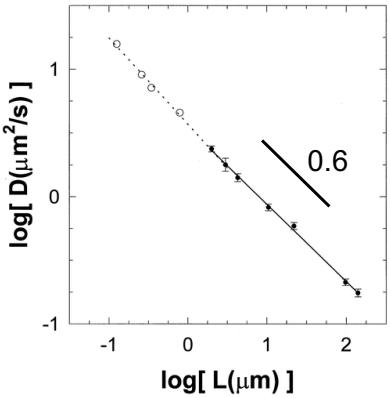
Experiment: chain diffusion (for ss-DNA)

Measure diffusion coefficient with dynamic light scattering or with video microscopy

Rouse: $D_R \sim \frac{1}{N} \sim \frac{1}{L}$



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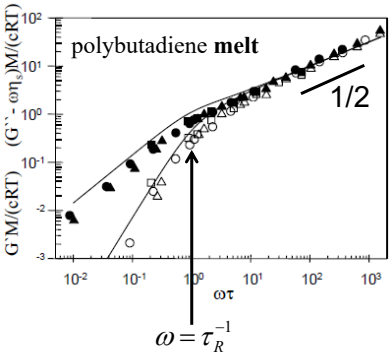
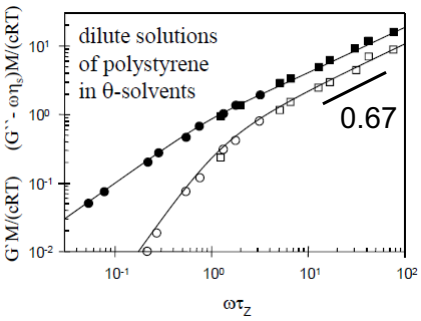
Experiment: relaxation modulus

$$G(t) \sim t^{-1/2} \quad \rightarrow \quad G'(\omega) \sim G''(\omega) \sim \omega^{1/2} \quad \left(\tau_R^{-1} < \omega < \tau_0^{-1}\right)$$





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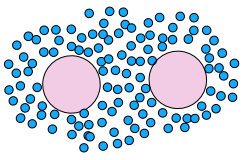
Rouse model is wrong for dilute flexible polymers!

Why ?

⟶ Hydrodynamic coupling between monomers



If one bead moves, it drags along the nearby solvent molecules and creates a flow field

$$v(r) \cong v(0)\frac{a}{r}$$

This leads to a solvent-mediated force on other particles

$$f_{ij}^{hyd} \cong \zeta v(r_{ij}) \sim \frac{1}{r_{ij}}$$

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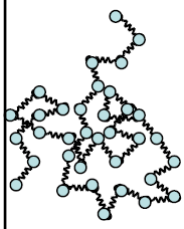
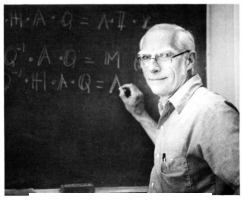
Langevin equation for a chain with hydrodynamic interactions



$$\zeta_i \frac{d\vec{r}_i}{dt} = \vec{f}_i^{\,R} + \frac{3kT}{a^2}\left[\left(\vec{r}_{i+1} - \vec{r}_i\right) + \left(\vec{r}_{i-1} - \vec{r}_i\right)\right] + \sum_{j=1}^{N} \vec{f}_{ij}^{\,hyd}\left(\vec{r}_j - \vec{r}_i\right)$$

Now all bead motions become coupled :
Very complicated problem !

Can be solved approximately by pre-averaging positions (Zimm, 1956)



Bruno H. Zimm
(1920 – 2005)

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The importance of hydrodynamic interactions

(Very crude estimate)

Total hydrodynamic force on particle i : $f_{tot}^{hyd} \sim \sum_j \frac{1}{r_{ij}} \sim N \cdot \frac{1}{R_{coil}} \sim N^{1-\nu}$

good solvent: ν =3/5, theta solvent: ν=1/2

For long polymers the hydrodynamic interactions are very important !

(Note: less important for stiff chains, $\nu \approx 1$)

Result :
effectively all solvent is dragged along; chain behaves as solid sphere

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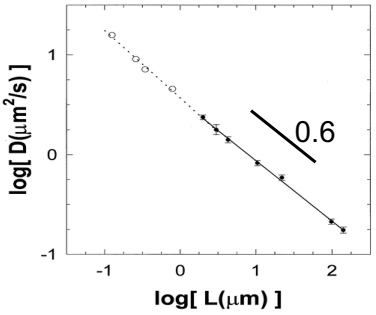
Zimm chain: trapped solvent

$$2R \cong aN^{\nu}$$

$$\nu = \begin{cases} 1/2 & (\text{theta solvent}) \\ 3/5 & (\text{good solvent}) \end{cases}$$

Friction of sphere: $\zeta_Z \cong \eta_s R$ (Stokes)

Diffusion coefficient: $D_Z = \frac{kT}{\zeta_Z} \cong \frac{kT}{\eta_s a N^{\nu}} \cong \frac{kT}{\zeta_0 N^{\nu}}$



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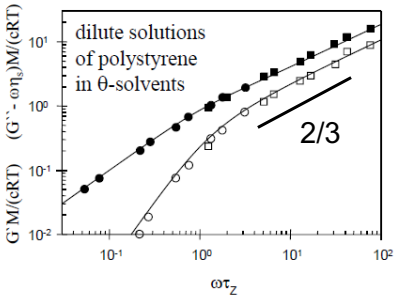
Zimm chains

Longest relaxation time: time needed for chain to diffuse its own size

$$\tau_Z \cong \frac{R^2}{D_Z} \cong \frac{a^2 N^{2\nu}}{\left(kT/\zeta_0 N^{\nu}\right)} \cong \tau_0 N^{3\nu}$$



Visco-elasticity (theta solvent):

$$G(t) \sim t^{-2/3}$$

$$G'(\omega) \sim G''(\omega) \sim \omega^{2/3} \quad \left(\tau_Z^{-1} < \omega < \tau_0^{-1}\right)$$

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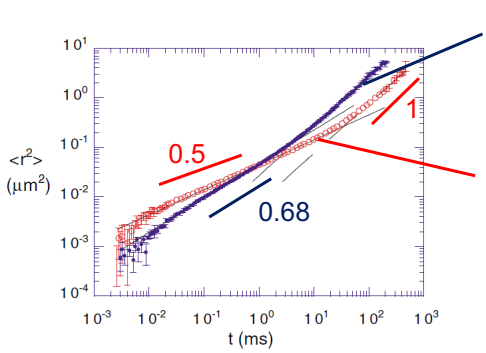
Zimm chains: monomer motion

$$\left\langle \Delta r^2(t) \right\rangle \cong a^2 \left(\frac{t}{\tau_0} \right)^{2/3} \qquad (\tau_0 < t < \tau_Z)$$

(faster than Rouse)

(exercise)



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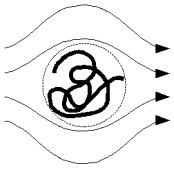
Dynamics of unentangled chains: Rouse versus Zimm



Rouse model

- no hydrodynamic coupling (free draining
- works for stiff polymers
- works in melts and concentrated solutions: screening of hydrodynamic interactions

Zimm model

- strong hydrodynamic coupling (no-draining)
- works for flexible polymers in dilute solution

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Entangled polymers

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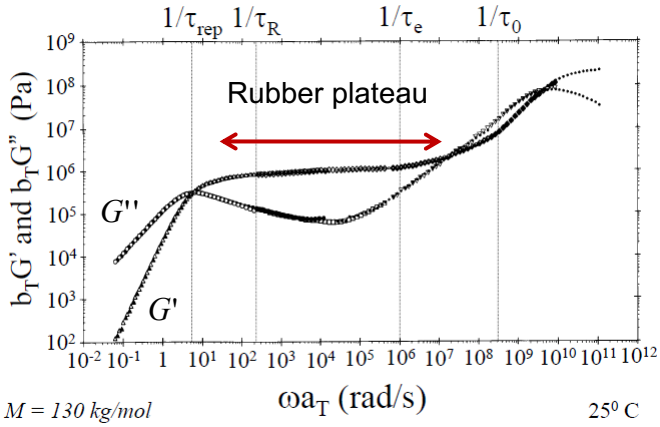
Concentrated polymer solutions: slow dynamics



At short times, polymer melts behave as elastic networks

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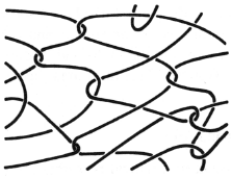
Concentrated polymer solutions: entanglements

Entanglements act as temporary cross-links



Plateau modulus: $G_e \cong \nu_e kT$

ν_e: # entanglements per unit volume

How much is ν_e ?

Polymer melt: $\nu_e \cong \frac{1}{a^3}\frac{1}{N_e}$

- $\frac{1}{a^3}$: # polymer-polymer contacts per unit volume
- N_e: Average number of Kuhn segments between entanglements

Experimentally found: $N_e \sim 10-100$ (independent of molar mass)

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Tube model

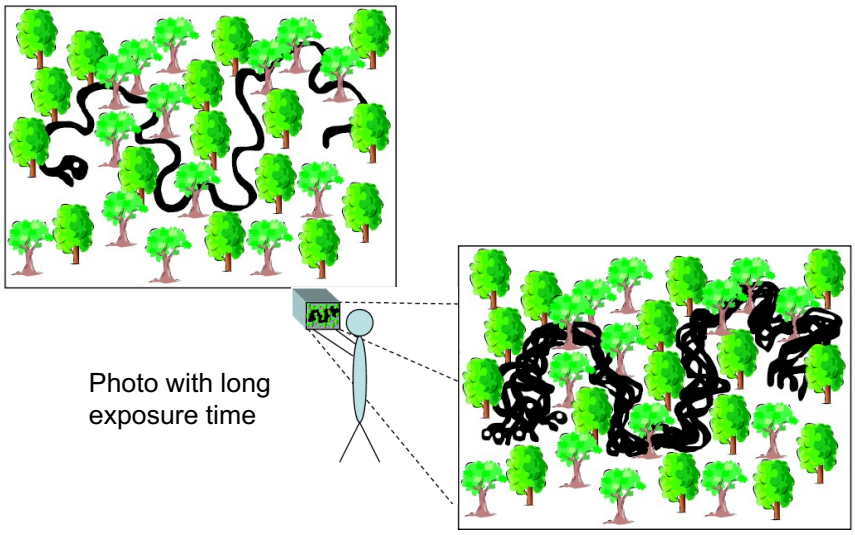

Photo with long exposure time

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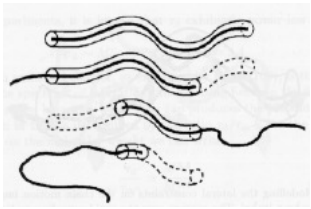
Escaping from the tube : reptation

P.G. De Gennes
1971



• Chain does a 1D curvilinear diffusion inside the tube

• Relaxation time: time needed to diffuse out of tube:

$$\tau_{rep} \cong \frac{L_{tube}^2}{D_{tube}}$$

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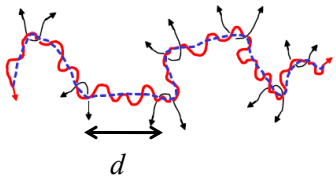
Tube length



What is the length L_{tube} of the tube ?

$$L_{tube} \cong d \frac{N}{N_e}$$

Distance between entanglements

$d \cong aN_e^{1/2}$ (ideal chain)

$$\rightarrow L_{tube} \cong d \frac{N}{N_e} \cong \frac{aN}{N_e^{1/2}}$$

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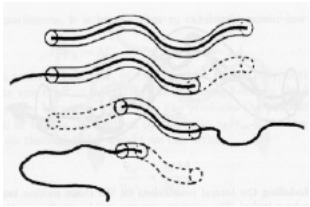
Reptation time



• Tube diffusion coefficient (Rouse):

$$D_{tube} \cong \frac{kT}{N\zeta_0}$$

• Relaxation time:

$$\tau_{rep} \cong \frac{L_{tube}^2}{D_{tube}} \cong \frac{\zeta_0 a^2 N^3}{kTN_e} \cong \tau_0 \frac{N^3}{N_e}$$

with $\tau_0 = \frac{\zeta_0 a^2}{kT}$

$$\tau_{rep} \sim 10^{-3}\text{-}100\,\text{s}$$

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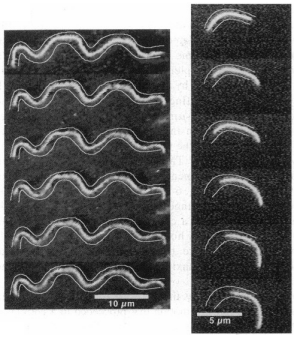
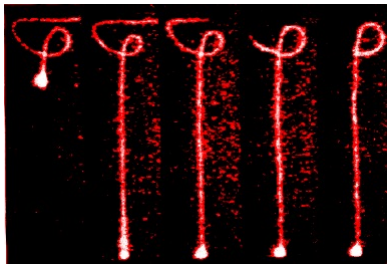
Observing reptating chains



Kas, Strey & Sackman
Nature 1994

Actin solution: $\tau_{rep} \sim 1\,\text{hour}$



Perkins, Quake, Smith & Chu
Science 1994

Labeled DNA in solution of unlabeled DNA; optical tweezer:

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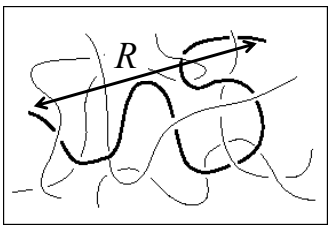
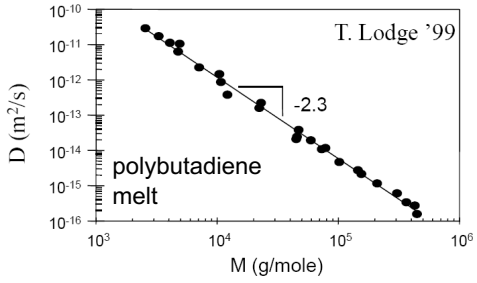
Self-diffusion coefficient of a polymer in a melt



Chain moves distance of order R in a time τ_{rep}:

$$D_{self} \cong \frac{R^2}{\tau_{rep}} \cong \frac{kTN_e}{\zeta_0 N^2}$$



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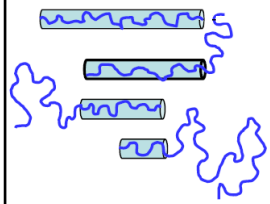
Visco-elasticity



← step strain at $t = 0$

← relaxation at $t > 0$

relaxation modulus: fraction of chain not yet escaped

Masao Doi & Sam Edwards, 1978:

$$G(t) = \frac{8G_e}{\pi^2} \sum_{p=1,3,\ldots} \frac{1}{p^2} \exp\left(-\frac{p^2 t}{\tau_{rep}}\right)$$

$$\approx G_e \exp\left(-\frac{t}{\tau_{rep}}\right)$$

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Stress relaxation modulus after step strain

Short times: chains do not feel tube

⟶ Rouse relaxation within tube:

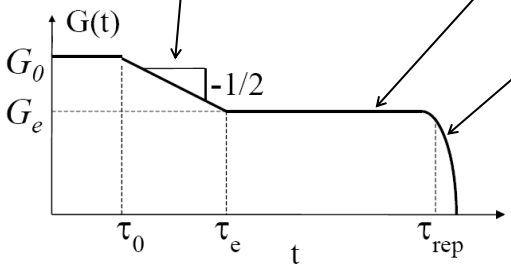
$$G(t) \cong G_0 \left(\frac{\tau_0}{t}\right)^{1/2} \quad \text{with} \quad G_0 \cong \frac{kT}{a^3}$$

Rubber Plateau:

$$G_e \cong \frac{kT}{a^3 N_e}$$

Reptation:

$$G(t) \cong G_e \exp\left(-\frac{t}{\tau_{rep}}\right)$$



$$\tau_e \cong \tau_0 N_e^2 \qquad \tau_{rep} \cong \tau_0 \frac{N^3}{N_e}$$

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The viscosity of a polymer melt

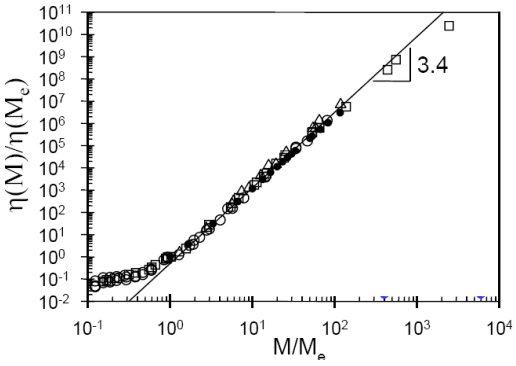
$$G_e \cong \frac{kT}{a^3 N_e} \qquad \tau_{rep} \cong \tau_0 \frac{N^3}{N_e}$$

Boltzmann superposition principle:

$$\eta = \int_0^\infty G(t)dt \approx G_e \tau_{rep} \cong \frac{\zeta_0 N^3}{a N_e^2}$$

Reptation theory: $\eta \sim M^3$

Experiment: $\eta \sim M^{3.4}$



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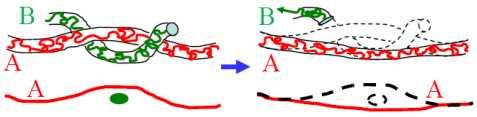
Modifications to reptation theory: constraint release



(reptation of surrounding chains)

De Gennes 1975

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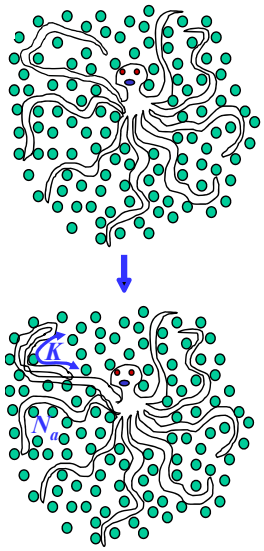
Dynamics of entangled stars

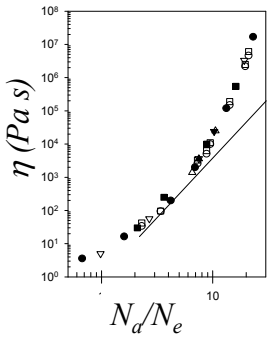


Arm retraction:
activated process

$$\tau \sim \exp\left(U_{ret}/kT\right)$$

$$\tau \sim \exp\left(\beta N_a\right)$$

De Gennes 1975



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Modifications to reptation theory: from 3 to 3.4

(Doi 1981)

Tube length fluctuations also for linear chains

Chain contracts in tube (other Rouse modes)

Tube length fluctuations and constraint release modify viscosity exponent from 3 to 3.4!

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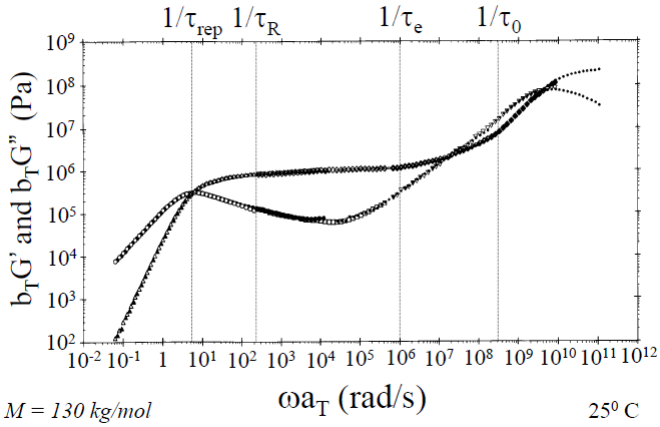
Time temperature superposition



M = 130 kg/mol

25^0 C

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Effect of temperature

Rouse: $\tau_R = \tau_0 N^2$

Zimm: $\tau_Z = \tau_0 N^{3\nu}$

Reptation: $\tau_{rep} = \tau_0 \frac{N^3}{N_e}$

Monomer time: $\tau_0 \approx \frac{\zeta a^2}{kT} \sim \frac{\zeta}{T}$

Relaxation time: $\tau \sim \frac{\zeta}{T}$

Modulus: $G \sim \rho T$

Viscosity: $\eta \approx G\tau \sim \rho\zeta$

Reference temperature T_0: $a_T = \frac{\zeta T_0}{\zeta_0 T}$ $b_T = \frac{\rho T}{\rho_0 T_0}$

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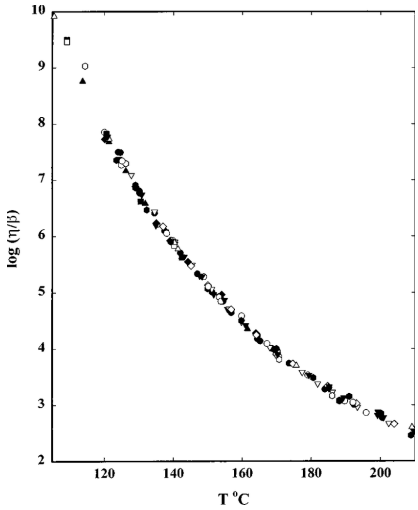
Temperature dependence



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