# Entanglements

**$M < M_e$**   **Rouse**

Zero-shear viscosity vs. M (note change of slope)
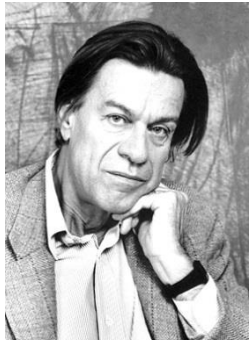


Poly(di-methylsiloxane)
Poly(iso-butylene)
Poly(ethylene)
Poly(butadiene)
Poly(tetra-methyl p-silphenyl siloxane)
Poly(methyl methacrylate)
Poly(ethylene glycol)
Poly(vinyl acetate)
Poly(styrene)

slope 3.4

slope 1

Log $\eta_m$ + constant

Log M + constant

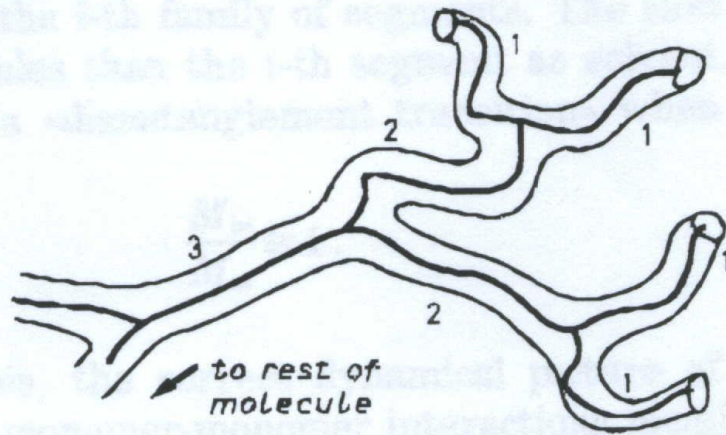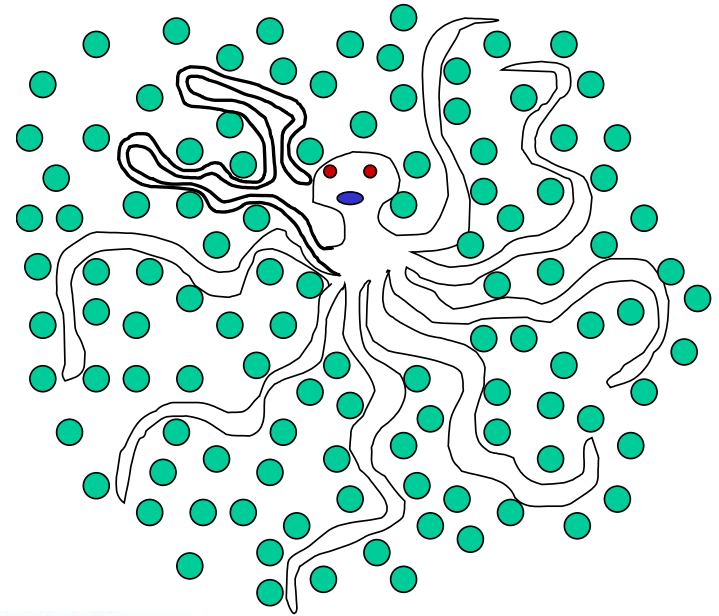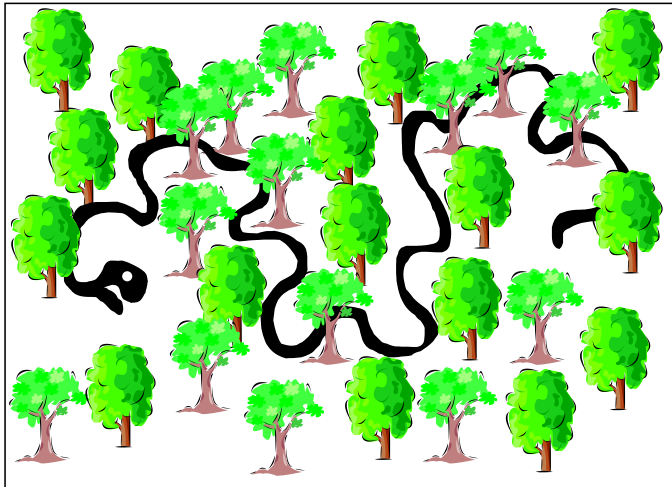**$M > M_e$**   **Edwards**
**deGennes**
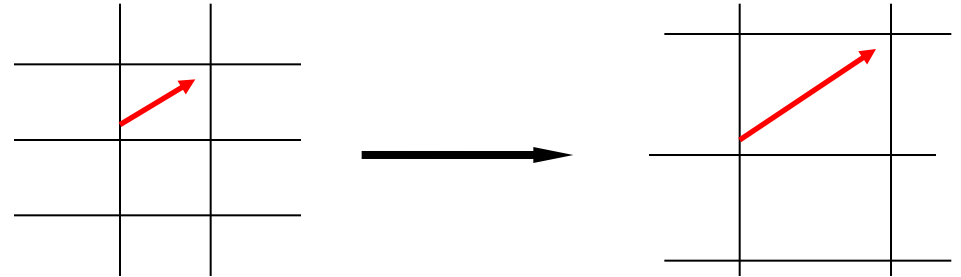**Doi**

Berry + Fox, 1968

<u>Question:</u>

Which factors affect the Me:
T, P, M, flexibility, concentration (solution), branching, microstructure?

to rest of molecule

# Dilution:  network swells in good solvent

$G(\Phi) = G_0\, \Phi^\beta$

$M_e(\varphi) = M_e\, \Phi^{-\alpha}$

$\beta = 2 \text{ or } 7/3 \quad \alpha = \beta - 1$

*Adam, 1975*
*Colby, Rubinstein, 1990*

**Table 13–I**

ENTANGLEMENT SPACINGS FROM INTEGRATION OF LOSS COMPLIANCE OR SIMILAR CALCULATIONS

| Polymer | Temperature, °C | $\log J_N^0$ (cm²/dyne) | $M_e$ | $j$ | $M_0$ | $jP_e$ | Ref. |
|---|---|---|---|---|---|---|---|
| *Methacrylate Polymers* | | | | | | | |
| Methyl (conventional) | 170 | −6.94 | 4,700 | 2 | 100 | 94 | 15 |
| Methyl (atactic)[a] | 220 | −6.59 | 10,000 | 2 | 100 | 200 | 16 |
| Methyl (atactic) | 131 | −6.90 | 4,800 | 2 | 100 | 96 | 15 |
| 2-Ethyl Butyl | 100 | −6.16 | 21,400 | 2 | 170 | 250 | 17 |
| *n*-Hexyl | 100 | −5.94 | 33,900 | 2 | 170 | 400 | 18 |
| *n*-Octyl | 100 | −5.52 | 87,000 | 2 | 198 | 880 | 19 |
| *Rubbers* | | | | | | | |
| Hevea rubber | 25 | −6.76 | 6,100 | 4 | 68 | 360 | 1 |
| Hevea rubber | −30 | −6.85 | 3,500 | 4 | 68 | 210 | 20 |
| 1,4-Polybutadiene[c] | 25 | −7.06 | 1,900 | 4 | 54 | 140 | 2 |
| 1,4-Polybutadiene[d] | 25 | −7.12 | 1,700 | 4 | 54 | 130 | 21 |
| 1,4-Polybutadiene, cis[e] | 25 | −6.88 | 2,900 | 4 | 54 | 220 | 22 |
| Polybutadiene[f] | −10 | −6.94 | 2,500 | — | — | — | 14 |
| 1,2-Polybutadiene[g] | 25 | −6.79 | 3,550 | 2 | 54 | 130 | 1 |
| Styrene-butadiene copolymer[h] | 25 | −6.89 | 3,000 | 4 | 65.5 | 180 | 23 |
| Butyl rubber[b] | 25 | −6.46 | 8,500 | 2 | 56 | 300 | 24 |
| Ethylene-propylene copolymer[i] | 25 | −7.10 | 1,660 | 2 | 34.3 | 100 | 25 |
| *General* | | | | | | | |
| Polyethylene | 190 | −7.36 | 1,250 | 2 | 28 | 90 | 25a |
| Polyisobutylene | 25 | −6.40 | 8,900 | 2 | 56 | 320 | 26 |
| Polyisobutylene | 25 | −6.46 | 7,600 | 2 | 56 | 270 | 30 |
| Poly(dimethyl siloxane)[j] | 25 | −6.47 | 8,100 | 2 | 74 | 220 | 27 |
| Poly(dimethyl siloxane) | 25 | −6.30 | 12,000 | 2 | 74 | 330 | 27a |
| Poly(dimethyl siloxane)[k] | 23 | — | 8,800 | 2 | 74 | 230 | 28 |
| Poly(dimethyl siloxane) | 25 | −6.33 | 11,300 | 2 | 74 | 300 | 29 |
| Polystyrene[l] | 160 | −6.30 | 18,100 | 2 | 104 | 350 | 3 |
| Polystyrene | 140 | −6.31 | 17,300 | 2 | 104 | 333 | 30a |
| Poly(α-methyl styrene) | 186 | −7.00 | 13,500 | 2 | 118 | 230 | 31,32 |
| Poly(vinyl acetate) | 60 | −6.55 | 9,100 | 2 | 86 | 210 | 30 |

Elastic element: $\boxed{\sigma = G\gamma}$

Viscous element: $\boxed{\eta \equiv \dfrac{\sigma}{\dot{\gamma}}}$

Viscoelastic element: $\boxed{\sigma = \eta\dot{\gamma} = \eta\dfrac{\gamma}{\lambda} = G\gamma \Rightarrow \color{red}{\eta = G\lambda}}$

Key relation
in linear viscoelasticity

$\boxed{\lambda}$  Characteristic relaxation time

Obtain time:

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

Einstein 1905

$\zeta$ = friction



$$\zeta = \eta R$$

$$f = \zeta u$$

Stokes 1905



$$D = \frac{R^2}{\lambda}$$



Fick 1905

$$\lambda = \frac{\eta R^3}{kT}$$

# Summary:

Synthesis:   N, b

Size:   $R = N^{1/2}b$

Distribution:   $P(R) \propto \exp\left(\dfrac{-3R^2}{2Nb^2}\right)$

Modulus:   $G = vkT$

Diffusion:   $\boxed{D = \dfrac{kT}{\zeta}}$

Hooke:   $F = Kx$

Newton:   $\eta \equiv \dfrac{\sigma}{\dot{\gamma}}$

Viscoelasticity:   $\eta = G\lambda$

# Importance of the time scale

granite



Halite (mineral form of salt)







*Even some apparent solids "flow" if they are observed long enough*

$\eta=4.5 \times 10^{19}$ Pa.s

**TABLE 2.3.1 / The Viscosity of Some Familiar Materials at Room Temperature**

| Liquid | Approximate Viscosity (Pa·s) |
|---|---|
| Glass | $10^{40}$ |
| Molten glass (500°C) | $10^{12}$ |
| Asphalt | $10^{8}$ |
| Molten polymers | $10^{3}$ |
| Heavy syrup | $10^{2}$ |
| Honey | $10^{1}$ |
| Glycerin | $10^{0}$ |
| Olive oil | $10^{-1}$ |
| Light oil | $10^{-2}$ |
| Water | $10^{-3}$ |
| Air | $10^{-5}$ |

Adapted from Barnes et al. (1989).

How many characteristic relaxation times exist in a polymer?

What are the implications for viscosity?

short time (local motion)

long time (global motion)

## A gross classification of viscoelastic materials:
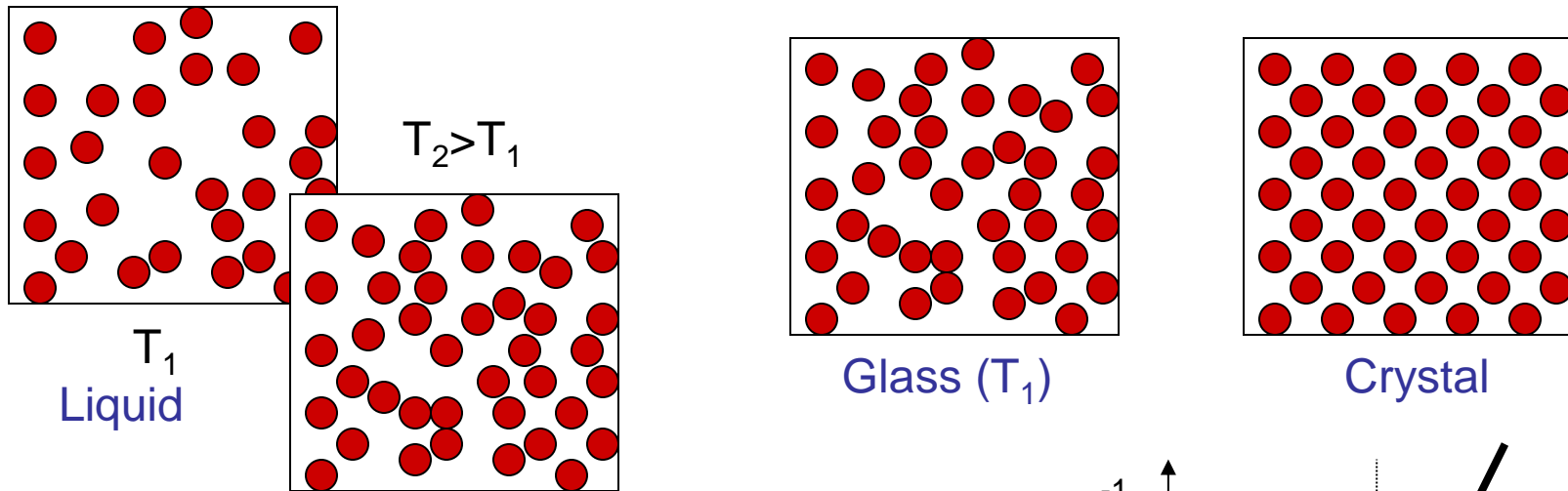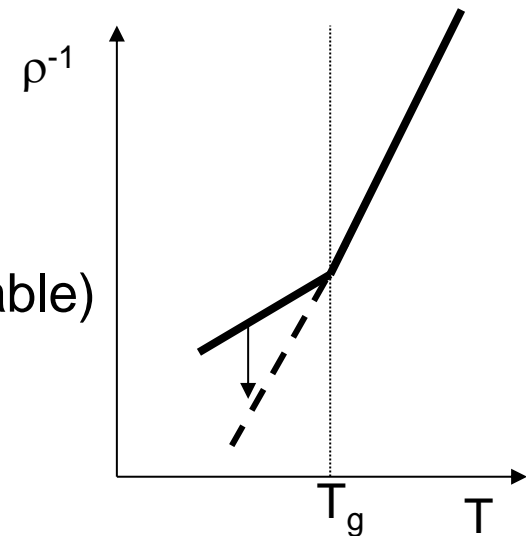
Glass  /  crystal

Rubber

Melt  /  solution

Important point:  For a solid, macroscopic motion if frozen (long time is infinite) whereas short-time (local) motion takes place
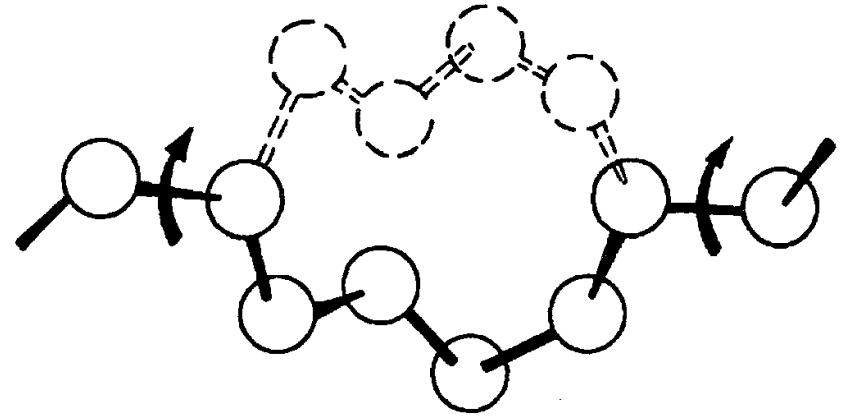
# Glass:

- Amorphous ("frozen") solid

$T_2 > T_1$

$T_1$
Liquid

Glass ($T_1$)

Crystal

- Non-equilibrium – (aging)

- Low temperatures (or short times)

- Glass transition: out of equilibrium (metastable)

- Cooling rate dependence

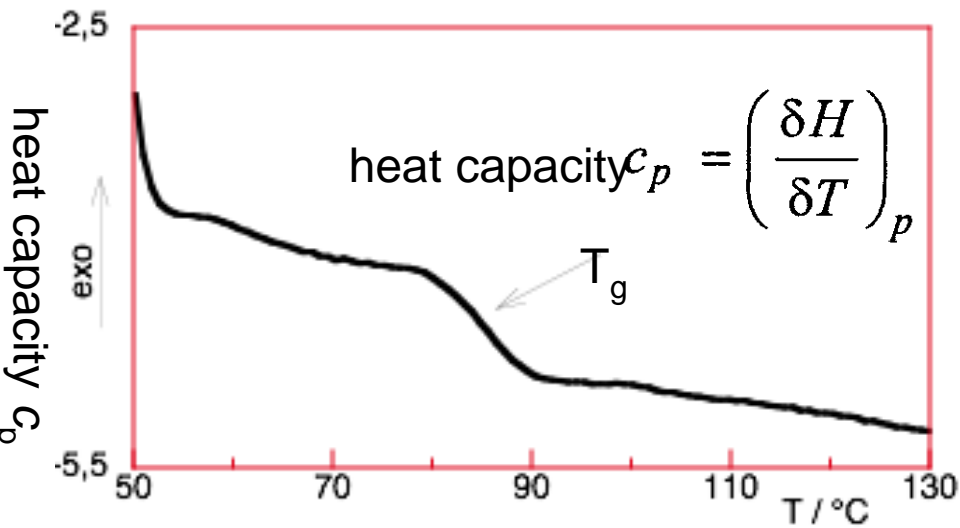- Local motions: free volume, cooperativity
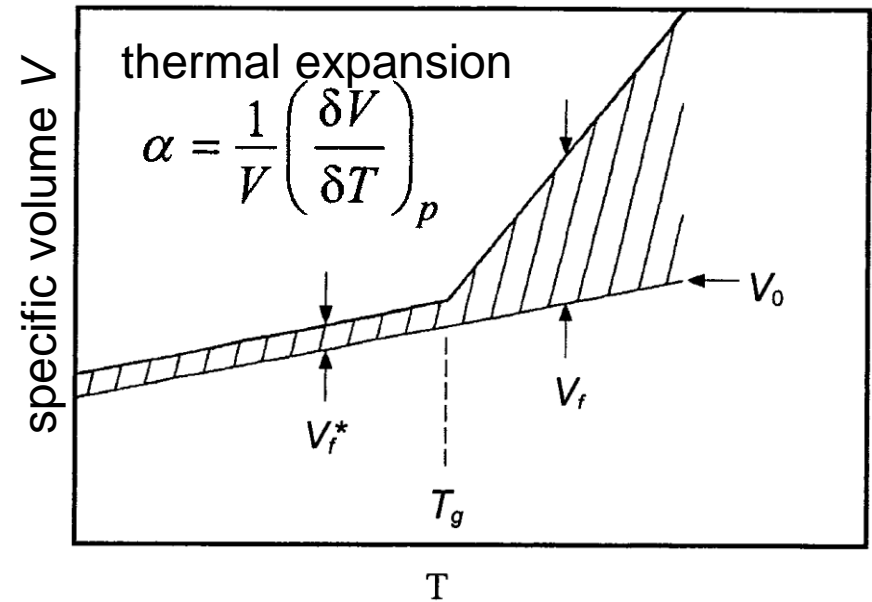
$\rho^{-1}$

$T_g$    $T$

# The Glass Transition

At the glass transition the polymer chain segments undergo increased local motions, which consume heat and leads to an increase in the volume requirement for the chain.
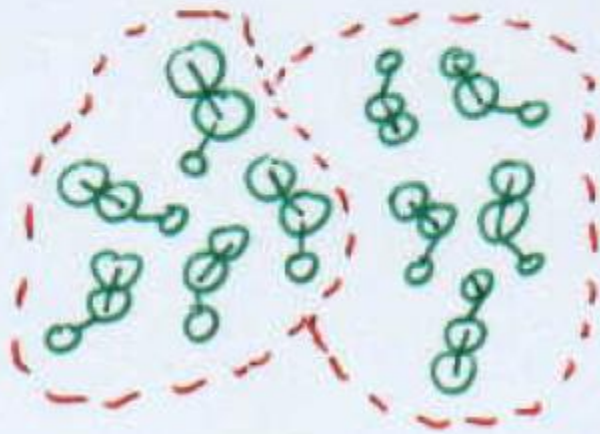


heat capacity change $c_p$

$$\text{heat capacity}\, c_p = \left( \frac{\delta H}{\delta T} \right)_p$$

$T_g$

specific volume change $V$

thermal expansion

$$\alpha = \frac{1}{V} \left( \frac{\delta V}{\delta T} \right)_p$$

$V_0$

$V_f$

$V_f^*$

$T_g$

T

heat capacity $c_p$

exo

T / °C

specific volume $V$

## Local motion in a dense polymer (melt)

Cooperativity:

$$P \sim \exp\left(-\frac{z\,\Delta E}{kT}\right) \qquad z \simeq 5-10 \text{ conformers}$$

## Vitrification:



$\rho^{-1}$
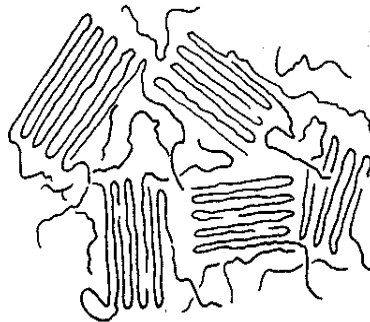
$T_g$    T

## Cotton candy



sugar    Fast cooling

Slow cooling



## Amorphous polymers:
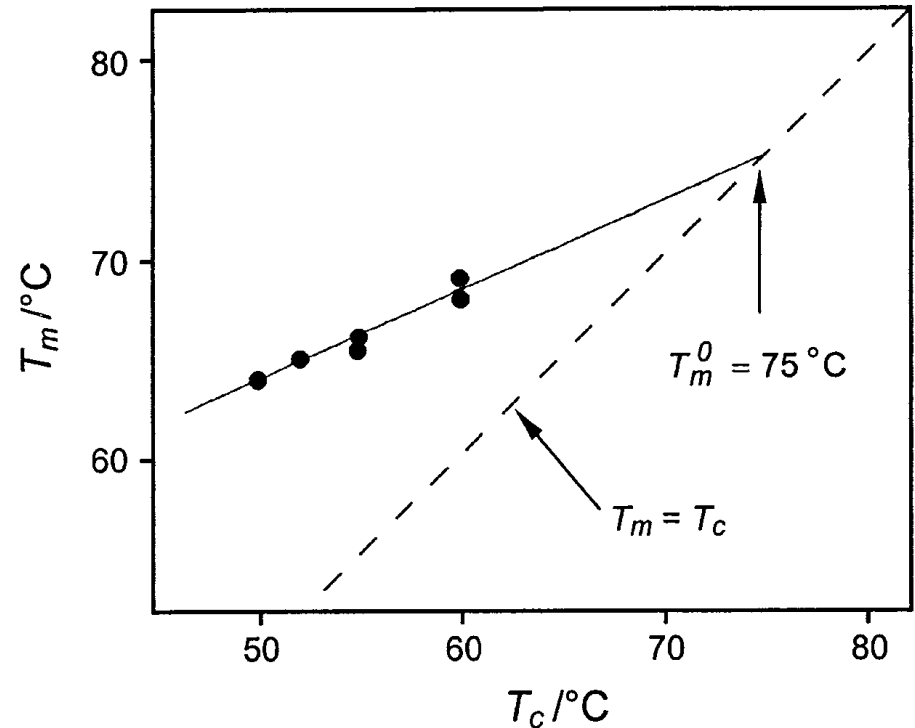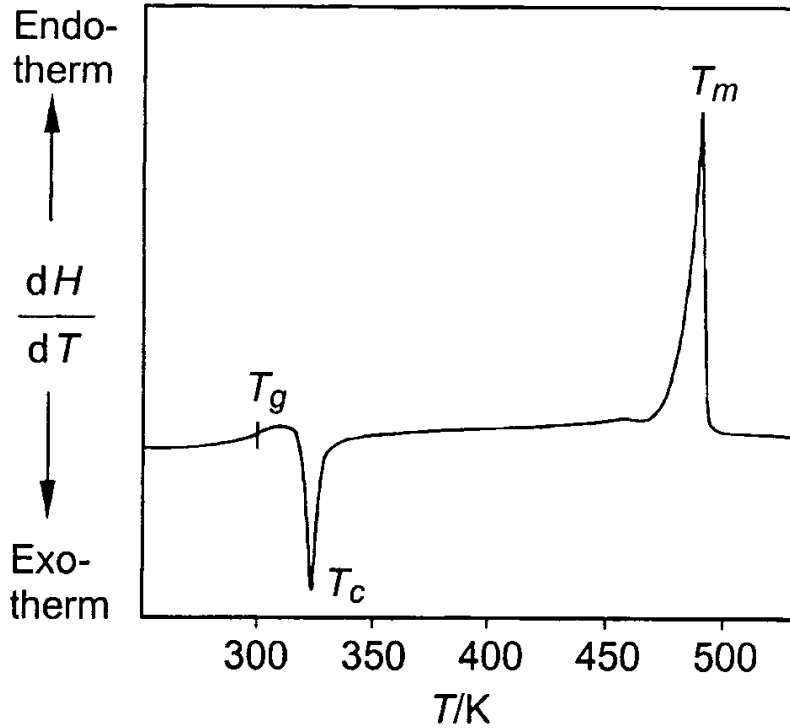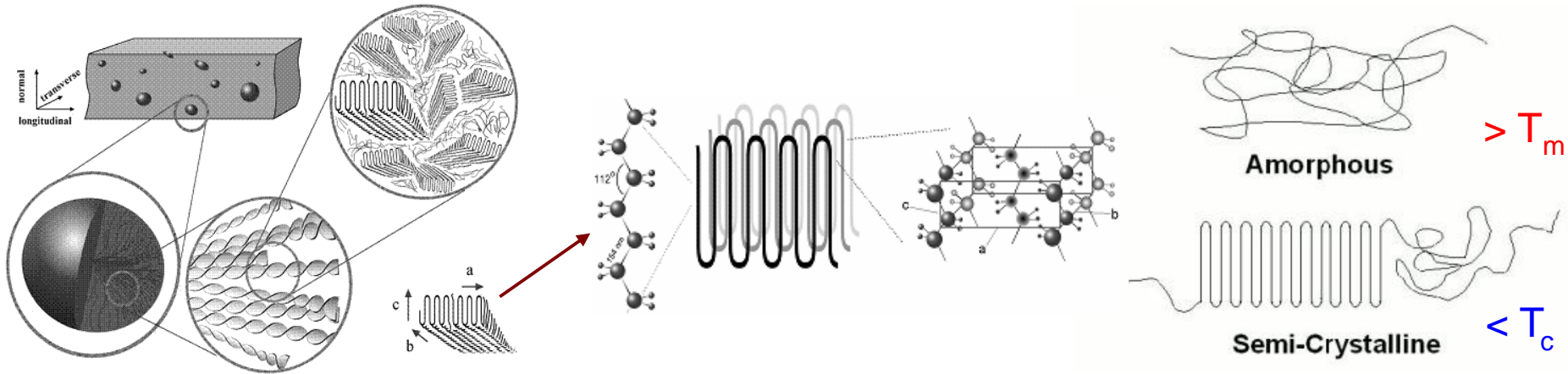


## Semi-crystalline polymer:



## Crystal



Journal of Crystal Growth 48, 1980, p. 303/20

Glass:  G~$10^9$ Pa                    Crystal: G<$10^7$ Pa

# Crystallization and Melting



Endo-therm

$\dfrac{\mathrm{d}H}{\mathrm{d}T}$

Exo-therm

$T_g$

$T_c$

$T_m$

$T$/K

$> T_m$

Amorphous

$< T_c$

Semi-Crystalline

$T_m$/°C

$T_m^0 = 75\,°C$

$T_m = T_c$

$T_c$/°C

<u>Question:</u>

Which are the implications of the existence of local short-time motion
in solids?

Think of self-healing (recent group seminar)

# Rubber (elastomer)  Thermosetting polymers (chemical network)

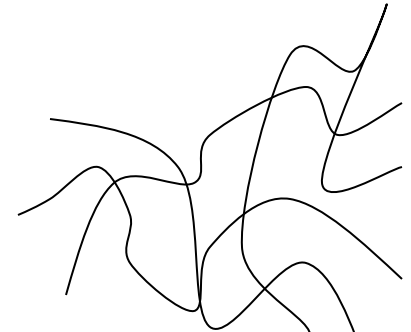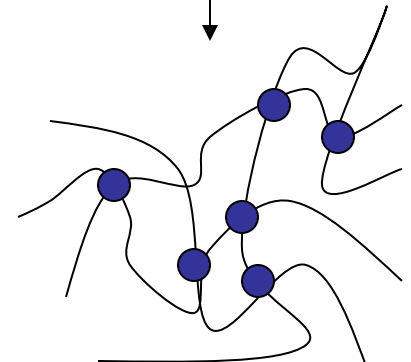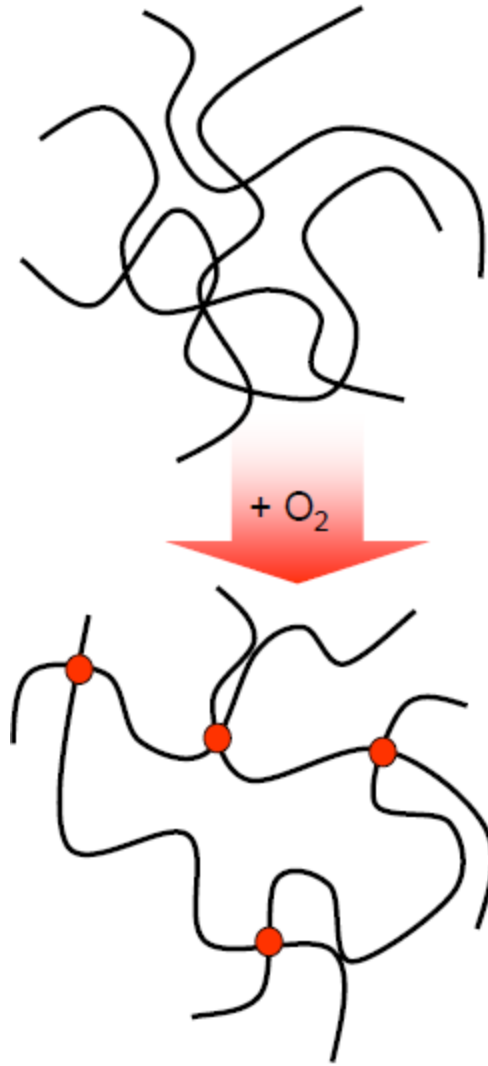- solid-like (permanent or temporary)

- network

- $T > T_g$

Vulcanisation:

Latex - liquid

Solid-like (gel)

*Hevea tree*

Natural rubber

A

B

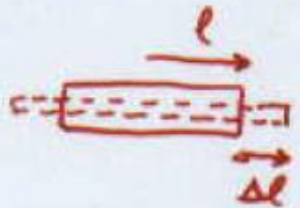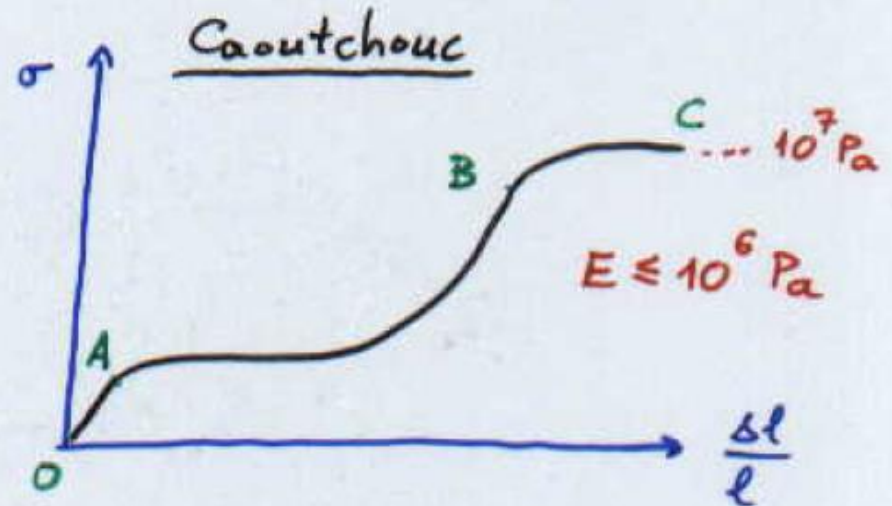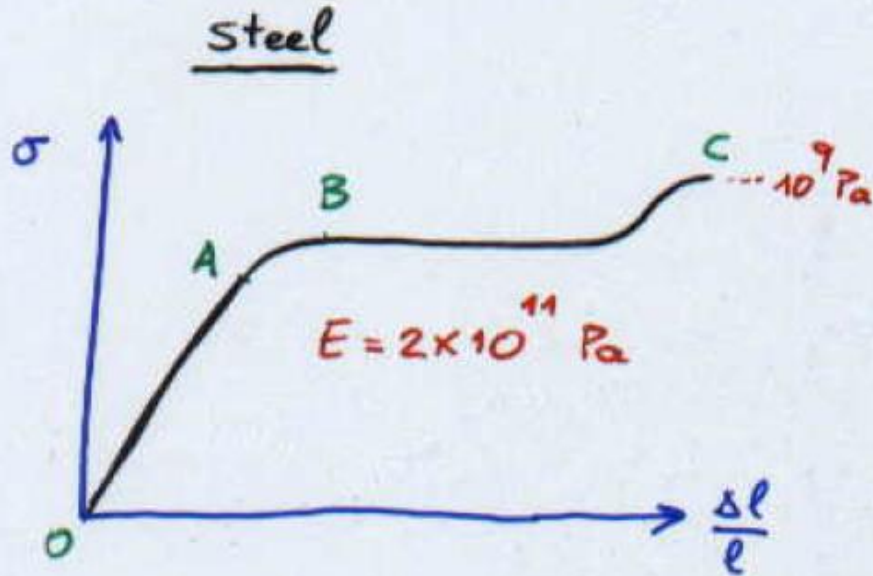$$G \approx \nu kT$$

$G \sim 10^5 - 10^6$ Pa

Scrap

Liquid

Cup

+ $O_2$

Indian 'boot'
Amazon (~500 bC)

How does vulcanization relate to the Indian boot example?

Think of Goodyear (~1839)

# Compare metal vs elastomer

## steel



$E = 2 \times 10^{11}\ P_a$

C $\cdots 10^9\ P_a$

## Caoutchouc



$E \leqslant 10^6\ P_a$

C $\cdots 10^7\ P_a$

$$\sigma = \frac{F}{A} = E\frac{\Delta l}{l}$$

$$\begin{cases} \text{OA} & \text{Linear reversible} \\ \text{AB} & \text{Non linear reversible} \\ \text{BC} & \text{Irreversible -- flow} \\ \text{C} & \text{Catastrophic failure} \end{cases}$$

# Thermoplastic polymers (physical network):

- Liquid

- temporary network

-  Large scale motions

entanglements



$$G_N^0 = \frac{\rho \; R \; T}{M_e}$$



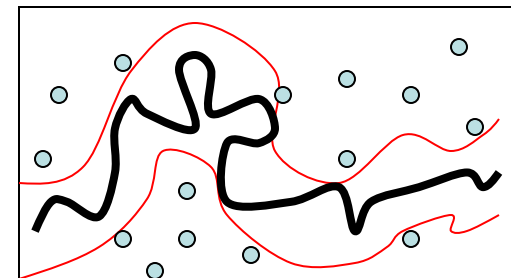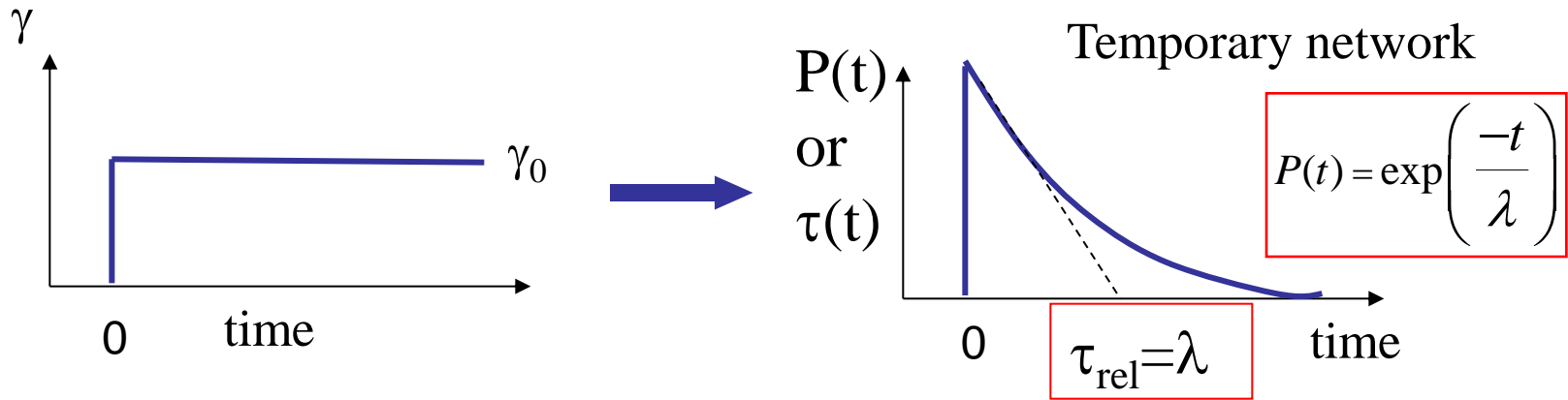High temperatures (T>Tg),

Low times

Tube model: de Gennes, Doi and Edwards (1986)

## Global motion (center of mass) in a flowing polymer melt

Coopevativity: $\quad P \sim \exp\left[-\dfrac{z\,\Delta E}{kT}\right] \qquad z = O(10^3)$

# Compare permanent and temporary networks



Temporary network

$$P(t) = \exp\left(\frac{-t}{\lambda}\right)$$

$\tau_{rel} = \lambda$

The molecules move in order to recover their stable coil-shape structure

Rubber (permanent network)

Can the same polymer behave as a glass <u>and</u> as a melt ?

Think of Tg

# Important point:

We can tune the state of a polymer (and hence modulus and time) with T
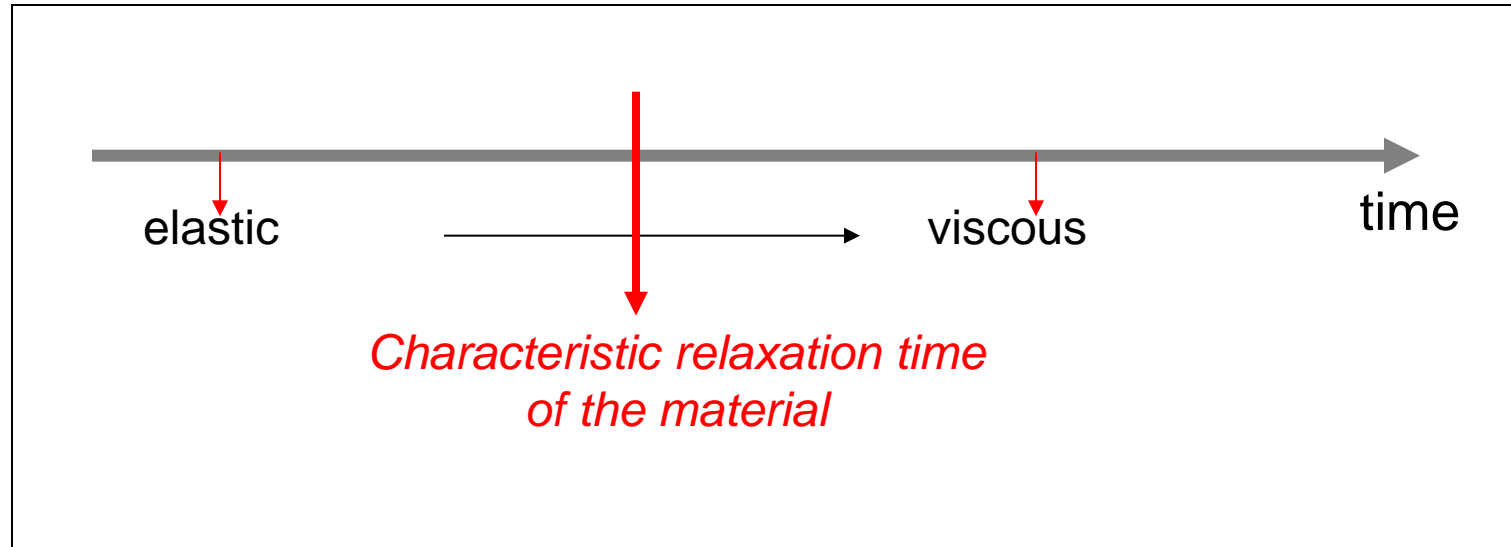
T<Tg  solid , glass

T>Tg  solid, rubber

T >> Tg  liquid

Alternatively, at a given temperature:  very short time:  glass ;  very long time: liquid

This means that there is an interplay of the characteristic time of the material and the temperature:

principle of time-Temperature Superposition (tTS) -  to be discussed below

# Importance of the time scale of the material in reference to observation time



The same material behaves like a liquid or a solid, depending on the observation time (experimental interrogation)

Use of dimensionless number:

Observation time versus Relaxation time

*Deborah number: (M. Reiner)*

$$De = \frac{\lambda}{t_{\exp}}$$

*" The mountains flowed before the Lord"*
*(song by prophetess Deborah, Bible,*
*Judges 5:5)*

• *De>>1* → *Elastic behaviour*

• *De<<1* → *viscous behaviour*

• *De ~ O(1)* → *viscoelastic behaviour*



Increasing Deborah number *De*

Silly Putty

# SONG OF DEBORAH

M. Reiner is credited with naming the Deborah Number after the song of Deborah, Judges 5:5- "The mountains flowed before the Lord"(Fig. 3.10). It was first mentioned in his article "The Deborah Number" in the January 1964 issue of Physics Today.
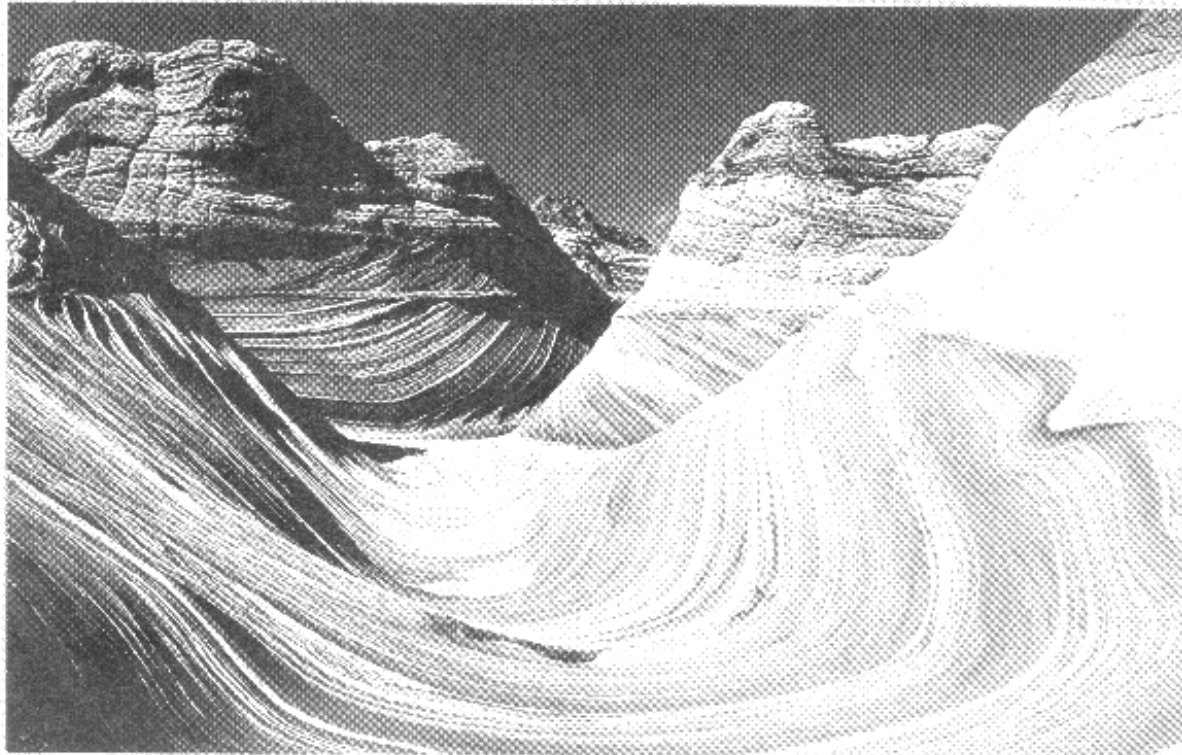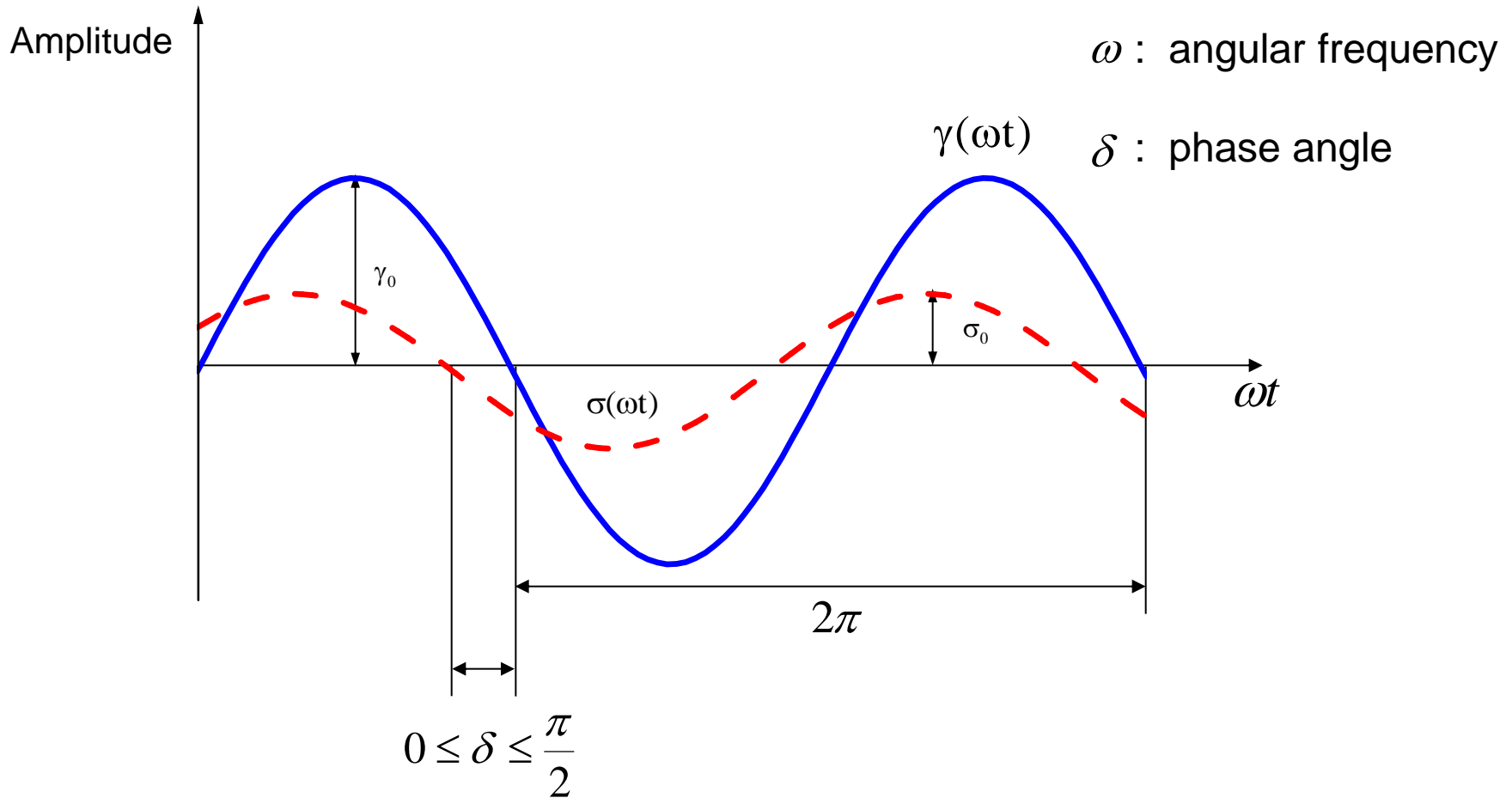


Figure. 3.10 Nestles Canyon, Arizona. Courtesy of Wolfgang Cohnen (©1997)

Amplitude

$\gamma(\omega t)$

$\omega$ : angular frequency

$\delta$ : phase angle

$\gamma_0$

$\sigma(\omega t)$

$\sigma_0$

$\omega t$

$2\pi$

$0 \leq \delta \leq \dfrac{\pi}{2}$

**impose**

$$\gamma(t) = \gamma_0 \cdot \sin(\omega t)$$

**probe**

Elastic response    Viscous response

$$\sigma(t) = \sigma_0 \cdot \sin(\omega t + \delta) = \gamma_0 \cdot G'(\omega) \cdot \sin(\omega t) + \gamma_0 \cdot G''(\omega) \cdot \cos(\omega t)$$

Deborah number in an oscillatory experiment: $\boxed{De = \lambda\omega}$    De > 1 → $t_{exp} < \lambda$

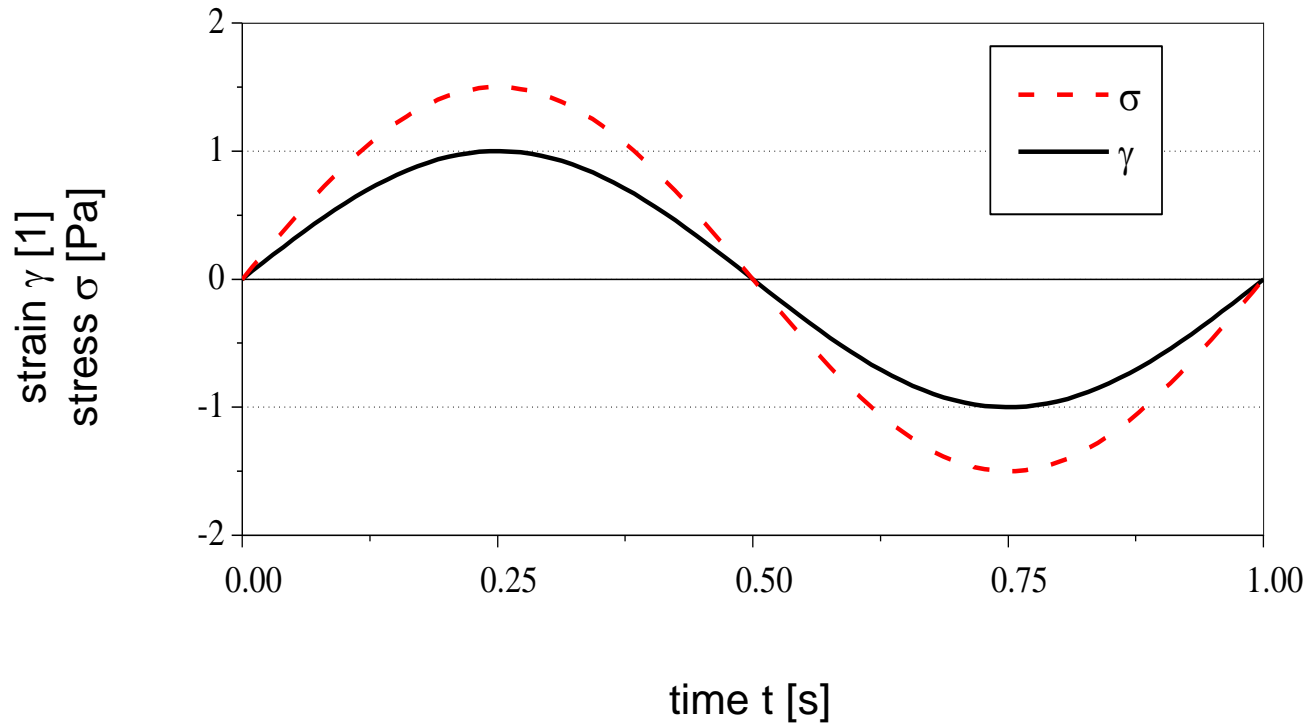Elastic element: $\boxed{\sigma = G\gamma \sim \omega^0}$

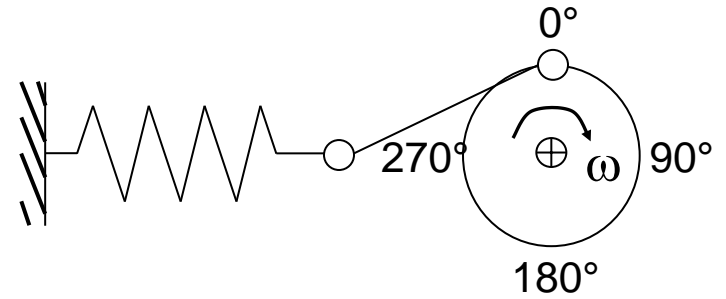Viscous element: $\boxed{\sigma = \eta\dot{\gamma} \sim \omega}$

G and η are material constants (do not depend on external mechanical stimulus)

# Ideal elastic solid
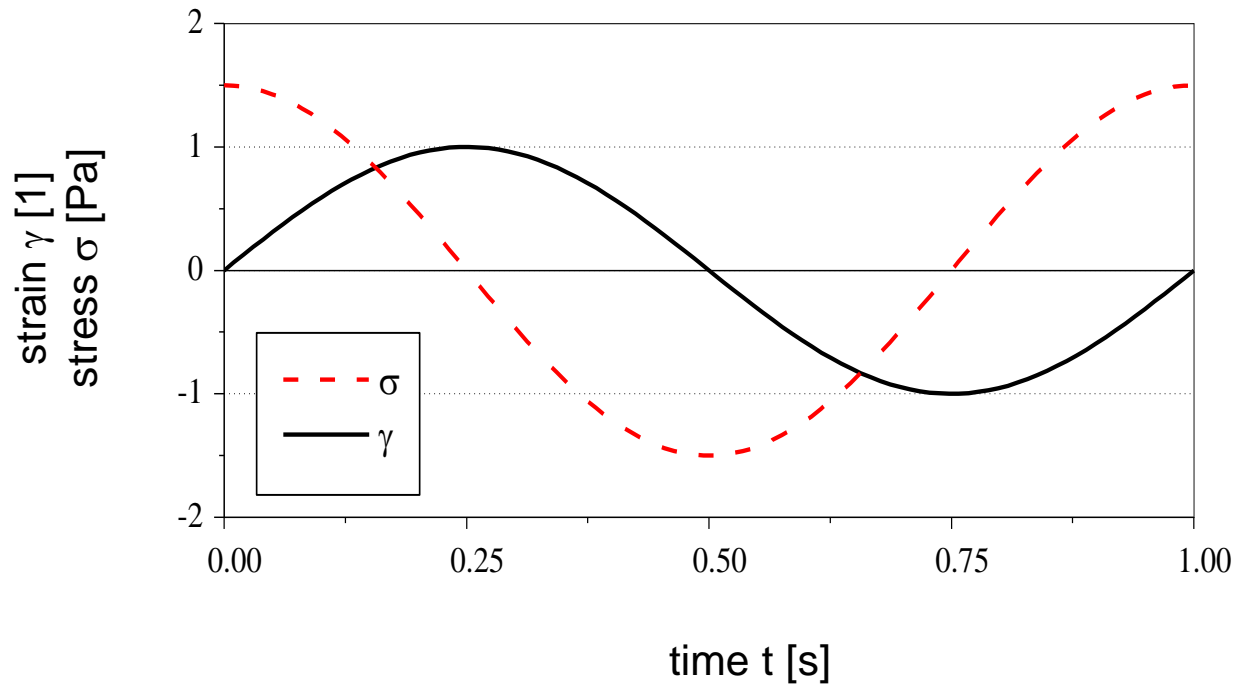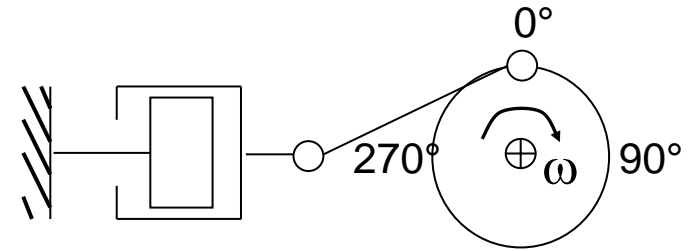
$$\gamma(t) = \gamma_0 \sin(\omega t)$$

$$\sigma(t) = G \cdot \gamma(t) = G \cdot \gamma_0 \sin(\omega t)$$

# Ideal viscous liquid

$$\gamma(t) = \gamma_0 \sin(\omega t)$$

$$\sigma(t) = \eta \cdot \dot{\gamma}(t) = \eta \cdot \gamma_0 \omega \cos(\omega t) = \eta \cdot \gamma_0 \omega \sin\left(\omega t + \frac{\pi}{2}\right)$$
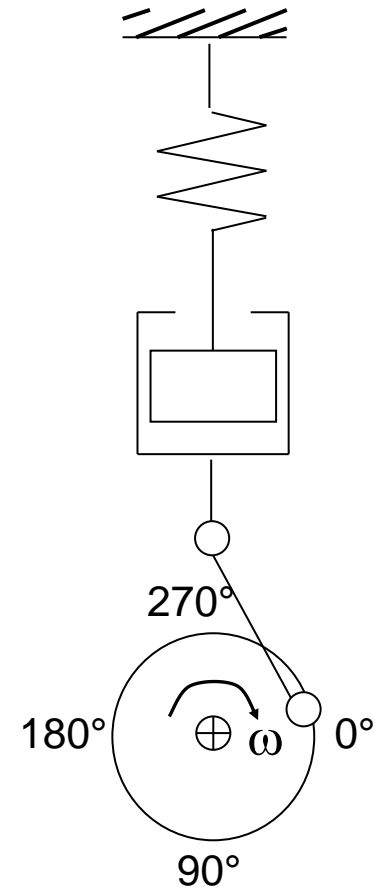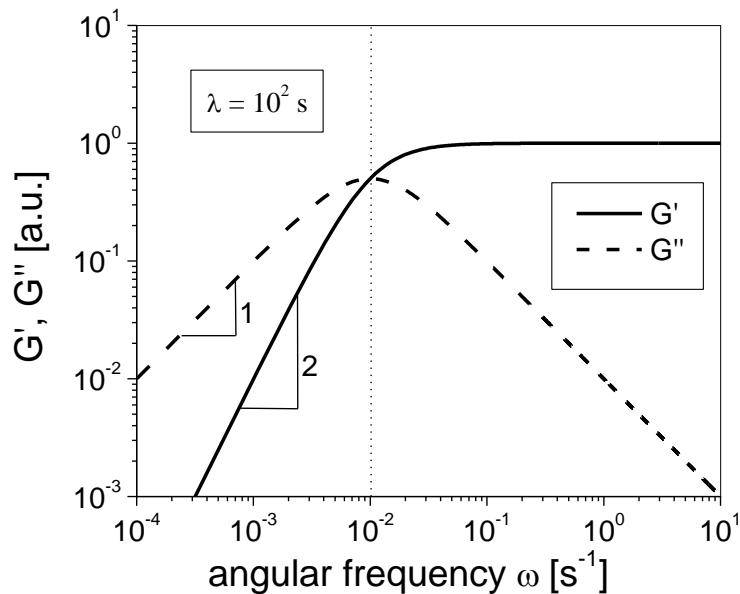
# Simplest viscoelastic liquid: Maxwell element

$$\sigma = \sigma_F = \sigma_D \qquad \gamma = \gamma_F + \gamma_D$$

$$\frac{d\gamma}{dt} = \frac{1}{G} \cdot \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \qquad \gamma_0 \omega \cos(\omega t) = \frac{1}{G} \cdot \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

$$\sigma = \left[ \frac{G \cdot \lambda^2 \cdot \omega^2}{1 + \lambda^2 \cdot \omega^2} \right] \cdot \sin(\omega t) + \left[ \frac{G \cdot \lambda \cdot \omega}{1 + \lambda^2 \cdot \omega^2} \right] \cdot \cos(\omega t)$$

$$\sigma = G'(G, \lambda, \omega) \cdot \sin(\omega t) + G''(G, \lambda, \omega) \cdot \cos(\omega t)$$



$\lambda = 10^2$ s

Legend: —— G'  - - - G''

Axes: G', G'' [a.u.] vs angular frequency $\omega$ [s$^{-1}$]

Slopes marked: 1, 2

270°
180° — $\oplus$ $\omega$ — 0°
90°

<u>Importance of time (frequency):</u>
Span time $\leftarrow\rightarrow$ Span responding length scale
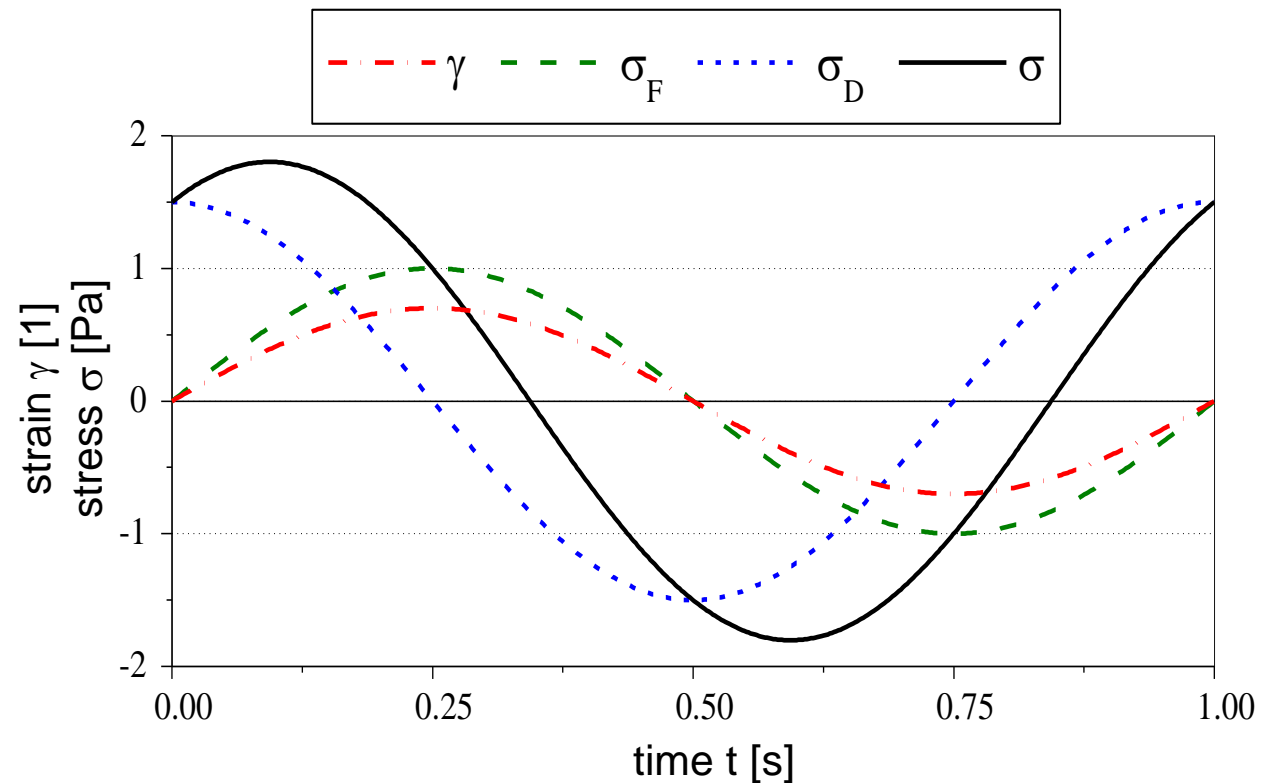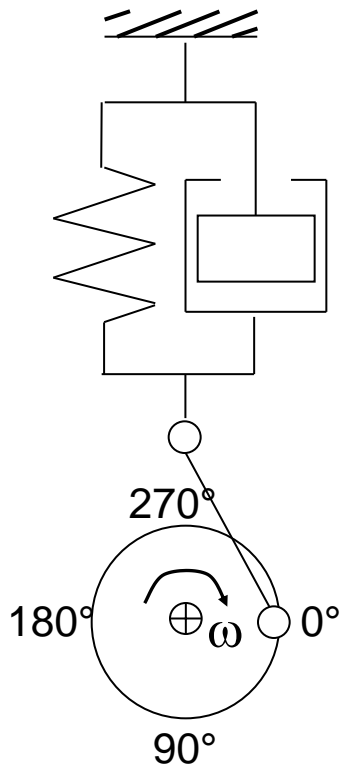<u>Spectroscopy</u>

# Simplest viscoelastic solid: Voigt-Kelvin element

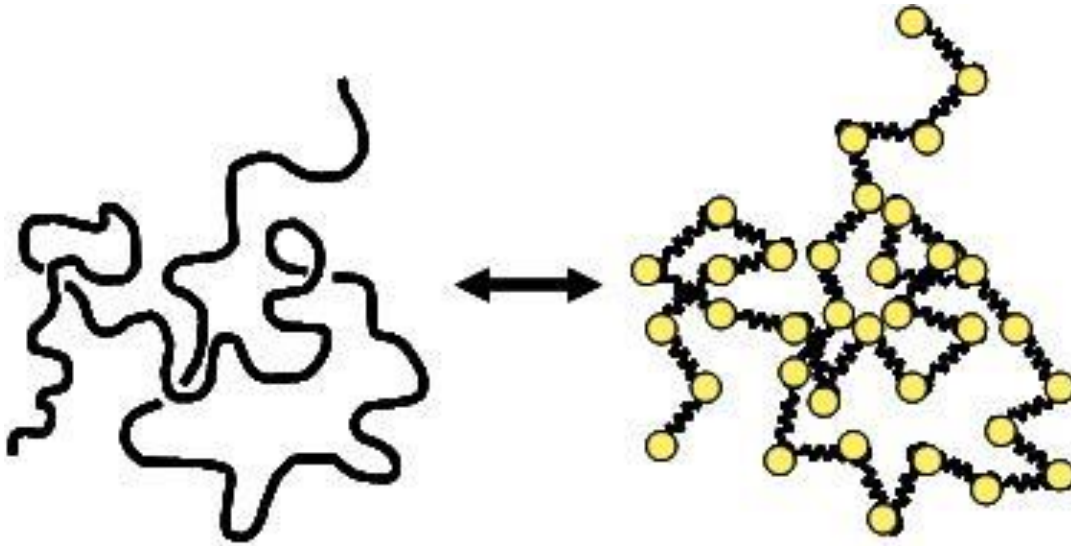$$\gamma = \gamma_F = \gamma_D$$

$$\sigma = \sigma_F + \sigma_D = G \cdot \gamma + \eta \cdot \dot{\gamma}$$

$$\delta = \arctan \frac{\eta \omega}{G}$$

$$\sigma(t) = G \cdot \gamma_0 \sin(\omega t) + \eta \cdot \gamma_0 \omega \sin\left(\omega t + \frac{\pi}{2}\right)$$
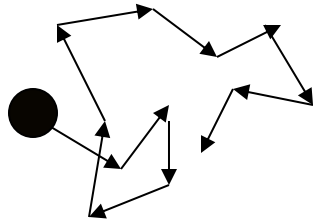
# Mesoscopic modeling: bead-spring models

Spring (constant k → G) : elastic element
Bead (friction ζ → η): viscous element

# I. Unentangled polymer dynamics (M<Me)

## I.1 Diffusion of a small colloidal particle:

<span style="color:red">random walk</span>

Simple diffusive motion: Brownian motion

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

Diffusion coefficient

## <span style="color:red">Friction coefficient:</span>

A constant force applied to the particle leads to a constant velocity:   $\vec{F} = \zeta \vec{v}$
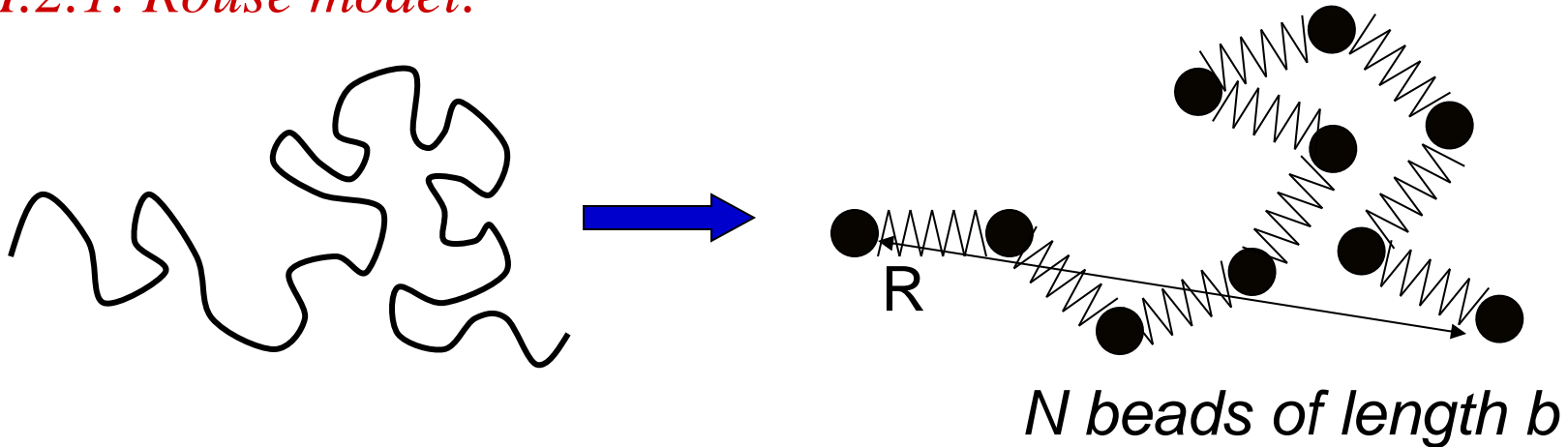
Friction coefficient

*Einstein relationship:*   $D = \dfrac{kT}{\zeta}$

*Stokes law:*   $\zeta = 6\pi\eta R$   (Sphere of radius R in a Newtonian liquid with a viscosity $\eta$)

*Stokes-Einstein-Sutherland*   $D = \dfrac{kT}{6\pi\eta R}$  ➡  Determination of   $R_H = \dfrac{kT}{6\pi\eta D}$

# I.2 Diffusion of an unentangled polymer chain:

## *I.2.1. Rouse model:*



*N beads of length b*

- Each bead has its own friction $\zeta$

- <u>Total friction</u>: $\zeta_R = N\zeta$ ➡️ $D_R = \dfrac{kT}{N\zeta}$

- Rouse time: $\tau_R \approx \dfrac{R^2}{D_R} \approx \dfrac{R^2}{kT/N\zeta} = \dfrac{\zeta}{kT}NR^2$

*$t < \tau_{Rouse}$: viscoelastic modes     $t > \tau_{Rouse}$: diffusive motion*

- Stokes law: $\zeta \approx \eta_s b$

- Kuhn monomer relaxation time: $\tau_0 \approx \dfrac{\zeta b^2}{kT} = \dfrac{\eta_s b^3}{kT}$ ➡️ $\tau_R \approx \tau_0 N^2$

# Rouse relaxation modes:

*The longest relaxation time:* $\tau_R \approx \tau_0 N^2$

*For relaxing a chain section of N/p monomers:*
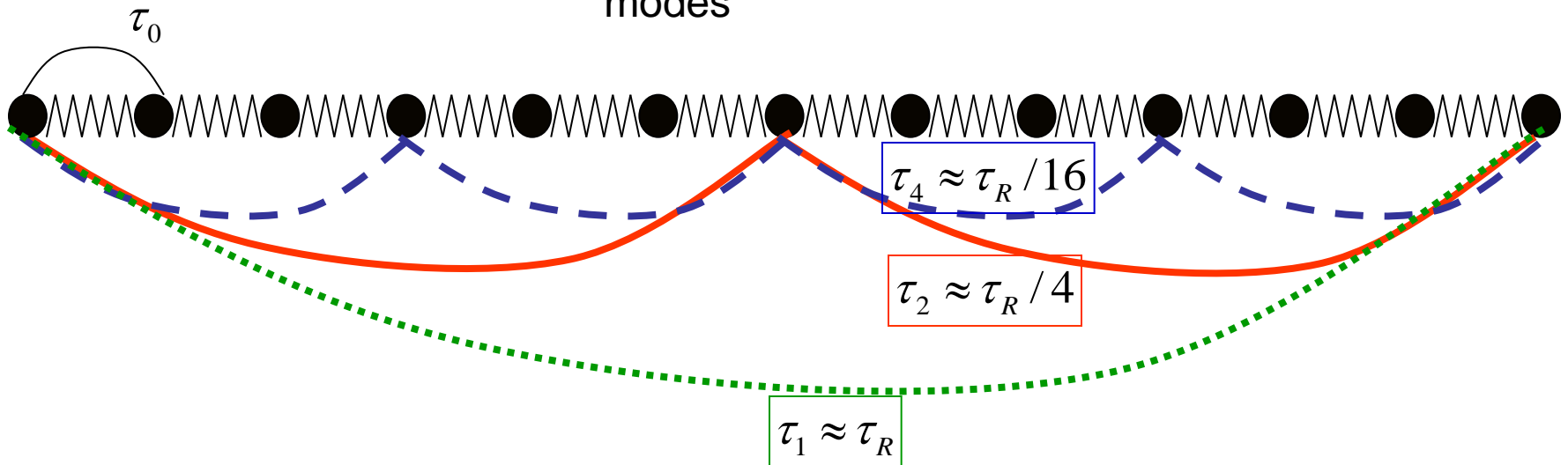
$$\tau_p \approx \tau_0 \left(\frac{N}{p}\right)^2$$

(p = 1,2,3,…,N)

$\tau_1 \approx \tau_R$

$\tau_i < \tau_{i-1}$

N relaxation modes

$\tau_0$

$\tau_4 \approx \tau_R / 16$

$\tau_2 \approx \tau_R / 4$

$\tau_1 \approx \tau_R$

- At time t = $\tau_p$, number of unrelaxed modes = p.

- Each unrelaxed mode contributes energy of order kT to the stress relaxation modulus:

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

(density of sections with N/p monomers: $\dfrac{v}{(N/p)b^3}$ )

Volume fraction

- Mode index at time t = $\tau_p$: $\quad p \approx \left(\dfrac{\tau_p}{\tau_0}\right)^{-1/2} N$
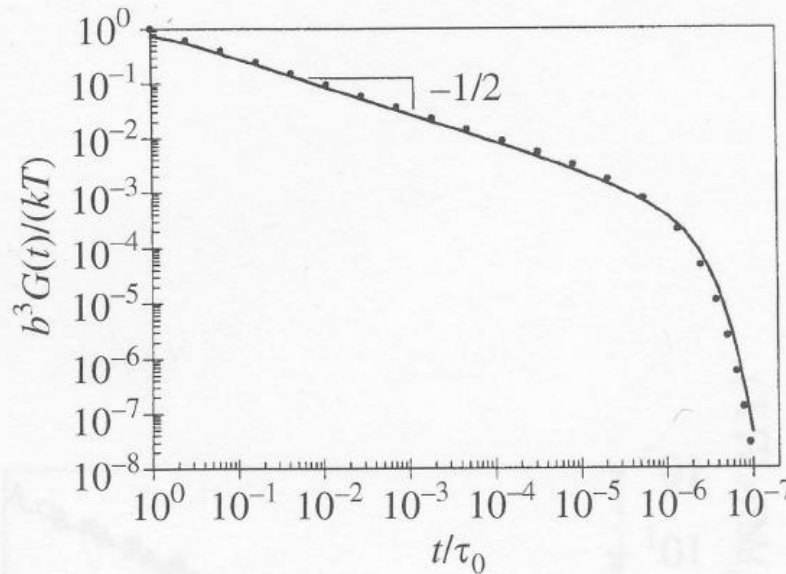
$$\Longrightarrow \quad G(t) \approx \frac{kT}{b^3} v \left(\frac{t}{\tau_0}\right)^{-1/2}$$ , for $\tau_0 < t < \tau_R$

Approximation: $G(t) \approx \dfrac{kT}{b^3} v \left(\dfrac{t}{\tau_0}\right)^{-1/2} \exp\left(\dfrac{-t}{\tau_R}\right)$ , for t > $\tau_0$

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

, for $\tau_0 < t < \tau_R$



Stress relaxation modulus predicted by the Rouse model for a melt of unentangled chains with $N = 10^3$. The solid curve is the exact Rouse result [Eq. (8.55)] and the dotted curve is the approximate Rouse result [Eq. (8.48)].

Viscosity of the Rouse model:

$$\eta = \int_0^\infty G(t)\,dt \approx \frac{kT}{b^3} \nu \int_0^\infty \left(\frac{t}{\tau_0}\right)^{-1/2} \exp\left(\frac{-t}{\tau_R}\right) dt$$

$$\approx \frac{kT}{b^3} \nu \sqrt{\tau_0 \tau_R} \int_0^\infty x^{-1/2} \exp(-x)\,dx \approx \frac{kT}{b^3} \nu \sqrt{\tau_0 \tau_R} \approx \frac{kT}{b^3} \nu \tau_0 N \approx \frac{\zeta}{b} N \nu$$

$$\Longrightarrow \quad \boxed{\eta \approx \frac{\zeta}{b} N}$$

Or:

$$\tau_R \approx \tau_0 N^2$$

$$G(\tau_R) \approx kT \frac{\nu}{N b^3}$$

$$\Longrightarrow \quad \boxed{\eta = \tau_R G(\tau_R) \approx \frac{\zeta}{b} N}$$

Exact solution of the Rouse model:

$$G(t) = \frac{kT}{Nb^3} \nu \sum_{p=1}^{N} \exp\left(\frac{-t}{\tau_p}\right) \qquad \text{with} \qquad \tau_p = \frac{\zeta b^2 N^2}{6\pi^2 kT p^2}$$
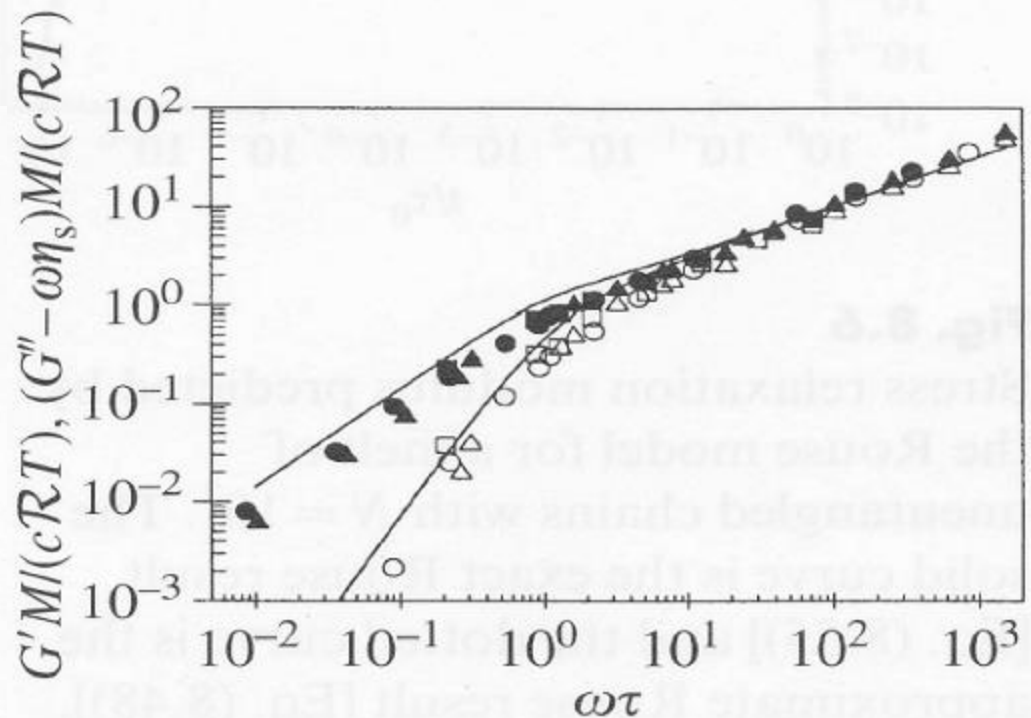
Each mode relaxes as a Maxwell element

# Example: Frequency sweep test:

$$G'(\omega) \simeq G''(\omega) \sim \omega^{1/2}$$  For $1/\tau_R < \omega < 1/\tau_0$
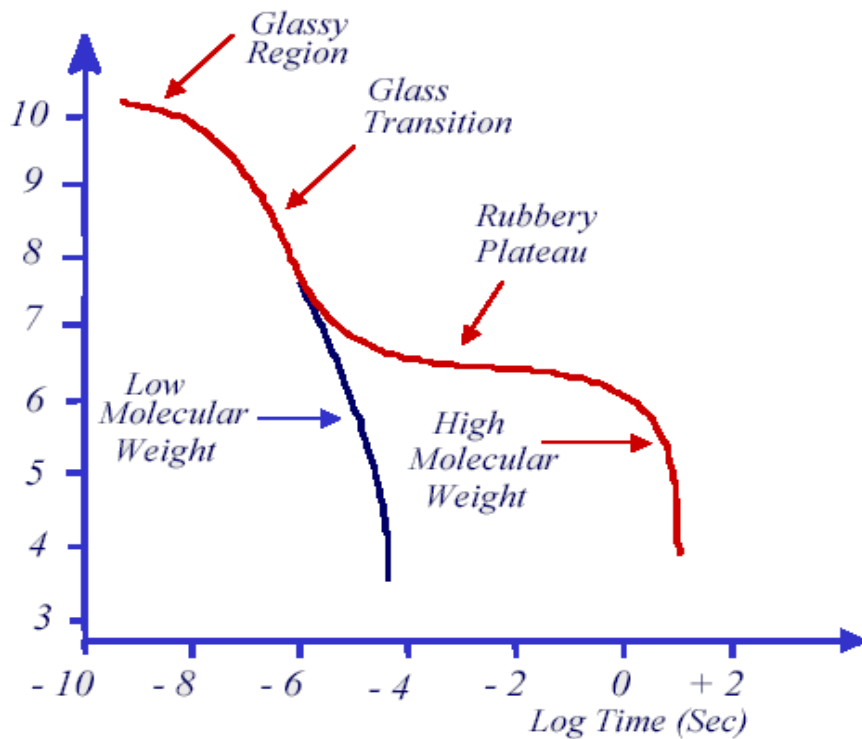
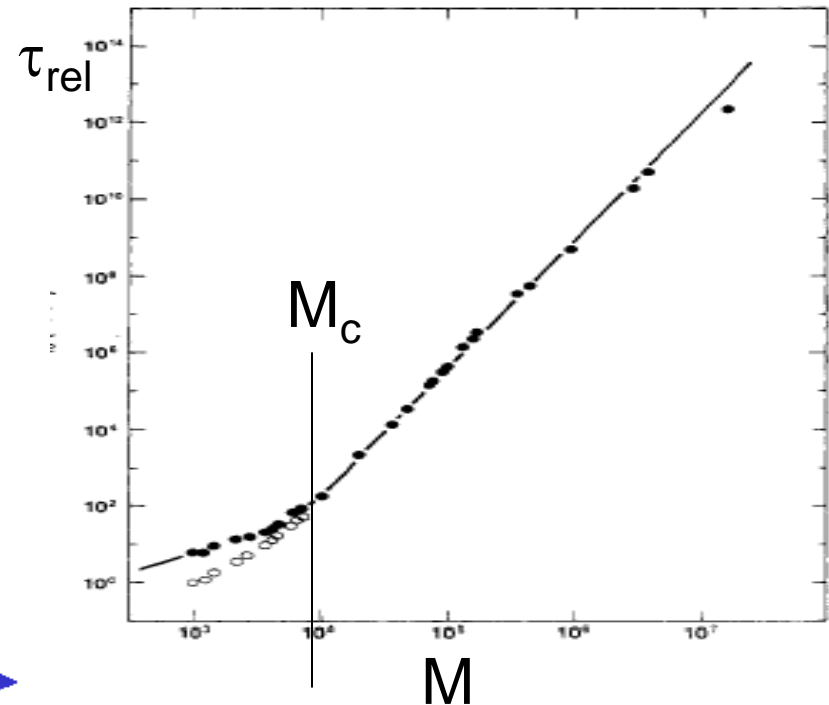$$\begin{cases} G'(\omega) \sim \omega \\ G''(\omega) \sim \omega^2 \end{cases}$$  For $\omega < 1/\tau_R$

Oscillatory shear data for solutions of poly(2-vinyl pyridine) in 0.0023 M HCl in water. Open symbols are the storage modulus $G'$ and filled symbols are the loss modulus $G''$. Squares have $c = 0.5\,\text{g L}^{-1}$, triangles have $c = 1.0\,\text{g L}^{-1}$, and circles have $c = 2.0\,\text{g L}^{-1}$. The curves are the predictions of the Rouse model [Eqs (8.49) and (8.50)]. Data from D. F. Hodgson and E. J. Amis, *J. Chem. Phys.* **94**, 4581 (1991).

# Rouse model: unentangled chains in polymer melts:

## Relaxation times



$\tau_{rel}$

$M_c$

M

For $M < M_c$ : $\tau \propto M^2$
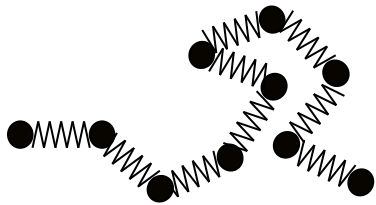
For $M > M_c$: $\tau \propto M^{3.4}$

Main issue with Rouse model: "phantom" chain (no interactions with environment (hence, it does not work for dilute solutions)

# *I.2.2. Account for hydrodynamic interactions: Zimm model*

*Viscous resistance from the solvent: the particle must drag some of the surrounding solvent with it.*

Hydrodynamic interaction: *long-range force acting on solvent (and other particles) that arises from motion of one particle.*

When one bead moves: interaction force on the other beads (Rouse: only through the springs)

The chain moves as a <u>solid object</u>: $\quad \zeta_Z \approx \eta_s R$

(no friction distribution in chain)

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

Zimm time:

$$\tau_Z \approx \frac{R^2}{D_Z} \approx \frac{\eta_s}{kT} R^3 \approx \frac{\eta_s b^3}{kT} N^{3/2} \approx \tau_0 N^{3/2} \quad \text{(In a theta solvent)}$$
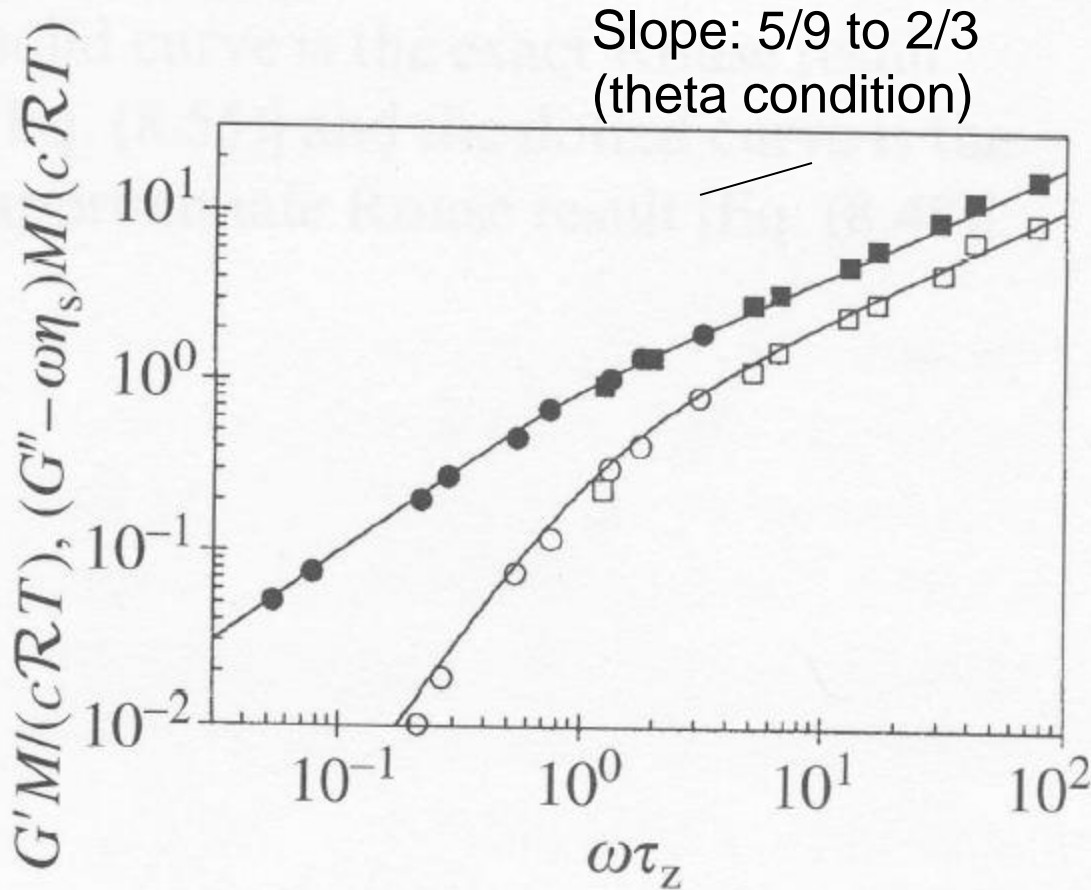
## Rouse time versus Zimm time:

$$\tau_R \approx \frac{R^2}{D_R} \approx \frac{R^2}{kT/N\zeta} \approx \frac{R^2}{kT/N\eta_s b} \approx \frac{\eta_s b^3}{kT} N^2$$

$$\tau_Z \approx \frac{R^2}{D_Z} \approx \frac{R^2}{kT/\zeta_Z} \approx \frac{R^2}{kT/\eta_s R} \approx \frac{\eta_s b^3}{kT} N^{3/2} \approx \tau_0 N^{3/2}$$

- $\tau_{Zimm}$ has a weaker M-dependence than $\tau_{Rouse}$.

- $\tau_{Zimm} < \tau_{Rouse}$ in dilute solution

- Zimm works better in dilute solution

Slope: 5/9 to 2/3 (theta condition)

Oscillatory shear data on dilute solutions of polystyrene with $M = 860\,000\ \mathrm{g\,mol^{-1}}$ in two $\theta$-solvents (circles are in decalin at 16 °C and squares are in di-2-ethylhexyl phthalate at 22 °C). Open symbols are the dimensionless storage modulus and filled symbols are the dimensionless loss modulus, both extrapolated to zero concentration. The curves are the predictions of the Zimm model [Eqs (8.67) and (8.68)]. Data from R. M. Johnson et al., Polym. J. 1, 742 (1970).

Dilute PS in Θ-solvent
  Zimm model

Undiluted short PS
  Rouse model



Polystyrene in 2 ☉-Solvents, M = 860,000

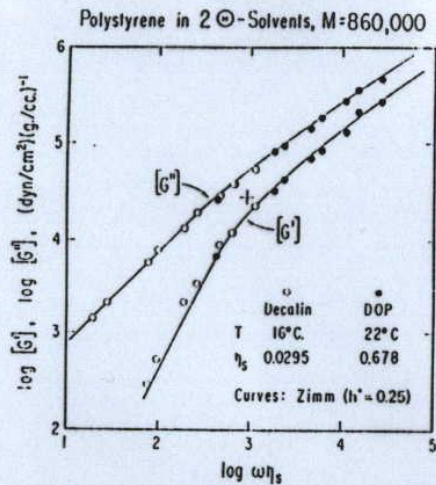|  | Decalin | DOP |
|---|---|---|
| T | 16°C. | 22°C |
| $\eta_s$ | 0.0295 | 0.678 |

Curves: Zimm (h* = 0.25)

Fig. 5.1. Intrinsic moduli for narrow distribution polystyrene (M = 860000) in two theta solvents (114). This comparison with theory is equivalent to that of reduced moduli described in the text. [Reproduced from Polymer J. 1, 747 (1970).]
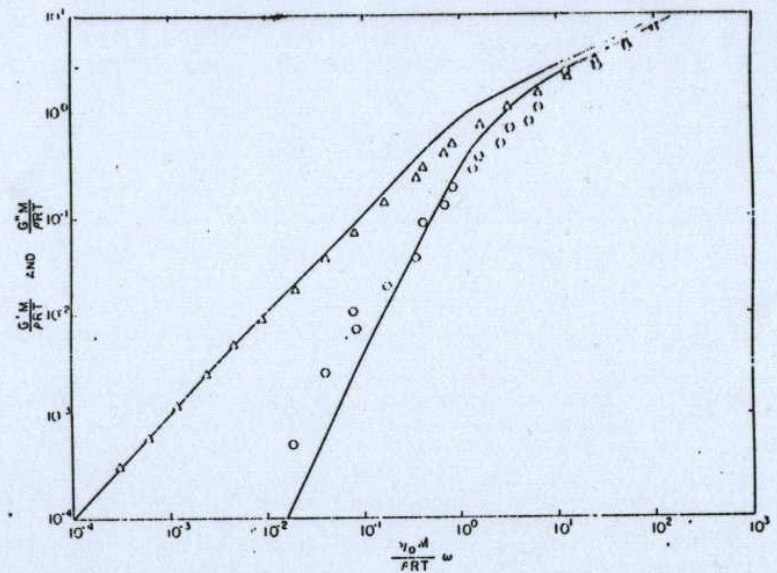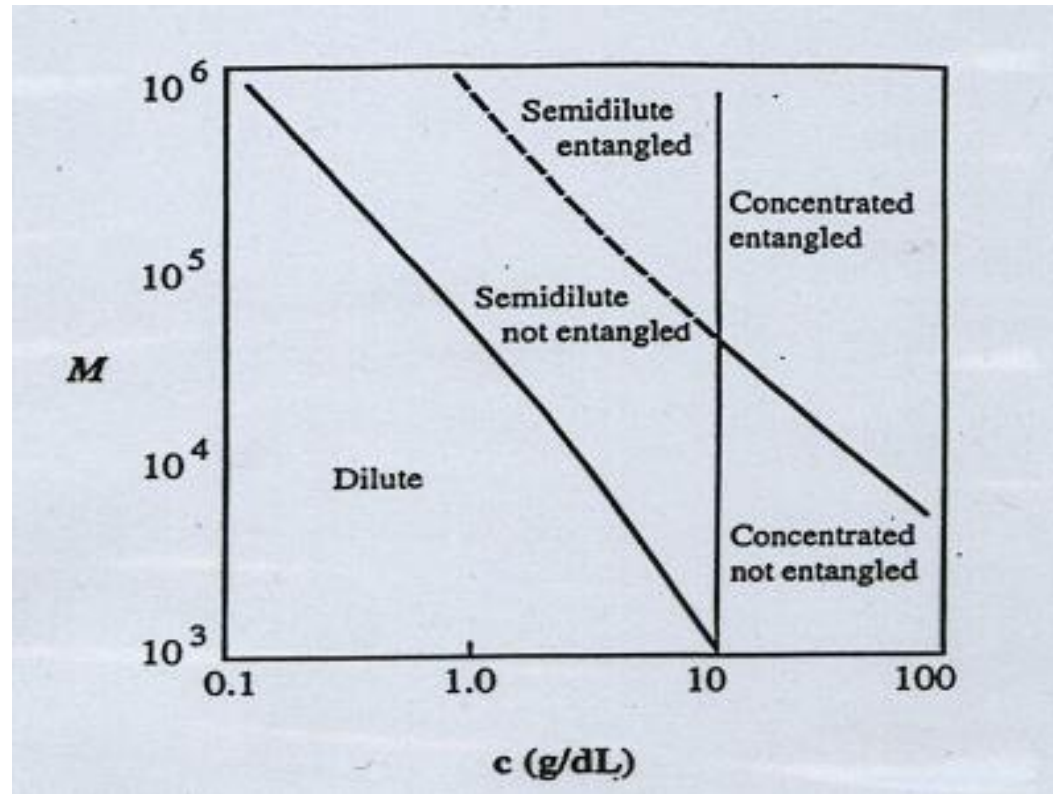


Fig. 5.2. Reduced dynamic moduli for undiluted narrow distribution polystyrene of low molecular weight. Data for a sample of $\bar{M}_w = 28\,900$ were reduced to 160 °C, for which $\varrho = 1.0$ gm/ml and $\eta_0 = 54\,500$ poise (124). The solid lines were calculated from the Rouse theory

$M_w = 28900$ g/mol
$M_e \simeq 13300$
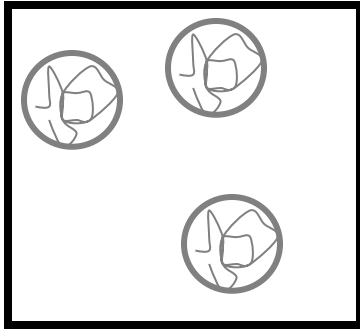
# Rheological Regimes:
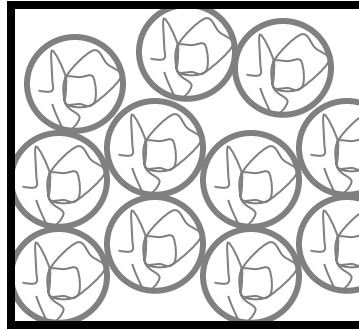
Dilute solutions: Zimm model – H.I. – no entanglement

Unentangled chains (Non diluted): Rouse model – no H.I. –  no entanglement

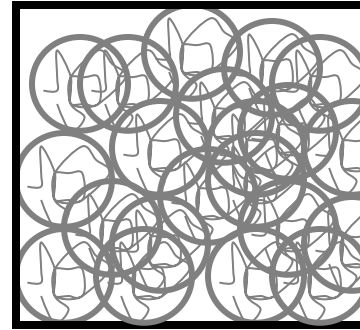Entangled chains: Reptation model – no H.I. –  entanglement

# III. Polymer: From diluted to concentrated state



c<c*

c=c*

c>c*

$$c* = \frac{M}{N_a \frac{4}{3}\pi R^3}$$

M: [g/mol]

c*: mass per volume

*Dilute solutions:*

$$\phi_{eff} = \frac{c_{Mass}}{c*} = c\frac{4}{3}\pi R^3 \ll 1$$

$$c = \frac{c_{Mass}N_a}{M}$$

$c_{Mass}$: mass per volume

c: number of molecules per volume

*Semi-dilute solutions:*

$c_{Mass} \approx c*$

*Concentrated solutions or melts:*

$c_{Mass} > c*$:     Interpenetration of the chains

c*: overlap concentration