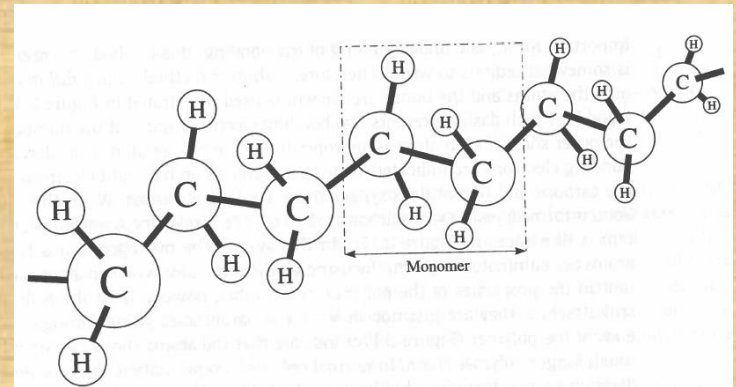


# Structure and Properties of Engineering Polymers

## Lecture: **Dynamics of Polymer Solutions and Melts**

Nikolai V. Priezjev



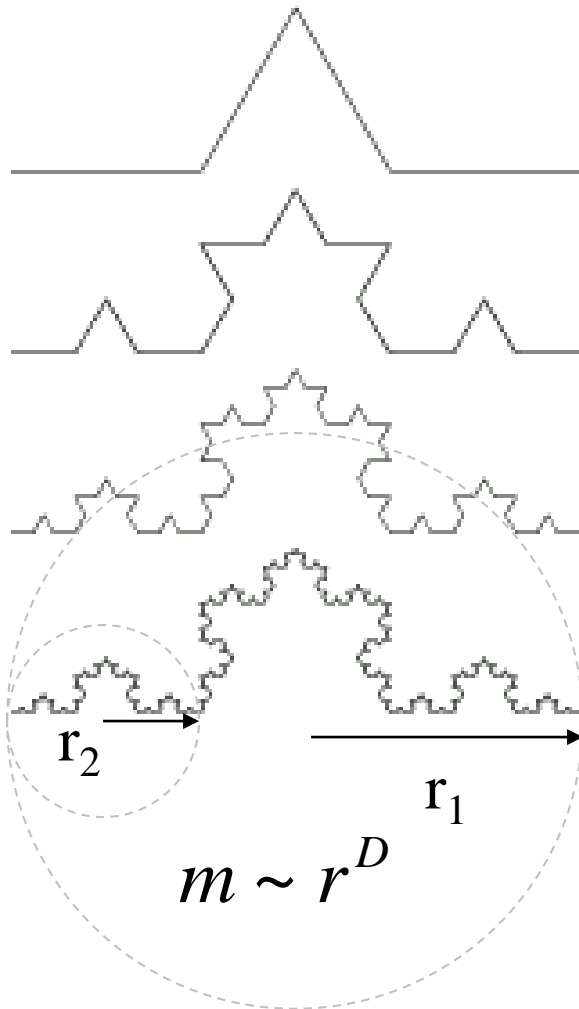
Textbook: *Plastics: Materials and Processing* (Third Edition), by A. Brent Young (Pearson, NJ, 2006).

# Dynamics of Polymer Solutions and Melts

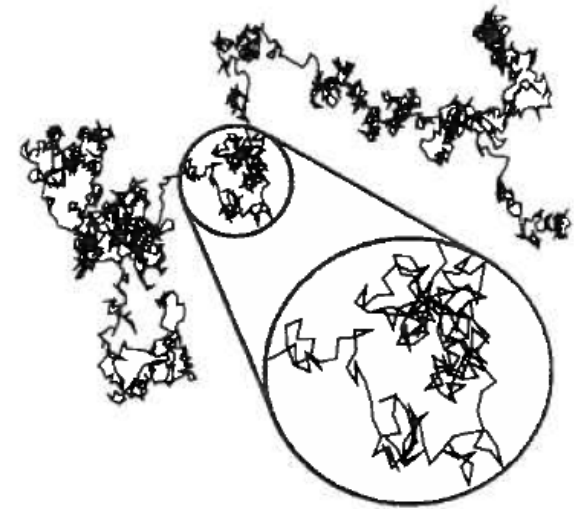
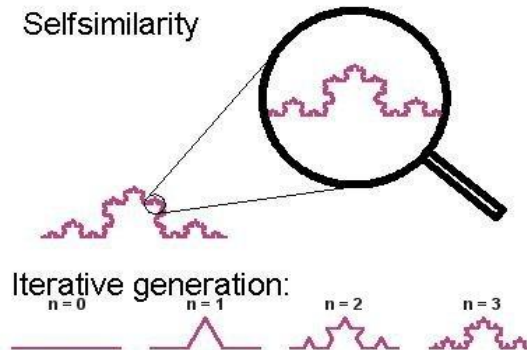
1. Length scales and fractal structure of polymer solutions
2. Brownian diffusion of a spherical particle in a viscous fluid
3. Review of dynamics of unentangled polymer solutions (Rouse and Zimm models)
4. Structure and dynamics of entangled polymer melts (primitive path analysis)

# Fractal Dimension

## The Koch Curve construction



$D = \text{Fractal Dimension}$



**Fig. 1.14**

Fractal structure of an ideal chain with fractal dimension  $D = 2$  obtained by computer simulation (courtesy of Q. Liao).

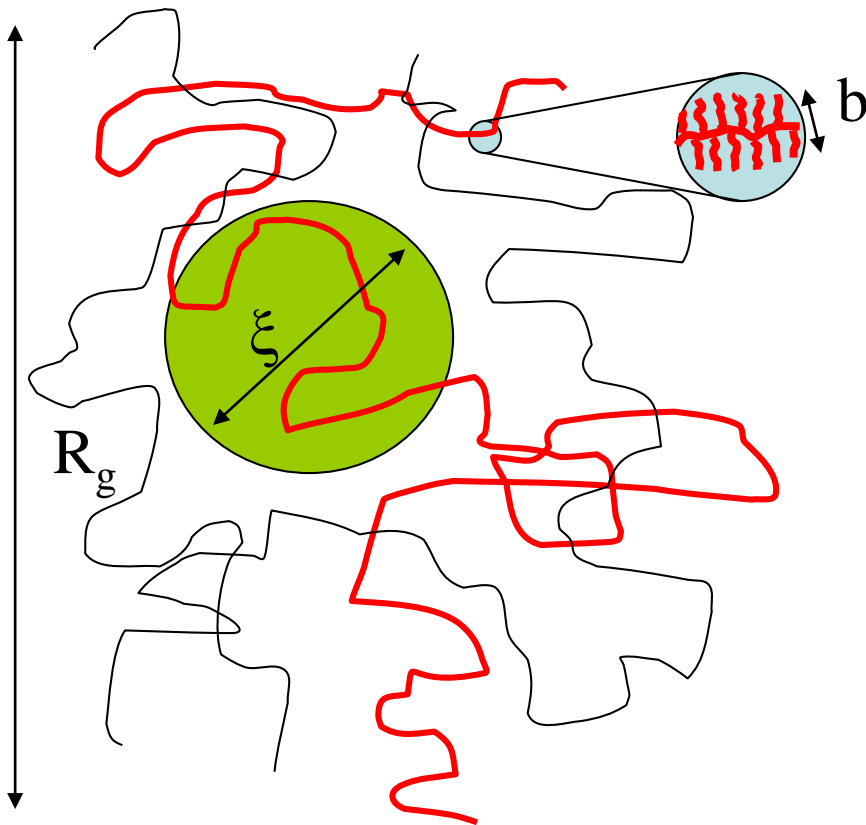
$$N^{1/D} \sim R$$

$$g \sim \langle r^2 \rangle$$

$$l < r < R$$

holds for any subsection of the ideal chain (no interaction between monomers far apart along the chain; random walk;  $D=2$ ) with  $g$  monomers and size  $r$ . Real chains (self-avoiding random walk) are swollen  $D=5/3$ .

# Fractal Structure of Mucins in Semidilute Solution



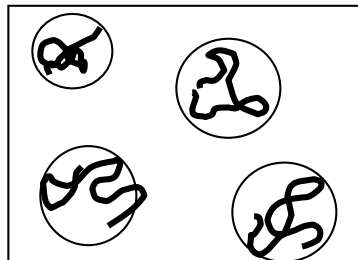
Contour length  $L=20\mu\text{m}$  ( $1\mu\text{m}=1000\text{nm}$ )

Molecular brush on scale  $b=5\text{-}10\text{nm}$

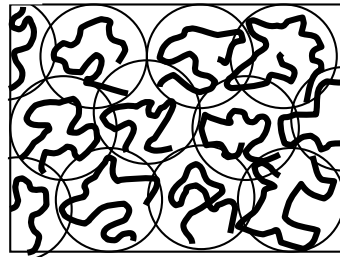
Correlation length  $\xi=50\text{nm}$  at mass concentration  $c=1\%$  (monomers interact with solvent and with monomers from the same section of its own chain)

On scale  $b < r < \xi$  excluded volume interactions swell mucins.

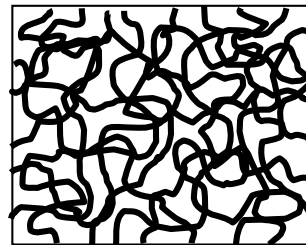
On larger length scales excluded volume interactions are screened.



$c < c^*$



$c = c^* \sim 0.1\%$



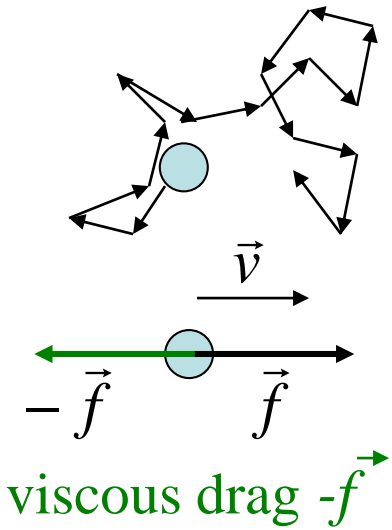
$c^* < c \ll 1$

Radius of gyration

$R_g \sim 200\text{-}300\text{nm}$

(depends on concentration  $c$ )

# Brownian (Diffusive) Motion



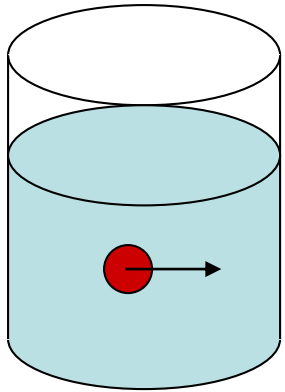
mean-square displacement:

$$\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle = 6Dt \quad D - \text{diffusion coefficient}$$

$\vec{v}$  – velocity of particle due to applied force  $\vec{f} = \vec{v}\zeta$

$\zeta$  – friction coefficient

**Einstein relation:**  $D = \frac{kT}{\zeta}$



Stokes Law:  $\zeta = 6\pi\eta R$

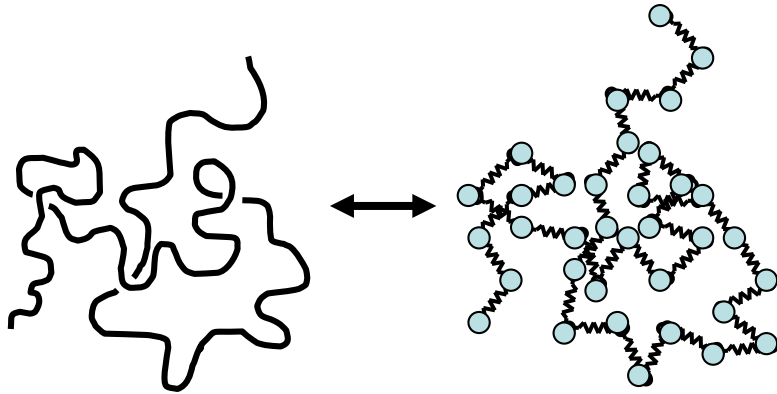
$R$  – radius of the particle  
 $\eta$  – viscosity of the fluid

$$D = \frac{kT}{6\pi\eta R} \quad - \text{Stokes-Einstein relation}$$

Time required for a particle to move a distance of order of its size:

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

# Rouse Model (1953)



$N$  beads connected by springs  
with root-mean square size  $b$ .

$\zeta$  – friction coefficient of a bead

$\zeta_R = N\zeta$  – total friction coefficient of the Rouse chain

$$D_R = \frac{kT}{\zeta_R} = \frac{kT}{N\zeta} \quad \text{– diffusion coefficient of the Rouse chain}$$



Time required for a chain to move a distance of order of its size  $R$

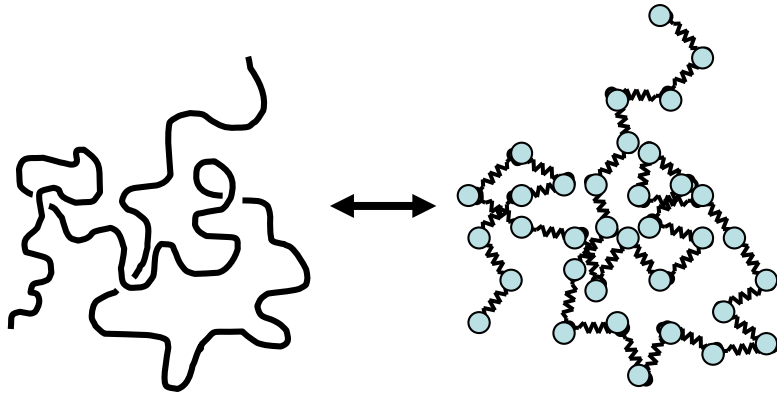
$$\tau_R \approx \frac{R^2}{D_R} \approx \frac{\zeta}{kT} NR^2 \quad \text{– Rouse time}$$

for  $t < \tau_R$  – viscoelastic modes

for  $t > \tau_R$  – diffusive motion

Ideal chain: no interaction between monomers that are far apart along the chain

# Rouse Model (continued)



$N$  beads connected by springs with root-mean square size  $b$ .

$\zeta$  – friction coefficient of a bead

$\eta_s$  – solvent viscosity

$$R \approx bN^\nu$$

Fractal structure

$$\tau_R \approx \frac{R^2}{D_R} \approx \frac{\zeta}{kT} NR^2$$

$$\tau_R \approx \frac{b^2 \zeta}{kT} N^{1+2\nu} \approx \tau_0 N^{1+2\nu}$$

where  $\tau_0 \approx \frac{b^2 \zeta}{kT}$  – Kuhn monomer relaxation time (time scale for motion of individual beads)

From the Stokes Law

$$\zeta \approx \eta_s b \longrightarrow \tau_0 \approx \frac{b^3 \eta_s}{kT}$$

Rouse model:  
draining limit

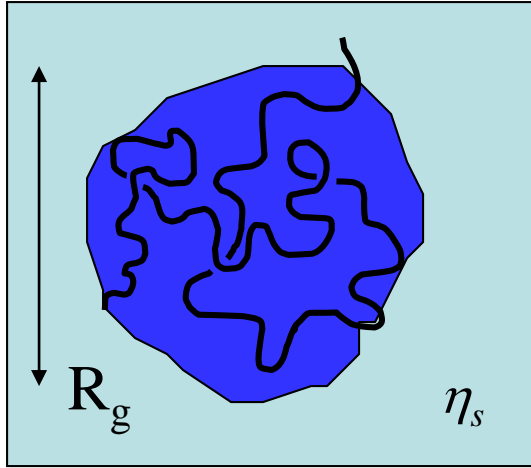
For ideal chain:  $\nu = 1/2$

$$\tau_R \approx \tau_0 N^2 \approx \frac{b^3 \eta_s}{kT} N^2$$

Rouse 1953

Ideal chain: no interaction between monomers that are far apart along the chain

# Zimm Model (1956)



Hydrodynamic interactions couple the motion of monomers with the motion of solvent.

Chain drags with it the solvent in its pervaded volume.

Friction coefficient of chain of size  $R$  in a solvent with viscosity  $\eta_s$  is  $\zeta_Z \approx \eta_s R$

$$R \approx bN^\nu$$

Fractal structure

Zimm diffusion coefficient:

$$D_Z = \frac{kT}{\zeta_Z} \approx \frac{kT}{\eta_s R}$$

Zimm time:  $\tau_Z = \frac{R^2}{D_Z} \approx \frac{\eta_s}{kT} R^3 \approx \frac{\eta_s b^3}{kT} N^{3\nu} \approx \tau_0 N^{3\nu}$

$3\nu < 1+2\nu$  for  $\nu < 1$  Zimm time is shorter than Rouse time in dilute solutions.

in  $\theta$ -solvent

$$\tau_z \sim N^{3/2}$$

in good solvent

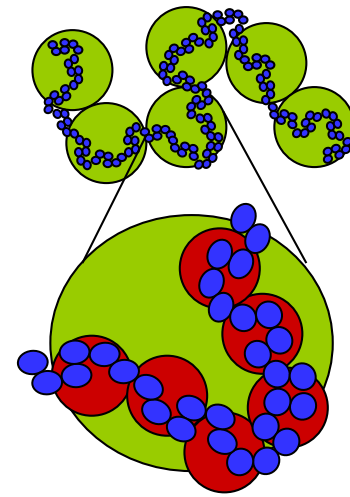
$$\tau_z \sim N^{9/5}$$

Hydrodynamic interactions are important in dilute solutions.



# Self-Similar Dynamics of Polymer Chains

Chains are fractal – they look the same on different length scales and move in the same way on different time scales.



## Rouse Model

## Zimm Model

Longest relaxation time:

$$\text{Rouse time } \tau_R \approx \tau_0 N^2$$

$$\text{Zimm time } \tau_Z \approx \tau_0 N^{3\nu}$$

$p$ -th mode involves relaxation of  $N/p$  monomers.

Smaller sections of the polymer chain with  $g=N/p$  monomers relax just like a  $g$ -mer.

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

$$\tau_p \approx \tau_0 \left( \frac{N}{p} \right)^{3\nu}$$

At time  $\tau_p$  modes with index higher than  $p$  have relaxed, while modes with index lower than  $p$  have not relaxed.

$\phi / (b^3 N / p)$   
number density  
of sections with  
 $N/p$  monomers

At time  $\tau_p$  there are  $p$  un-relaxed modes per chain each contributing energy of order  $kT$  to the stress relaxation modulus:

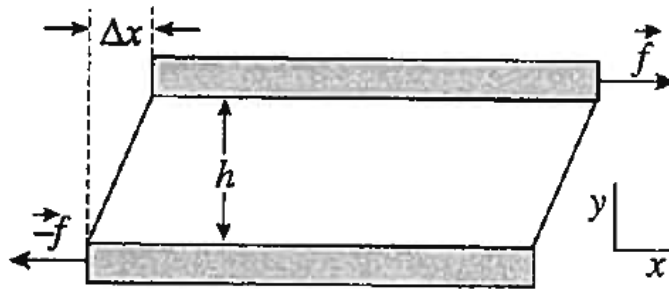
$\phi = V_{\text{pol}}/V_{\text{sol}}$  – volume fraction of the polymer in solution

$$G(\tau_p) \approx \frac{kT}{b^3} \frac{\phi}{N} p$$

# Stress Relaxation Modulus After a Step Strain

$G(t)$  is the “stress relaxation modulus”  $G(t) = \frac{\sigma_s(t)}{\gamma_s} \approx G(\tau)e^{-t/\tau}$

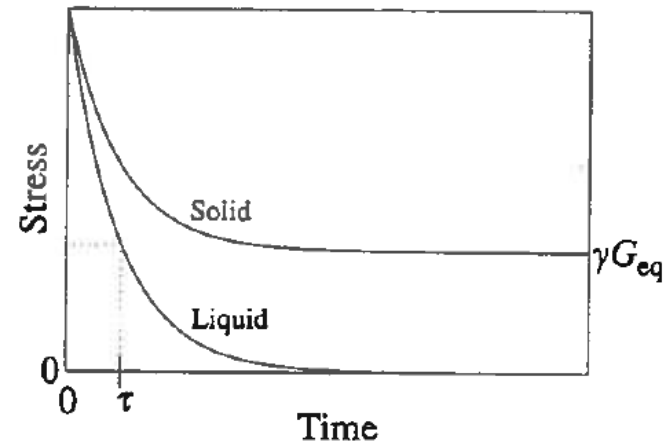
$G(t)$  can be determined by applying a constant strain,  $\gamma_s$ , and observing stress relaxation over time:



**Fig. 7.20**

Deformation in simple shear requires application of equal and opposite forces to the two plates. The shear strain is  $\gamma = \Delta x/h$ . The figure is a two-dimensional representation.

$$\text{viscosity: } \eta = \int_0^{\infty} G(t) dt \approx G(\tau)\tau$$



**Fig. 7.22**

Stress relaxation in step strain experiments on a viscoelastic solid (upper curve) and a viscoelastic liquid (lower curve). The dashed lines show the value of the stress at the relaxation time  $\tau$  of the liquid. The solid has the same relaxation time.

# Self-Similar Dynamics of Polymer Chains

## Rouse Model

$$G(\tau_p) \approx \frac{kT}{b^3} \frac{\phi}{N} p$$

Index  $p$  of the mode that relaxes at  $t = \tau_p \approx \tau_0 \left( \frac{N}{p} \right)^\alpha$

$$p \approx \left( \frac{t}{\tau_0} \right)^{-1/2} N$$

$$p \approx \left( \frac{t}{\tau_0} \right)^{-1/3\nu} N$$

Stress relaxation modulus interpolation at intermediate times  $\tau_0 < t < \tau_{relax}$

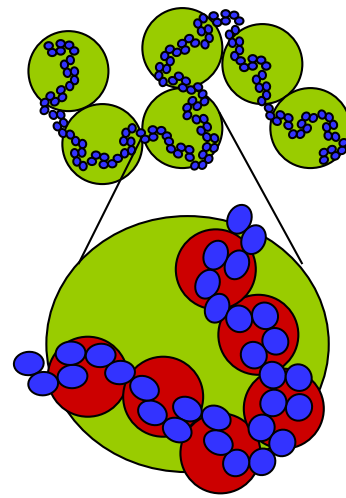
$$G(t) \approx \frac{kT}{b^3} \phi \left( \frac{t}{\tau_0} \right)^{-1/2}$$

$$G(t) \approx \frac{kT}{b^3} \phi \left( \frac{t}{\tau_0} \right)^{-1/3\nu}$$

Stress relaxation modulus approximation for all  $t > \tau_0$

$$G(t) \approx \frac{kT}{b^3} \phi \left( \frac{t}{\tau_0} \right)^{-1/2} \exp\left(-\frac{t}{\tau_R}\right)$$

$$G(t) \approx \frac{kT}{b^3} \phi \left( \frac{t}{\tau_0} \right)^{-1/3\nu} \exp\left(-\frac{t}{\tau_Z}\right)$$



# Stress Relaxation Modulus: Rouse Model

Scaling approximation  $G(t) \approx \frac{kT}{b^3} \phi \left( \frac{t}{\tau_0} \right)^{-1/2} \exp \left( -\frac{t}{\tau_R} \right)$

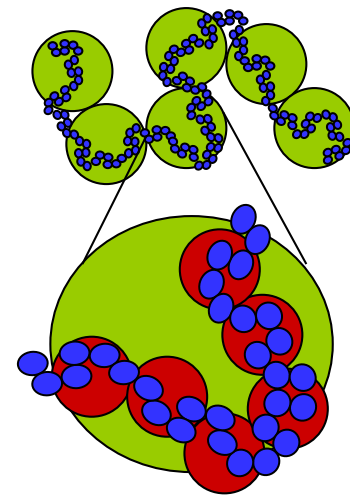
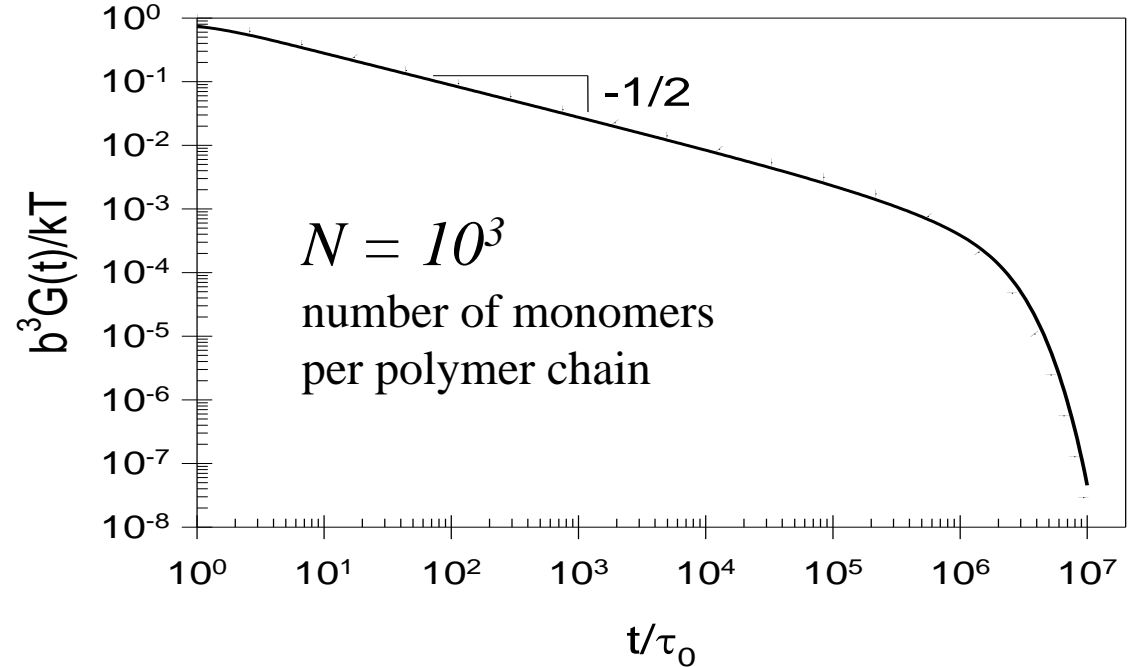
Exact Rouse solution:

$$G(t) = kT \frac{\phi}{Nb^3} \sum_{p=1}^N \exp \left( -\frac{t}{\tau_p} \right)$$

relaxation time  
of p-th mode

$$\tau_p = \frac{b^2 \zeta}{6\pi^2 kT} \left( \frac{N}{p} \right)^2$$

(solid line)



Rouse model applies to melts  
( $\phi=1$ ) with short unentangled  
chains

$$\eta \approx \frac{\zeta}{b} N \quad \eta = \int_0^{\infty} G(t) dt$$

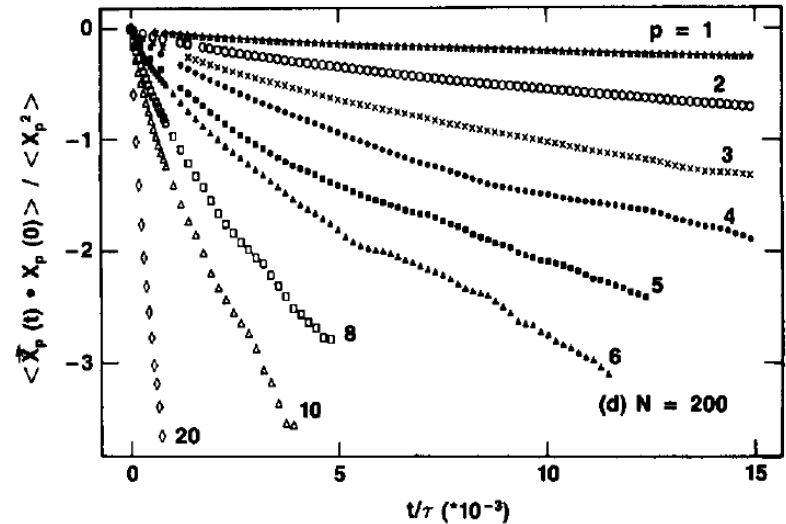
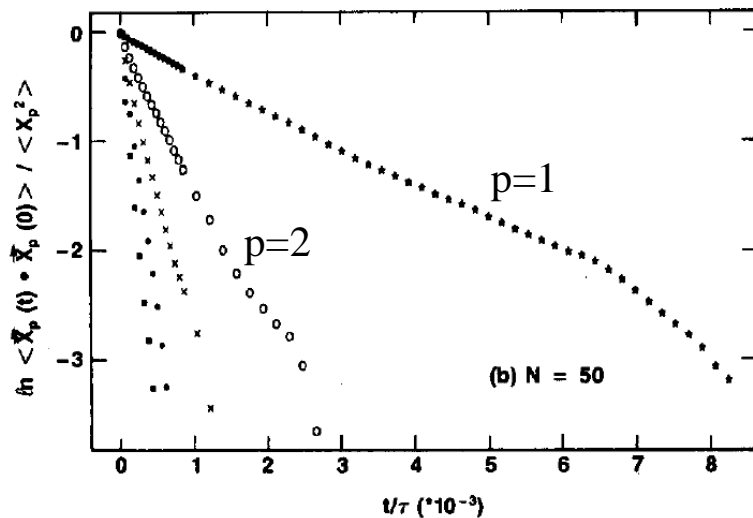
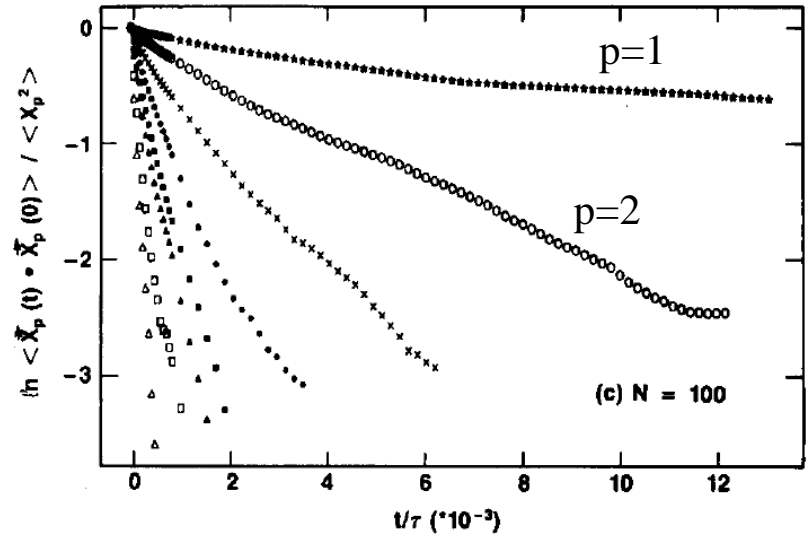
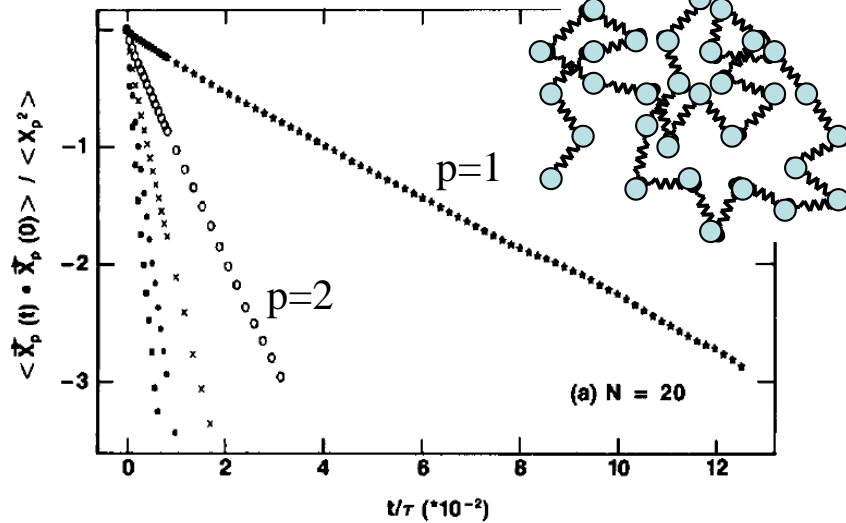
# Normal Mode Analysis: MD simulations of Bead-Spring Model

$$\mathbf{X}_p(t) = \frac{1}{N} \left[ \sum_{i=1}^N \mathbf{r}_i(t) \cos \frac{p\pi(i-1)}{N-1} \right]$$

Rouse modes;  
p = mode #

$$g_p(t) = \frac{\langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle}{\langle \mathbf{X}_p(0) \cdot \mathbf{X}_p(0) \rangle} = \exp(-t/\tau_p)$$

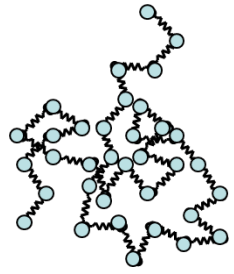
$$\tau_p \approx \tau_0 \left( \frac{N}{p} \right)^2$$



# Mean Square Displacement of Monomers

## Rouse Model

## Zimm Model



Section of  $N/p$  monomers moves by its size  $b(N/p)^{1/2}$  during its relaxation time  $\tau_p$

ok for melts

$$\langle [\vec{r}_j(\tau_p) - \vec{r}_j(0)]^2 \rangle \approx b^2 \left( \frac{N}{p} \right)^{2\nu}$$

ok for dilute solutions

for ideal chain  $\nu = 1/2$

$$p/N = (t/t_0)^{-1/2}$$

$$p/N = (t/t_0)^{-1/3\nu}$$

Mean square monomer displacement for  $\tau_0 < t < \tau_{\text{relax}}$

$$\langle [\vec{r}_j(t) - \vec{r}_j(0)]^2 \rangle \approx b^2 (t/\tau_0)^{1/2}$$

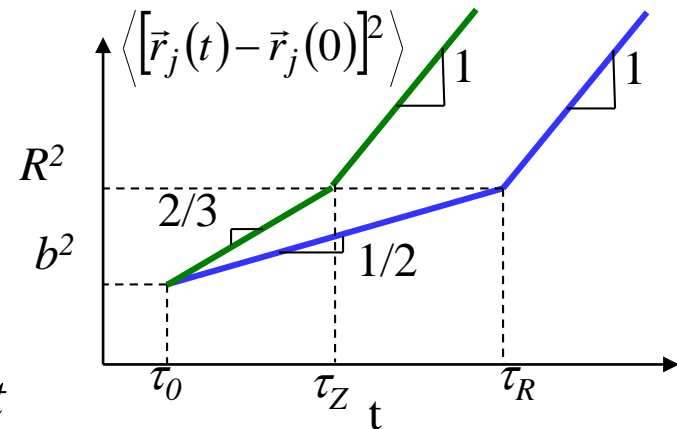
$$\langle [\vec{r}_j(t) - \vec{r}_j(0)]^2 \rangle \approx b^2 (t/\tau_0)^{2/3}$$

## Sub-diffusive motion

Sections of  $N/p$  monomers move coherently on time scale  $\tau_p$

Monomer motion in Zimm model is faster than in Rouse model

$$\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle = 6Dt$$



# Summary of Unentangled Dynamics

**Rouse model** – local monomer friction  $\zeta$  and no hydrodynamic interactions. It is applicable to unentangled polymer melts.

Rouse friction coefficient of an N-mer is  $N\zeta$  and diffusion coefficient

$$D_R = kT / (N\zeta)$$

**Zimm model** – motion of monomers is hydrodynamically coupled. Polymer chain drags solvent in its pervaded volume. It is applicable to dilute solutions. Diffusion coefficient  $D_Z = kT / (\eta_s R)$

Polymer diffuses distance of order of its size during its relaxation time

$$\tau_R \approx \frac{\zeta}{kT} NR^2$$

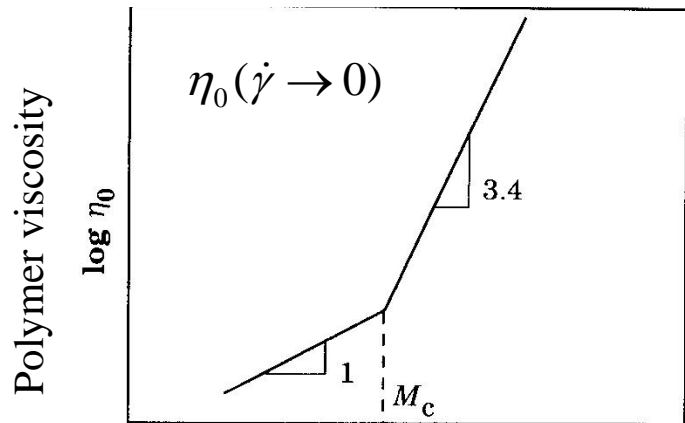
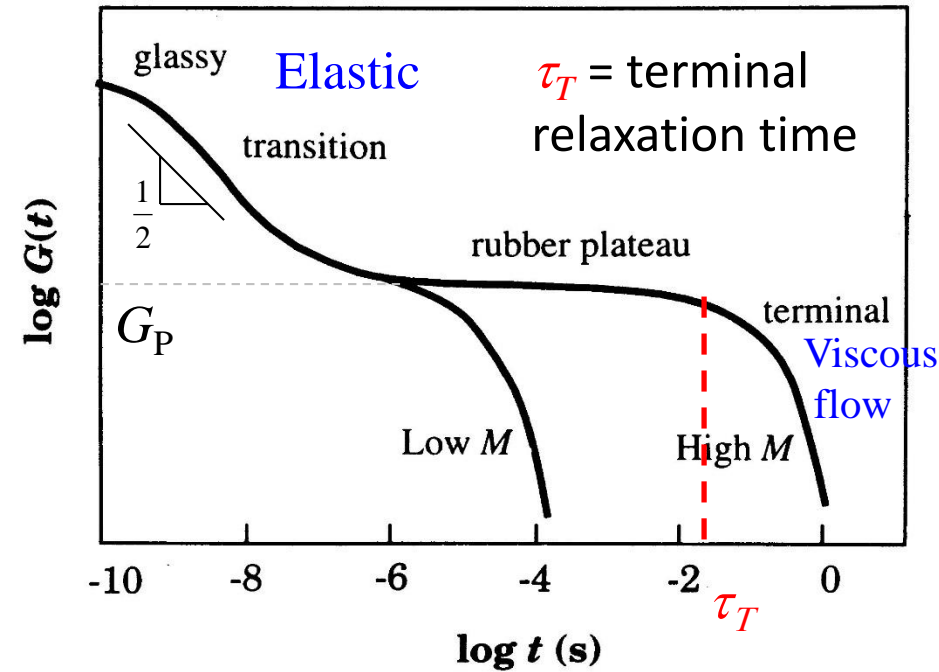
$$\tau_Z \approx \frac{\eta_s}{kT} R^3$$

Hydrodynamic interactions in semidilute solutions are important up to the scales of hydrodynamic screening length.

On larger length scales both excluded volume and hydrodynamic interactions are screened by surrounding chains.

# Viscoelasticity of Entangled Polymer Melts

## Relaxation Modulus for Polymer Melts



Molecular weight (chain length)

The stress relaxation  $G(t)$  for two polymers with different molecular weights.

At short time the curves are identical.

At intermediate times we have a plateau with a *constant modulus* – **the plateau modulus**.

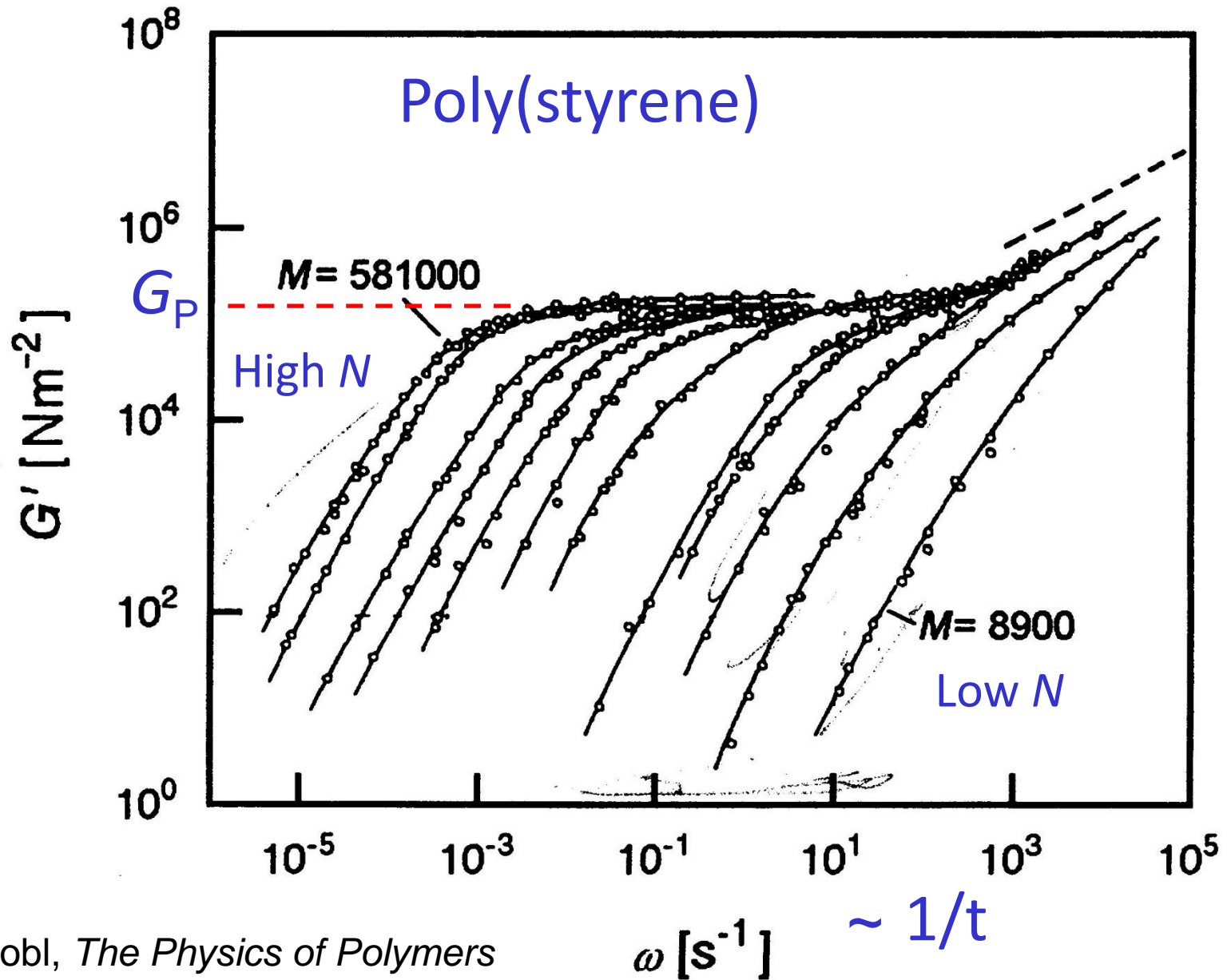
The plateau ends at a **terminal time**  $\tau_T$  which depends strongly on molecular weights ( $N$ ) according to a power law  $\tau_T \sim N^m$  where the exponent  $m \approx 3.4$

Two Q's arises: 1) Why is  $m \approx 3.4$  almost universal? 2) why do we have an almost purely elastic behaviour at the plateau?

$$\eta \approx \int_0^{\infty} G(t) dt \approx G_P \tau_T \sim N^{3.4}$$

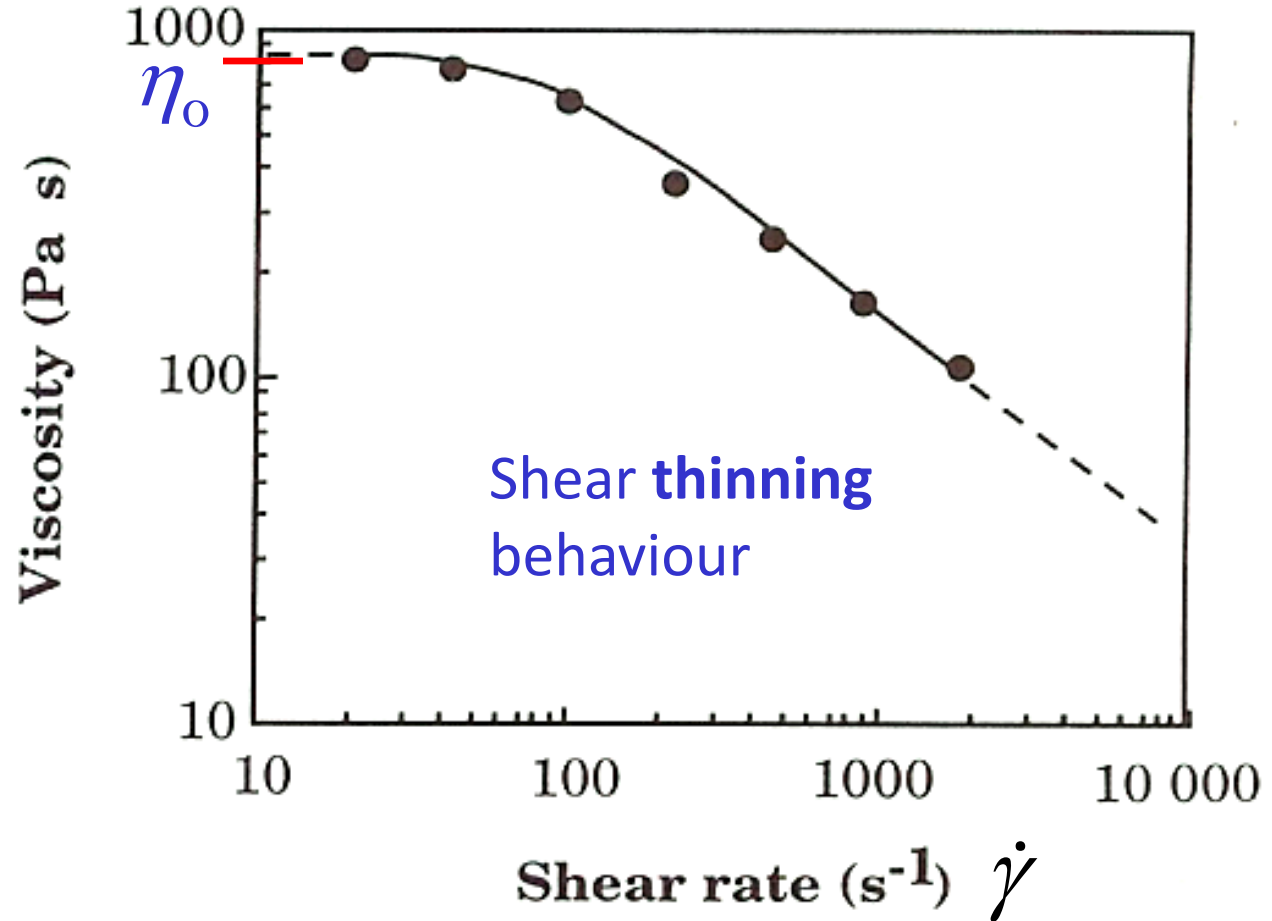


# Experimental Shear Relaxation Moduli



# Viscosity of Polymer Melts

Extrapolation to low shear rates gives us a value of the “zero-shear-rate viscosity”,  $\eta_0$ .



For comparison:  $\eta$  for water is  $10^{-3}$  Pa s at room temperature.

Poly(butylene terephthalate) at 285 °C

From Gedde, *Polymer Physics*

# Scaling of Viscosity: $\eta_o \sim N^{3.4}$

$$\eta \sim \tau_T G_P$$

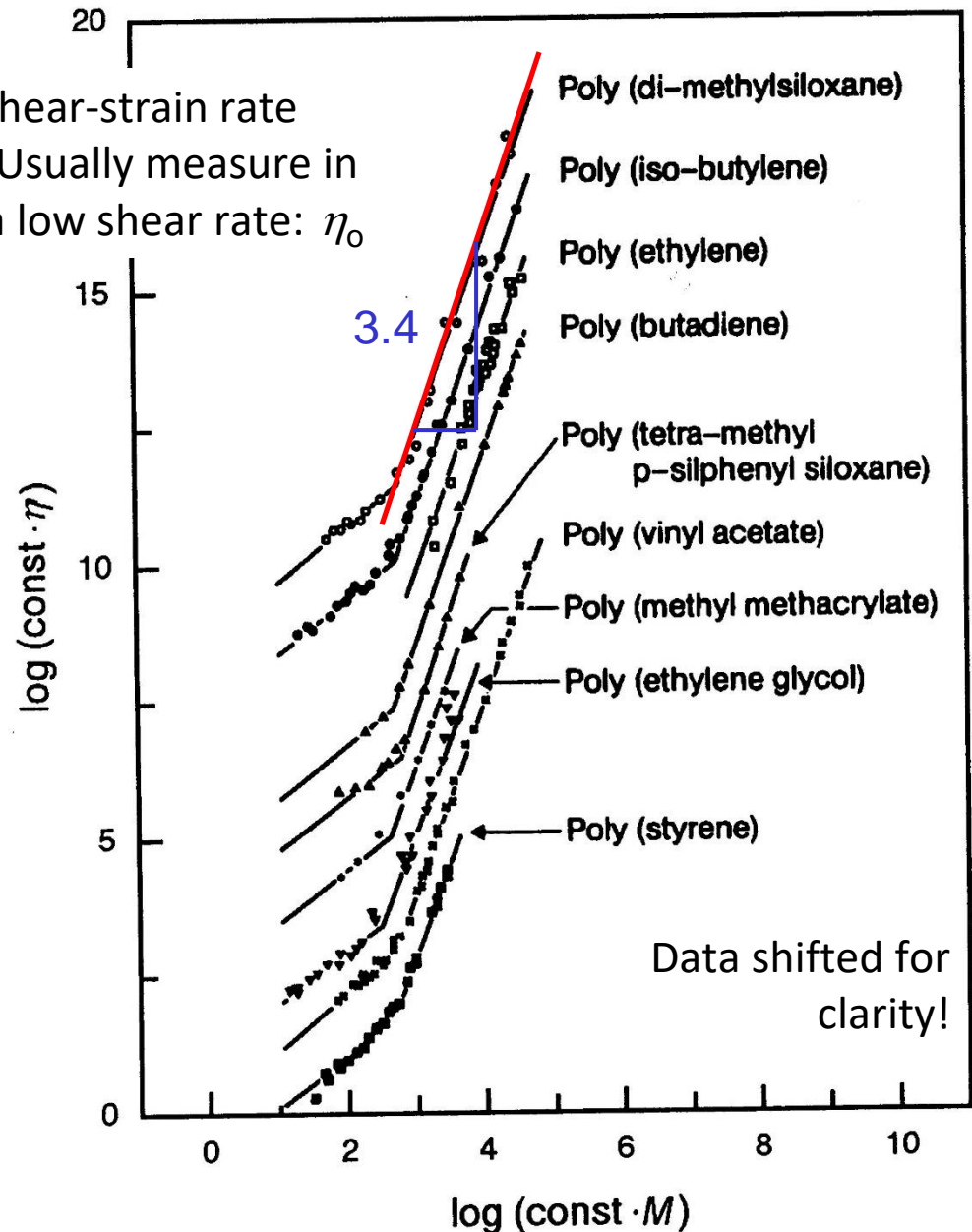
$$\eta_o \sim N^{3.4} \quad N^0 \sim N^{3.4}$$

Universal behavior for  
linear polymer melts

Applies for higher  $N$ :  
 $N > N_c$

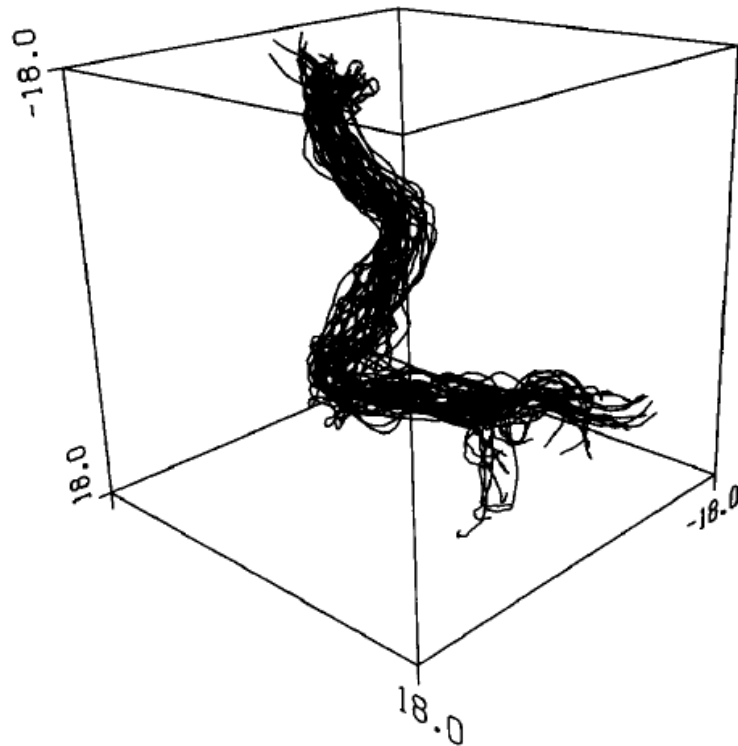
**Why?**

Viscosity is shear-strain rate dependent. Usually measure in the limit of a low shear rate:  $\eta_o$



# Simulation of the tube: polymer melt with linear chains of N beads

Lennard-Jones potential:

$$V_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{r}{\sigma} \right)^{-12} - \left( \frac{r}{\sigma} \right)^{-6} \right]$$


MD simulations of a chain with  $N=400$  monomers in an entangled polymer melt. Forty configurations of the chain are shown at equally spaced time intervals  $600\tau$ .

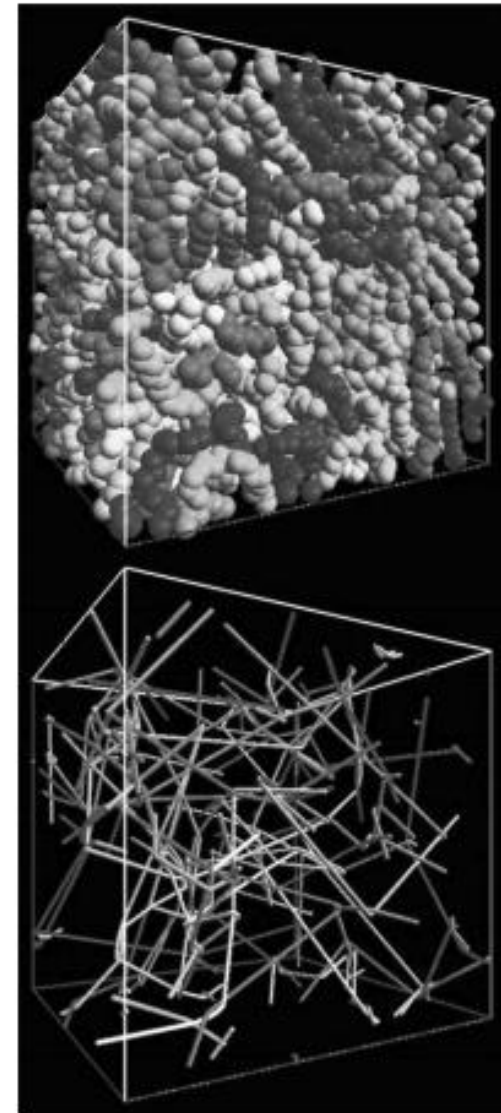
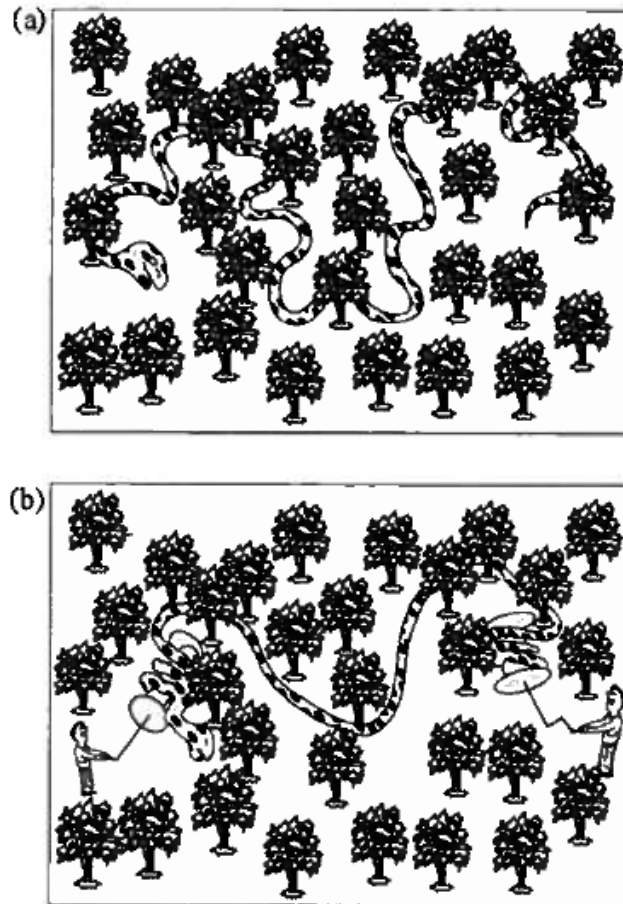


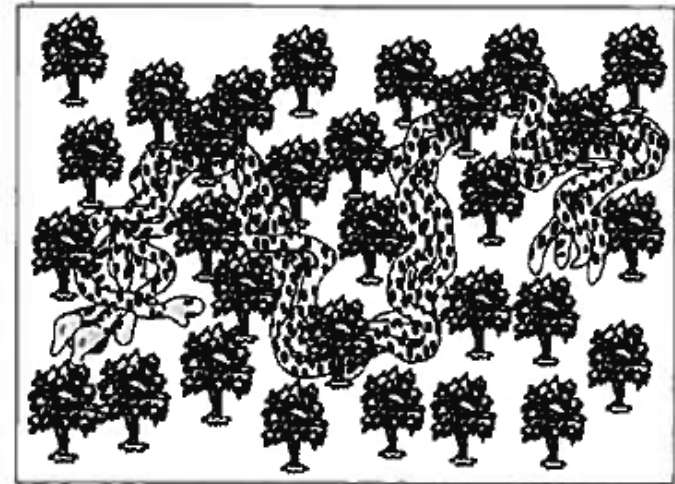
Fig. 3. A representative amorphous polymer sample and the corresponding network of primitive paths.

# Entangled Polymer System: Reptation and the Tube Model



**Fig 9.11**

Frame (a) shows a two-dimensional model of a chain in a permanent entanglement network: a giant snake in a forest. Frame (b) shows two students reeling-in the ends of the snake to construct the primitive path.



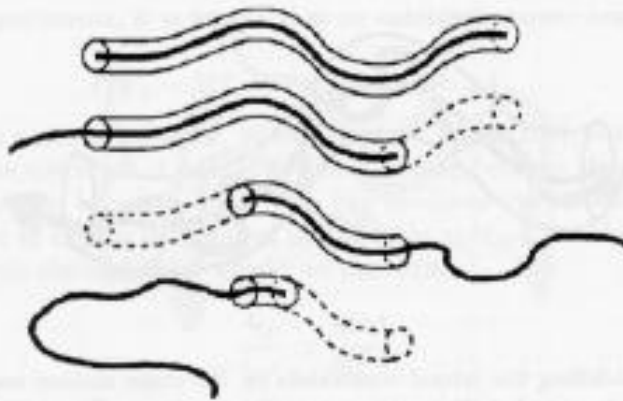
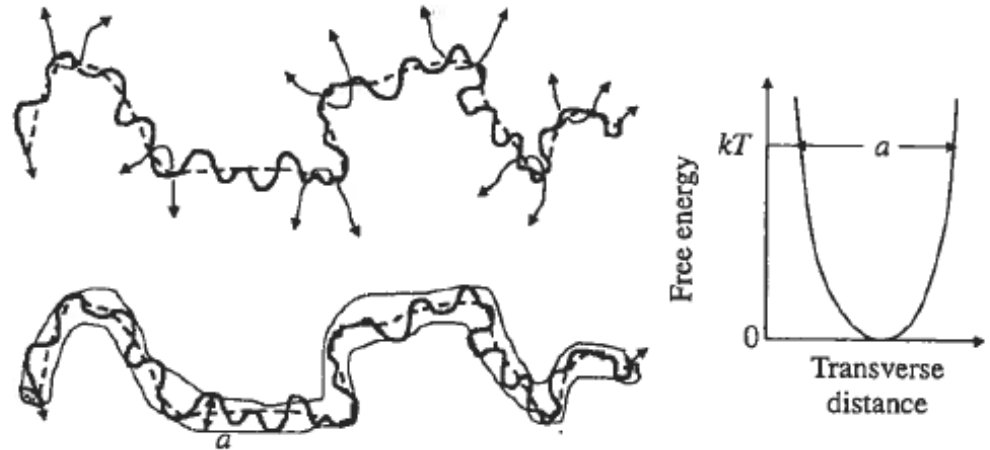
**Fig. 9.12**

A long-exposure photograph of the giant snake in the forest clearly defines its confining tube.

# Entangled Polymer System: Reptation and the Tube Model

**Fig. 7.10**

A chain or network strand (thick curve) is topologically constrained to a tube-like region by surrounding chains. The primitive path is shown as the dashed curve. The roughly quadratic potential defining the tube is also sketched.

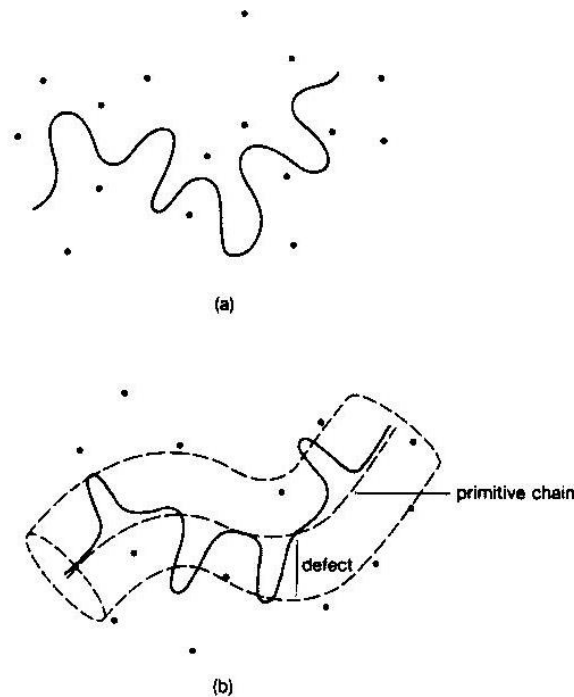


**Fig. 6.11.** Reptation model: Decomposition of the tube resulting from a reptative motion of the primitive chain. The parts which are left empty disappear

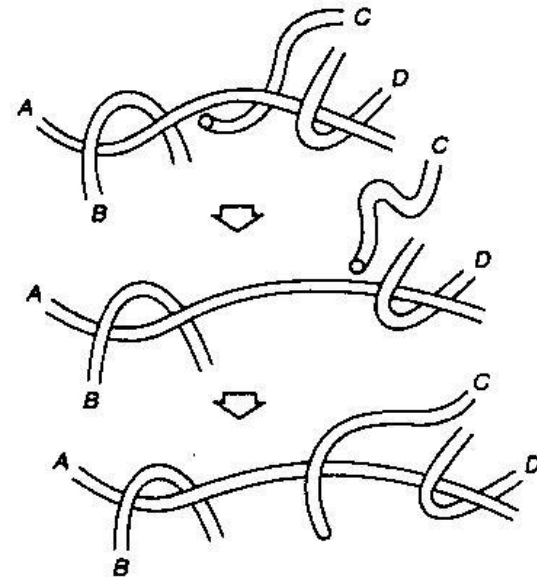


# Entangled Polymer System: Reptation and the Tube Model

A 2D projected viewpoint



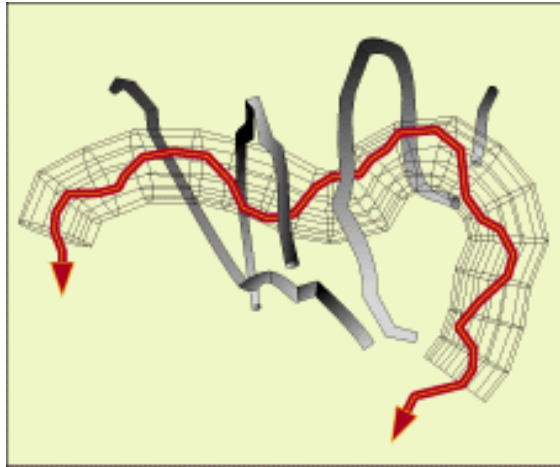
Constraint Release & Re-entangled Mechanisms



A chain in a fixed network of obstacles

M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, pps. 189-194, Oxford Science: New York (1986).

# Q1: The tube model and the idea of reptation (P. de Gennes)



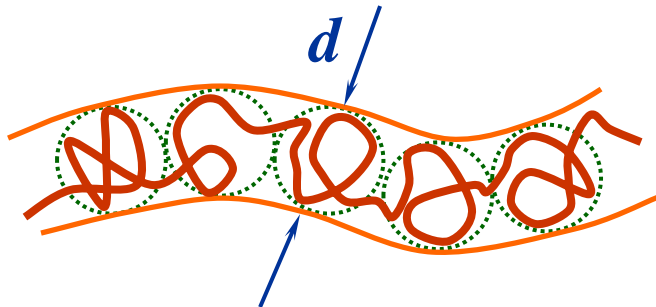
A polymer chain escapes from its own tube of length  $L$  after a time  $\tau_T$

Every segment in the tube have a mobility,  $\mu_{\text{seg}}$  restricted by the surrounding “resistance”.

The tube with  $N$  segments have a mobility,  $\mu_{\text{tube}} = \mu_{\text{seg}}/N$

Brownian motion within the tubes confinement – use Einstein relation to calculate a diffusion coefficient  $\Rightarrow$

$$\Rightarrow D_{\text{tube}} = k_B T \mu_{\text{tube}} = k_B T \mu_{\text{seg}}/N$$



$$\tau_T \cdot D_{\text{tube}} = L^2$$

$$\tau_T = \frac{L^2}{D_{\text{tube}}} \propto \frac{N^3}{\text{const}}$$

This relationship is close to the best experimental fit

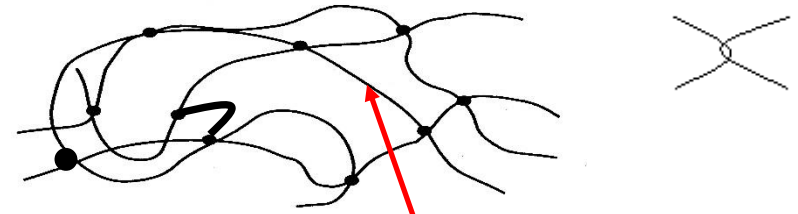
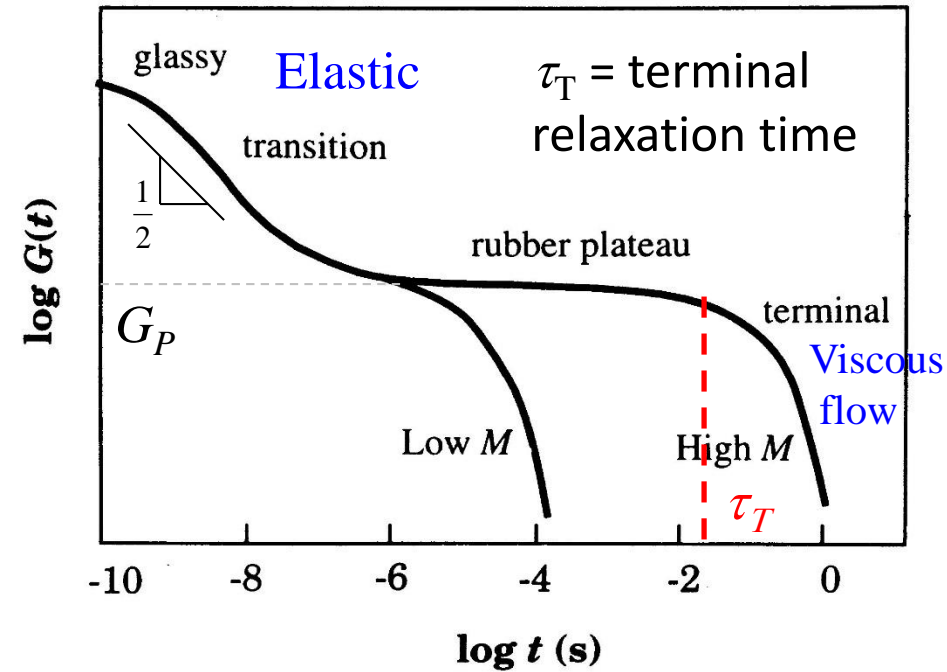
$$\eta \sim N^{3.4}$$



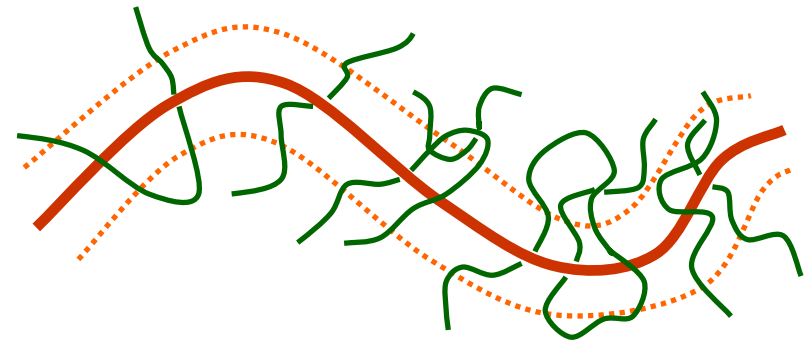
# Q2: The rubber plateau and entanglements

## Relaxation Modulus for Polymer Melts

Rubber plateau arises from chain entanglements.



$G_P = nkT$ , where  $n$  is # of strands per unit volume.



It can be shown that in a rubber, a *cross-linked polymer*, the elastic modulus depends on the average molecular mass between cross-links  $M_x$ ,  $R$ ,  $T$  and the density  $\rho$ :

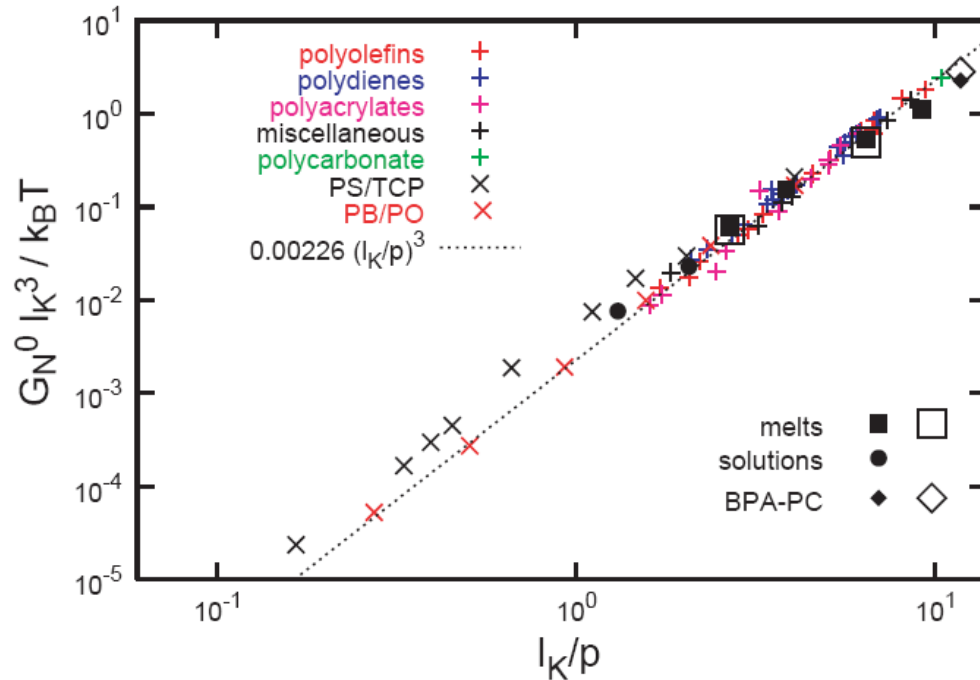
Adopting an identical relation and treating the entanglements as *temporary cross-links* with a lifetime of the order of  $\tau_T$  we can calculate an average mass of the molecular mass between the entanglements ( $M_x$ ).

$$G_P = \frac{\rho RT}{M_x}$$

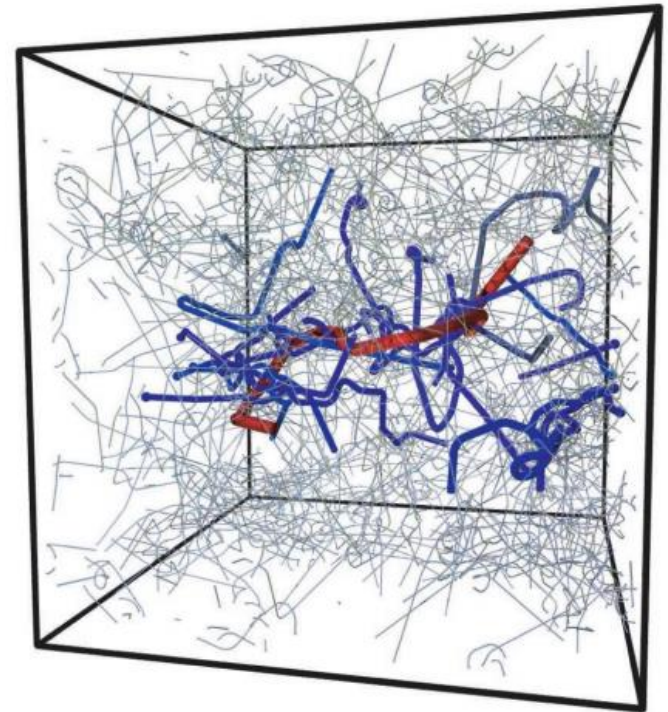
The value of  $G_P$  is independent of  $N$  for a given polymer

# Rheology and Topology of Entangled Polymers

## Primitive Path Analysis (PPA):

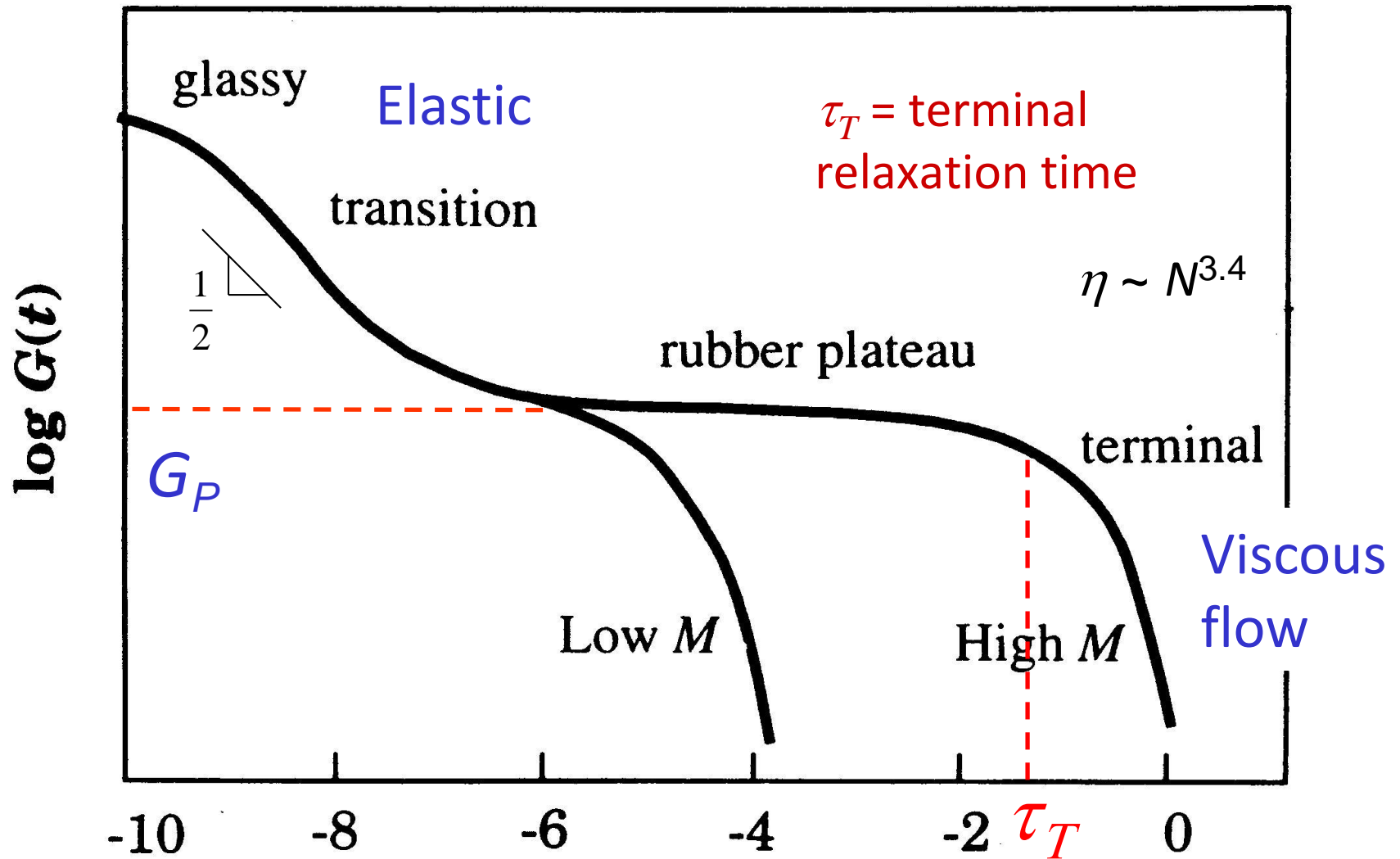


**Fig. 2.** Dimensionless plateau moduli  $G_N^0 l_K^3 / k_B T$  as a function of the dimensionless ratio  $l_K/p$  of Kuhn length  $l_K$  and packing length  $p$ .



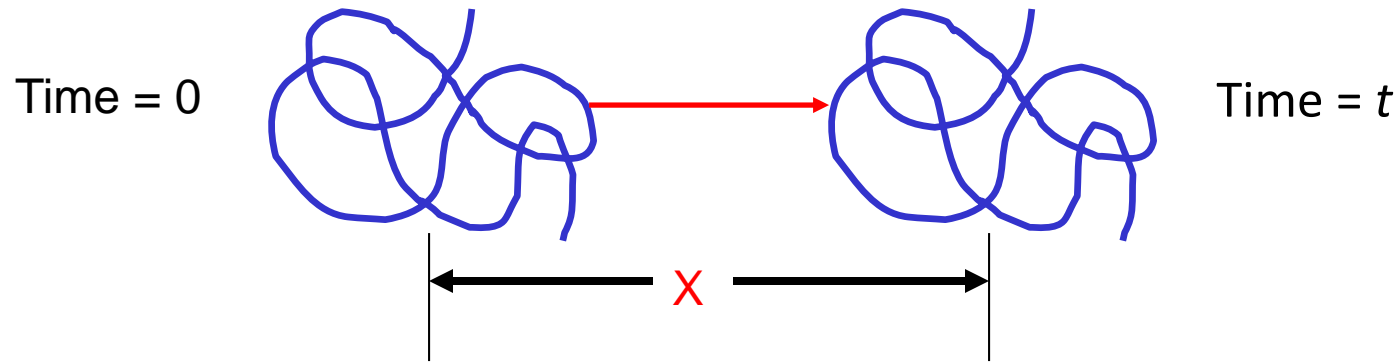
**Fig. 3.** Result of the primitive-path analysis of a melt of 200 chains of  $N + 1 = 350$  beads. We show the primitive path of one chain (red) together with all of those it is entangled with (blue). The primitive paths of all other chains in the system are shown as thin lines.

# Summary of Entangled Dynamics



$G_P$  is independent of  $N$  for a given polymer:  $G_P \sim N^0$ .

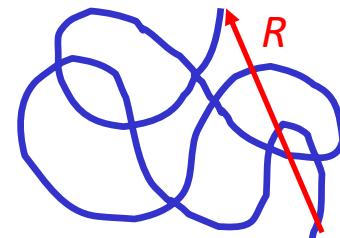
# Polymer Self-Diffusion



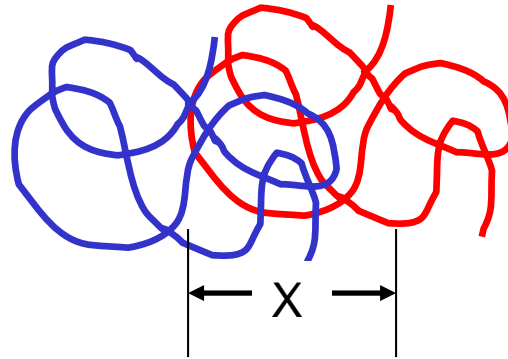
Reptation theory can also describe the self-diffusion of polymers, which is the movement of the centre-of-mass of a molecule by a distance  $X$  in a matrix of the same type of molecules.

In a time  $\tau_{tube}$ , the molecule will diffuse the distance of its entire length. But, its centre-of-mass will move a distance on the order of its r.m.s. end-to-end distance,  $R$ .

In a polymer melt:  $\langle R^2 \rangle^{1/2} \sim aN^{1/2}$



# Polymer Self-Diffusion Coefficient



A self-diffusion coefficient,  $D_{\text{self}}$ , can then be defined as:

$$D_{\text{self}} \sim \frac{x^2}{t} \sim \frac{(aN^{1/2})^2}{\tau_{\text{tube}}} = \frac{a^2 N}{\tau_{\text{tube}}}$$

But we have derived this scaling relationship:

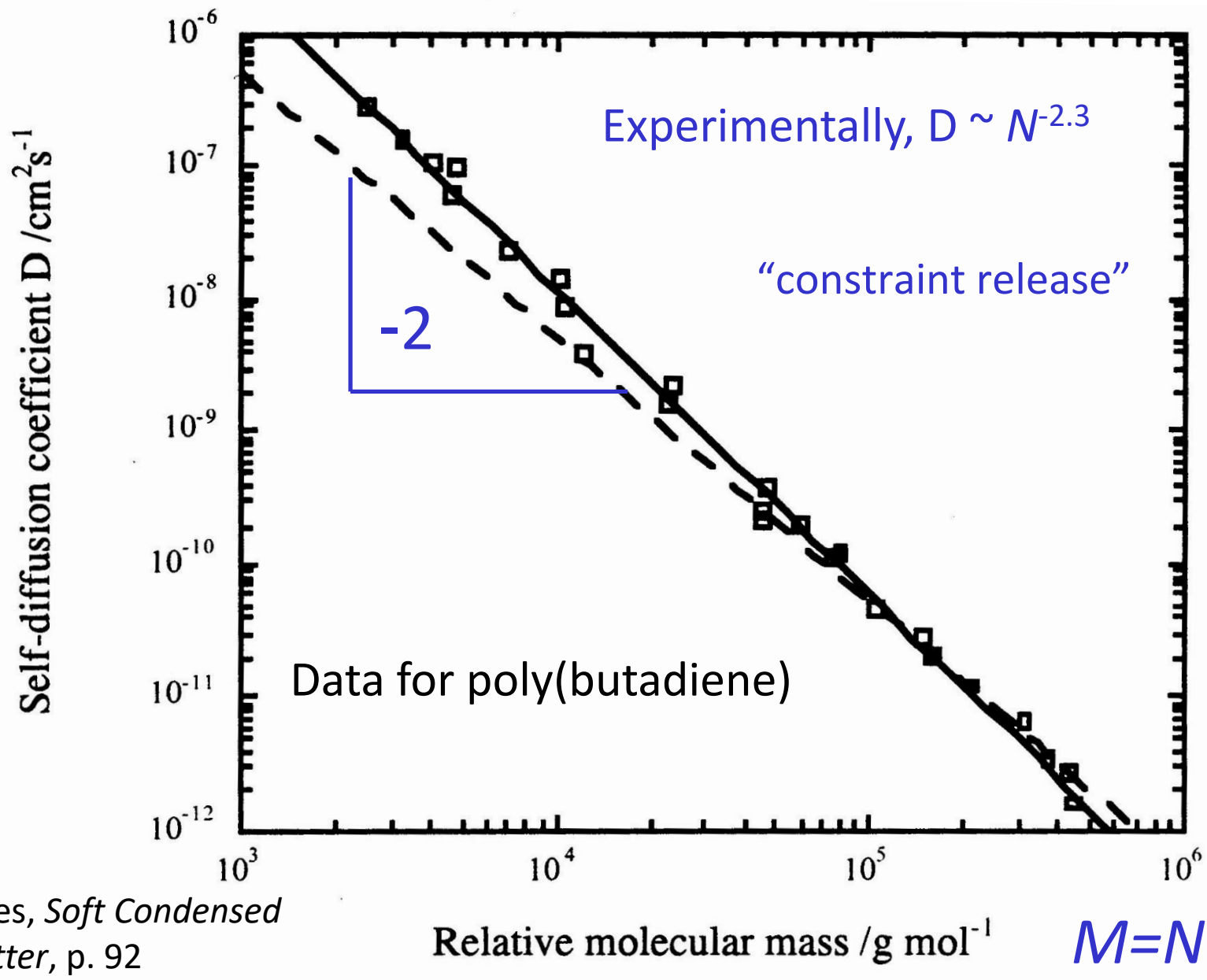
$$\tau_{\text{tube}} \sim N^3$$

Substituting, we find:

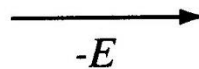
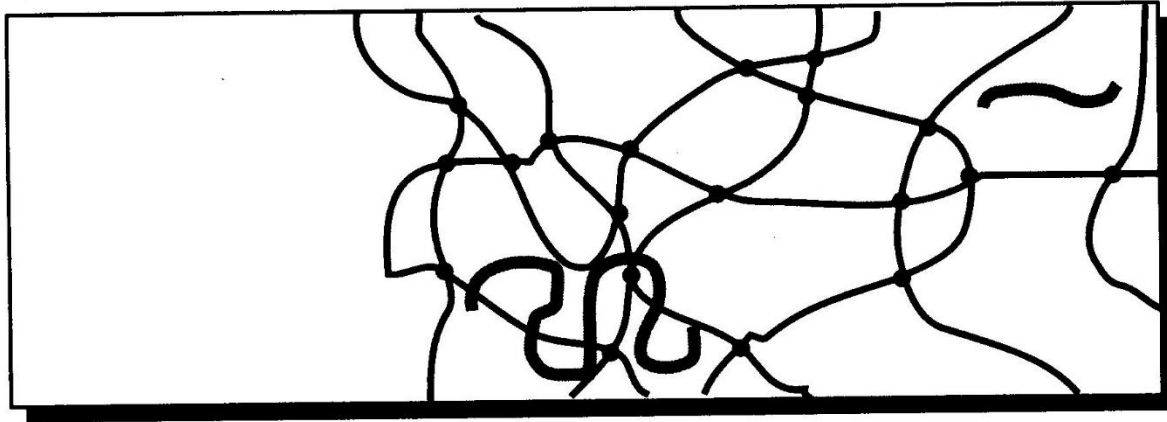
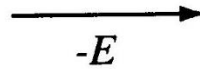
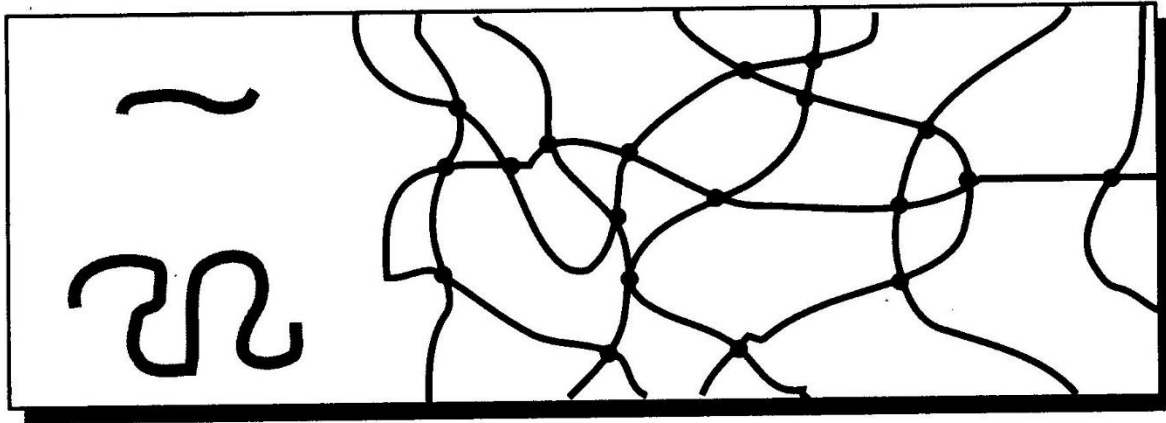
$$D_{\text{self}} \sim \frac{Na^2}{N^3} \sim N^{-2}$$

Larger molecules are predicted to diffuse much more slowly than smaller molecules.

# Testing of Scaling Relation: $D \sim N^{-2}$

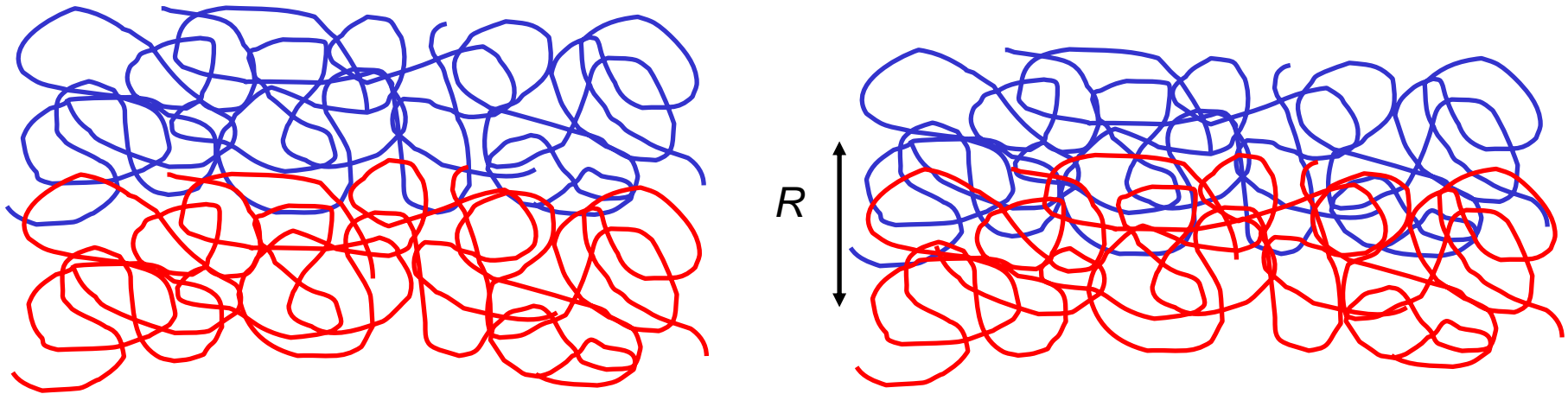


# Application of Theory: Electrophoresis



# Relevance of Polymer Self-Diffusion

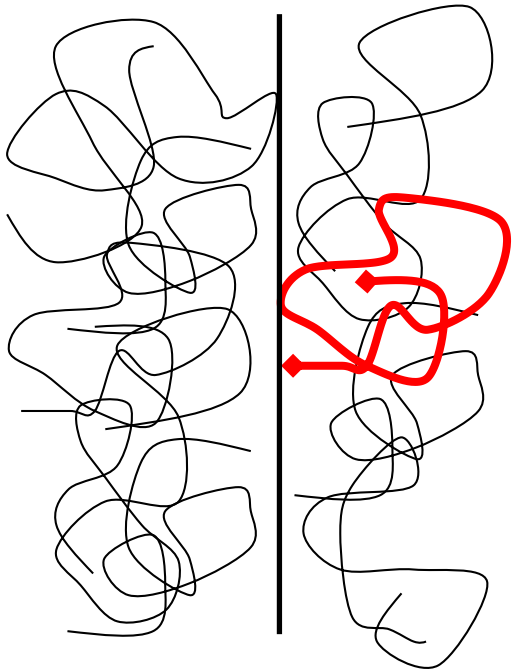
When **welding two polymer surfaces together**, such as in a manufacturing process, it is important to know the time and temperature dependence of the diffusion coefficient  $D$ .



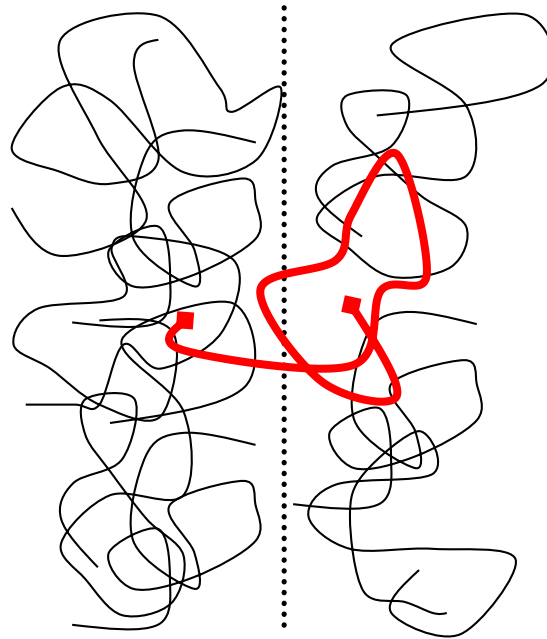
Good adhesion is obtained when the molecules travel a distance comparable to  $R$ , such that they entangle with other molecules.



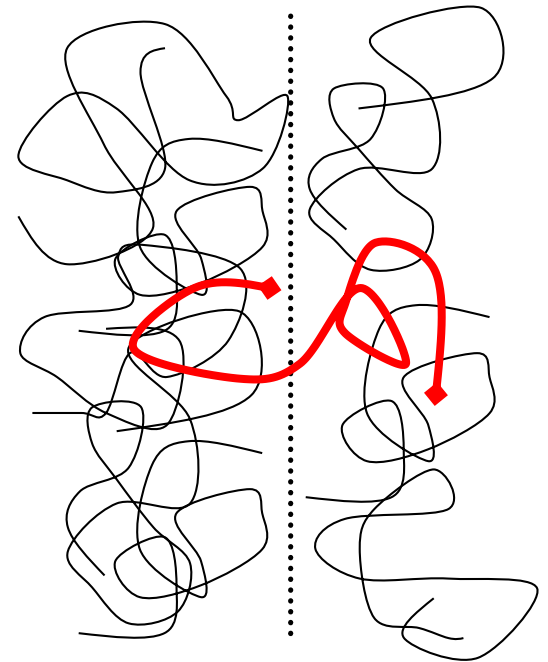
# Stages of Interdiffusion at Polymer/Polymer Interfaces



**Interfacial wetting:** weak adhesion from van der Waals attraction



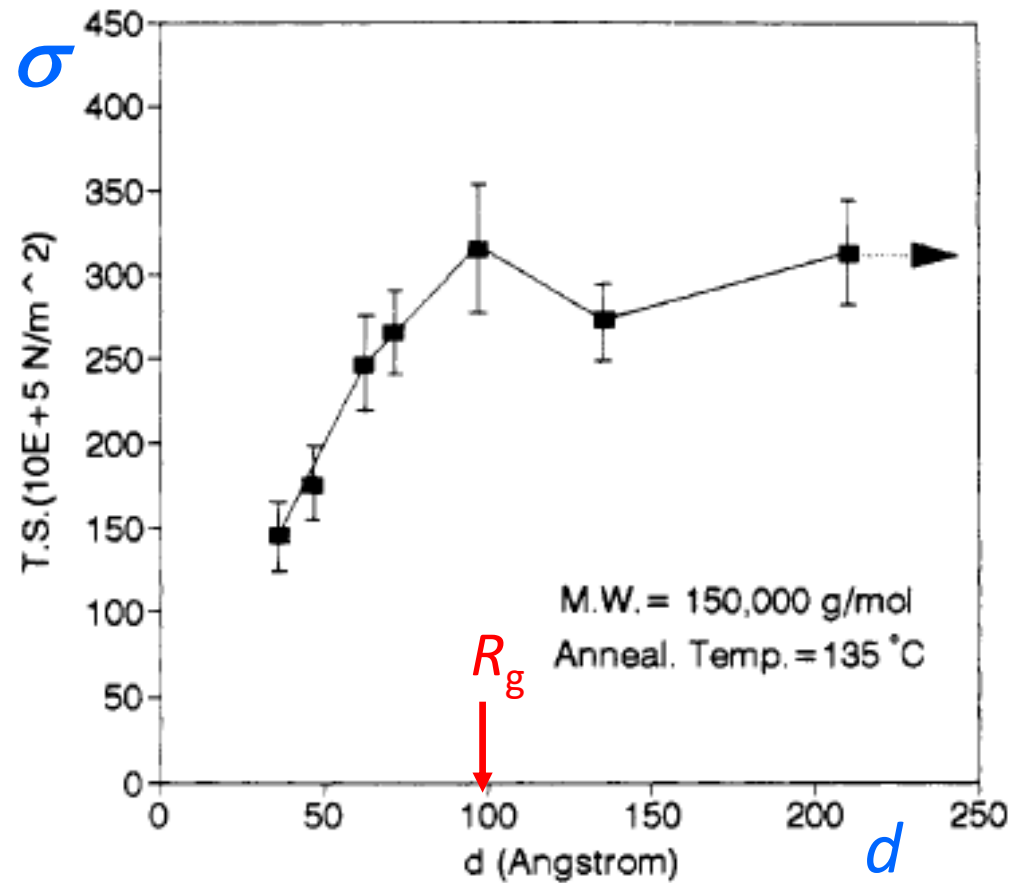
**Chain extension across the interface:** likely failure by chain “pull-out”



**Chain entanglement across the interface:** possible failure by chain scission (*i.e.* breaking)

# Strength Development with Increasing Diffusion Distance

Full strength is achieved when  $d$  is *approximately* the radius of gyration of the polymer,  $R_g$ .



K.D. Kim et al, *Macromolecules* (1994) **27**, 6841