Chapt. 5 Amorphous State of Polymers

5.1 Molecular motions of polymers

特点, 基本类型

5.2 Viscous flow of polymers

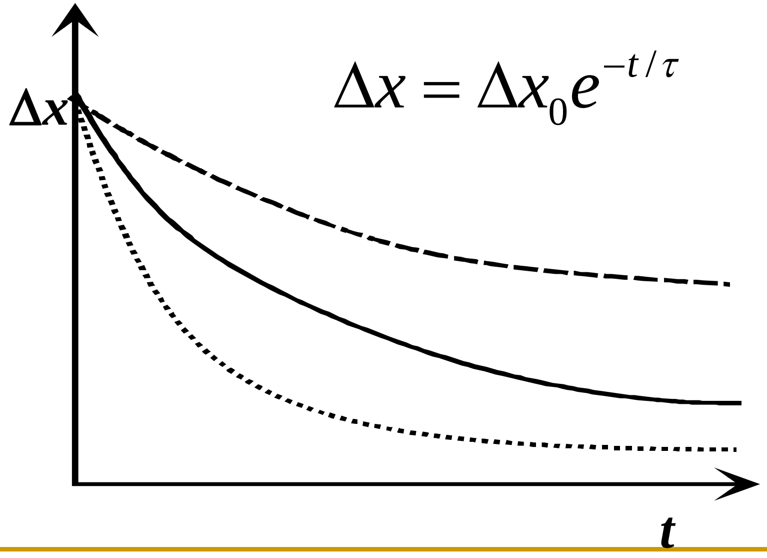
特点, 表征, 影响因素

5.3 Glass transition of polymers

意义, 表征, 理论

5.1 高聚物的分子热运动

- 1. 主要特点
- 运动单元的多重性
- 布朗运动/微布朗运动
- 与温度有关的松弛过程



τ : relaxation time

(1) 与运动单元有关

(2) 与温度有关

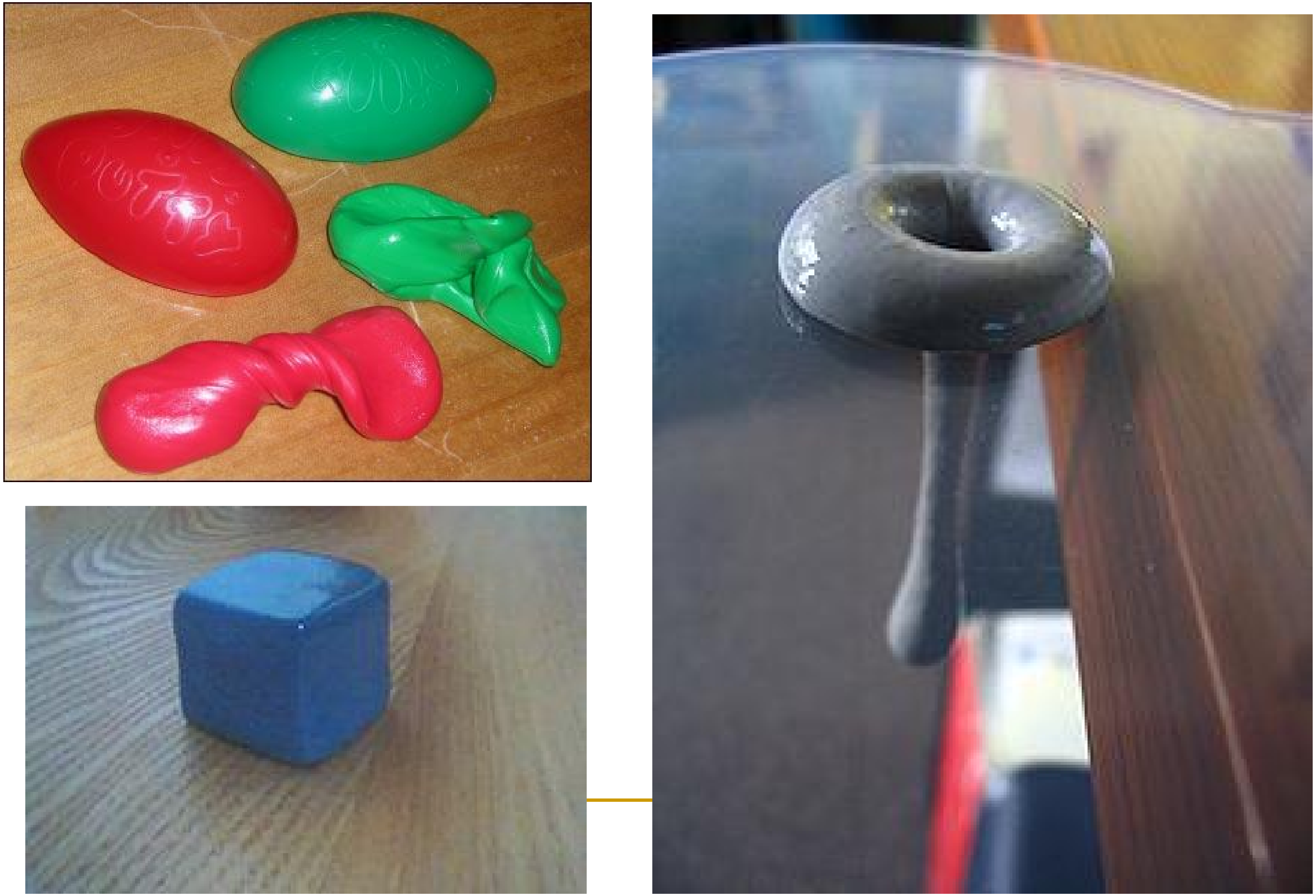
a. 指数形式 $\tau = \tau_0 e^{\Delta E/RT}$

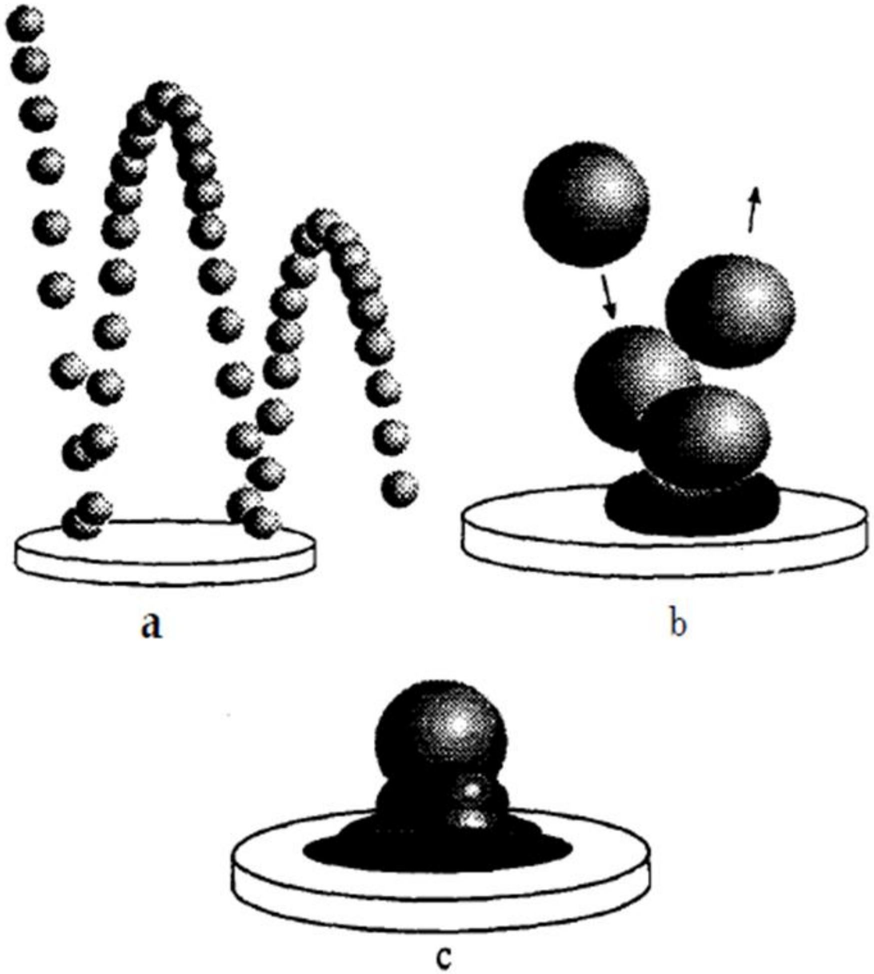
b. WLF 方程 (*T*g附近)

(3) 与观察时的时间标尺有关

比如：升降温速度，振动频率

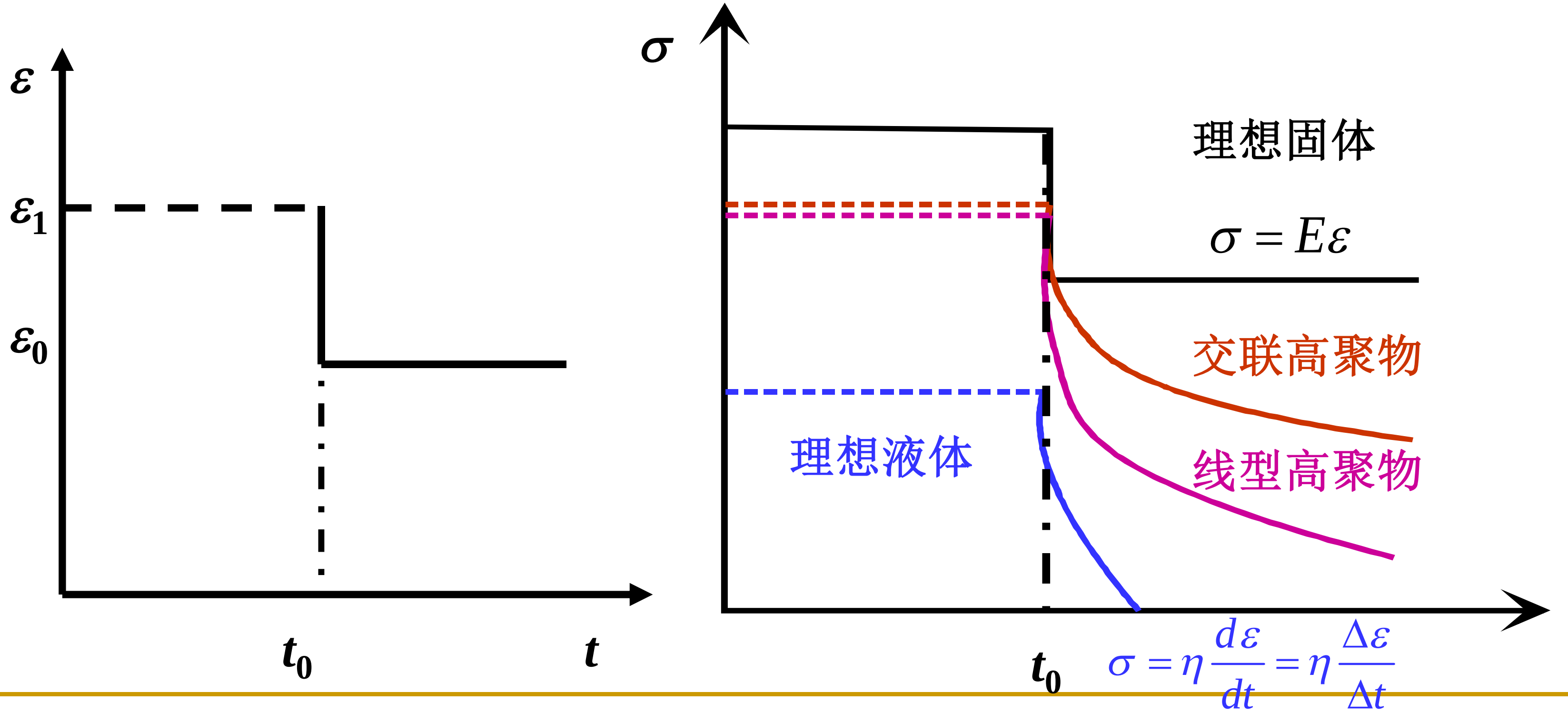
Time Dependent Behavior – Example: Silly Putty




a
b
c

Stress relaxation

在恒定温度和形变保持不变的情况下，高分子材料内部的应力随时间增加而逐渐衰减的现象

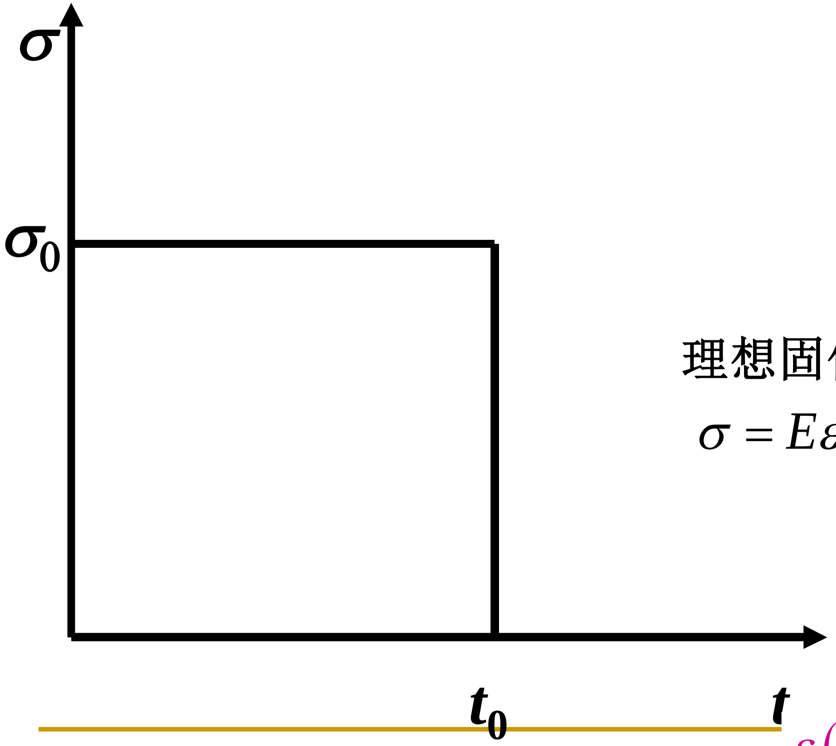


$$\sigma = \eta \frac{d\varepsilon}{dt} = \eta \frac{\Delta\varepsilon}{\Delta t}$$

$$\frac{\sigma(t)}{\varepsilon_0} = E(t) = E_0 \exp(-t/\tau)$$

Creep

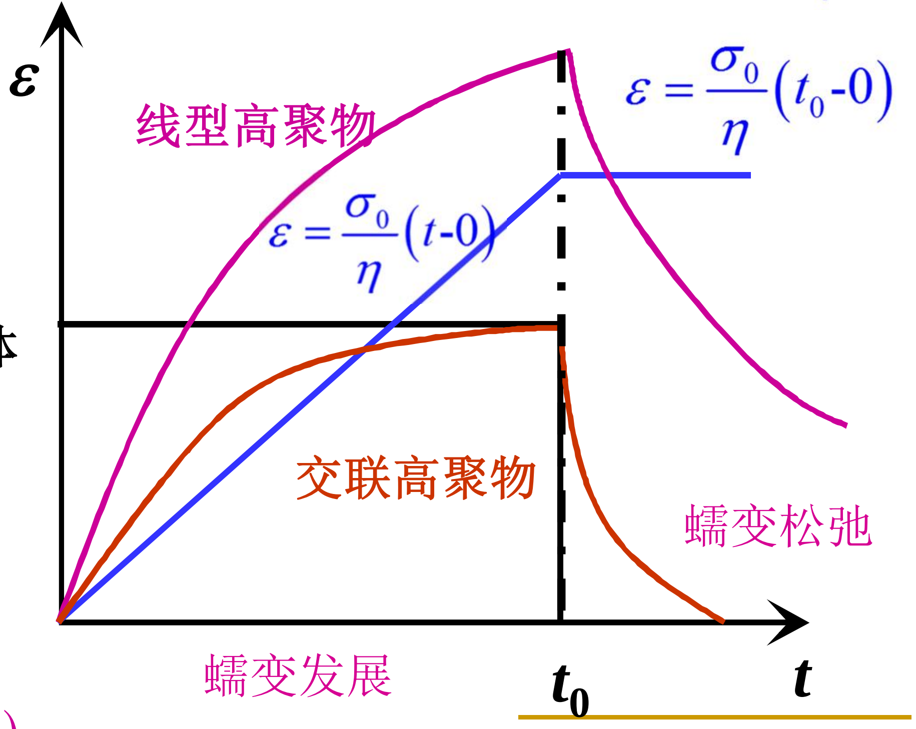
指一定温度和较小的恒定外力作用下，材料的形变随时间的增加而逐渐变化的现象



理想液体 $\sigma = \eta \frac{d\varepsilon}{dt}$ $\varepsilon = \int \frac{\sigma_0}{\eta} dt$

理想固体

$\sigma = E\varepsilon$



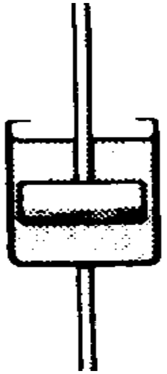
$$\frac{\varepsilon(t)}{\sigma_0} = D(t) = D(\infty)\left(1-e^{-t/\tau}\right)$$

$$\varepsilon(t) = \varepsilon(\infty)e^{-t/\tau}$$

Relaxation Time Originates from Viscoelastic Properties of Polymers

- **Elasticity and viscosity**
  - **Hooke's law describes the behavior of a linear elastic solid and Newton's law that of a linear viscous liquid:**

Spring as a model:
Modulus: E



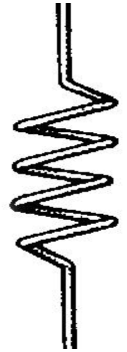
Dashpot as a model:
Viscosity (粘度): η

- **Hooke's law: $\sigma = E\varepsilon$**
- **Newton's law: $\sigma = \eta(d\varepsilon/dt)$**

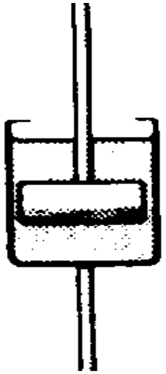
σ : stress (应力); ε : strain (应变)

Phenomenological models for linear viscoelasticity

Elasticity **Viscosity**



+



= **Viscoelasticity ?**

$\sigma = E\varepsilon$

$\sigma = \eta(d\varepsilon/dt)$

Model I - Maxwell model **Combining the spring and dashpot in series**

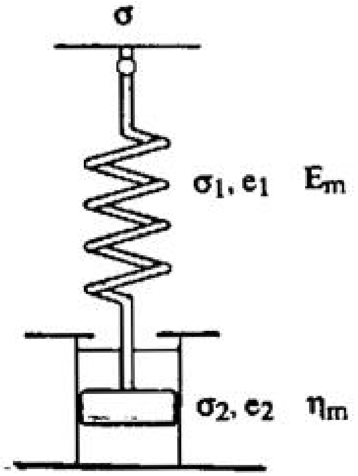
Model II -Voigt-Kelvin model **Combining the spring and dashpot in parallel**

Model III – Burger’s Model **Combining the Maxwell and Voigt elements in series**

....

Elasticity + Viscosity = Viscoelasticity ?

Model I: Maxwell Model



$\sigma_1 = E_m \varepsilon_1$

$\sigma_2 = \eta_m (d\varepsilon_2/dt)$

$$\frac{d\varepsilon_1}{dt} = \frac{1}{E_m}\frac{d\sigma}{dt}$$

$$\frac{d\varepsilon_2}{dt} = \frac{\sigma}{\eta_m}$$

$$\left.\begin{matrix} \sigma = \sigma_1 = \sigma_2 \\ \varepsilon = \varepsilon_1 + \varepsilon_2 \end{matrix}\right\}$$

→

$$\frac{d\varepsilon}{dt} = \frac{1}{E_m}\frac{d\sigma}{dt} + \frac{\sigma}{\eta_m}$$

For stress relaxation, $d\varepsilon/dt = 0$,

$$\frac{d\sigma}{\sigma} = -\frac{E_m}{\eta_m}dt$$

At time $t = 0$, $\sigma = \sigma_0$,

$$\sigma(t) = \sigma_0 \exp\left(\frac{-E_m}{\eta_m}\right)t$$

Relaxation time: $\tau = \eta_m / E_m$:

$$\boxed{\sigma(t) = \sigma_0 \exp\left(\frac{-t}{\tau}\right)}$$

松弛模量 $E(t) = \dfrac{\sigma(t)}{\varepsilon_0} = E_0 e^{-t/\tau}$

Maxwell Model fails to describe Creep

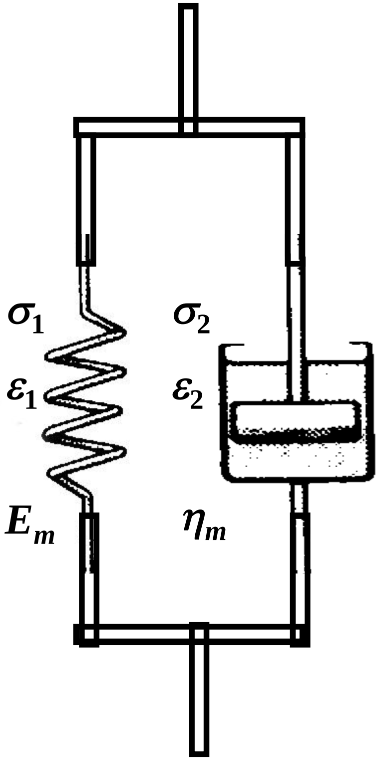
$$\frac{d\varepsilon}{dt}=\frac{1}{E_m}\frac{d\sigma}{dt}+\frac{\sigma}{\eta_m}$$

For creep, $\sigma = \sigma_0$,

$$\frac{d\varepsilon}{dt}=\frac{1}{E_m}\frac{d\sigma_0}{dt}+\frac{\sigma_0}{\eta_m}=\frac{\sigma_0}{\eta_m}$$

the “creep” behavior of viscous liquids.

Model II - Voigt-Kelvin model



Total stress: $\sigma = \sigma_1 + \sigma_2$;
strain: $\varepsilon = \varepsilon_1 = \varepsilon_2$

$$\left.\begin{aligned}\sigma_1 &= E_m \varepsilon_1 \\ \sigma_2 &= \eta_m \frac{d\varepsilon_2}{dt}\end{aligned}\right\} \Rightarrow \sigma_1 + \sigma_2 = \sigma = E_m \varepsilon + \eta_m \frac{d\varepsilon}{dt}$$

For stress relaxation, dε/dt = 0, $\sigma = E_m \varepsilon_0$

It fails to describe the stress relaxation behavior.

For creep, $\sigma = \sigma_0$,

$$\sigma_0 = E_m \varepsilon + \eta_m \frac{d\varepsilon}{dt}$$

At time $t = 0$, $\varepsilon = 0$, 柔量

$$\varepsilon(t) = \frac{\sigma_0}{E_m}\left(1 - e^{-(E_m/\eta_m)t}\right)$$

Relaxation time:
Retardation time $\tau = \eta_m / E_m$:

$$\varepsilon(t) = \frac{\sigma_0}{E_m}\left(1 - e^{-t/\tau}\right)$$

Model II - Voigt-Kelvin model

Creep compliance

$$\varepsilon(t)/\sigma_0 = \frac{\sigma_0}{E_m}/\sigma_0\left(1-e^{-t/\tau}\right)$$

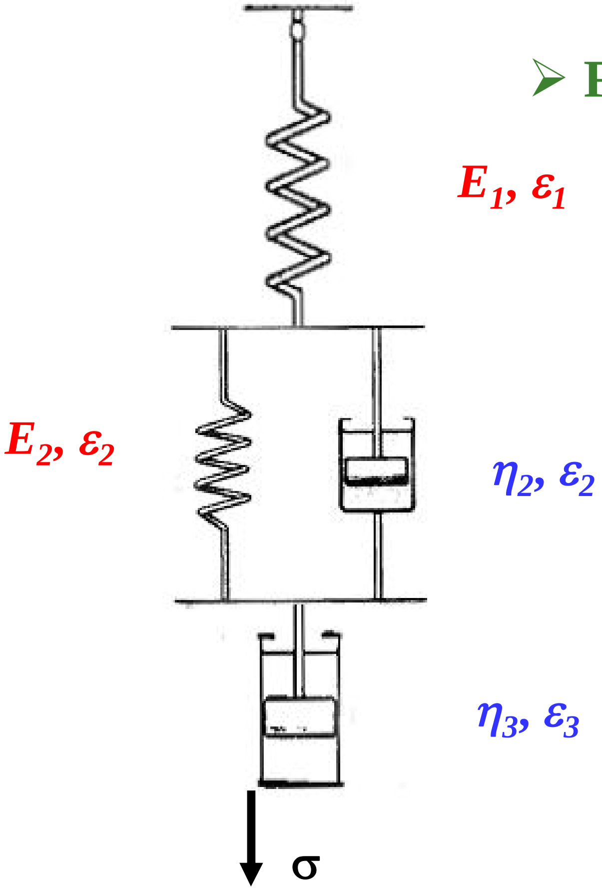
$$D(t) = D(\infty)\left(1-e^{-t/\tau}\right)$$

For creep recovery, $\sigma = 0$,

$$0 = E_m\varepsilon + \eta_m\frac{d\varepsilon}{dt}$$

$$\varepsilon(t) = \varepsilon(\infty)e^{-t/\tau}$$

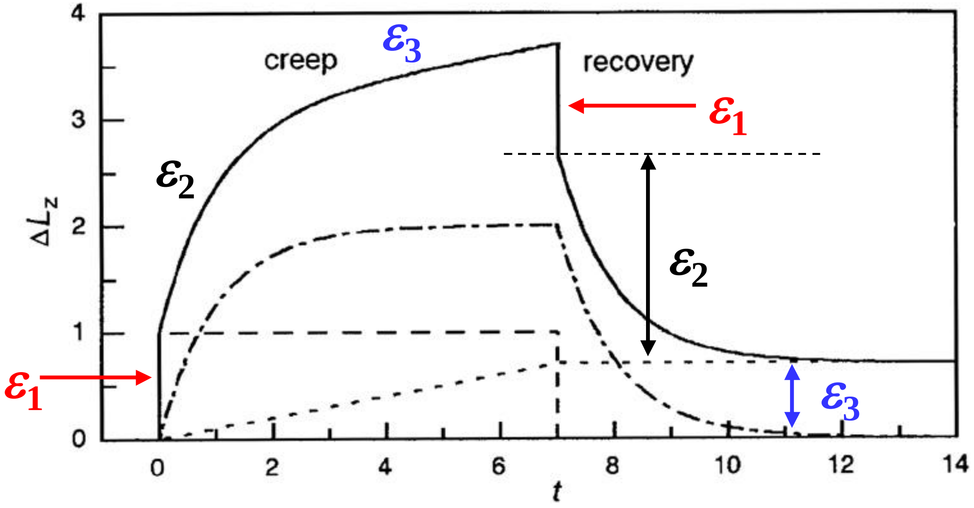
Model III – Burger's Model



- **For creep, $\sigma = \sigma_0$:**

$$\varepsilon(t) = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \frac{\sigma_0}{E_1} + \frac{\sigma_0}{E_2}\left(1 - e^{-t/\tau}\right) + \frac{\sigma_0}{\eta_3} t$$

where $\tau = \dfrac{\eta_2}{E_2}$



粘弹性-分子和力学的松弛行为

力学性能随时间改变而演化，变化的快慢可由材料本身的松弛时间估算

$$\boxed{\tau = \eta_m/E_m}$$

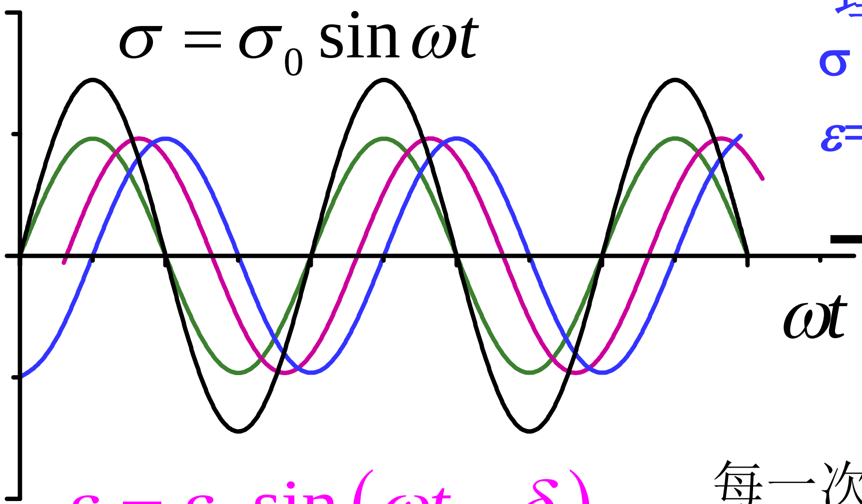
粘弹性的微观起源：

弹性由熵弹性即构象熵的改变贡献

粘性由构象改变过程中受到的粘滞阻力导致

Dynamical Mechanics Analysis

高聚物在交变应力作用下，形变落后于应力变化的现象称为滞后现象



$$\sigma = \sigma_0 \sin \omega t$$

$$\varepsilon = \varepsilon_0 \sin\left(\omega t - \delta\right)$$

将落后一个δ的相位

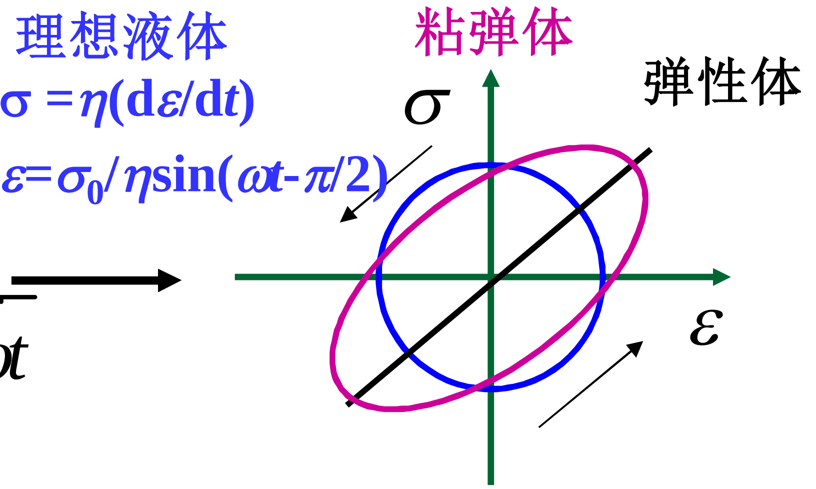
即：滞后现象

hysteresis and mechanics loss

理想液体

$\sigma = \eta(d\varepsilon/dt)$

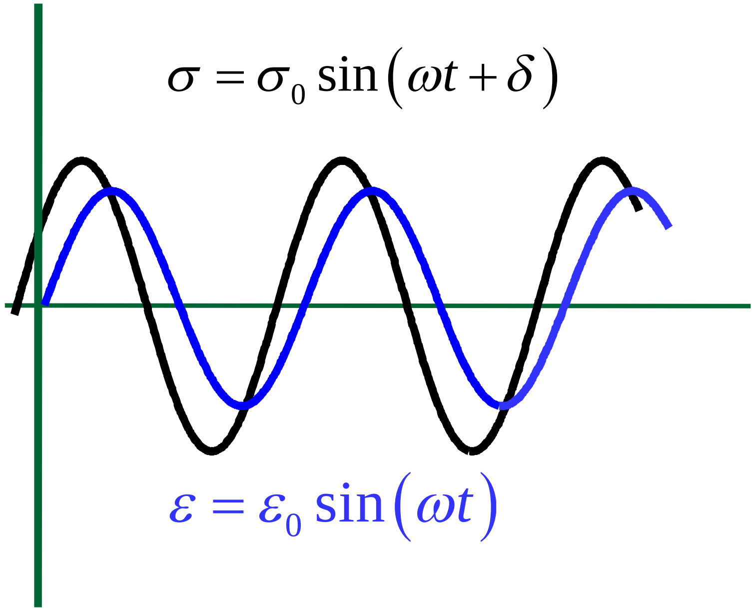
$\varepsilon = \sigma_0/\eta \sin(\omega t - \pi/2)$



每一次循环将消耗功—**力学损耗**或叫**内耗**，δ又称为**力学损耗角**

$$\Delta W = \oint \sigma(t) d\varepsilon(t) = \pi \sigma_0 \varepsilon_0 \sin\delta$$

Complex Modulus: As “Solid”



$$\sigma = \sigma_0 \sin(\omega t + \delta)$$

$$\varepsilon = \varepsilon_0 \sin(\omega t)$$

$$\sigma(t) = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta$$

synchronization **asynchronism**

Modulus of synchronization part

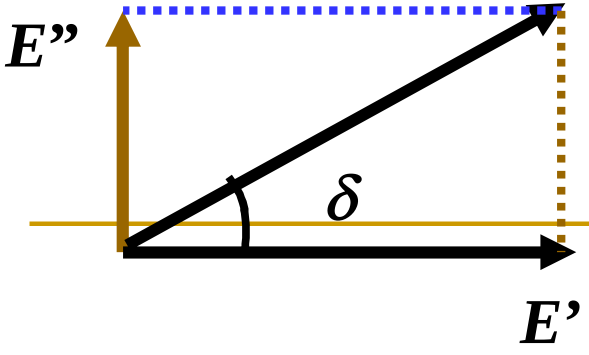
Modulus of asynchronism part

$$E' = \left(\frac{\sigma_0}{\varepsilon_0}\right)\cos\delta \quad E'' = \left(\frac{\sigma_0}{\varepsilon_0}\right)\sin\delta$$

$$E \neq E' + E''$$

$$\vec{E} = \vec{E}' + \vec{E}''$$ **or** $$E^* = E' + iE''$$

$$E^* = \left(\frac{\sigma_0}{\varepsilon_0}\right)e^{i\delta}$$



$$\tan\delta = \frac{E''}{E'}$$

内耗的量度

偏向液体的程度

Complex Viscosity: As "Liquid"

$$\varepsilon = \varepsilon_0 \sin(\omega t) \qquad \sigma(t) = \sigma_0 \sin\omega t \cos\delta + \sigma_0 \cos\omega t \sin\delta$$

$$\downarrow \qquad\qquad \downarrow \qquad\qquad \downarrow$$

$$\dot{\gamma} = \frac{d\varepsilon}{dt} = \varepsilon_0 \omega \cos(\omega t)$$

asynchronism **synchronization**

Viscosity of asynchronism part

Viscosity of synchronization part

$$\eta'' = \left(\frac{\sigma_0}{\varepsilon_0 \omega}\right)\cos\delta \qquad \eta' = \left(\frac{\sigma_0}{\varepsilon_0 \omega}\right)\sin\delta$$

$$E' = \left(\frac{\sigma_0}{\varepsilon_0}\right)\cos\delta \ \downarrow \qquad \downarrow\ E'' = \left(\frac{\sigma_0}{\varepsilon_0}\right)\sin\delta$$

$$\eta'' = \frac{E'}{\omega} \qquad \eta' = \frac{E''}{\omega}$$

For dynamic mechanics

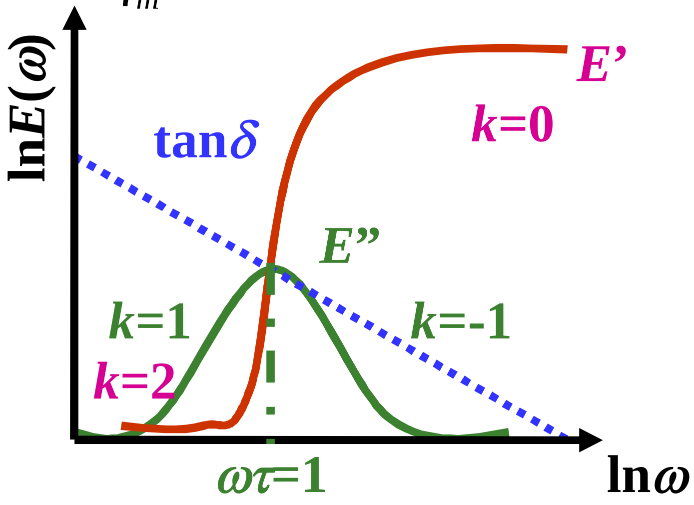
Model I - Maxwell model

$$\frac{d\varepsilon}{dt}=\frac{1}{E_m}\frac{d\sigma}{dt}+\frac{\sigma}{\eta_m} \qquad \sigma=\sigma_0 e^{i\omega t}$$

$$\frac{d\varepsilon(t)}{dt}=\frac{\sigma_0}{E_m}i\omega e^{i\omega t}+\frac{\sigma_0}{\eta_m}e^{i\omega t}=\left(\frac{\sigma_0}{E_m}i\omega+\frac{\sigma_0}{\eta_m}\right)e^{i\omega t}$$

$$\int d\varepsilon(t)dt=\int\left(\frac{\sigma_0}{E_m}i\omega+\frac{\sigma_0}{\eta_m}\right)e^{i\omega t}dt$$

$$E^*=\frac{\Delta\sigma(t)}{\Delta\varepsilon(t)}=\frac{E_m\omega^2\tau^2}{1+\omega^2\tau^2}+i\frac{E_m\omega\tau}{1+\omega^2\tau^2}$$



Model II - Voigt-Kelvin model

$$\sigma=E_m\varepsilon+\eta_m\frac{d\varepsilon}{dt} \qquad \varepsilon=\varepsilon_0 e^{i\omega t}$$

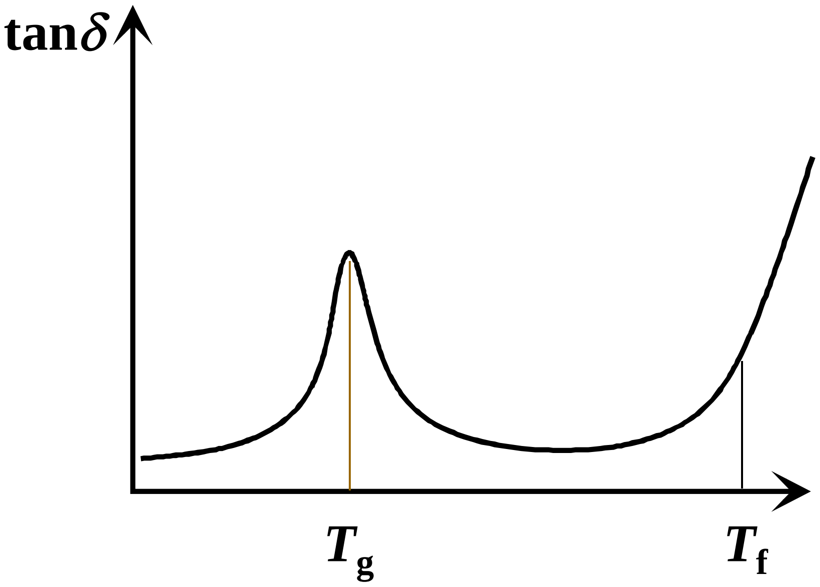
Complex compliance

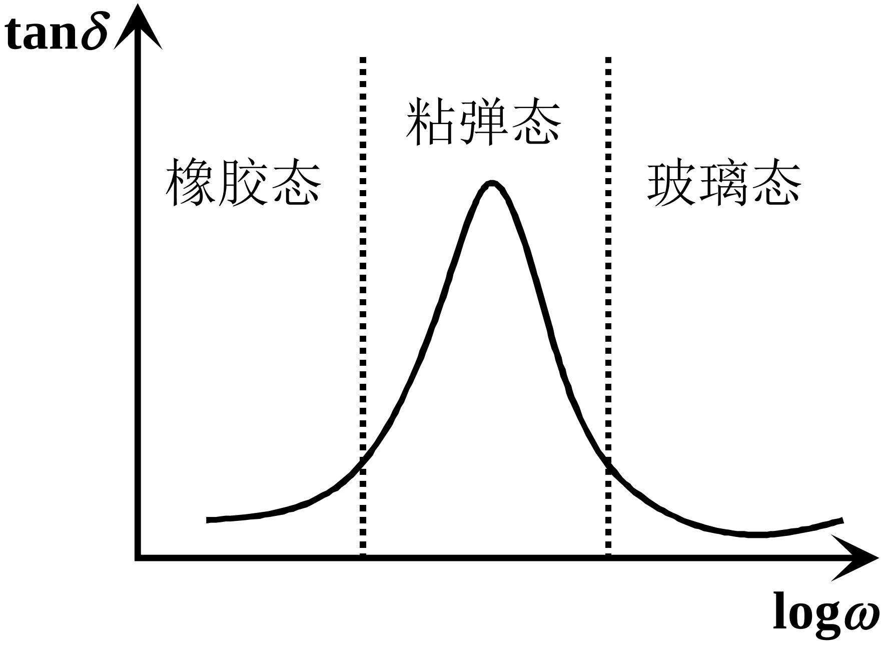
$$D^*=\frac{1}{E^*}=\frac{1}{E_m\left(1+\omega^2\tau^2\right)}-i\frac{\omega\tau}{E_m\left(1+\omega^2\tau^2\right)}$$

$\tau=\eta_m/E_m$

internal friction 高聚物的内耗与温度、频率的关系

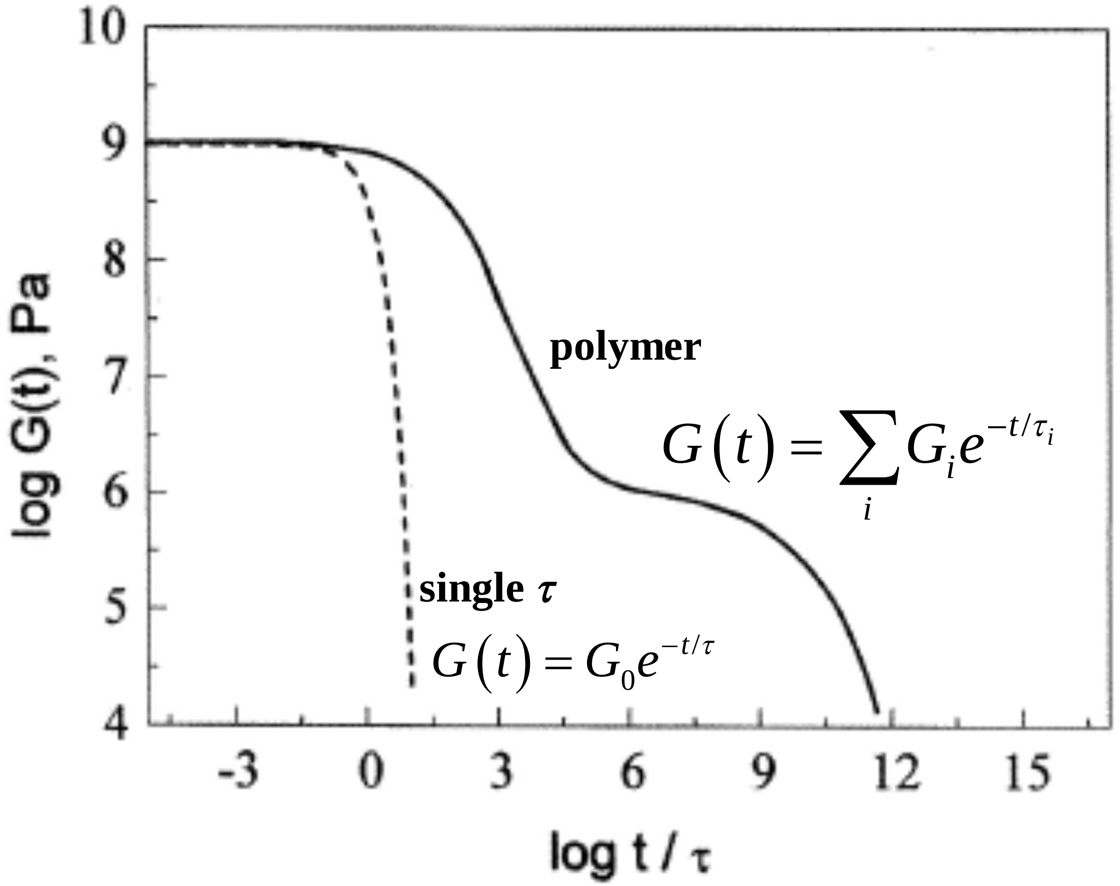
可用力学损耗角的正切tanδ来表示内耗的大小





玻璃化转变区域是粘弹性表现最强烈的区域

单松弛与多松弛时间与性能的关系



General Maxwell Model

For stress relaxation

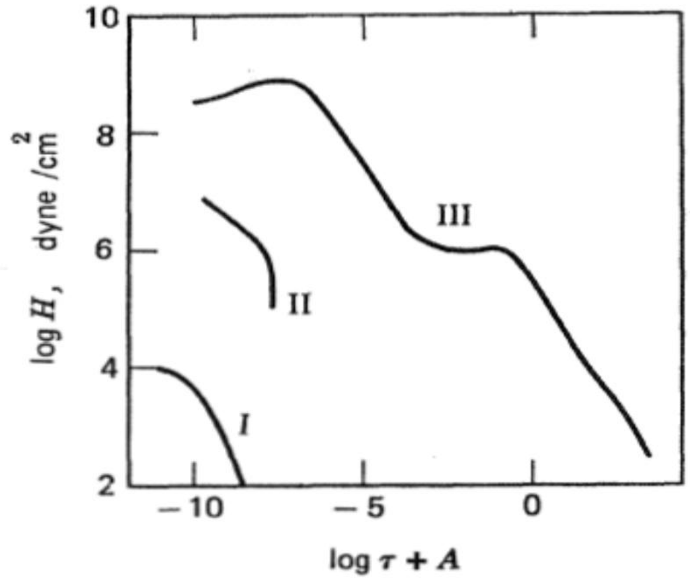
relaxation time spectrum (松弛时间谱)

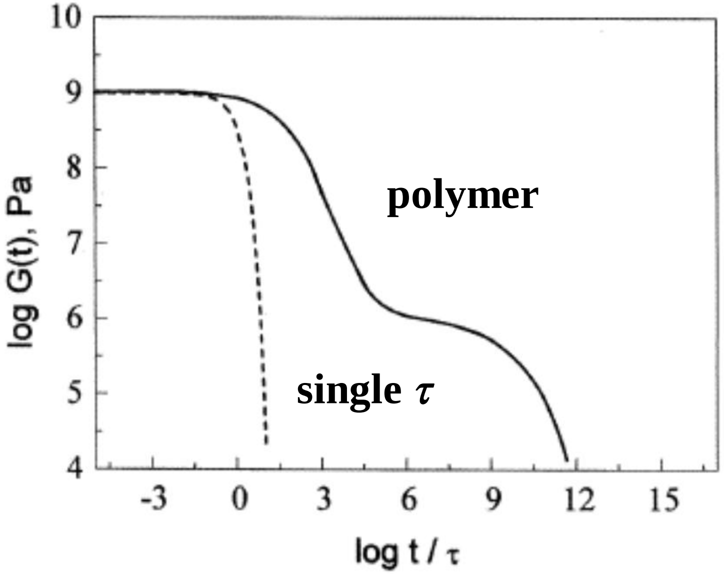
$$E(t)=\sum_i E_i e^{-t/\tau_i}$$

$$E(t)=\int_0^{\infty} f(\tau)e^{-t/\tau}d\tau$$

$$\xrightarrow{H(t)=\tau f(\tau)}$$

$$E(t)=\int_{-\infty}^{\infty} H(\tau)e^{-t/\tau}d\ln\tau$$





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Viscosity & Relaxation Modulus

$$E_i(t) = E_i e^{-t/\tau_i} \qquad \eta_i = \tau_i E_i$$

$$E(t) = \sum_i E_i e^{-t/\tau_i}$$

$$\int_0^\infty E_i(t)dt = \int_0^\infty E_i e^{-t/\tau_i} dt = E_i \int_0^\infty e^{-t/\tau_i} dt = E_i \tau_i = \eta_i$$

$$\eta = \sum_i \eta_i = \sum_i \int_0^\infty E_i(t)\,dt = \int_0^\infty \sum_i E_i(t)\,dt = \int_0^\infty E(t)\,dt$$

$$\eta(T) = \int_0^\infty E(T,t)\,dt$$

General Voigt Model

For creep

retardation time spectrum (推迟时间谱)

$$D_1(t)=\int_{-\infty}^{\infty}L_1(\tau)\left(1-e^{-t/\tau}\right)d\ln\tau$$

For creep recovery

$$D_2(t)=\int_{-\infty}^{\infty}L_2(\tau)e^{-t/\tau}d\ln\tau$$

For dynamic mechanics

General Maxwell Model

$$E^*=\sum_i\frac{E_i\omega^2\tau_i^2}{1+\omega^2\tau_i^2}+i\sum_i\frac{E_i\omega\tau_i}{1+\omega^2\tau_i^2}$$

or

General Voigt Model

$$D^*=\sum_i\frac{1}{E_i\left(1+\omega^2\tau_i^2\right)}-i\sum_i\frac{\omega\tau_i}{E_i\left(1+\omega^2\tau_i^2\right)}$$

Viscosity & Modulus & Relaxation Time

Solid Elasticity(short) Liquid Viscosity(long)

$$\sigma = E\varepsilon$$

$$\sigma = \eta(d\varepsilon/dt)$$

Viscoelasticity of Polymer

$\tau_i = \eta_i / E_i$ *i*-th movement mode

Modulus *vs* Relaxation Time

$$E(T,t) = \sum_i E_i(T) e^{-t/\tau_i}$$

⇒

$$E(T,t) = \int_{-\infty}^{\infty} H(T,\tau) e^{-t/\tau} d\ln\tau$$

relaxation time spectrum

Viscosity *vs* Modulus

1. oscillatory shear

$$\eta'(T,\omega) = \frac{E''(T,\omega)}{\omega} \qquad \eta''(T,\omega) = \frac{E'(T,\omega)}{\omega}$$

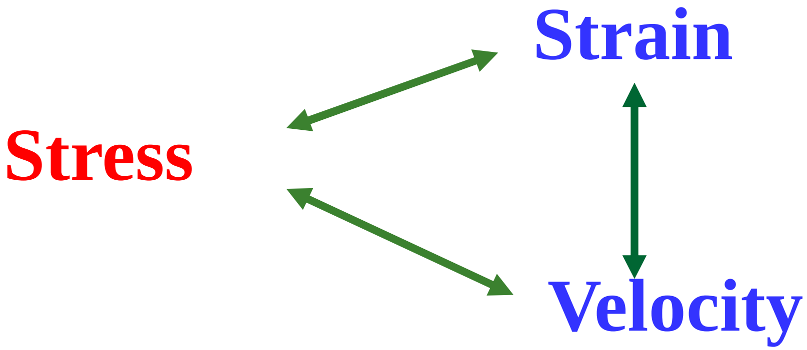
2. static shear

$$\eta(T) = \int_0^{\infty} E(T,t)\,dt$$

5.2 Viscous Flow of Polymers

- **The rheological properties (流变性质) of polymers is extremely important for polymer processing**

Rheology: The study of the deformation and flow of matter.



Stress

Strain

Velocity

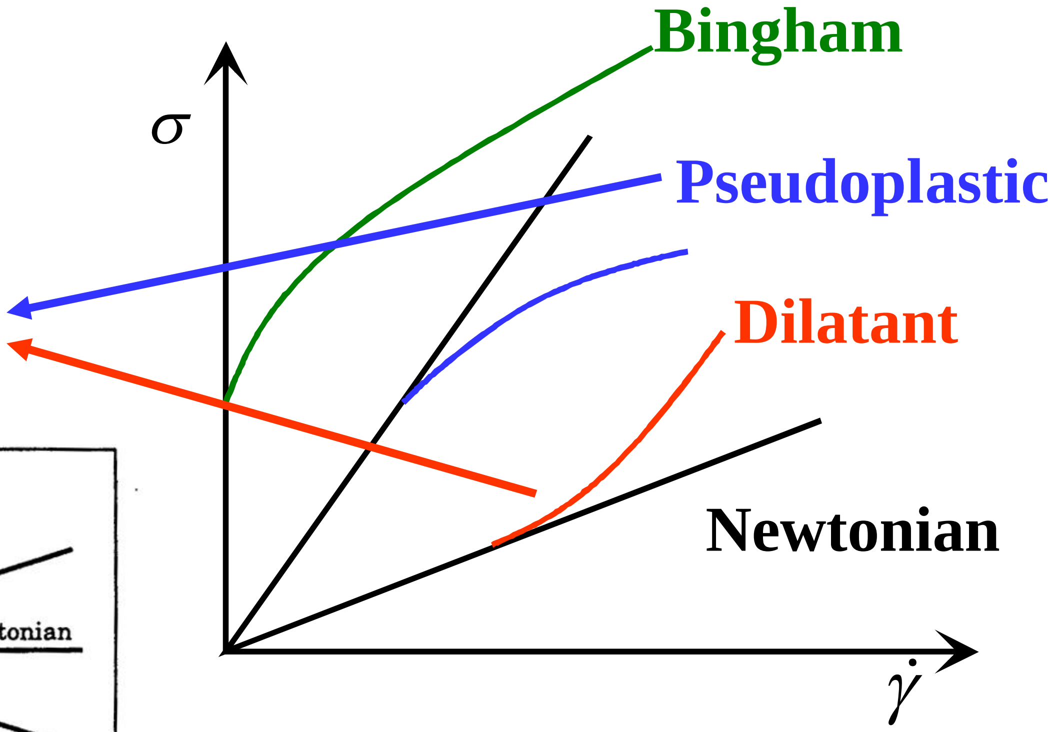
Characteristic of polymer viscous flow

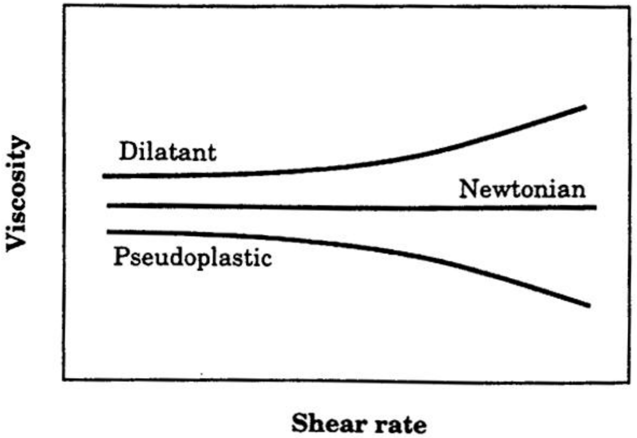
1. 链段的蠕动实现整个分子的迁移

2. 不符合牛顿流体的流动规律

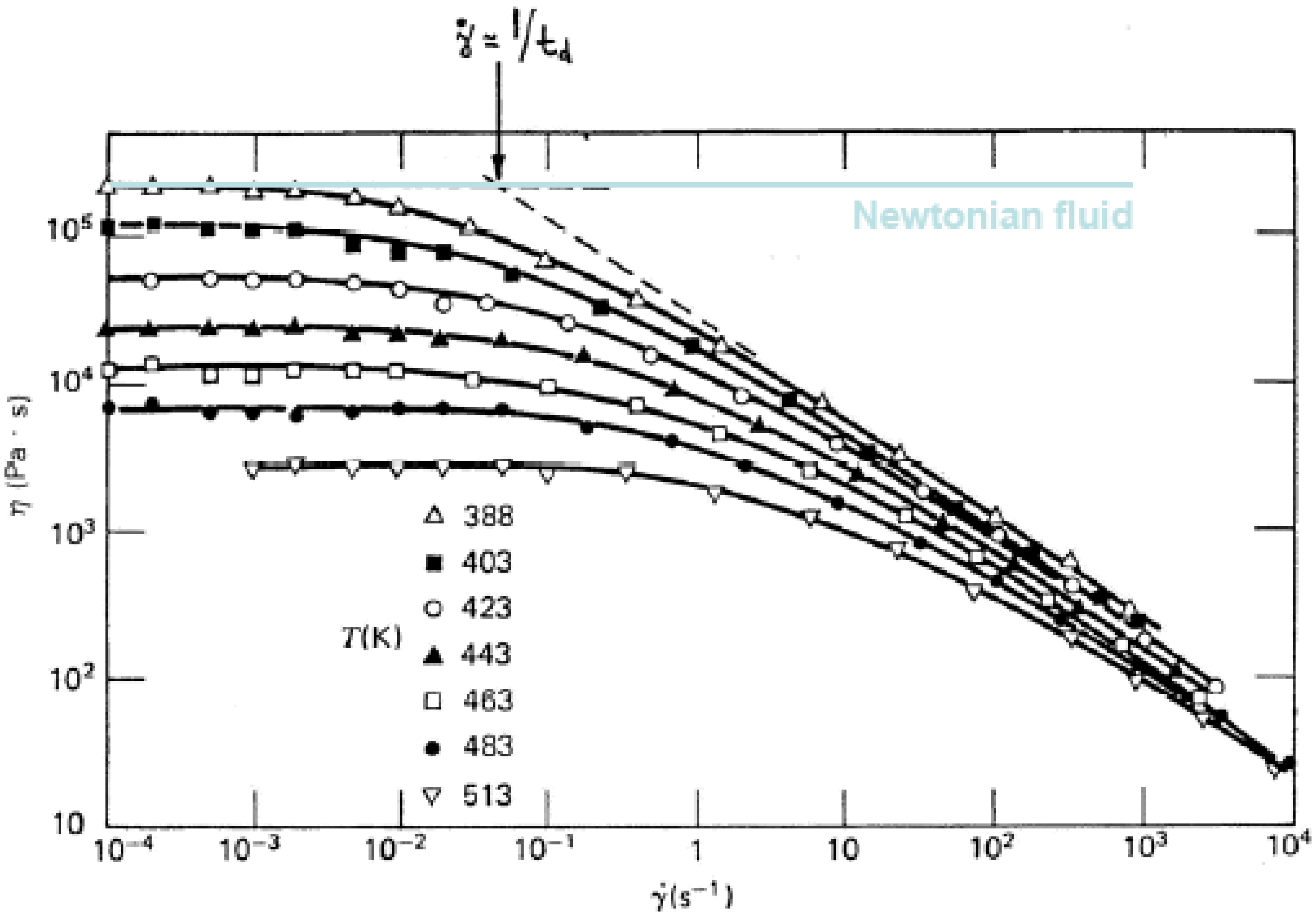
$$\sigma \neq \eta \frac{d\gamma}{dt} = \eta\dot{\gamma}$$

$$\sigma = K\dot{\gamma}^{n}$$



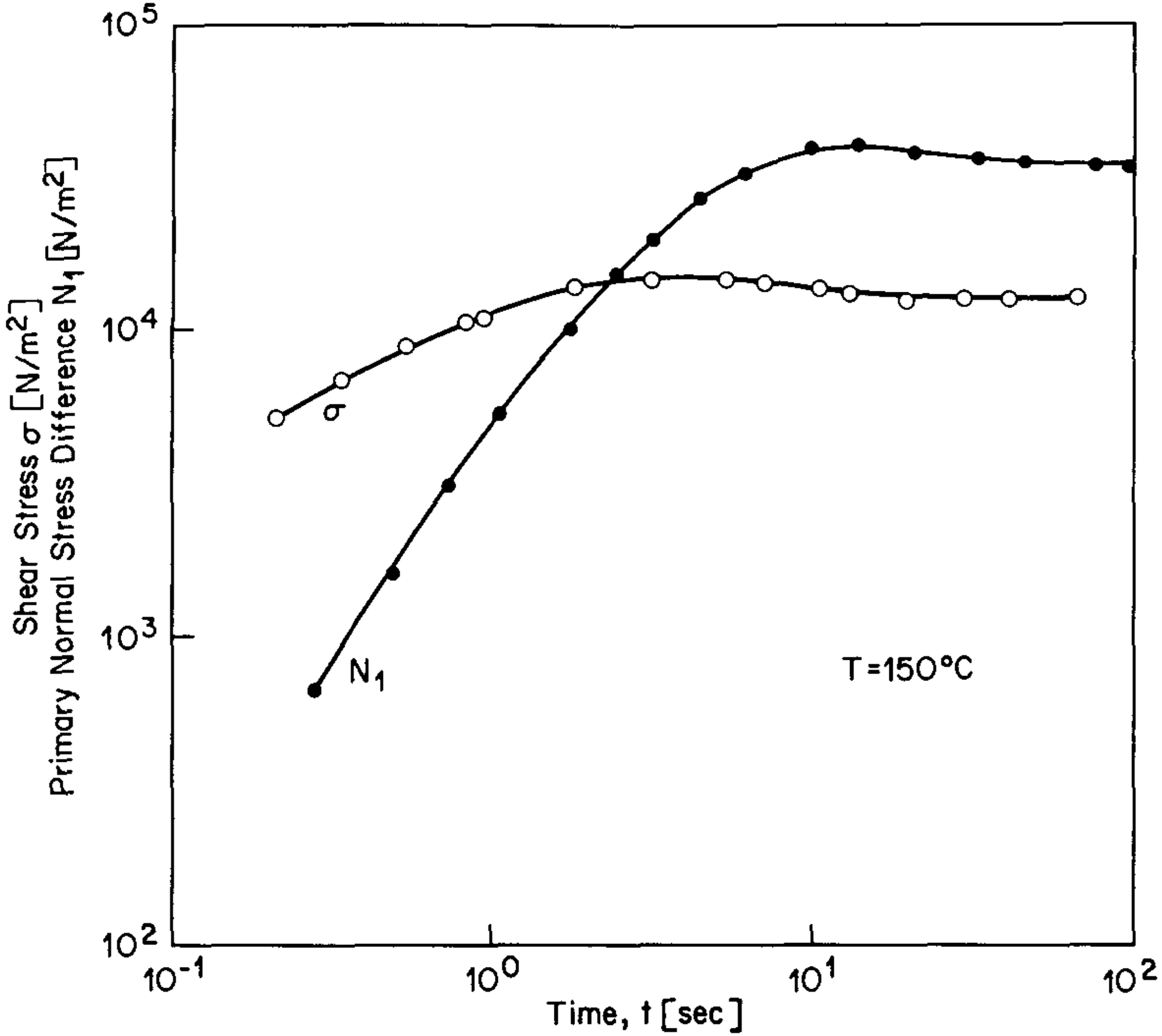


Shear thinning (剪切变稀)

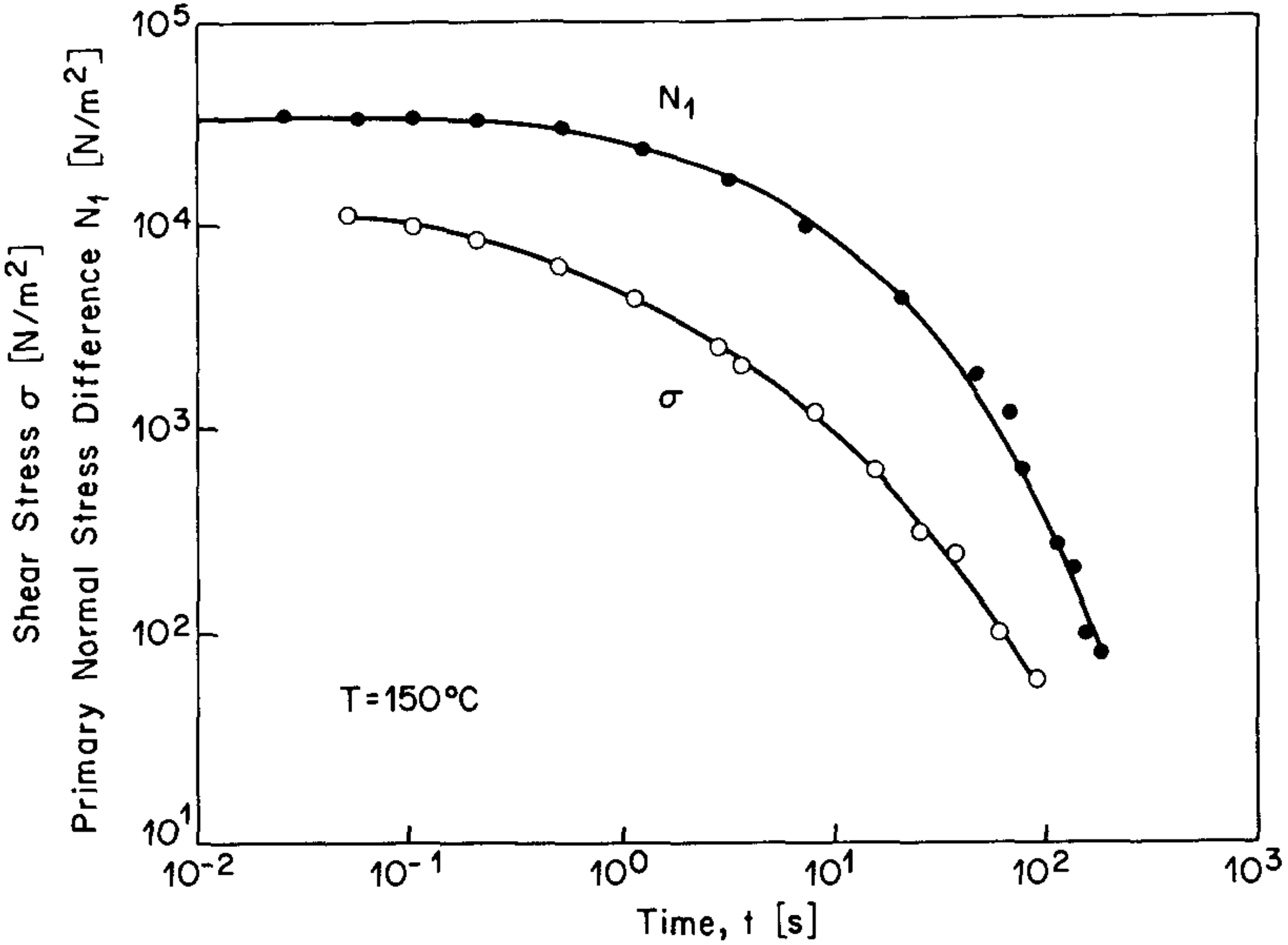


3. 流动时伴有高弹形变

Time-dependent shear stress and primary normal stress difference after start-up of steady shearing

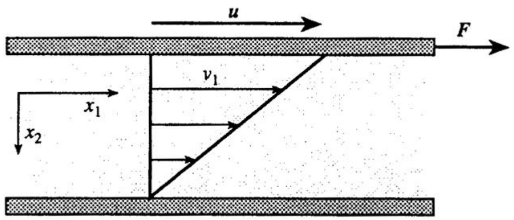


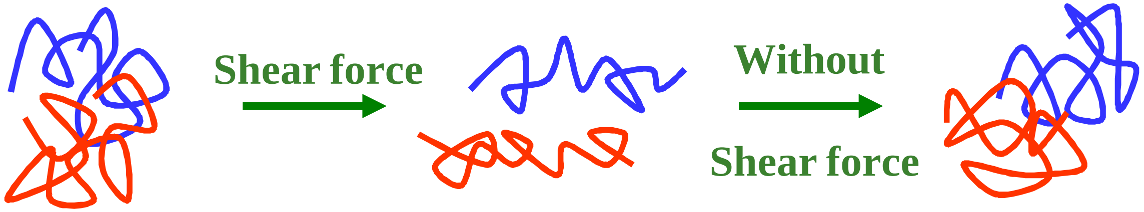
Relaxation of shear stress and primary normal stress difference after cessation of steady-state shearing



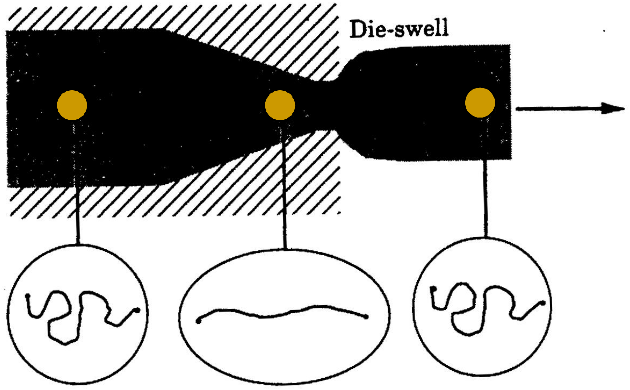
3. 流动时伴有高弹形变

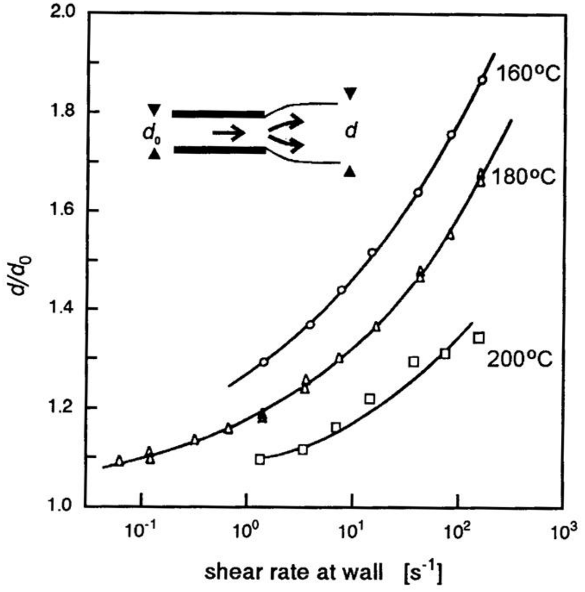
- Consider a steady simple shear flow





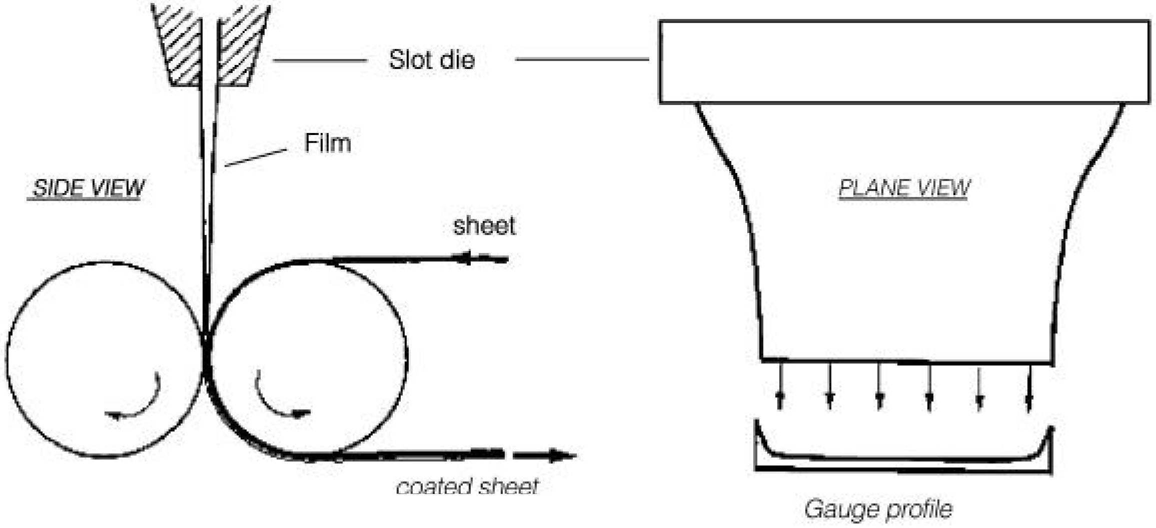
- Die-swell (出口胀大)

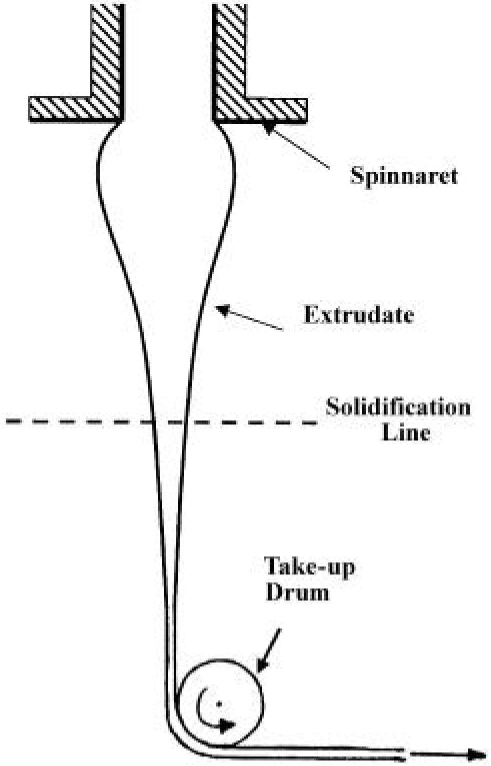


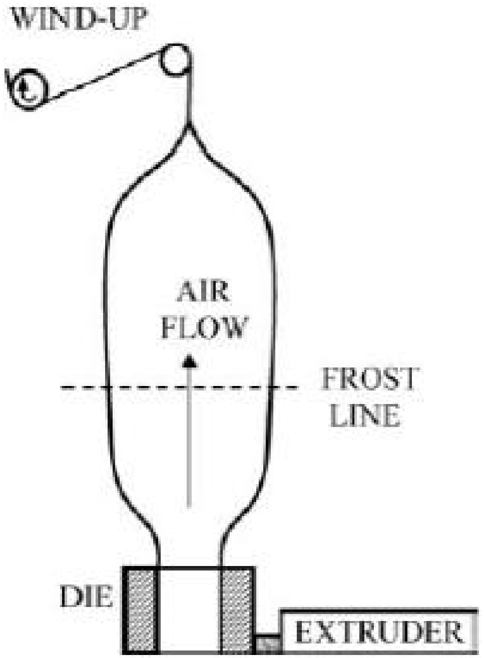


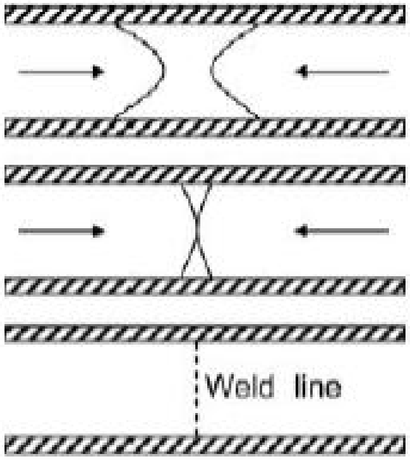
Extrudate swell observed for a melt of PS for various shear rates and temperatures. (Burke, J. J.; etc. *Characterization of Materials in Research*, Syracuse Univ. Press, 1975.)

Polymer Processing

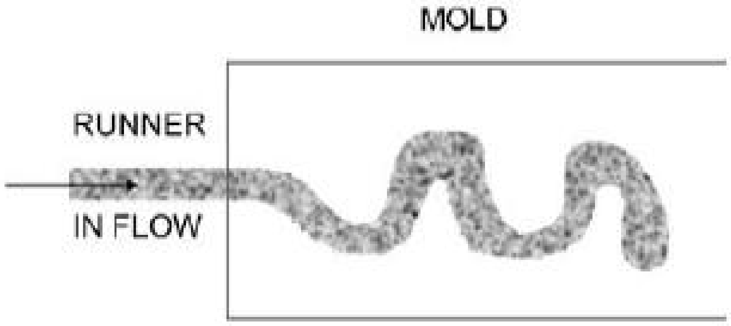






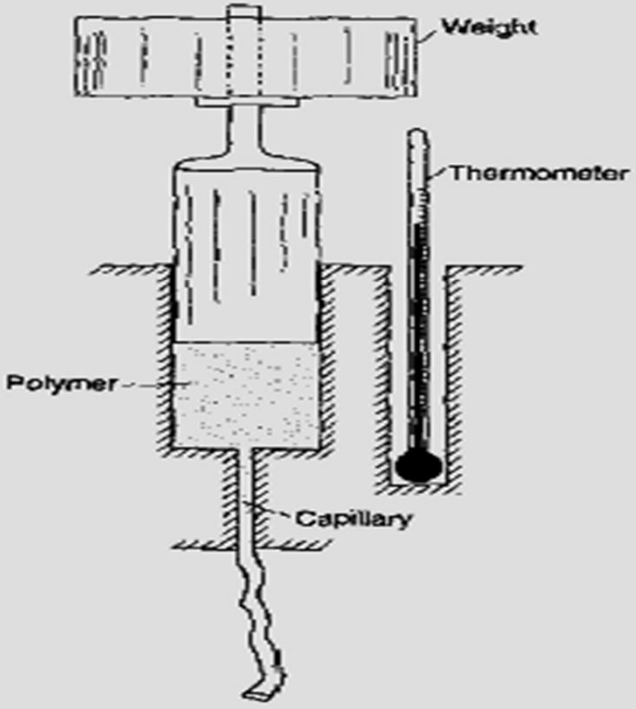


(a)



(b)

Melt flow index (MFI)



ASTM D1238

DIN 53735

Corresponds to simplyfied capillary viscometer (see practical course)

Fig.4.12. Schematic diagram of an extrusion plastometer used to measure melt flow index.

Polymer granules in heatable cylinder.

After melting extrusion through standard capillary by standard weight

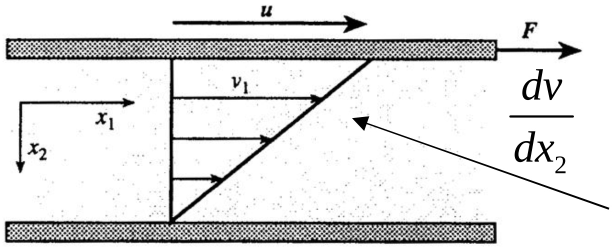
Melt flow index: polymer weight in grains/10 min. extrusion time

Characterization of viscous flow

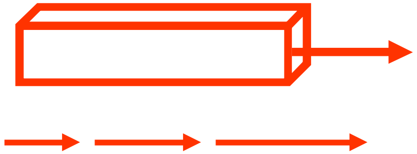
复杂流动方式的分解：三种最基本的流动(变形)方式

a.剪切流动(形变)-shear viscosity η_s

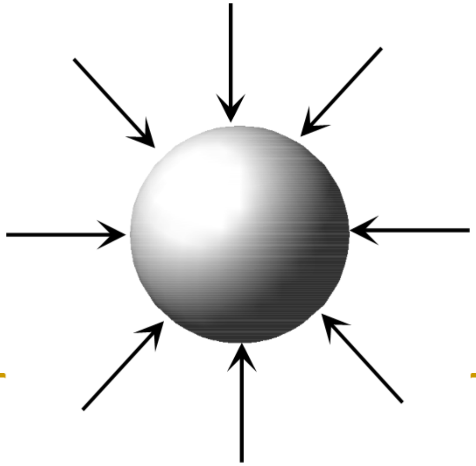
b.拉伸流动(形变)-tensile viscosity η_t



velocity gradient



c. 压缩流动(形变)-bulk viscosity



for incompresible fluids $\eta_b \rightarrow \infty$

Melt viscosities of polymers

shear viscosity剪切粘度和

$$\eta_s = \frac{\sigma_s(\dot{\gamma})}{\dot{\gamma}}_{\text{1-D}} = \sigma_s \Big/ \left(\frac{dv}{dh}\right)_{\text{2-D}}$$

extensional viscosity拉伸粘度

$$\eta_t = \frac{\sigma_t(\dot{\varepsilon})}{\dot{\varepsilon}}$$

- apparent viscosity表观粘度

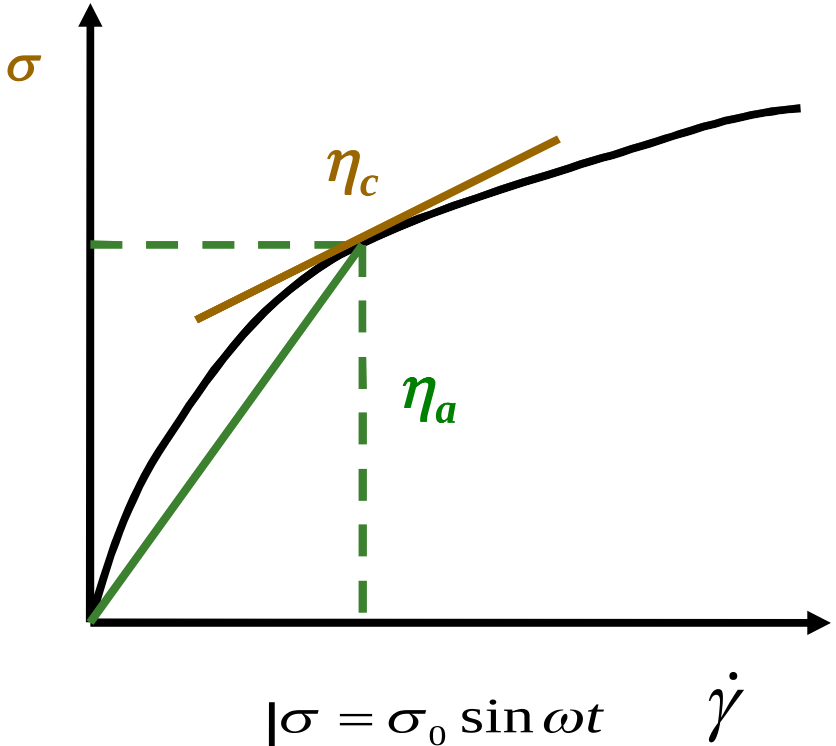
$$\eta_a = \eta(\dot{\gamma}) = \frac{\sigma(\dot{\gamma})}{\dot{\gamma}} = \sigma \Big/ \left(\frac{dv}{dh}\right)$$

- differential viscosity微分粘度

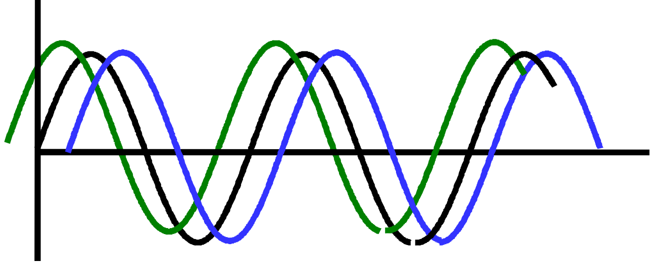
$$\eta_c = \frac{\mathrm{d}\sigma(\dot{\gamma})}{\mathrm{d}\dot{\gamma}}$$

- complex viscosity复数粘度(动态力学)

$$\eta^* = \eta' - i\eta''$$



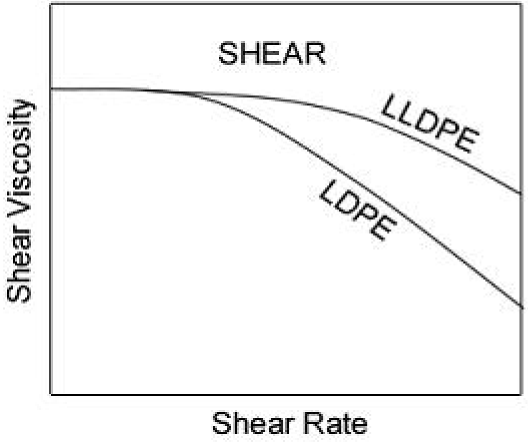
$$\sigma = \sigma_0 \sin \omega t$$

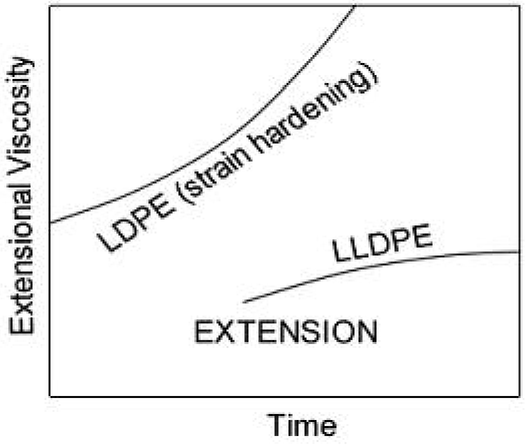


$$\varepsilon = \varepsilon_0 \sin(\omega t - \delta)$$

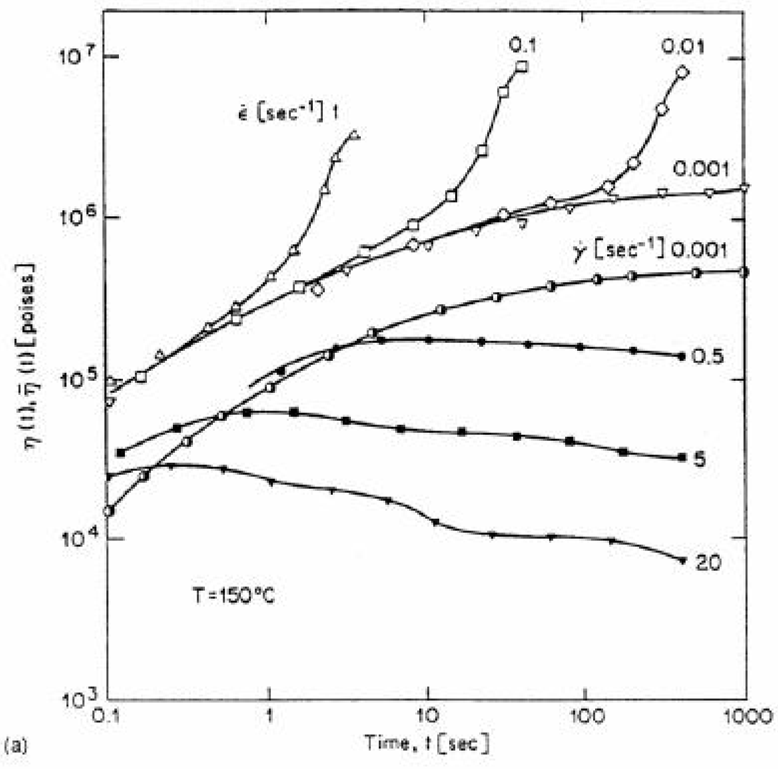
$$\dot{\varepsilon} = \varepsilon_0 \omega \sin(\omega t - \delta + \pi/2)$$

拉伸粘度的性质



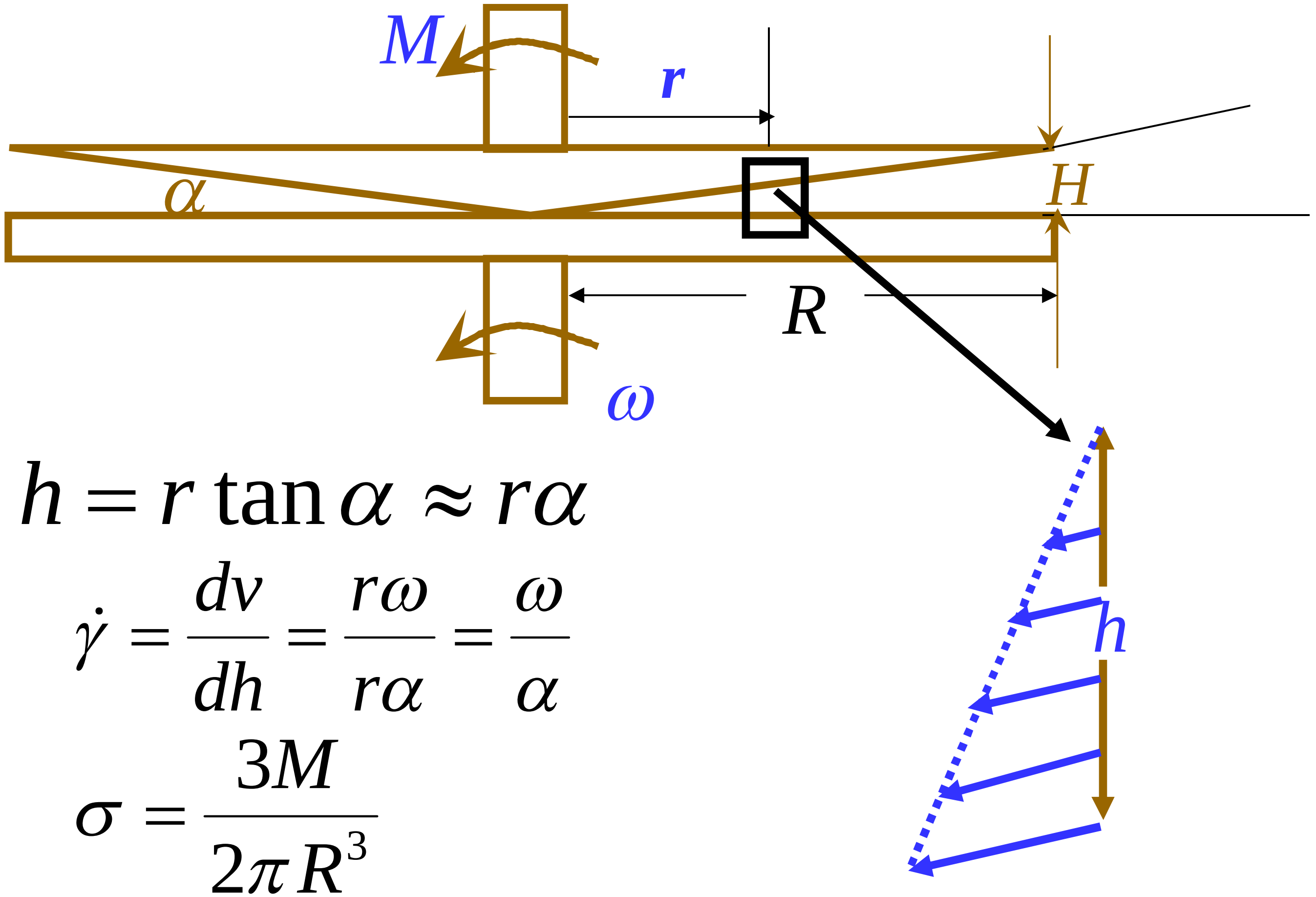


Improves stability in extensions flows



Measurement of shear viscosity

Cone-plate viscometer (锥板粘度计)- an example



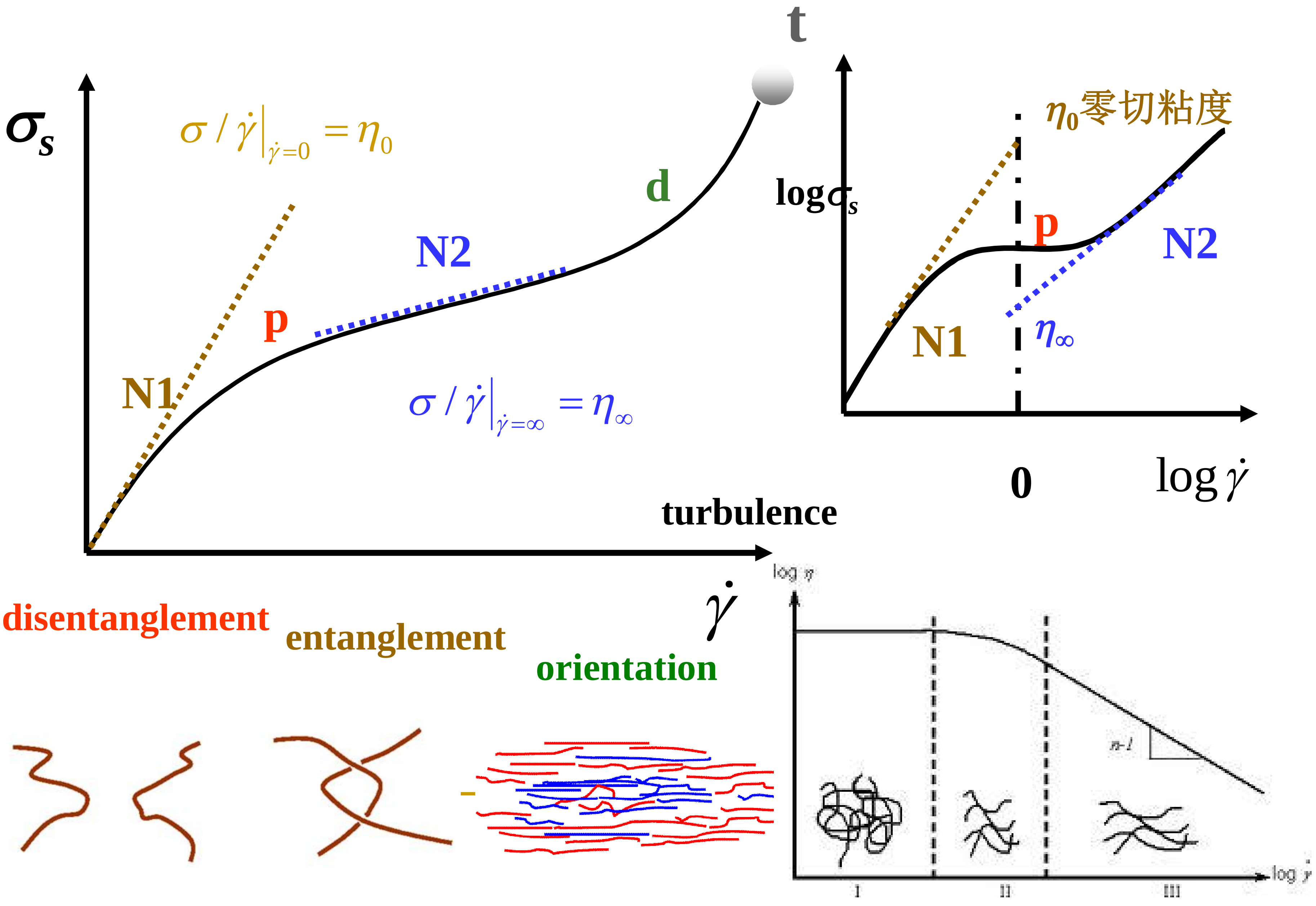
$$h = r\tan\alpha \approx r\alpha$$

$$\dot{\gamma} = \frac{dv}{dh} = \frac{r\omega}{r\alpha} = \frac{\omega}{\alpha}$$

$$\sigma = \frac{3M}{2\pi R^3}$$

$$\eta_a = \frac{\sigma}{\dot{\gamma}} = \frac{M}{b\omega} \qquad b = \frac{2\pi R^3}{3\alpha}$$

As liquids: The flow curve of polymer melts



η_0 dependent of M

- **Critical molecular weight at the entanglement (缠结) limit: M_c**

Exp.

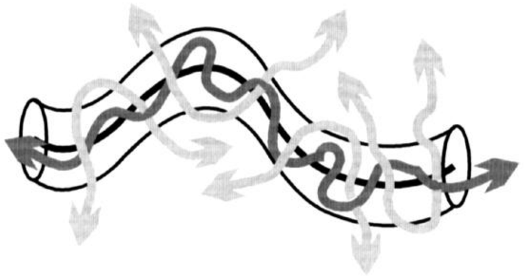
$\eta_0 \sim M_w^{1} \qquad (M < M_c)$

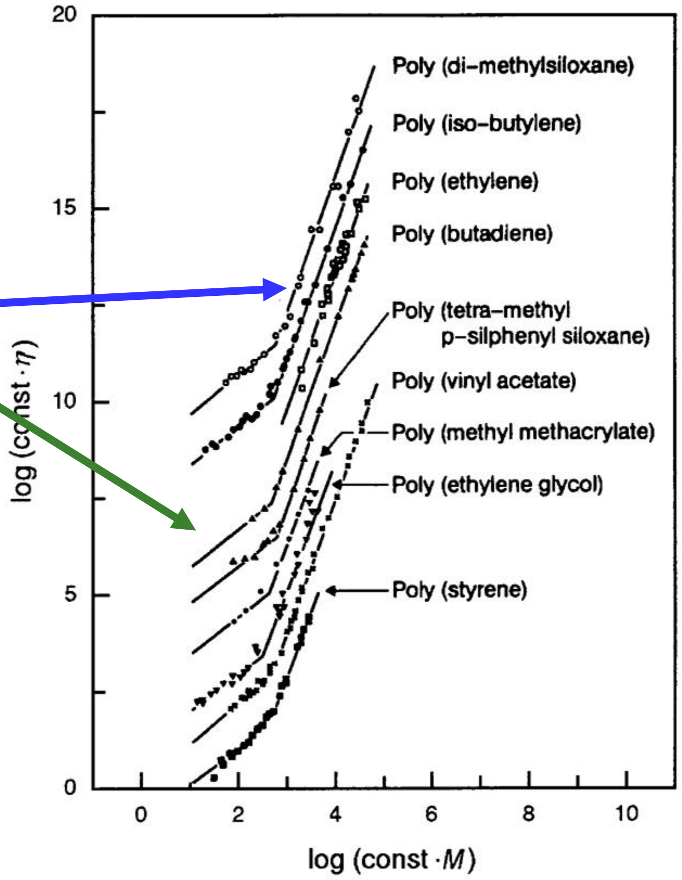
$\eta_0 \sim M_w^{3.3\sim3.4} \qquad (M > M_c)$

Theory

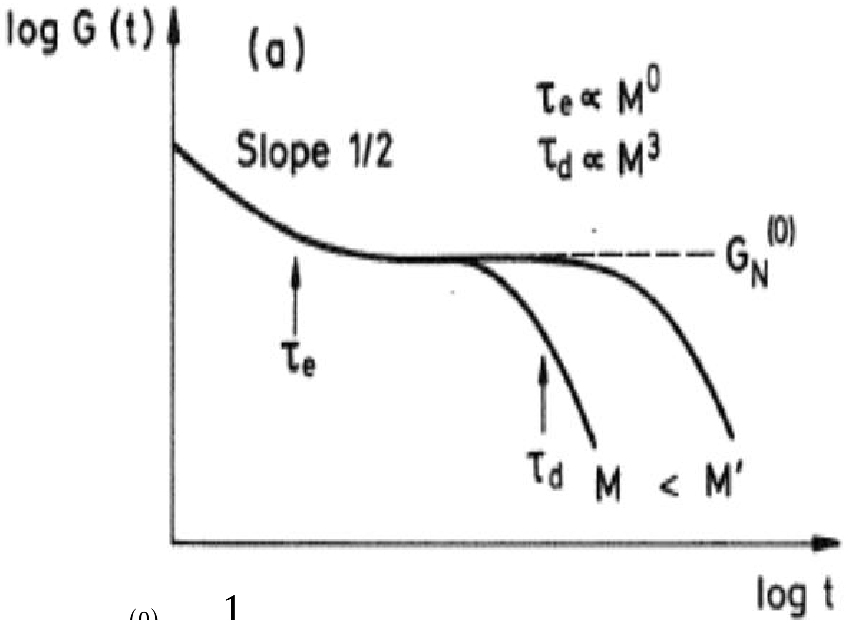
$\eta_0 \sim M^{1}$ Rouse Model

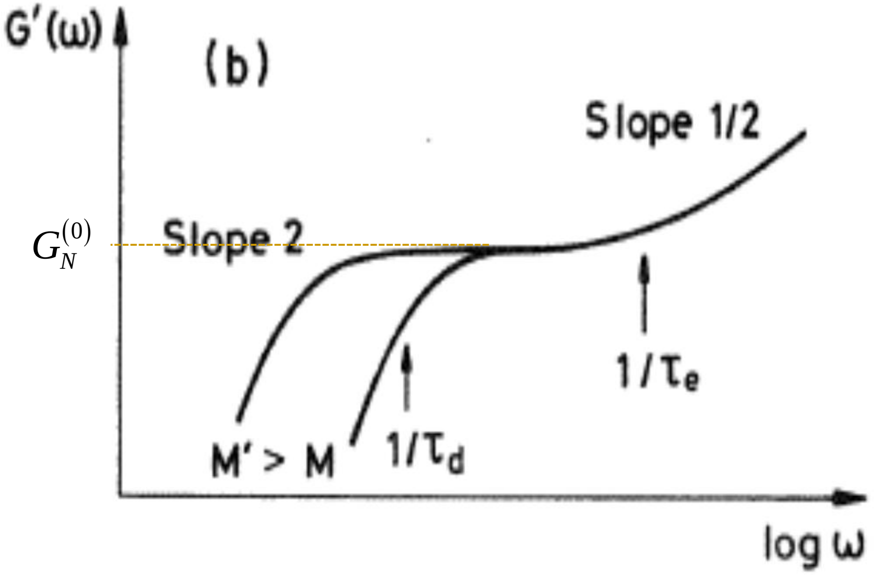
$\eta_0 \sim M^{3}$ Tube (Reptation) Model





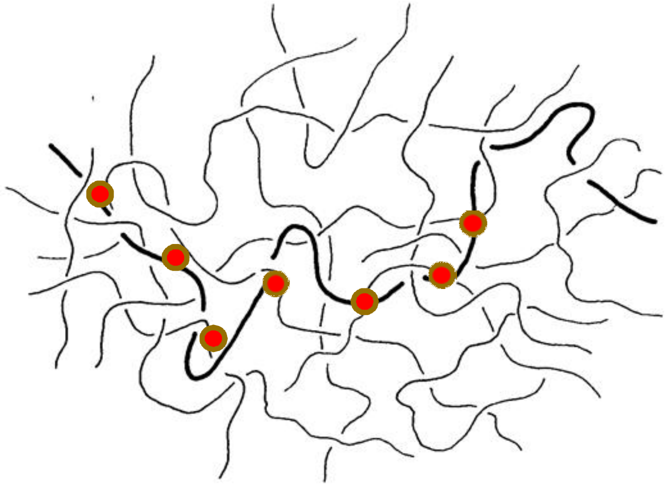
As Solids: Time *vs.* Frequency *vs.* Temp at Low Deformations

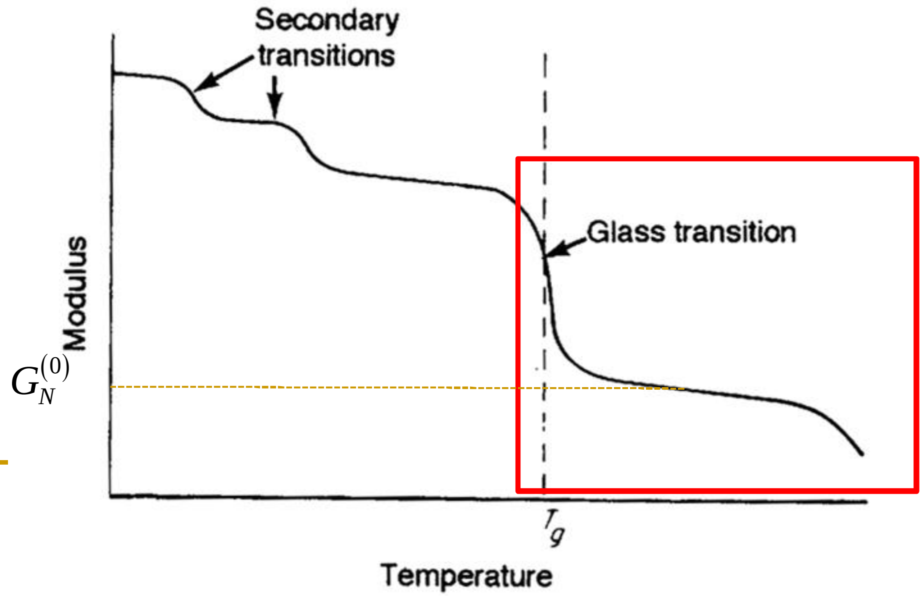




$$G_N^{(0)} \sim \frac{1}{M_e}$$

缠结点之间的分子量





熔体粘度的影响因素

1. 分子量与分子量分布
2. 温度-Vogel-Fuchler 方程

$$\eta = A\exp\left[B/\left(T-T_0\right)\right]$$

$B_{\mathrm{rigid}}>B_{\mathrm{flexible}}$

3. 剪切应力与剪切速率
4. 链结构-支化

T_f的影响因素

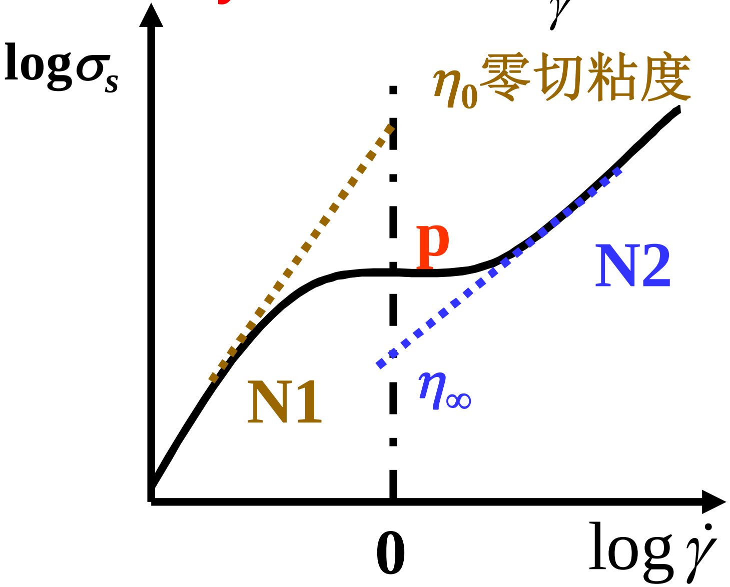
1. 分子结构的柔顺性
2. 分子量
3. 分子间相互作用
4. 外力作用

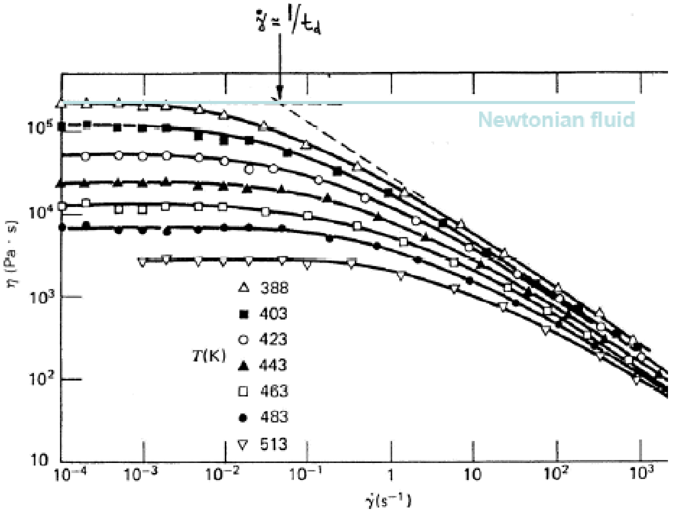
Viscosity & Modulus in Polymer Melts

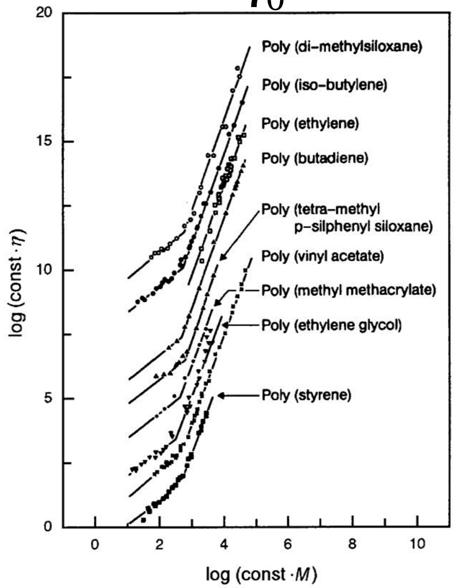
Viscosity

$$\log\eta = \log\frac{\sigma_s}{\dot{\gamma}} = \log\sigma_s - \log\dot{\gamma}$$

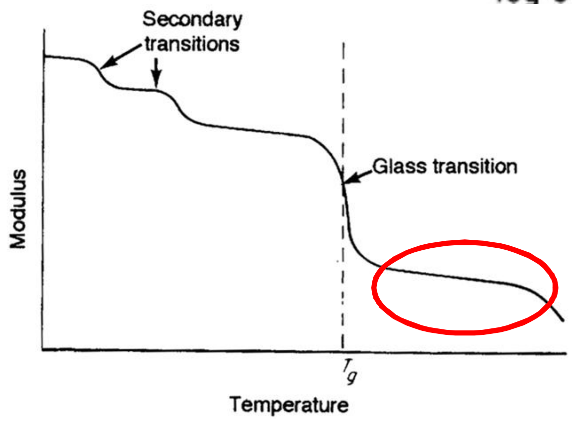
$$\eta_0 \propto M^1 \quad \text{or} \quad \eta_0 \propto M^{3.3}$$

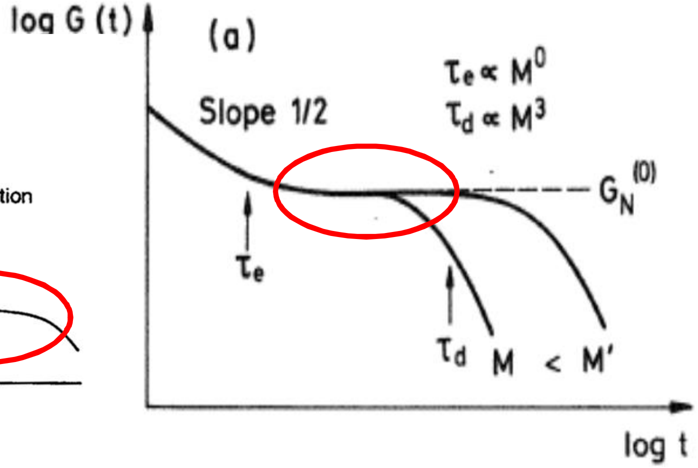


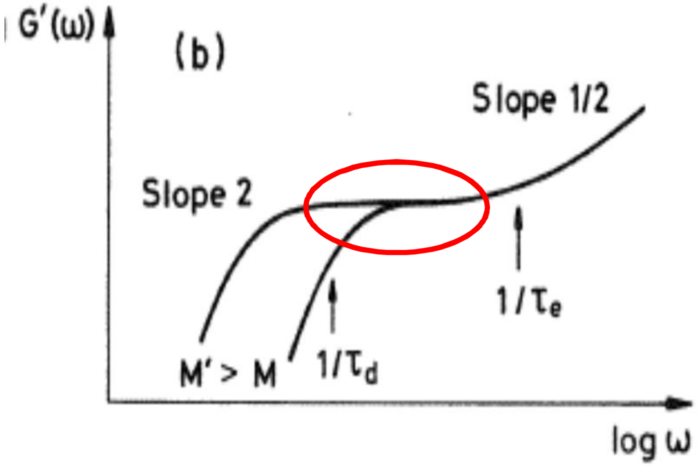




Modulus

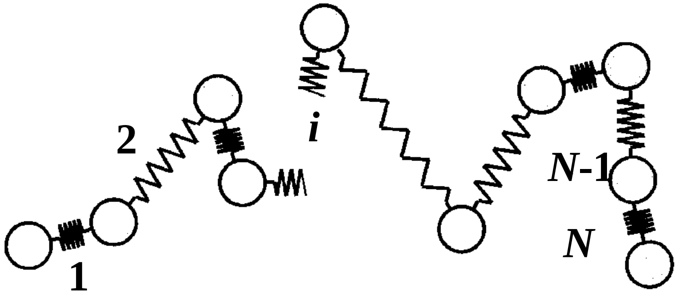






Molecular Theory of Viscous Flow and Viscoelasticity of Polymer – How to get τ?

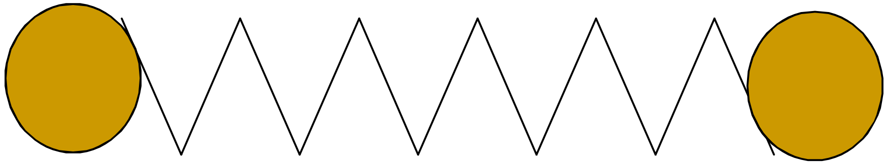
- **Rouse model**
  - **Rouse-chain:**
    - **The chain is subdivided in *N* 'Rouse-sequences', each sequence being sufficiently long so that Gaussian properties are ensured.**
    - **Each Rouse sequence is substituted by a bead and a spring. The springs are the representatives of the elastic tensile force, while the beads play the role of centers whereon friction forces apply.**



Rouse-chain composed of *N*+1 beads connected by springs

When a bead is displaced from its equilibrium position there are two types of forces acting on it: (1) those that result from the viscous interaction with the surrounding molecules, and (2) those that represent the tendency of the molecular chains to return to a state of maximum entropy by Brownian diffusion movement.

Potential of a Spring



Hook’s law

$$F(R) = k(R - R_0)$$

$$U(R) = \frac{1}{2}k(R - R_0)^2$$

Boltzmann Factor

$$\Omega \sim \exp\left[-U(R)/k_B T\right]$$

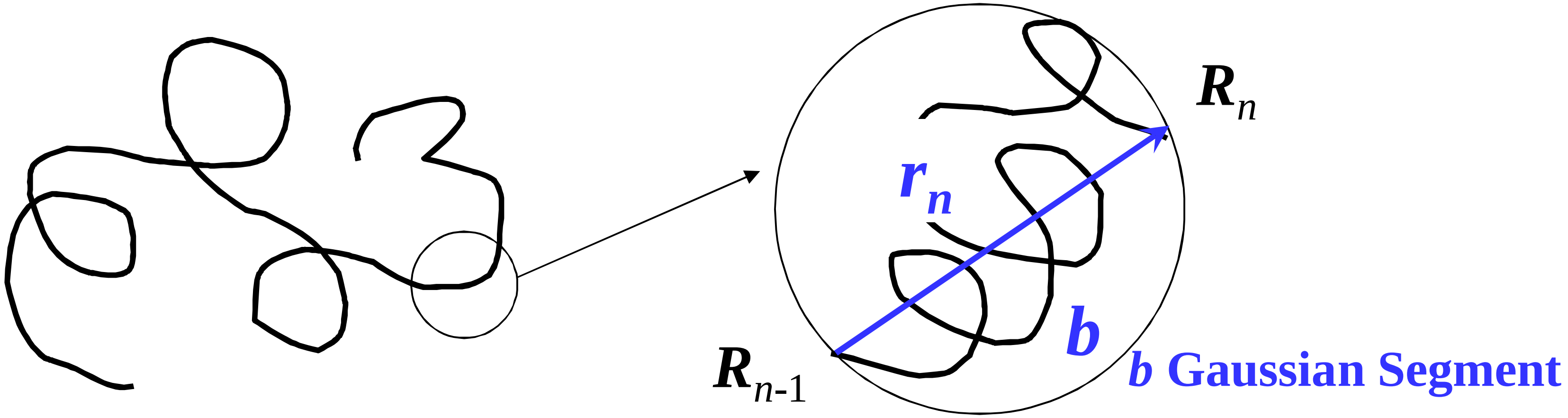
Partition Function

$$Z \sim \sum_i \exp\left[-U_i(R)/k_B T\right]$$

Free Energy

$$F = -k_B T \ln Z$$

A Brief Review of Gaussian Model



小高斯链段的末端距分布
$$\psi=\left(\frac{3}{2\pi b^2}\right)^{3/2}\exp\left(-\frac{3\boldsymbol{r}_n^{\,2}}{2b^2}\right)=A\exp\left(-\frac{u_0\left(\boldsymbol{r}_n\right)}{k_BT}\right)$$

$$u_0\left(\boldsymbol{r}_n\right)=\frac{3}{2b^2}k_BT\left(\boldsymbol{R}_n-\boldsymbol{R}_{n-1}\right)^2$$

熵弹簧

高斯长链
$$\Phi\left(\boldsymbol{R}\right)=\prod_{n=1}^{n_k}\psi=\left(\frac{3}{2\pi b^2}\right)^{3n_k/2}\exp\left(-\frac{1}{k_BT}\sum_{n=1}^{n_k}u_0\left(\boldsymbol{r}_n\right)\right)$$

$$=\left(\frac{3}{2\pi b^2}\right)^{3n_k/2}\exp\left(-\frac{U_0\left(\left\{\boldsymbol{r}_{n_k}\right\}\right)}{k_BT}\right)$$

$$U_0\left(\left\{\boldsymbol{r}_{n_k}\right\}\right)=\frac{3}{2b^2}k_BT\sum_{n=1}^{n_k}\left(\boldsymbol{R}_n-\boldsymbol{R}_{n-1}\right)^2$$

Rouse model

For the Brownian motion of a harmonic oscillator

$$U\left(R\right)=\frac{1}{2}kR^{2}$$

f: Random force of Brownian Motion

$$\zeta\frac{dR}{dt}=-\frac{\partial U}{\partial R}+f=-F+f=-kR+f$$

Langevin equation

For the Brownian motion of the bead-spring model

$$U\left(R_i\right)=\frac{1}{2}k\left[\left(R_{i+1}-R_i\right)^{2}+\left(R_i-R_{i-1}\right)^{2}\right]$$

Consideration of the restoring force when a bead is displaced from its equilibrium position leads to the expression

$$\zeta\frac{dR_i}{dt}=-\frac{3k_BT}{b^2}\frac{\partial U\left(R_i\right)}{\partial R_i}=-\frac{3k_BT}{b^2}(2R_i-R_{i-1}-R_{i+1})+f_i$$

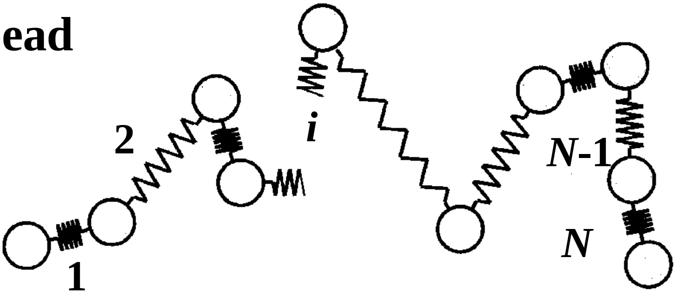
d*x*/d*t*: the time differential of the displacement of *i*th bead

: the friction coefficient of a bead

***l*: the length of each link in a chain**

***N*: the number of the links in a macromolecule**

(for *N* submolecules there are 3*N* of these equations)



Normal Coordinates of Rouse Model

$$\boxed{\zeta \frac{\partial \boldsymbol{R}_i}{\partial t} = -k\left(-R_{i-1}+2R_i-R_{i+1}\right)+\boldsymbol{f}_i}$$

$$\begin{aligned}
\frac{dR_1}{dt} &= -\frac{k}{\zeta}\left(R_1-R_2\right) && + \quad 0 \quad + f_1 \\
\frac{dR_2}{dt} &= -\frac{k}{\zeta}\left(-R_1+2R_2-R_3\right) && + \quad 0 \quad + f_2 \\
\frac{\partial \boldsymbol{R}_i}{\partial t} &= \quad 0 \quad -\frac{k}{\zeta}\left(-R_{i-1}+2R_i-R_{i+1}\right) && + \quad 0 \quad + \boldsymbol{f}_i \\
\frac{dR_n}{dt} &= \quad 0 \quad -\frac{k}{\zeta}\left(-R_{n-1}+R_n\right) && + f_n
\end{aligned}$$

$$\frac{d\boldsymbol{Q}}{dt} = -\frac{k}{\zeta}\boldsymbol{ZQ}+f\boldsymbol{I}$$

$$\boldsymbol{Q} = \begin{bmatrix} R_1 \\ \vdots \\ R_n \end{bmatrix}$$

$$\boldsymbol{Z} = \begin{pmatrix}
1 & -1 & & & & \\
-1 & 2 & -1 & & 0 & \\
0 & -1 & 2 & -1 & & \\
 & & & \cdots & & \\
 & 0 & & -1 & 2 & -1 \\
 & & & & -1 & 1
\end{pmatrix}$$

Rouse-Zimm Matrix

$$k = \frac{3k_BT}{b^2}$$

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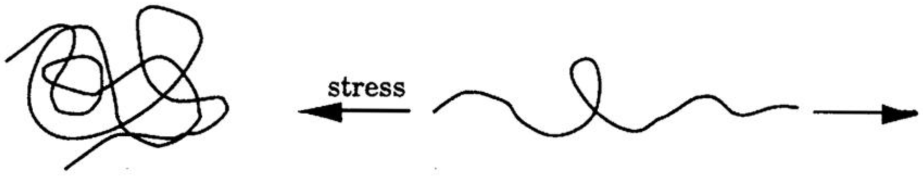
Applications of Gaussian Chain Model: Stretching of an Ideal Chain



$$S = k \ln \Psi(h)$$

$$\Phi = \Psi / \Omega$$

$$\Phi' = \Psi' / \Omega$$

$$\Delta S = k \ln \Phi / \Phi'$$

$$\Phi(\boldsymbol{h}, N_g) = \left(\frac{3}{2\pi N_g l^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}^2}{2N_g l^2}\right)$$

$$\Phi(\boldsymbol{h}, N_g) = \Psi(\boldsymbol{h}, N_g) / \Omega(N_g)$$

$$\Psi(\boldsymbol{h}, N_g) = \Phi(\boldsymbol{h}, N_g)\,\Omega(N_g) = \left(\frac{3}{2\pi N_g l^2}\right)^{3/2} \exp\left(-\frac{3\boldsymbol{h}^2}{2N_g l^2}\right)\Omega(N_g)$$

$$S(\boldsymbol{h}, N_g) = -\frac{3}{2} k_B \frac{\boldsymbol{h}^2}{N_g l^2} + \frac{3}{2} k_B \ln\left(\frac{3}{2\pi N_g l^2}\right) + k_B \ln \Omega(N_g)$$

$$G(\boldsymbol{h}, N_g) = U - TS = \frac{3}{2} k_B T \frac{\boldsymbol{h}^2}{N_g l^2} + G(N_g)$$

$$\boldsymbol{f} = \frac{\partial G(\boldsymbol{h}, N_g)}{\partial h} = \frac{3k_B T}{N_g l^2}\boldsymbol{h} \qquad \boldsymbol{f} = k\boldsymbol{x}$$

相当于拉一根弹簧，弹性系数=???

简正(正则)变换

$X = TQ$ 简正坐标系变换矩阵: ***T***

$TZT^{-1} = \Lambda$ 对角矩阵***Λ***是***Z***的本征值:

$$\begin{pmatrix} \lambda_1 & & & \\ & \lambda_2 & & \\ & & \cdots & \\ & & & \lambda_n \end{pmatrix}$$

$$\frac{dT\mathbf{Q}}{dt} = -\frac{k}{\zeta} T\mathbf{Z}T^{-1}T\mathbf{Q} + Tf\mathbf{I}$$

$$\frac{d\mathbf{X}}{dt} = -\frac{3k_BT}{b^2\zeta}\boldsymbol{\Lambda}\mathbf{X} \qquad \mathbf{X}(t) = \mathbf{X}(0)\exp\left(-\frac{3k_BT}{b^2\zeta}t\boldsymbol{\Lambda}\right)$$

X: 简正坐标系中的本征向量

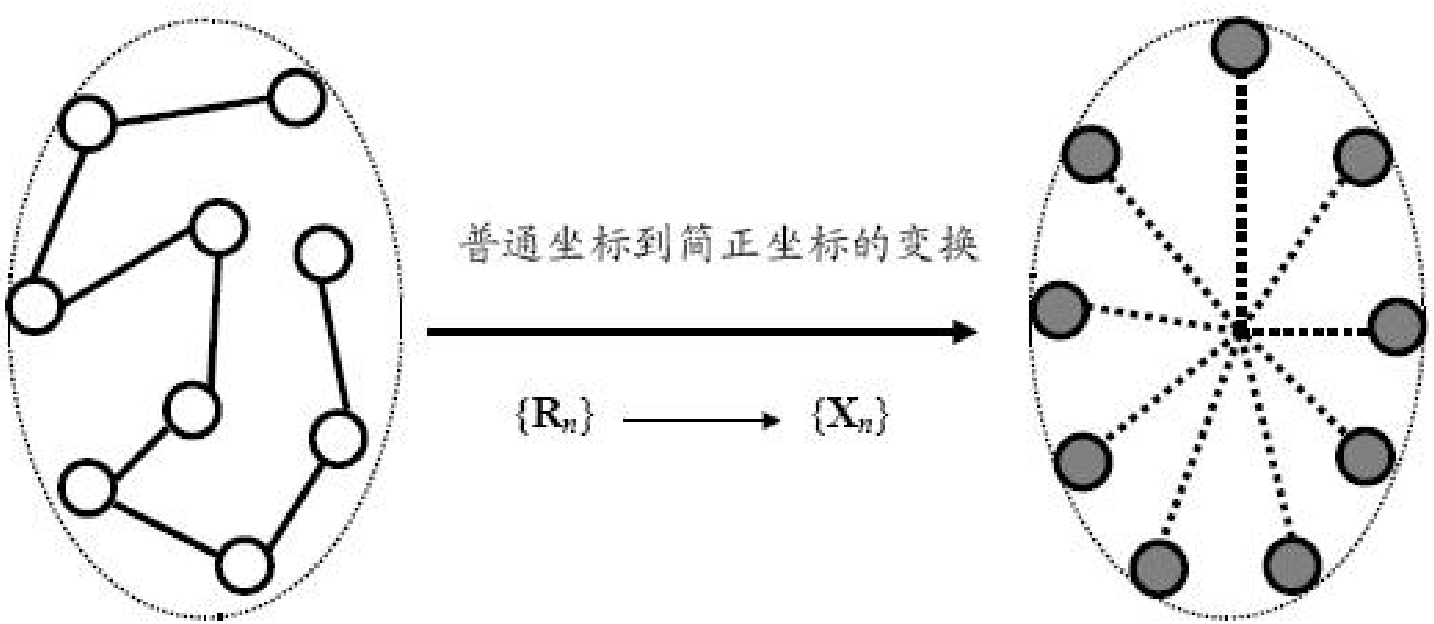
$$X_p(t) = X_p(0)\exp\left(-\frac{t}{\tau_p}\right) \qquad \tau_p = \frac{b^2\zeta}{3k_BT\lambda_p} \qquad \lambda_p = 4\sin^2\left(\frac{p\pi}{2N}\right) \approx 4\left(\frac{p\pi}{2N}\right)^2$$

$$\tau_p = \frac{b^2\zeta}{3k_BT\,4\sin^2\left(\frac{p\pi}{2N}\right)} \simeq \frac{N^2b^2\zeta}{3\pi^2k_BT}\frac{1}{p^2} = \tau_1\frac{1}{p^2} \qquad \tau_1 = \frac{N^2b^2\zeta}{3\pi^2k_BT}$$

Terminal relaxation time

末端(最长)松弛时间

高分子链的简正坐标

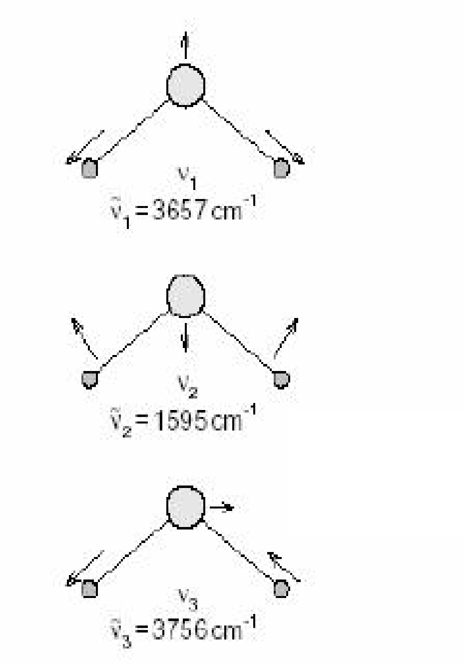


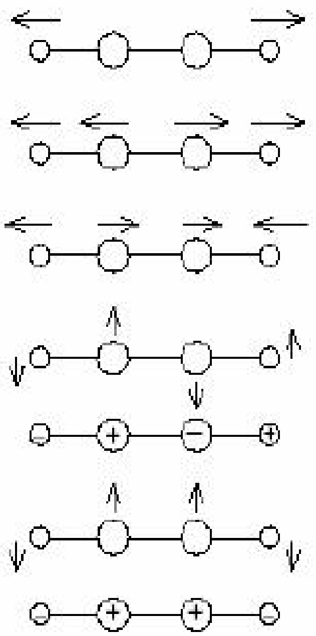
高分子链内的运动是相互偶合的。而在简正坐标中，每个简正运动模式之间是相互去偶的。高分子链的任一种运动状态，则是各种简正运动模式的线性叠加。

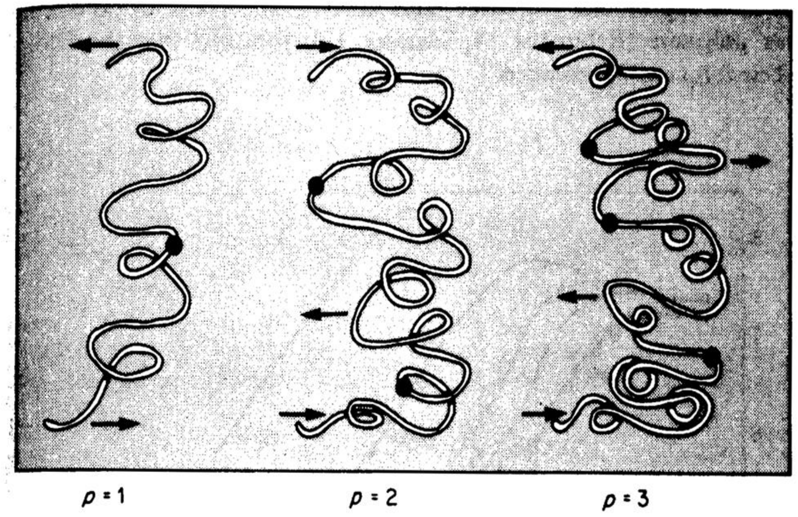
简正坐标系和简正振动

高分子链内的运动是相互偶合的。而在简正坐标中，每个简正运动模式之间是相互去偶的。高分子链的任一种运动状态，则是各种简正运动模式的线性叠加。

例：水， C_2H_4 和 高分子链的简正振动模式

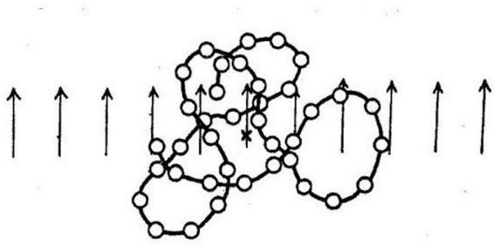






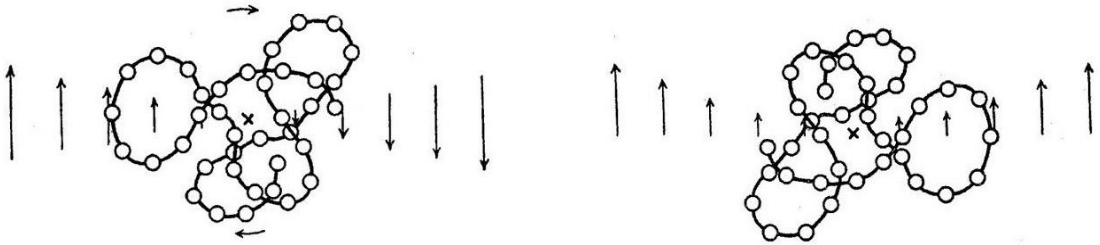
用经典力学的方法将全部原子的坐标作线性组合所得到的一种集体坐标－简正坐标。原子在3*n*个自由度上的坐标变化，变换为3*n*个简正坐标的变化， 3*n*个简正坐标中的任意一个都与全部原子的坐标有关。可以把耦合振动分解为简正振动, 每个简正坐标表征的是一套分子内部运动的组合，而这种组合一定是符合分子所属的对称性群的一个对称类。

The Zimm Model



自由穿流

Rouse Model



非自由穿流

Zimm Model

引入相关函数 $\boldsymbol{H}_{nm}$ 表示由第*m*个bead运动产生的流场对第*n*个bead产生的扰动

$$\boldsymbol{v}(\boldsymbol{r}_n)=\sum_m \boldsymbol{H}(\boldsymbol{r}_m-\boldsymbol{r}_n)\cdot\boldsymbol{F}(\boldsymbol{r}_m)$$

$$\boxed{\frac{\partial \boldsymbol{R}_n}{\partial t}=\sum_m H_{nm}\left[-k\frac{\partial U}{\partial \boldsymbol{R}_m}+\boldsymbol{f}(m,t)\right]}$$

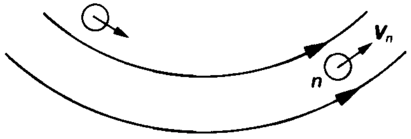
$$\boldsymbol{H}_{nm}=\begin{cases}\dfrac{\boldsymbol{I}}{\zeta} & \text{Rouse model}\\[2ex] \dfrac{1}{8\pi\eta\left|r_{nm}\right|}\left(I+\hat{\boldsymbol{r}}_{nm}\hat{\boldsymbol{r}}_{nm}\right) & \text{Zimm model}\end{cases}$$

Oseen Tensor 奥森张量

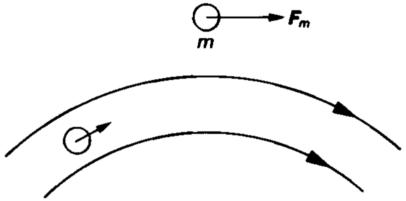
附录：Oseen Tensor

The Momentum Equation of Fluids – Navier-Stokes Equation

$$\rho\frac{\partial \boldsymbol{v}}{\partial t} = \eta\nabla\cdot\boldsymbol{\sigma} + \nabla P + \boldsymbol{F}(\boldsymbol{r}) = \eta\nabla^2\boldsymbol{v} + \nabla P + \boldsymbol{F}(\boldsymbol{r})$$



$$\nabla\cdot\boldsymbol{v} = 0$$



Stokes Approximation:

$$\eta\nabla^2\boldsymbol{v} + \nabla P = -\boldsymbol{F}(\boldsymbol{r})$$

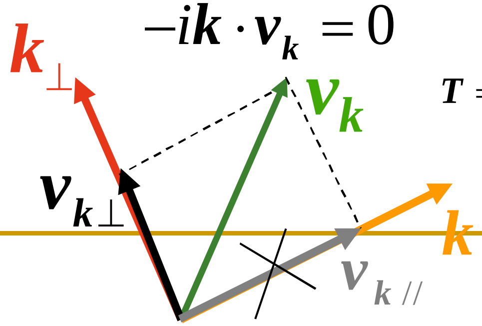
$$\nabla\cdot\boldsymbol{v} = 0$$

Doi, Edwards, The Theory of Polymer Dynamics, p89

In Fourier Space: $\nabla \to -i\boldsymbol{k}$ $\nabla^2 \to (-i\boldsymbol{k})^2$

$$-\eta\boldsymbol{k}^2\boldsymbol{v}_{\boldsymbol{k}} - i\boldsymbol{k}P_{\boldsymbol{k}} = -F_{\boldsymbol{k}} \quad \Rightarrow \quad \left(-\eta\boldsymbol{k}^2\boldsymbol{v}_{\boldsymbol{k}} + \boldsymbol{F}_{\boldsymbol{k}}\right)_{\perp} = 0$$

$$-i\boldsymbol{k}\cdot\boldsymbol{v}_{\boldsymbol{k}} = 0$$



$$\boldsymbol{T} = \left(\boldsymbol{I} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\right)$$

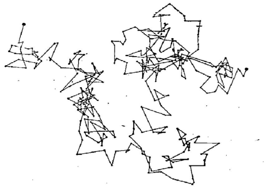
$$v_{\boldsymbol{k}} = \frac{1}{\eta\boldsymbol{k}^2}\left(\boldsymbol{I} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\right)\cdot\boldsymbol{F}_{\boldsymbol{k}} = \boldsymbol{H}(\boldsymbol{k})\cdot\boldsymbol{F}_{\boldsymbol{k}}$$

$$\boldsymbol{v}(\boldsymbol{r}) = \int d\boldsymbol{r}'\,\boldsymbol{H}(\boldsymbol{r}-\boldsymbol{r}')\cdot\boldsymbol{F}(\boldsymbol{r}')$$

$$\boxed{\boldsymbol{H}(\boldsymbol{r}) = \frac{1}{(2\pi)^3}\int d\boldsymbol{k}\,\frac{1}{\eta\boldsymbol{k}^2}\left(\boldsymbol{I} - \hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\right)e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} = \frac{1}{8\pi\eta r}\left(\boldsymbol{I} + \hat{\boldsymbol{r}}\hat{\boldsymbol{r}}\right)}$$

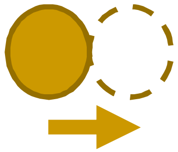
Estimating The Longest Relaxation Times

Brownian Motion



$$\left\langle \left[\boldsymbol{r}(t)-\boldsymbol{r}(0)\right]^2 \right\rangle^{1/2} = (6Dt)^{1/2}$$

Friction coefficient $\boldsymbol{f} = \zeta \boldsymbol{v}$ Einstein Relation $\boxed{D = \frac{k_B T}{\zeta}}$



$\boldsymbol{R} = l$

$$R^2 = 6D\tau_0 \quad \tau_0 \approx \frac{R^2}{6D} = \frac{\zeta l^2}{6k_B T} \approx \frac{\pi \eta_s l^3}{k_B T}$$

Stokes Law $\boxed{\zeta = 6\pi\eta_s R_h}$ Stokes-Einstein Relation $\boxed{D = \frac{k_B T}{6\pi\eta_s R_h}}$ $\boxed{R_h = \frac{k_B T}{6\pi\eta_s D}}$

Rouse Model:

$$D_R = \frac{k_B T}{\zeta_R} \quad \zeta_R = N\zeta \quad \boxed{\zeta \approx \eta_s l}$$

$$R_g \approx N^{\upsilon} l$$

$$\tau_R = \frac{R_g^2}{D_R} = \frac{\zeta N R_g^2}{k_B T} \approx \frac{\zeta l^2}{k_B T} N^{1+2\upsilon}$$

$$\approx \frac{\eta_s l^3}{k_B T} N^{1+2\upsilon}$$

Zimm Model:

$$D_Z = \frac{k_B T}{\zeta_Z} \quad \zeta_Z \approx \eta_s R_g$$

$$\tau_Z = \frac{R_g^2}{D_Z} = \frac{\zeta_Z R_g^2}{k_B T} \approx \frac{\eta_s R_g^3}{k_B T} \approx \frac{\eta_s l^3}{k_B T} N^{3\upsilon}$$

Relaxation times of Rouse-Zimm Model

relaxation time of different mode

Rouse model

$$\tau_p = \frac{N^2 b^2 \zeta}{3\pi^2 k_B T} p^{-2}$$

$$= \tau_{1,\mathrm{Rouse}} p^{-\mu}$$

$$\mu = 2$$

Zimm model in
good or θ solvent

$$\tau_p = \frac{\eta N^{3\nu} b^3}{k_B T} p^{-3\nu}$$

$$= \tau_{1,\mathrm{zimm}} p^{-\mu}$$

$$\mu = 3\nu = 9/5$$ or

$$\mu = 3/2$$

Terminal relaxation time

$$\boxed{\tau_{1,\mathrm{Rouse}} = \frac{N^2 b^2 \zeta}{3\pi^2 k_B T}}$$

$\sim M^2$ or $\sim M^{11/5}$

$$\tau_{1,\mathrm{zimm}} = \frac{\eta N^{3\nu} b^3}{k_B T}$$

$\sim M^{9/5}$ or $\sim M^{3/2}$

Rouse-Zimm model

For $N >> 1$

Relaxation time for the *p*th mode:

$$\tau_p = \tau_1 p^{-\mu}$$

$$p = 1, 2, \ldots, m.$$

- **Stress relaxation modulus and complex modulus (Maxwell-element model):**

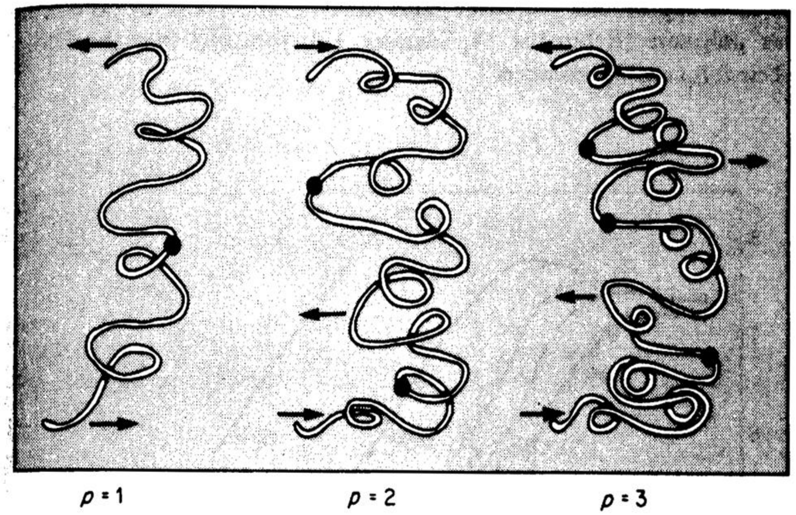
$$G(t) = nk_BT\sum_{p=1}^{m}\exp(-\frac{t}{\tau_p})$$

$$= \frac{c}{N}k_BT\int_0^\infty dp\exp\left(-2tp^2/\tau_R\right)$$

$$= \frac{c}{2\sqrt{2}N}k_BT\left(\frac{\tau_R}{t}\right)^{1/2}$$

$$G'(\omega) = nk_BT\sum_{p=1}^{m}\left(\frac{\omega^2\tau_p^2}{1+\omega^2\tau_p^2}\right)$$

$$G''(\omega) = \omega\eta + nk_BT\sum_{p=1}^{m}\left(\frac{\omega\tau_p}{1+\omega^2\tau_p^2}\right)$$



The first three normal modes of a chain

- **R-Z model is good for $M < M_C$**

$$[\eta] = 0.425\frac{N_A}{M}\left(\sqrt{N}a\right)^3$$

$$\phi_{0(\mathrm{RZ})} = 0.425N_A = 2.56\times10^{23}$$

$$\phi_{0(\exp)} = 2.2 \sim 2.87\times10^{23}$$

Prediction of Viscoelasticity by Rouse-Zimm Model

Rouse: **(μ=2 or 11/5)** Zimm: **(μ=3/2, θ solvents) or (μ=9/5 , good solvents)**

$$G'(\omega) = nk_B T \sum_{p=1}^{m} \left(\frac{\omega^2 \tau_p^2}{1+\omega^2\tau_p^2} \right) \qquad G''(\omega) = \omega\eta + nk_B T \sum_{p=1}^{m} \left(\frac{\omega\tau_p}{1+\omega^2\tau_p^2} \right)$$

1. $\omega\tau_1 \ll 1$

$$G'(\omega) = (\omega\tau_1)^2 \sum_{p=1} p^{-2\mu} \sim \omega^2 \qquad G''(\omega) = (\omega\tau_1) \sum_{p=1} p^{-\mu} + \omega\eta \sim \omega$$

2. $\omega\tau_1 \gg 1$

$$G'(\omega) = \int_0^\infty dp \frac{(\omega\tau_1)^2 p^{-2\mu}}{1+(\omega\tau_1)^2 p^{-2\mu}} \qquad G''(\omega) = \int_0^\infty dp \frac{(\omega\tau_1) p^{-\mu}}{1+(\omega\tau_1)^2 p^{-2\mu}}$$

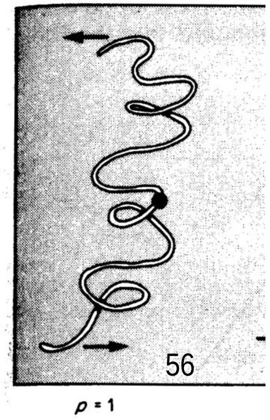
$$= (\omega\tau_1)^{1/\mu} \frac{1}{\mu} \int_0^\infty dx \frac{x^{1-1/\mu}}{1+x^2} \qquad = (\omega\tau_1)^{1/\mu} \frac{1}{\mu} \int_0^\infty dx \frac{x^{-1/\mu}}{1+x^2}$$

$$= (\omega\tau_1)^{1/\mu} \frac{\pi}{2\mu \sin(\pi/2\mu)} \sim \omega^{1/\mu} \qquad = (\omega\tau_1)^{1/\mu} \frac{\pi}{2\mu \cos(\pi/2\mu)} \sim \omega^{1/\mu}$$

3. $\omega\tau_1 \approx 1: \quad G'(\omega) \approx G''(\omega)$

τ_1 terminal relaxation time

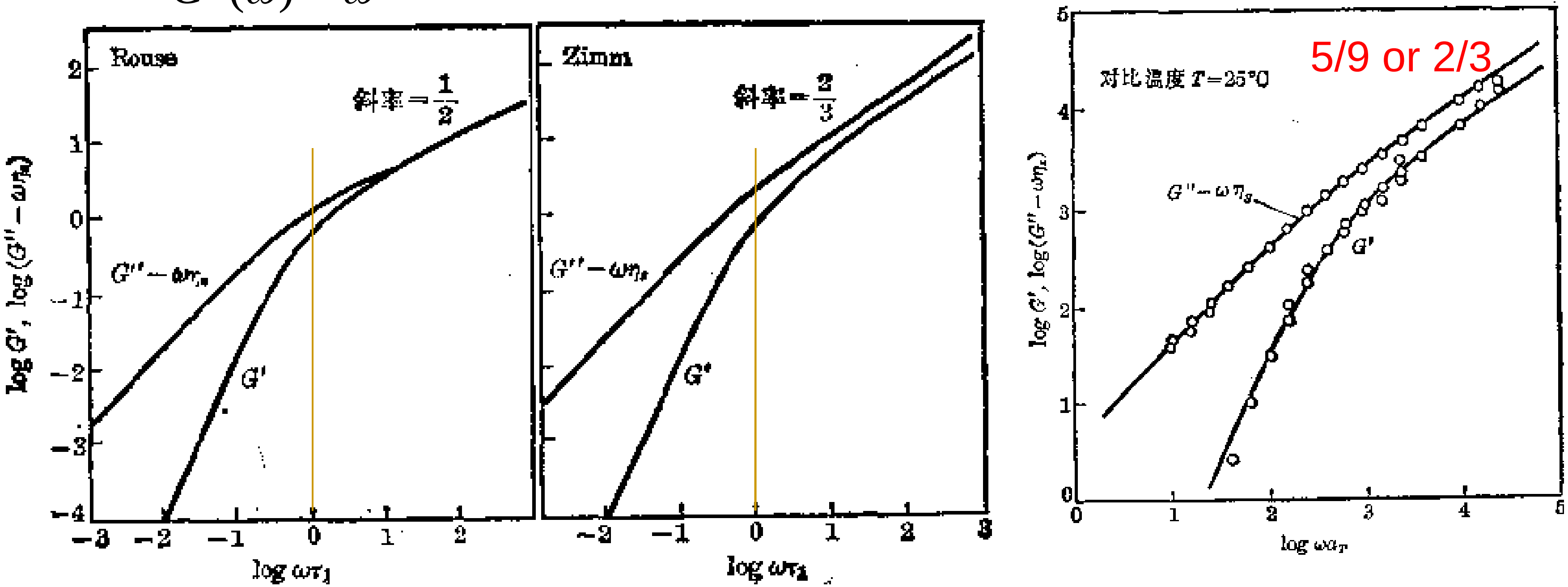
末端松弛时间



Dynamic Modulus of Polymer in Dilute Solution

$\omega\tau_1 \ll 1$ $G'(\omega) \sim \omega^2$ 与高分子结构无关，反映高分子链整体的流动

$G''(\omega) \sim \omega$



Rouse (μ=2) Zimm (μ=3/2, θ solvents) Experiments

$\omega\tau_1 \ll 1$ $G'(\omega) \sim \omega^2$

$G''(\omega) \sim \omega^1$

与高分子结构有关，反映高分子链局部的运动

$G'(\omega) \sim \omega^{1/\mu}$

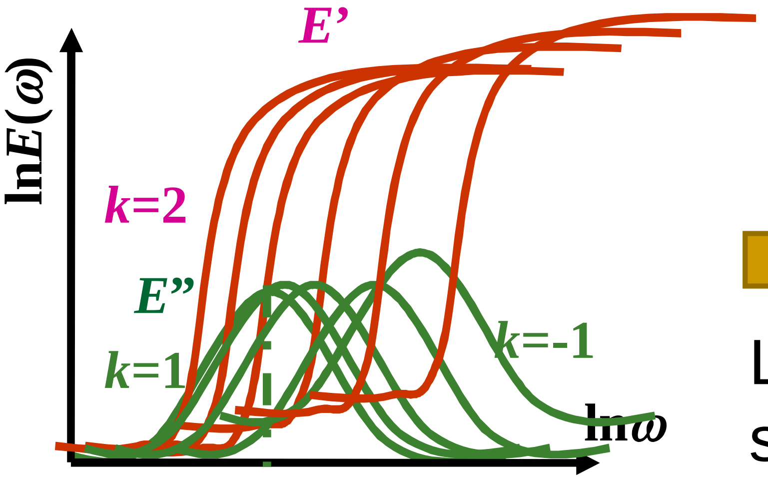
$\omega\tau_1 \gg 1$

$G''(\omega) \sim \omega^{1/\mu}$

末端松弛时间τ_1—高分子内部对外频开始有响应的临界时间

From Maxwell Model to General Maxwell Model or Rouse-Zimm Model

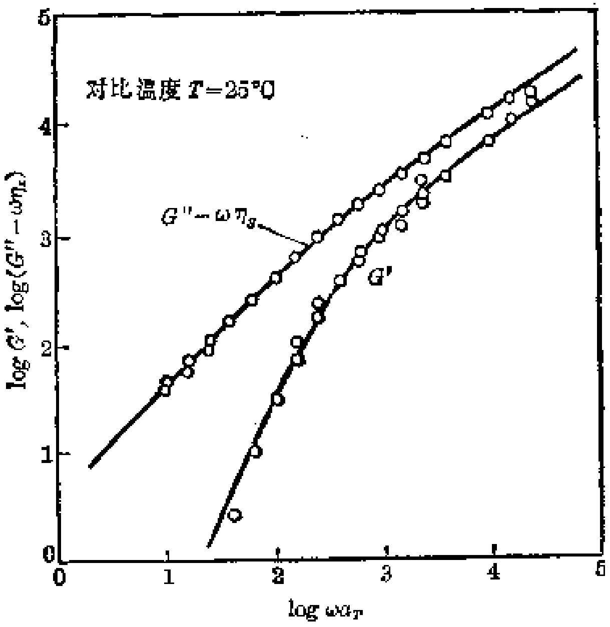
Maxwell Model



Single Relaxation Time

Linear superpose of Multiple Relaxation Time Spectrum

Rouse-Zimm Model



Multiple Relaxation Time

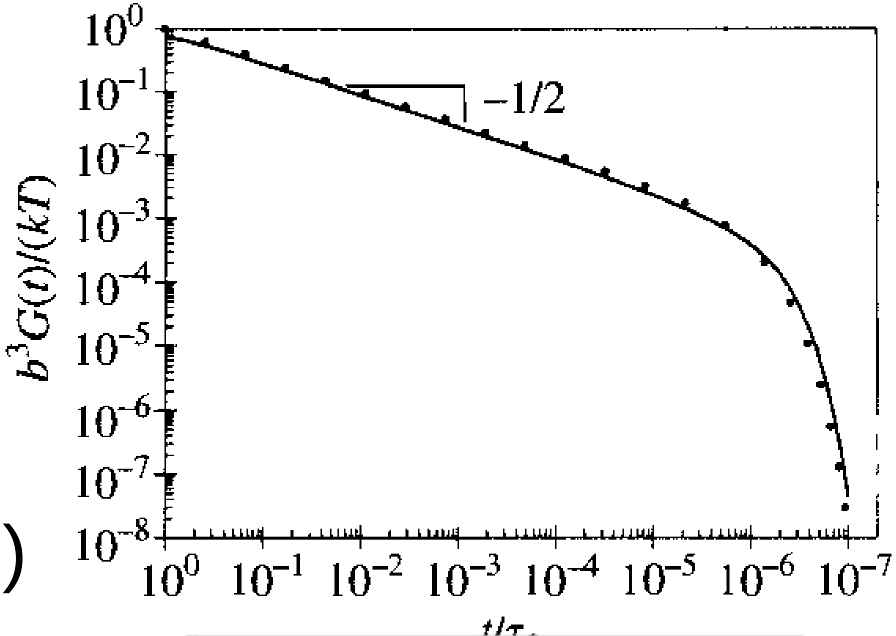
Relaxation Modulus and Dynamic Modulus of Rouse Model

$$G(t) = nk_BT\sum_{p=1}^{m}\exp(-\frac{t}{\tau_p})$$

$$= \frac{c}{N}k_BT\int_0^\infty dp\exp\left(-2tp^2/\tau_R\right)$$

$$= \frac{c}{2\sqrt{2}N}k_BT\left(\frac{\tau_R}{t}\right)^{1/2} \qquad (t<\tau_R)$$

$$G(t) \approx \frac{c}{N}k_BT\left(\frac{\tau_R}{t}\right)^{1/2}\exp\left(-t/\tau_R\right) \qquad (t>>\tau_R)$$



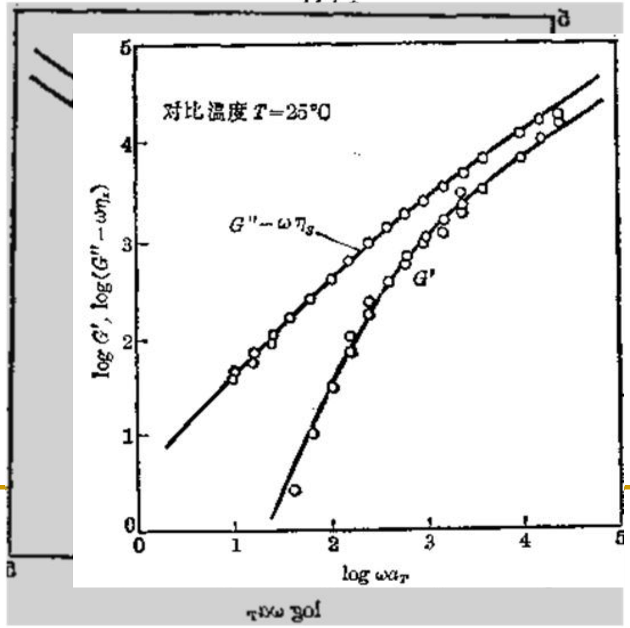
Note: $$\int_0^\infty e^{-a^2x^2}dx = \frac{\sqrt{\pi}}{2a} \qquad (a>0)$$

零切粘度 $$\eta_0 = \int_0^\infty dtG(t)$$

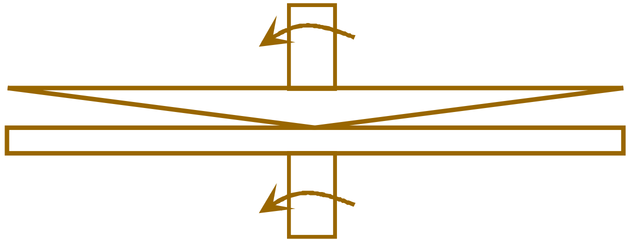
$$= \frac{c}{Nk_BT}\sum_{p=1}^{\infty}\int_0^\infty dt\exp\left(-2tp^2/\tau_R\right)$$

$$= \frac{c}{Nk_BT}\frac{\tau_R}{2}\sum_{p=1}^{\infty}p^{-2}$$

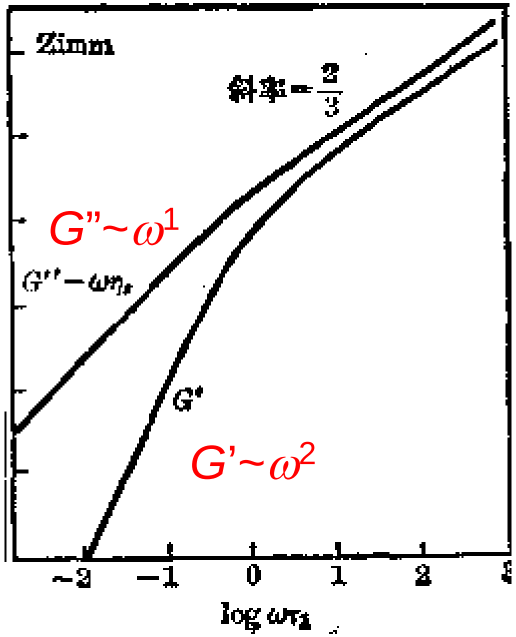
$$= \frac{c\zeta}{36}Nb^2 \propto M \qquad (M<M_c)$$



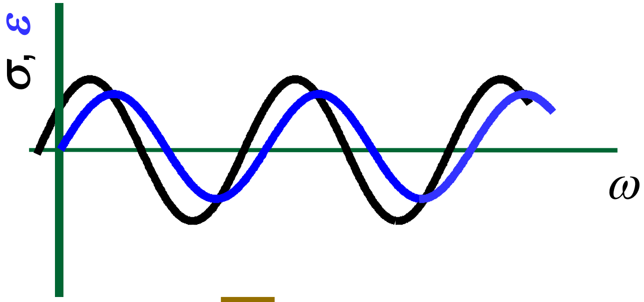
高分子溶液和熔体的动态力学实验



高分子稀溶液

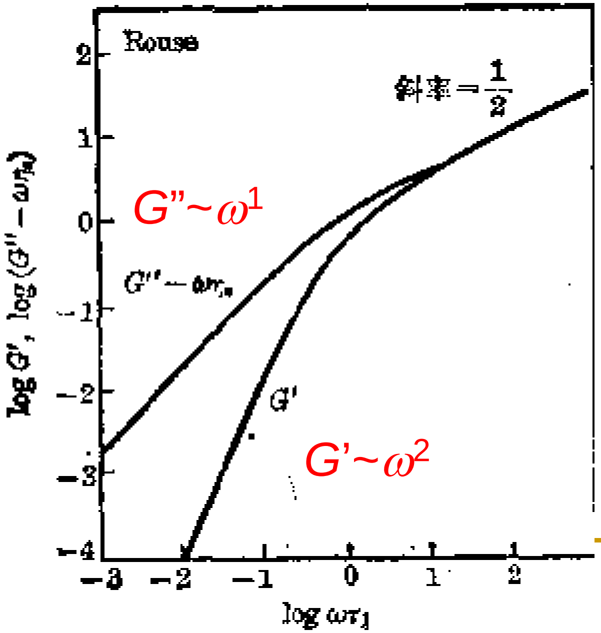


Zimm Model



高分子熔体

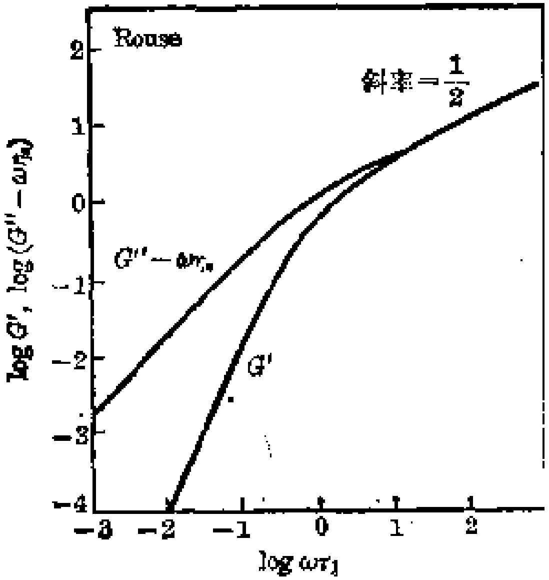
$M<M_c$

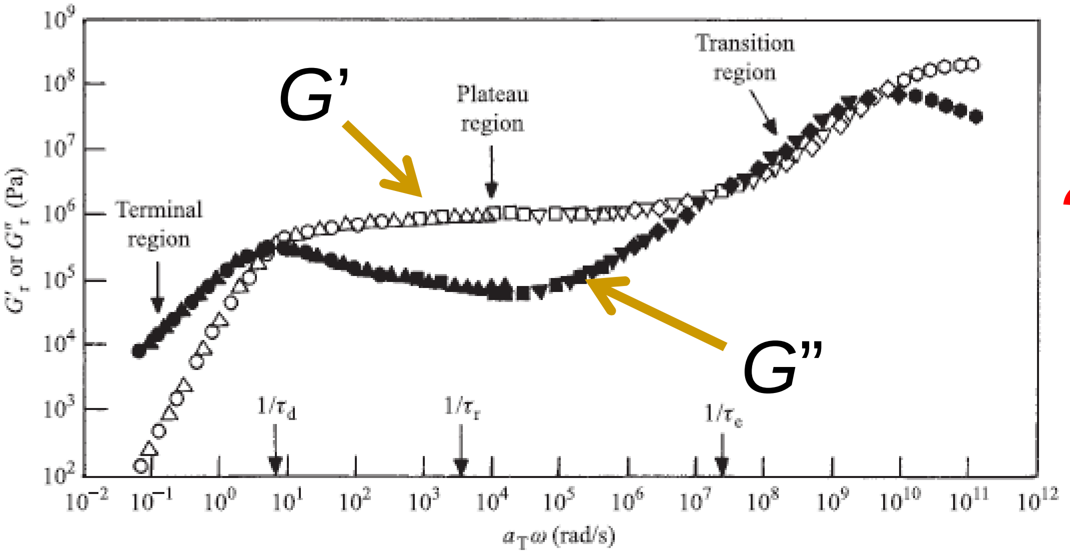


Rouse Model

$$G' = \left(\frac{\sigma_0}{\varepsilon_0}\right)\cos\delta \qquad G'' = \left(\frac{\sigma_0}{\varepsilon_0}\right)\sin\delta$$

Dynamics Modulus of Polymer Melts ($M>M_c$)

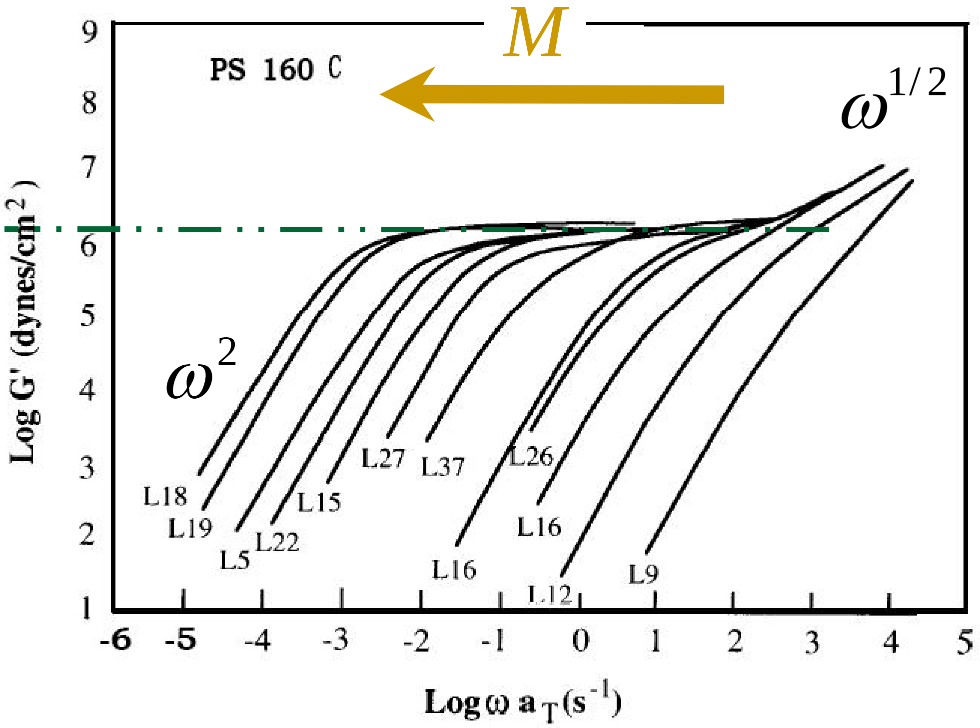




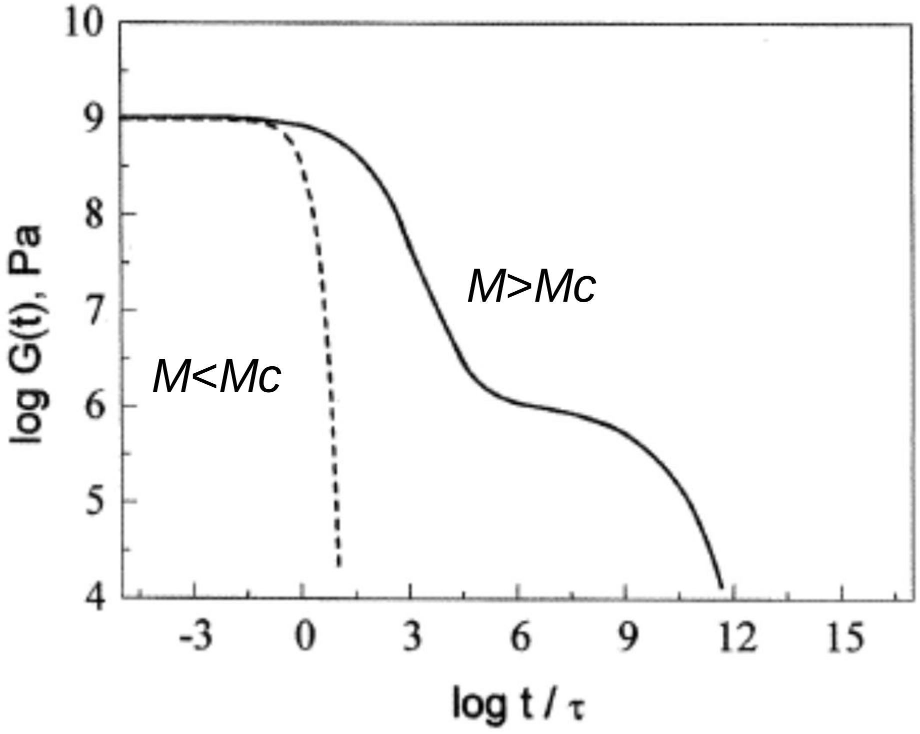
???

Plateau modulus

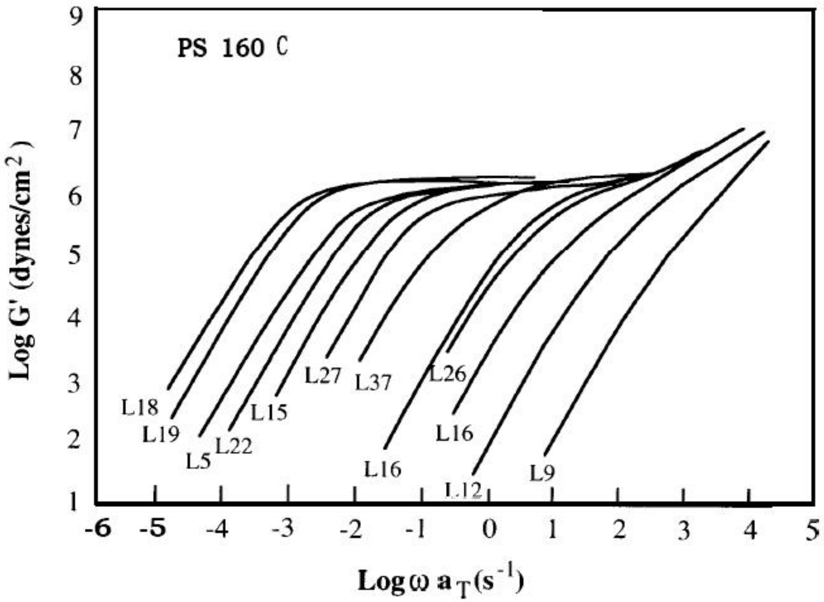
$$G_N^{(0)} \sim \frac{1}{M_e}$$

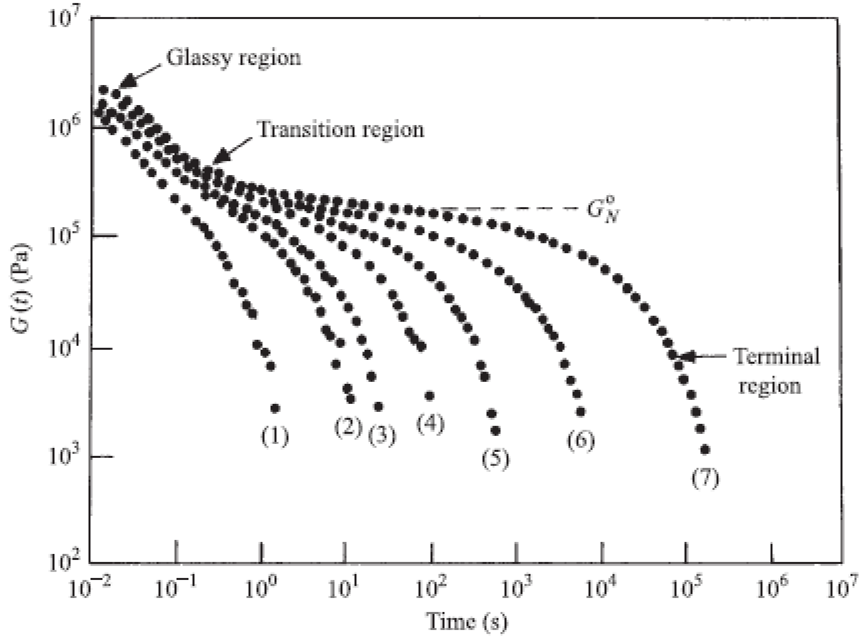


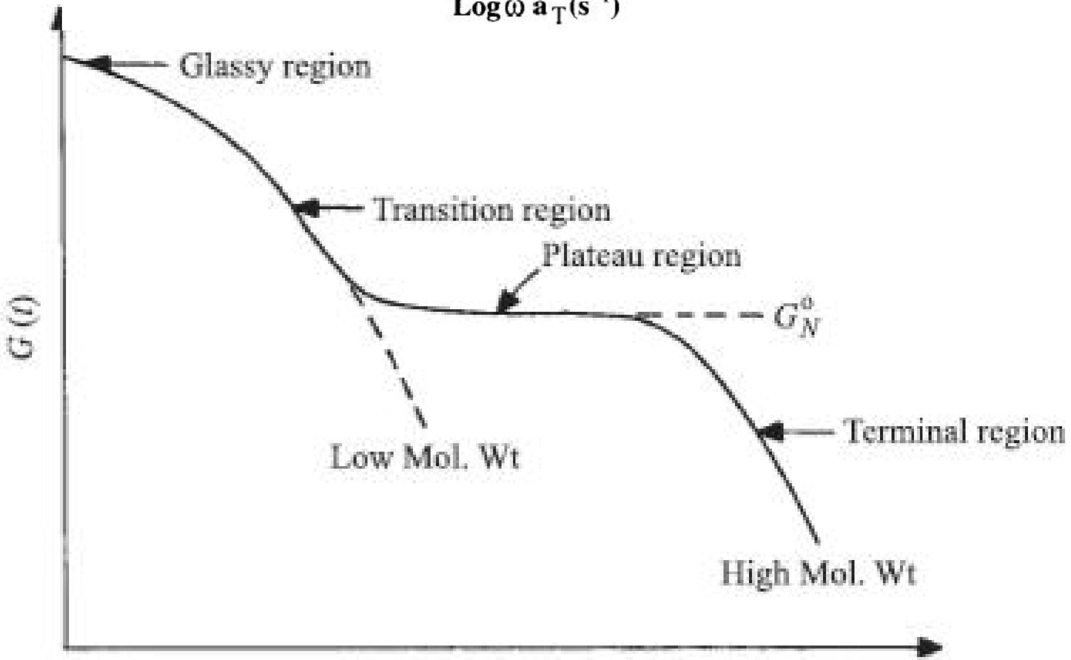
Relaxation Modulus of Polymer Melts

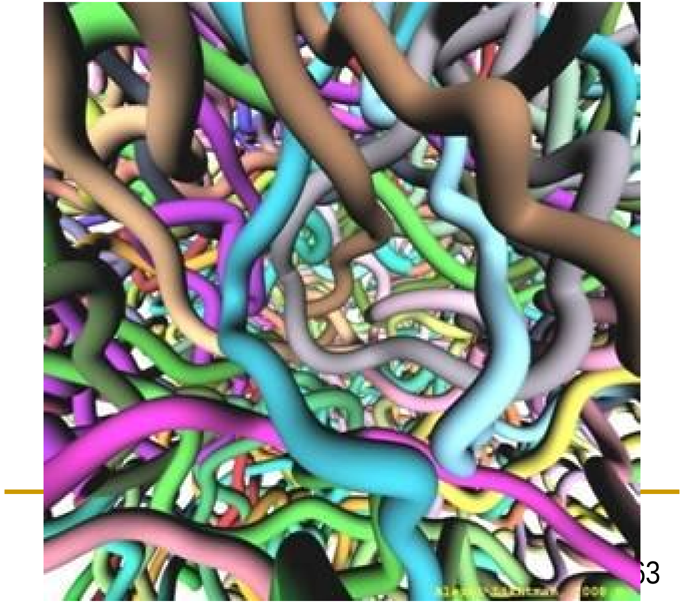


Relaxation Modulus *vs* Dynamic Modulus in Melts

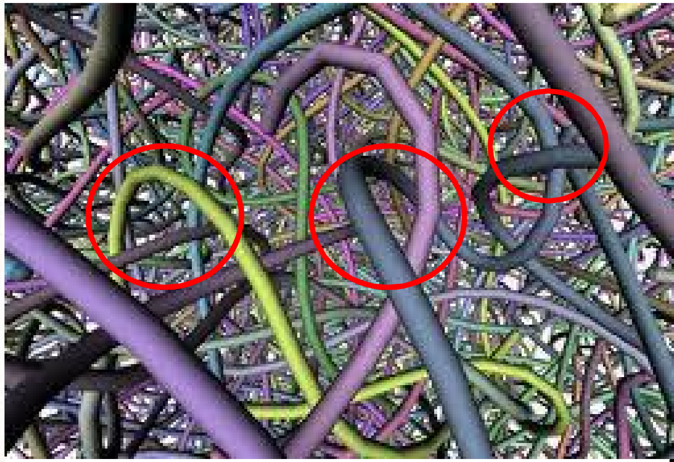


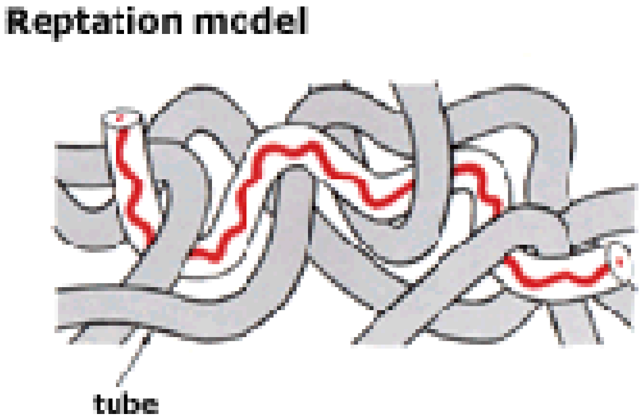


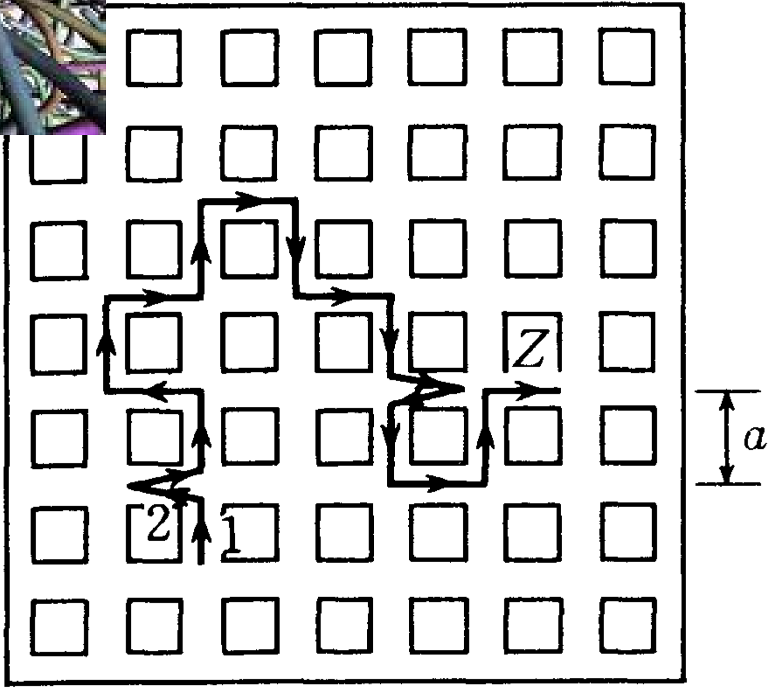


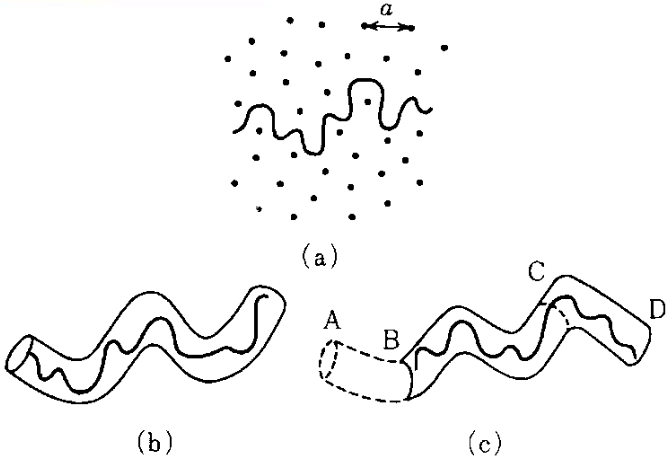


Tube & Reptation Model for Entanglement







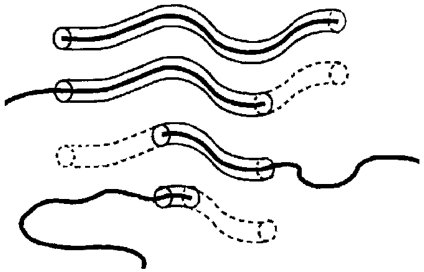


Contour length of the primitive tube: L_{pr}

Length between entanglement: a_{pr}

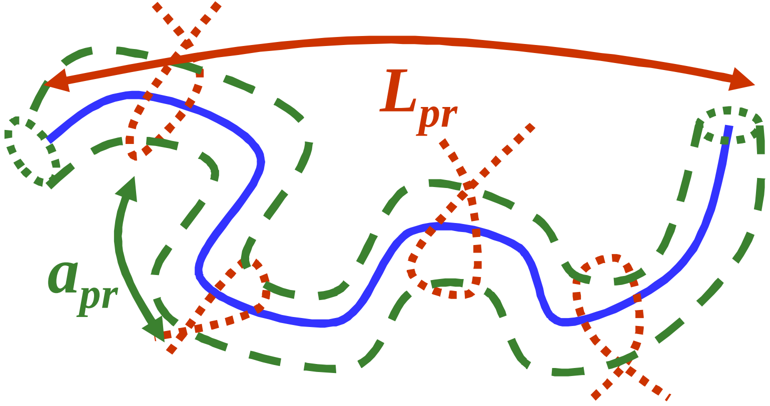
Microscopic Dynamical Model of Polymers

- **Reptation model**



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

$$\left\langle \left(\boldsymbol{R}_n(t) - \boldsymbol{R}_n(0) \right)^2 \right\rangle = \left(k_B T b^2 \tau_e \zeta \right)^{1/2} = a_{pr}^2$$



Relation of entanglement and reptation model

Define the contour length of the primitive path L_{pr}:

$$R_0^2 = Nb^2 \doteq L_{pr} a_{pr} \qquad L_{pr} = Nb^2 / a_{pr}$$

a_{pr} is the associated sequence length, which describes the stiffness of the primitive path and is determined by the topology of the entanglement network.

$$\tau_e = \frac{a_{pr}^4 \zeta}{k_B T b^2}$$ entanglement time

Curvilinear diffusion coefficient D:

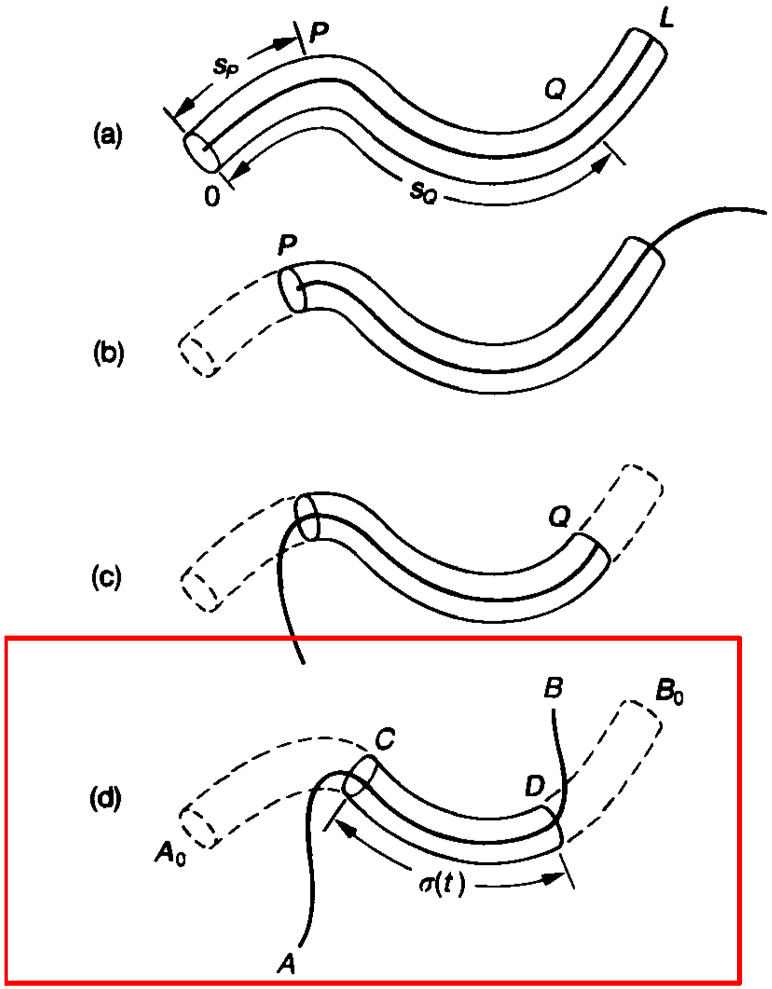
$$D = \frac{k_B T}{\zeta_P}$$ **(Einstein relation)**

$\zeta_P = N\zeta_b$ **(ζ_b: friction coefficient of bead)**

In order to get disentangled, chain have to diffuse over a distance l_{pr}, and this requires a time:

$$\tau_d \approx \frac{L_{pr}^2}{D}$$

Therefore, $\tau_d \sim \zeta_b N^3$ disentanglement time



Time correlation function of End-to-end Vector

$$\langle \boldsymbol{P}(t)\cdot\boldsymbol{P}(0)\rangle = \left\langle\left(\overrightarrow{A_0C}+\overrightarrow{CD}+\overrightarrow{DB_0}\right)\cdot\left(\overrightarrow{AC}+\overrightarrow{CD}+\overrightarrow{DB}\right)\right\rangle$$

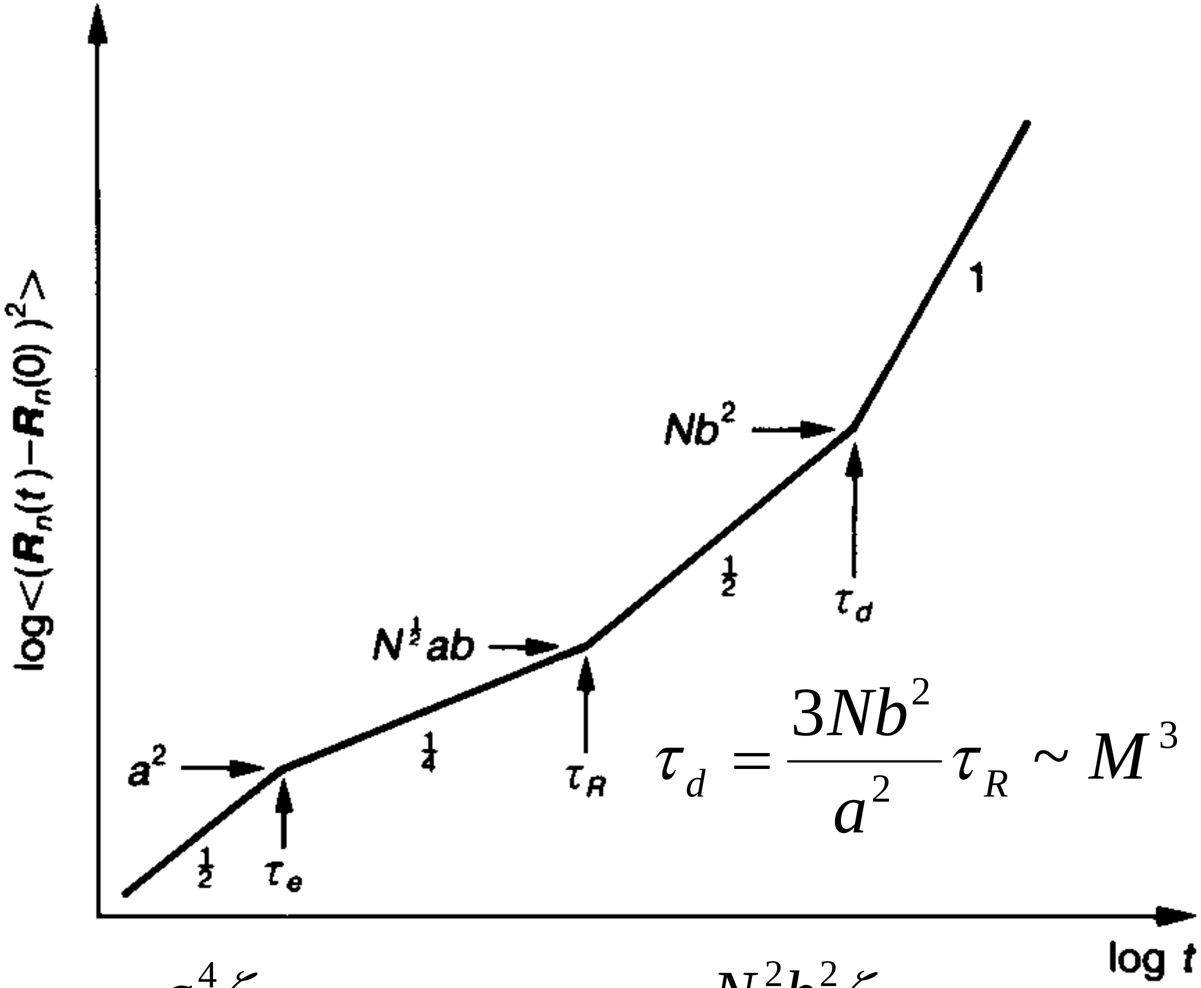
$$= \left\langle \overrightarrow{CD}^2 \right\rangle = a\langle\sigma(t)\rangle$$

$$\langle\sigma(t)\rangle = \langle\sigma(t)\rangle_0 \exp\left(-p^2 t/\tau_d\right)$$

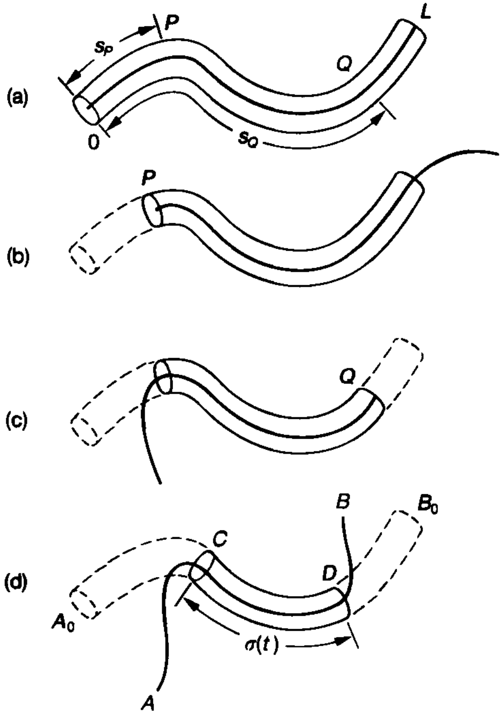
$$\tau_d = L^2/D\pi^2 = \frac{1}{\pi^2}\frac{\zeta_b N^3 b^4}{k_B T a^2} = \frac{3Nb^2}{a^2}\tau_R$$

Doi, M., Edward, S. F., The Theory of Polymer Dynamics, Oxford, 1986, p.194

Comparison of relaxation times



$$\tau_d = \frac{3Nb^2}{a^2}\tau_R \sim M^3$$



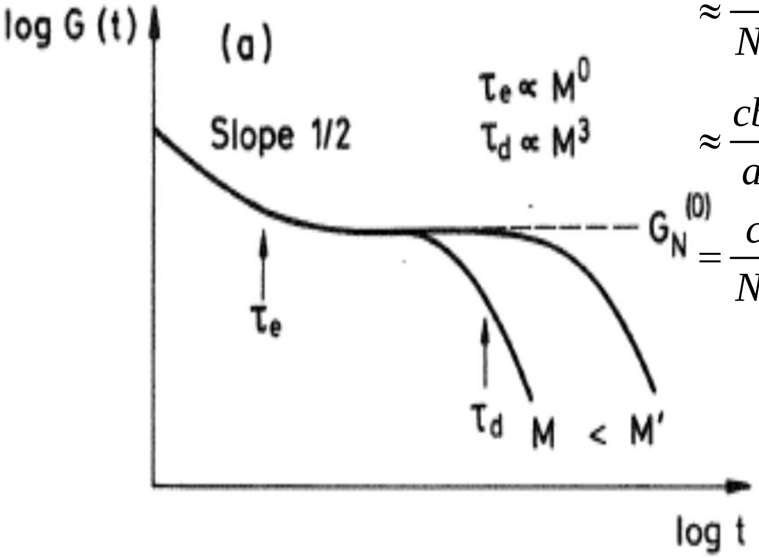
$$\tau_e = \frac{a^4\zeta}{k_BTb^2} \sim M^0 \quad \tau_{1,\mathrm{Rouse}} = \frac{N^2b^2\zeta}{3\pi^2 k_BT} \sim M^2$$

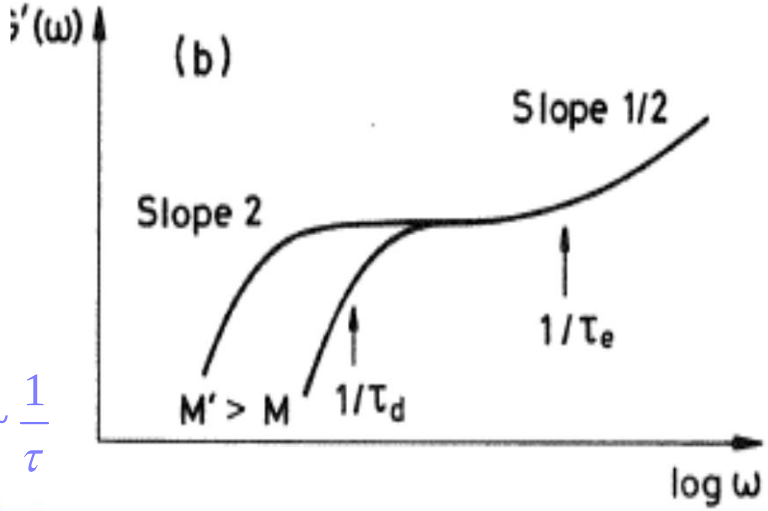
Effects of Entanglement on Relaxation Modulus

Step Shear $G(t)=\frac{c}{2\sqrt{2N}}k_BT\left(\frac{\tau_R}{t}\right)^{1/2}$

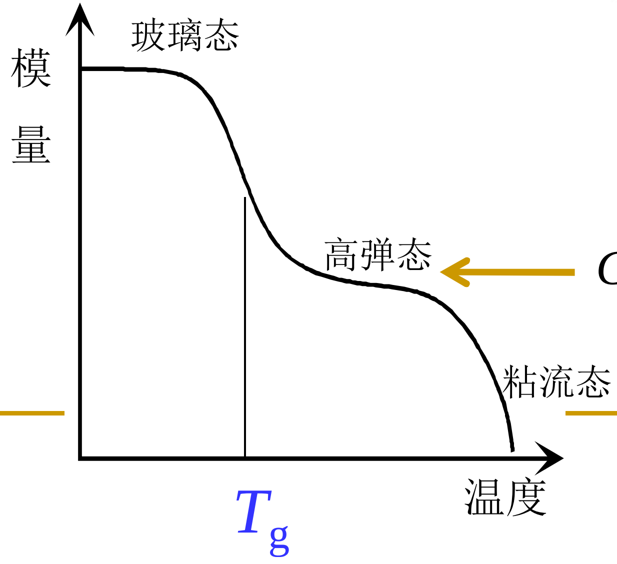
$$G(t=\tau_e)=G_N^{(0)}$$
$$\approx\frac{c}{N}k_BT\left(\frac{\tau_R}{\tau_e}\right)^{1/2}$$
$$\approx\frac{cb^2}{a^2}k_BT$$
$$=\frac{cb^2}{N_eb^2}\sim\frac{1}{M_e}$$

Dynamically Shear

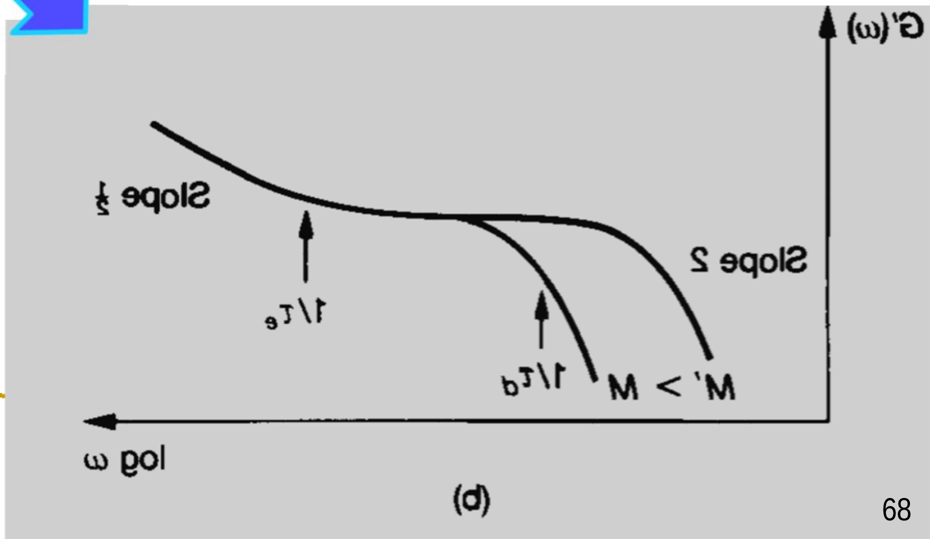




$\omega\sim\frac{1}{\tau}$



$G(t)=G_N^{(0)}$



Viscosity

Rouse $M < M_c$

$$\tau_R = \frac{N^2 b^2 \zeta}{3\pi^2 k_B T}$$

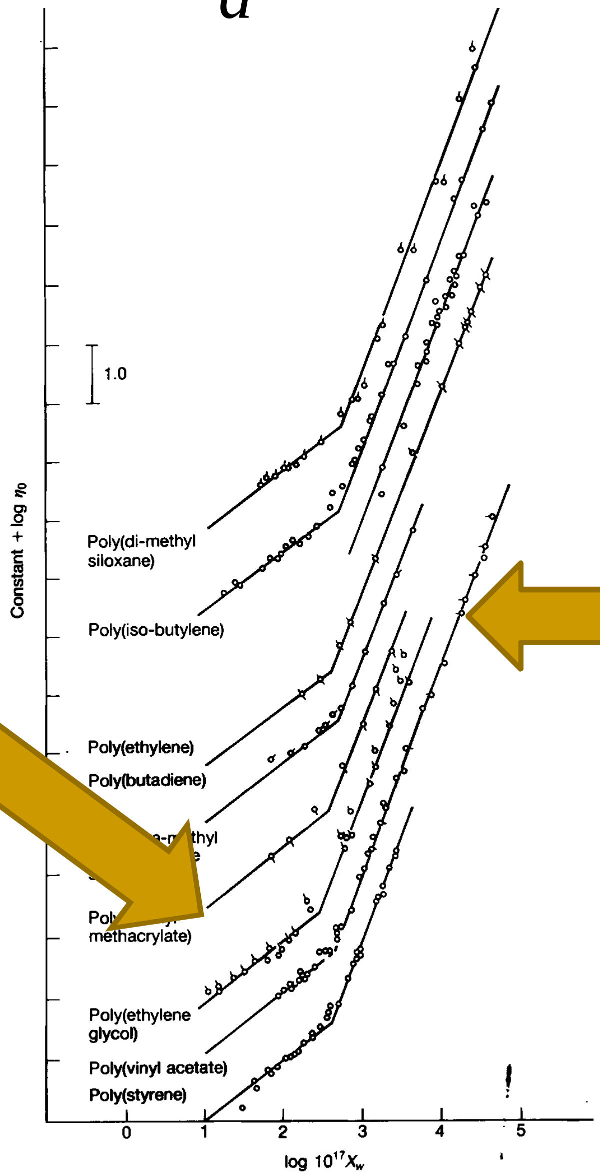
$$\eta_0 = \int_0^\infty dt G(t)$$

$$= \frac{c}{N k_B T} \sum_{p=1}^{\infty} \int_0^\infty dt \exp\left(-2tp^2 / \tau_R\right)$$

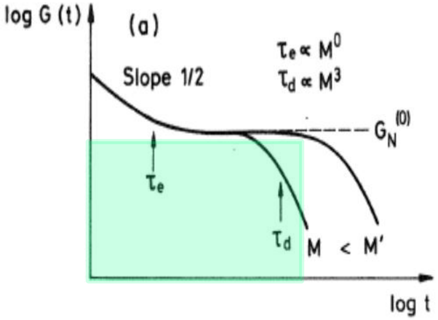
$$= \frac{c}{N k_B T} \frac{\tau_R}{2} \sum_{p=1}^{\infty} p^{-2}$$

$$= \frac{c\zeta}{36} N b^2 \propto M$$

$$\tau_d = \frac{3Nb^2}{a^2} \tau_R \sim M^3$$



Tube $M > M_c$



$$\eta_0 = \int_0^\infty dt G(t)$$

$$= \frac{\pi^2}{12} G_N^{(0)} \tau_d$$

$$\sim M^3$$

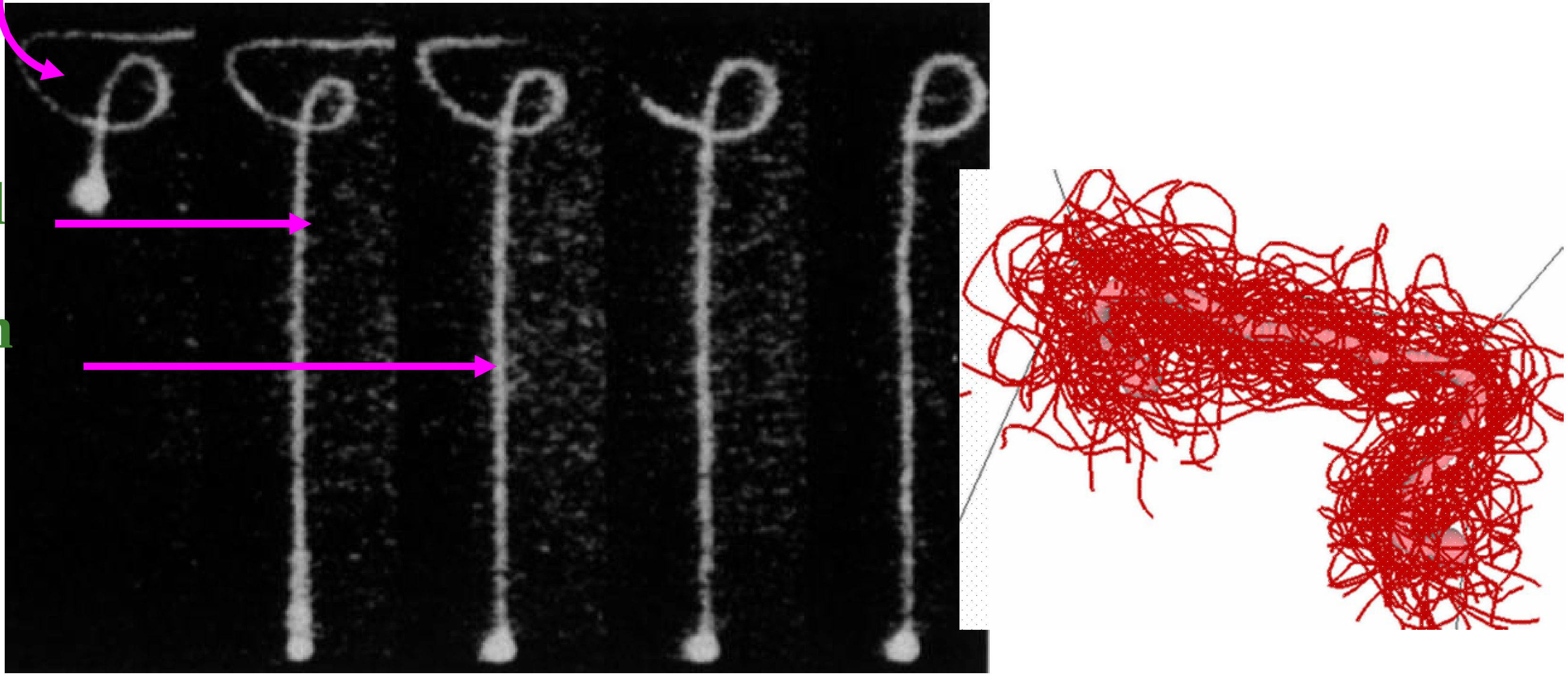
- **Note, $\tau \sim \eta \sim M^{\nu}$ with $\nu \approx 3.3 - 3.4$ for molecular weight higher than M_c.**

Experiments & Simulations

Initial conformation

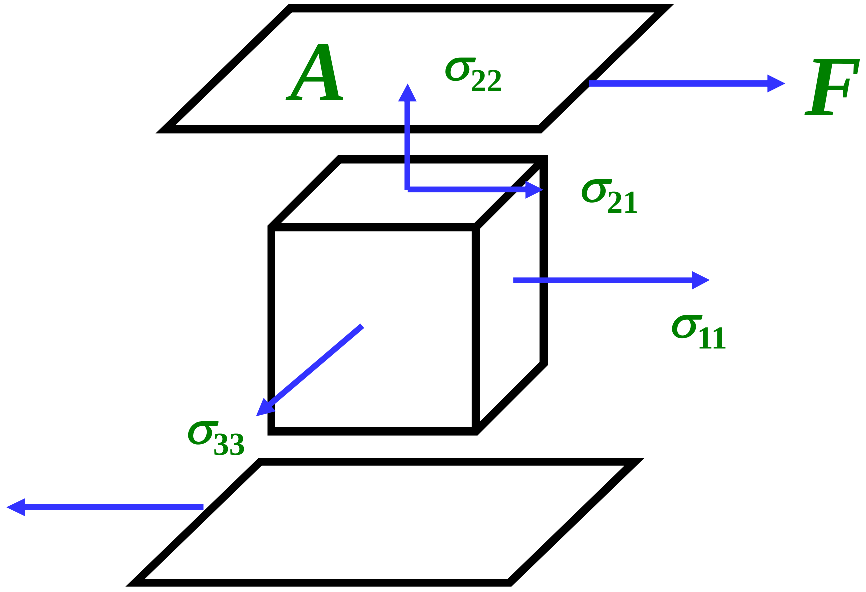
Stretched

Reptation starts

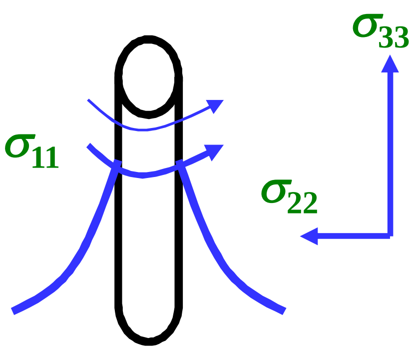


Series of image of a fluorescent stained DNA chain embedded in a concentrated solution of unstained chains. (Chu. S. etc. *Science* **1994**, *264*, 819.)

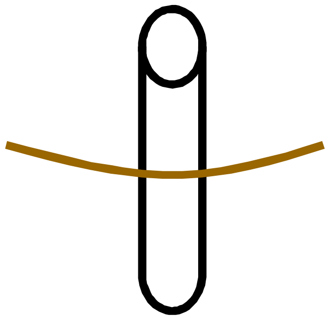
Normal stress difference and Elastic effects on viscous flow of polymers



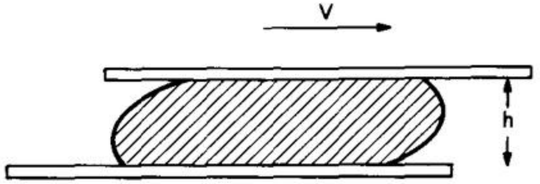
$F/A=\sigma_s=\sigma_{21}$



Weissenberg effect



For polymer melts



$N_1=\sigma_{11}-\sigma_{22}>0$

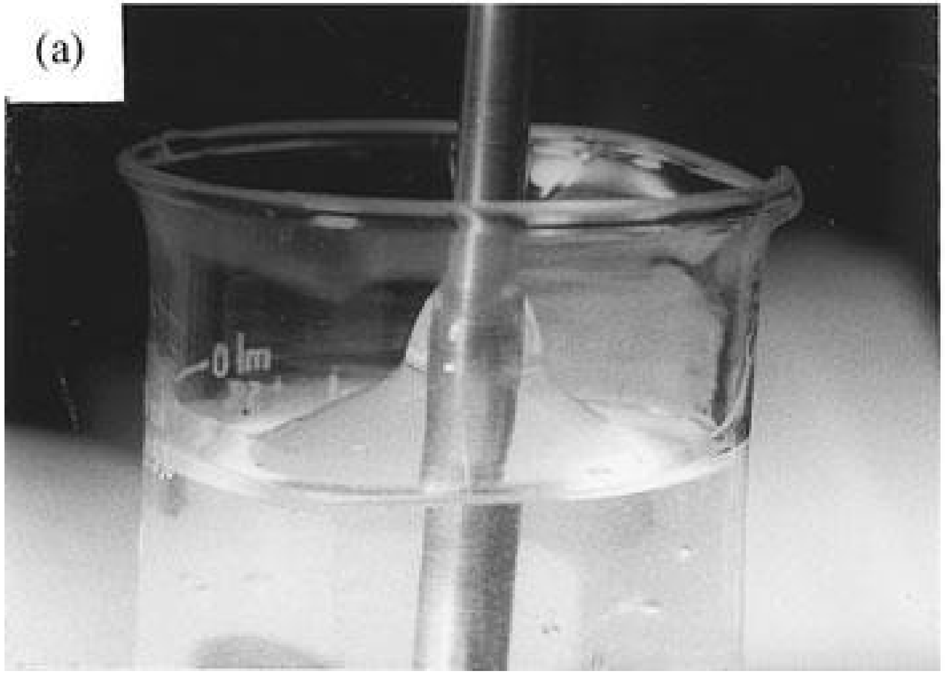
$N_2=\sigma_{22}-\sigma_{33}<0$

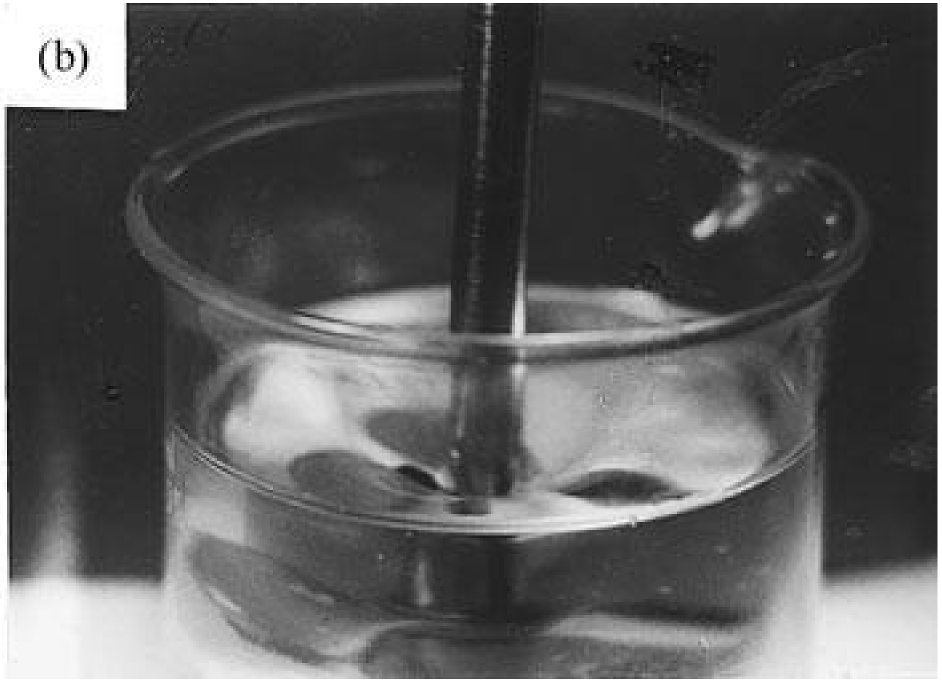
For low molecular weight liquids

$N_1=\sigma_{11}-\sigma_{22}=0$

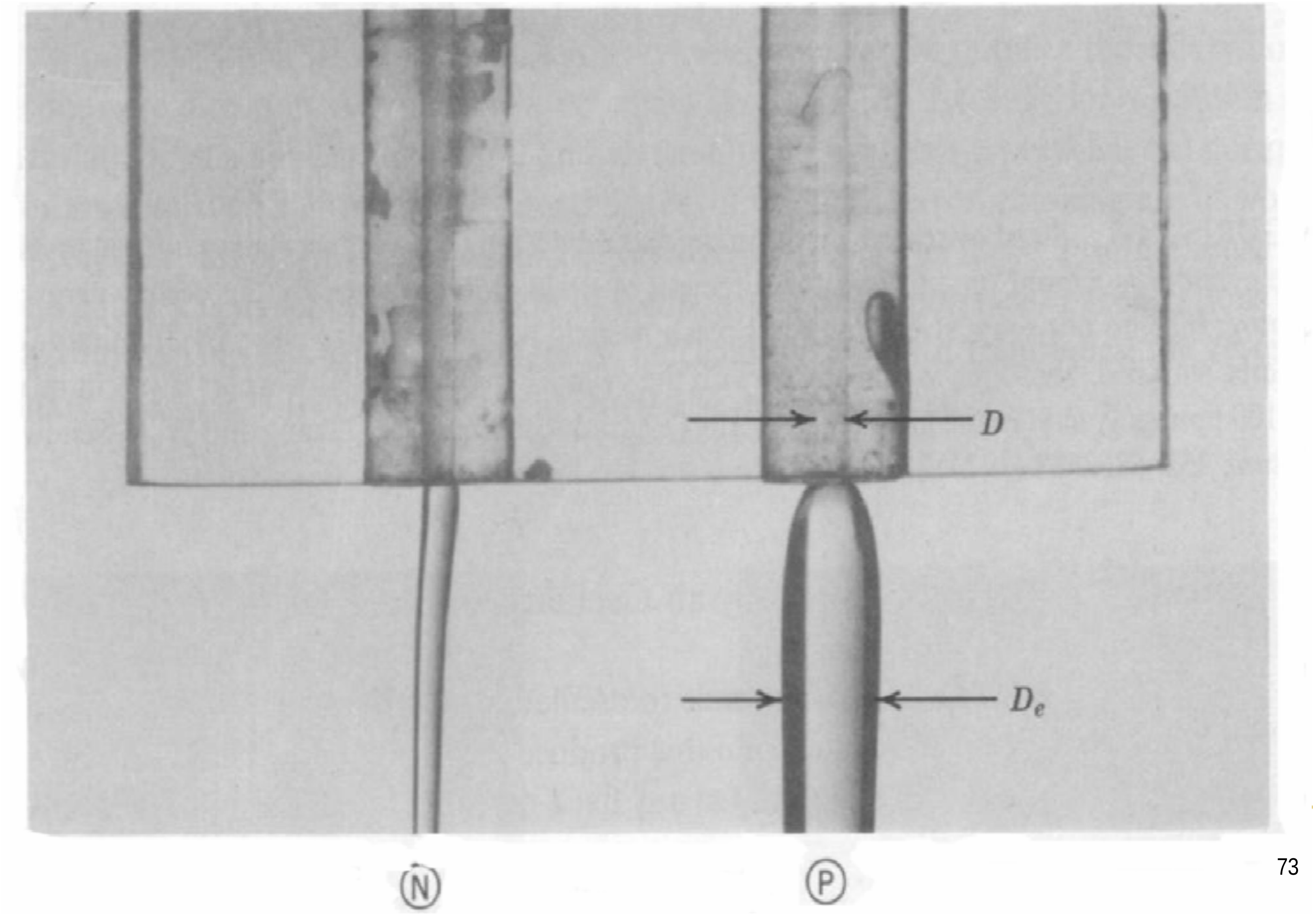
$N_2=\sigma_{22}-\sigma_{33}=0$

Rod-climbing

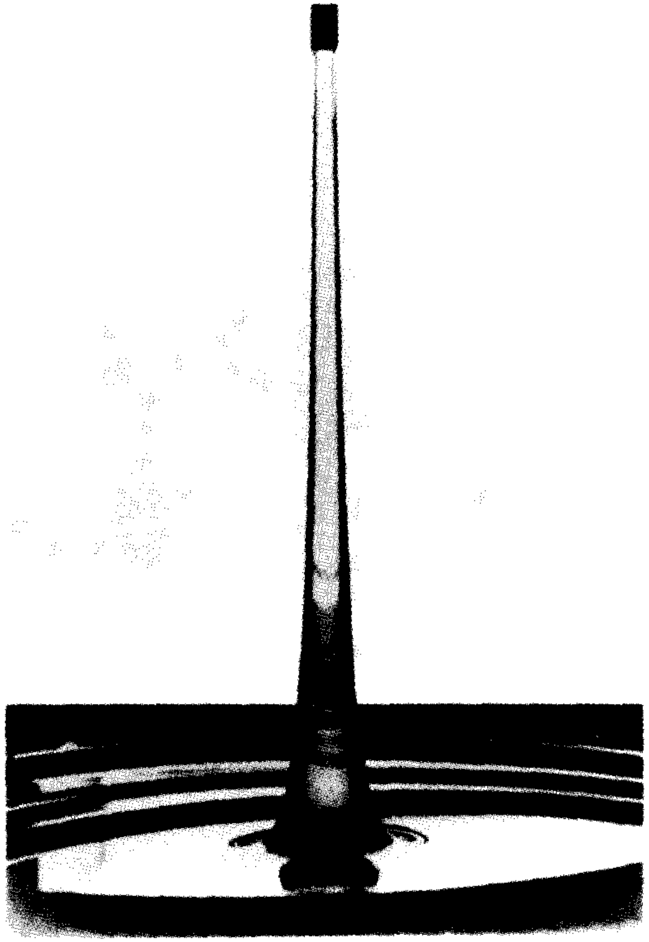

(a)


(b)

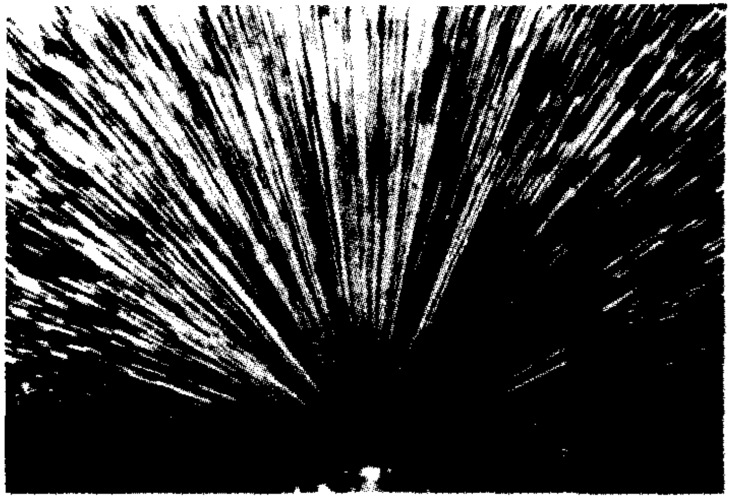
Extrudate swell



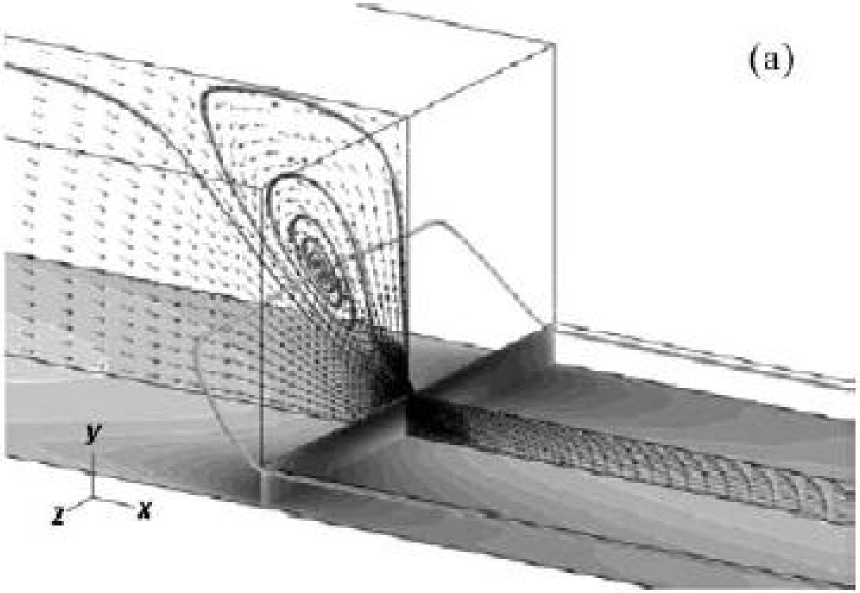
tubeless siphon (无管虹吸)



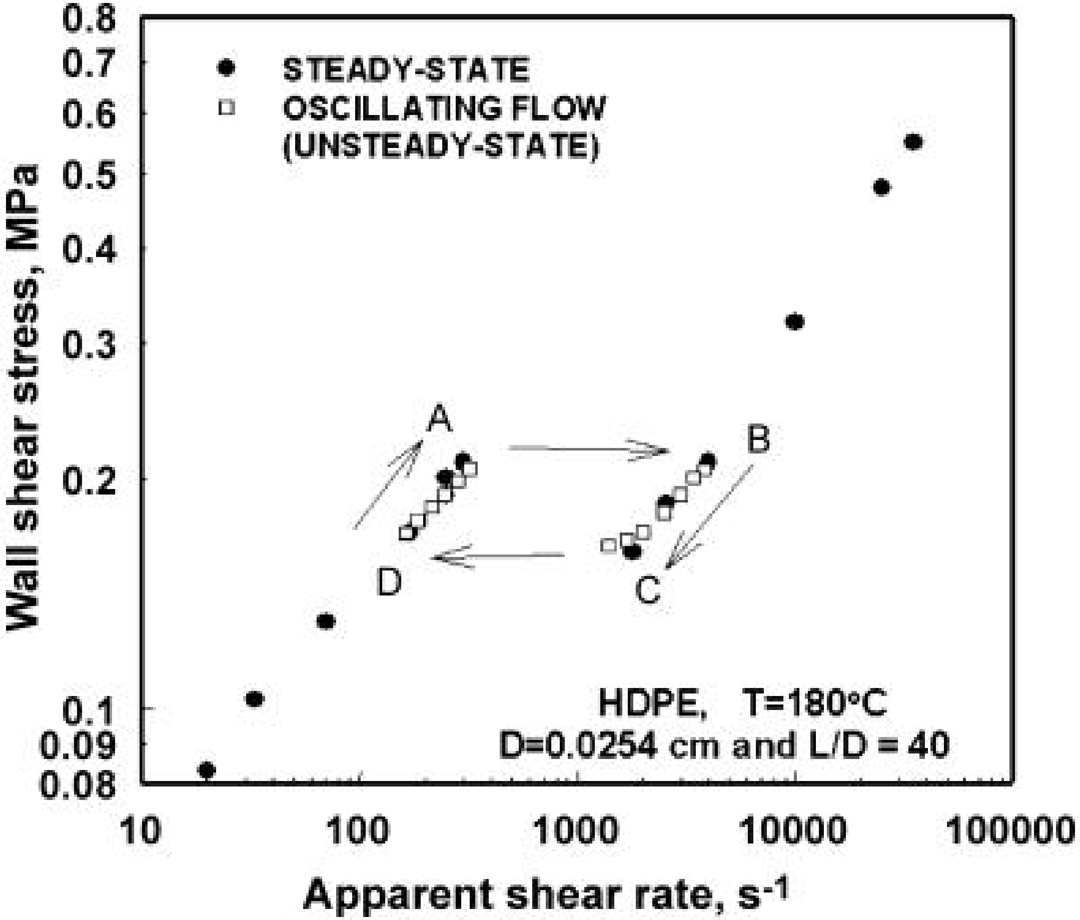
toroidal eddy (环形涡流)

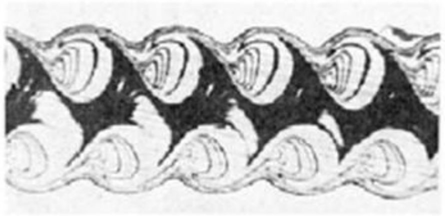


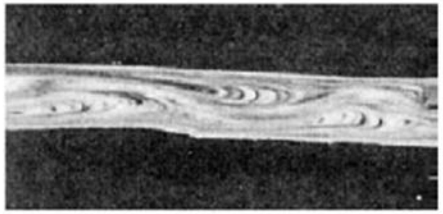
(N)



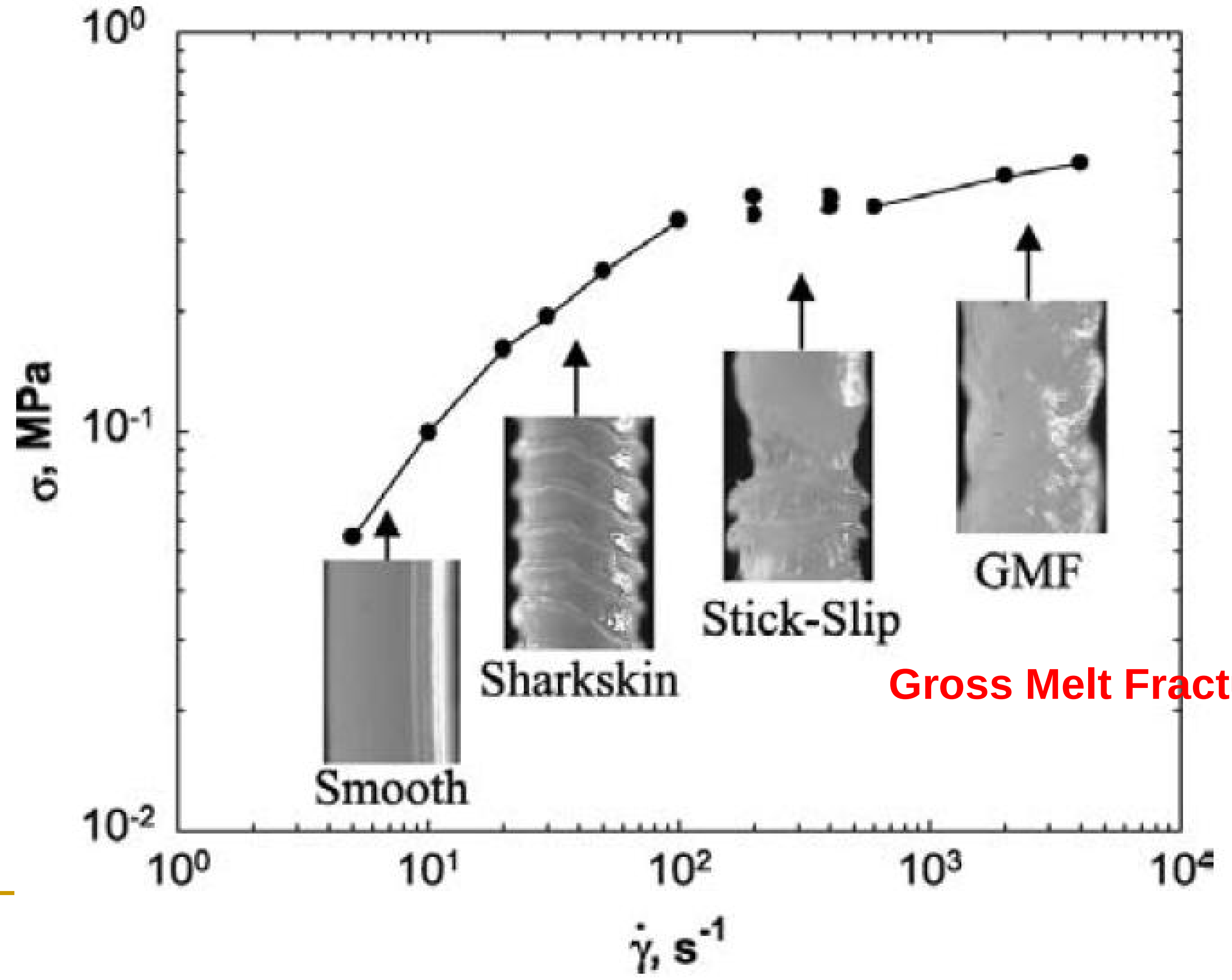
Instability in Processing




(a)

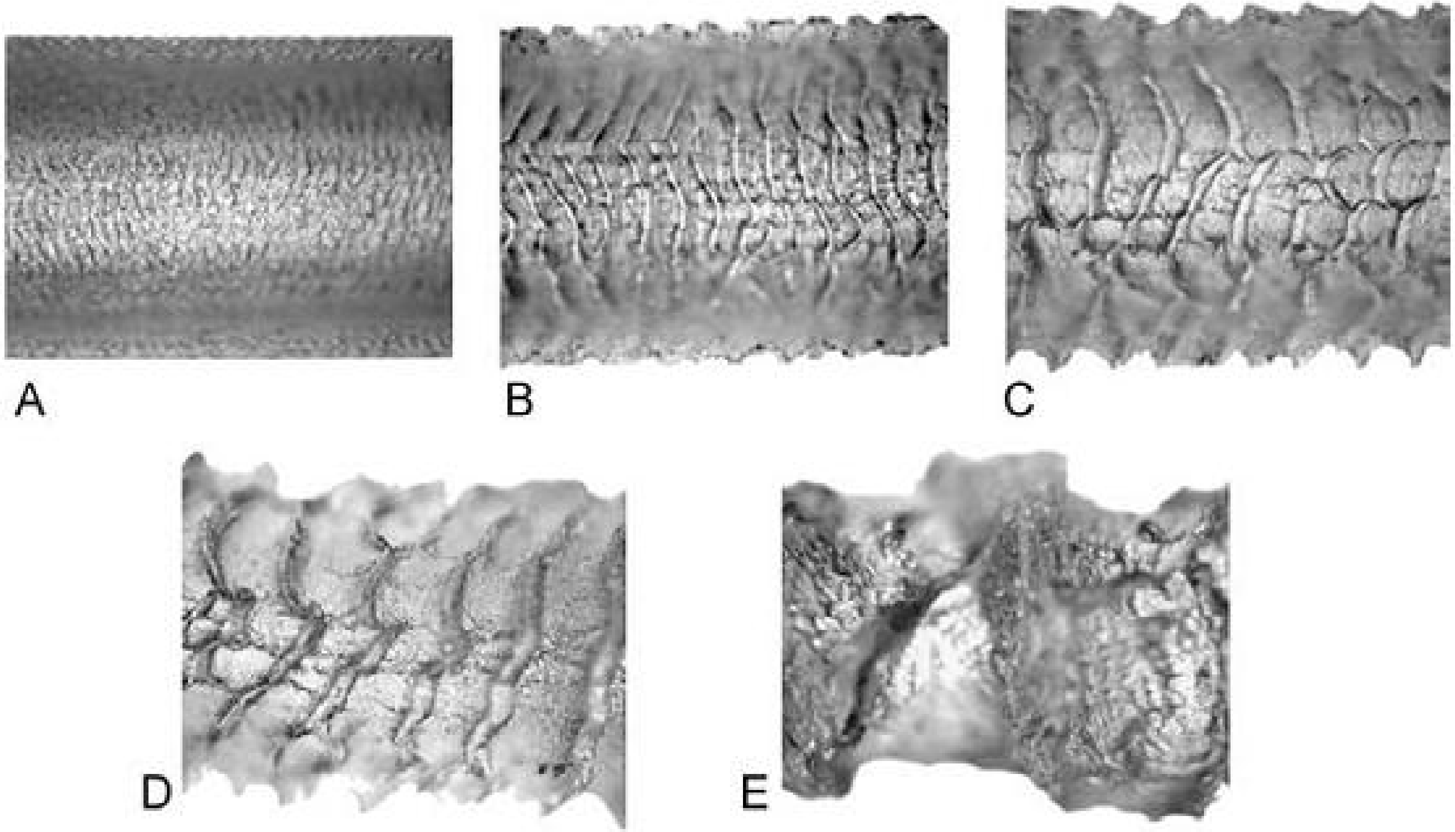

(b)

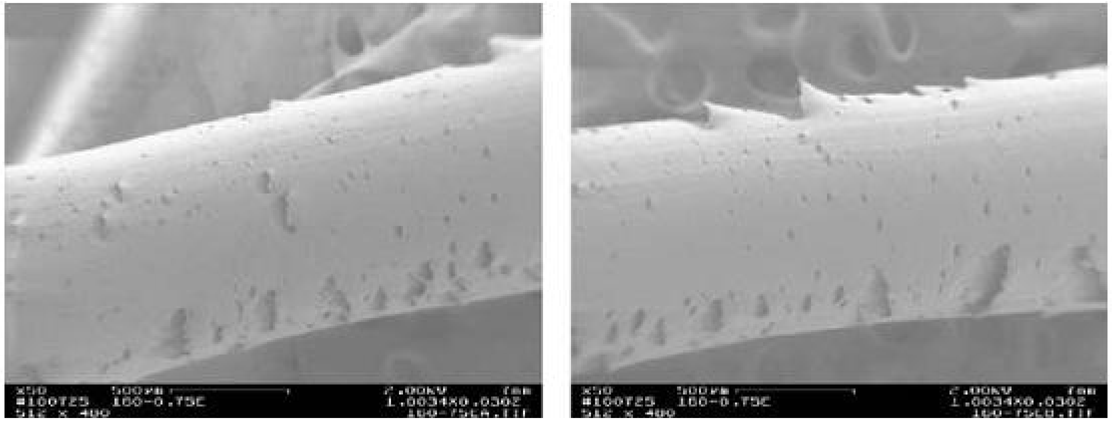
Instability in Processing



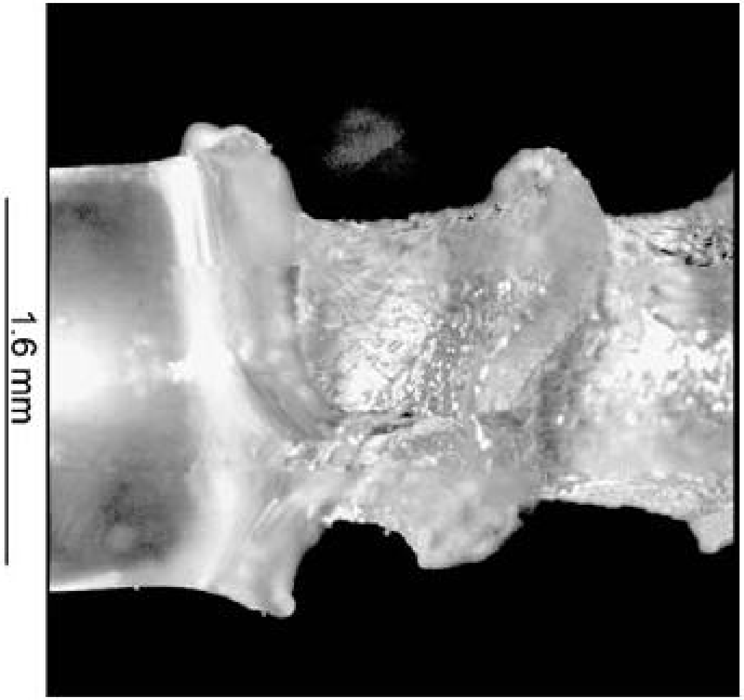
Gross Melt Fracture

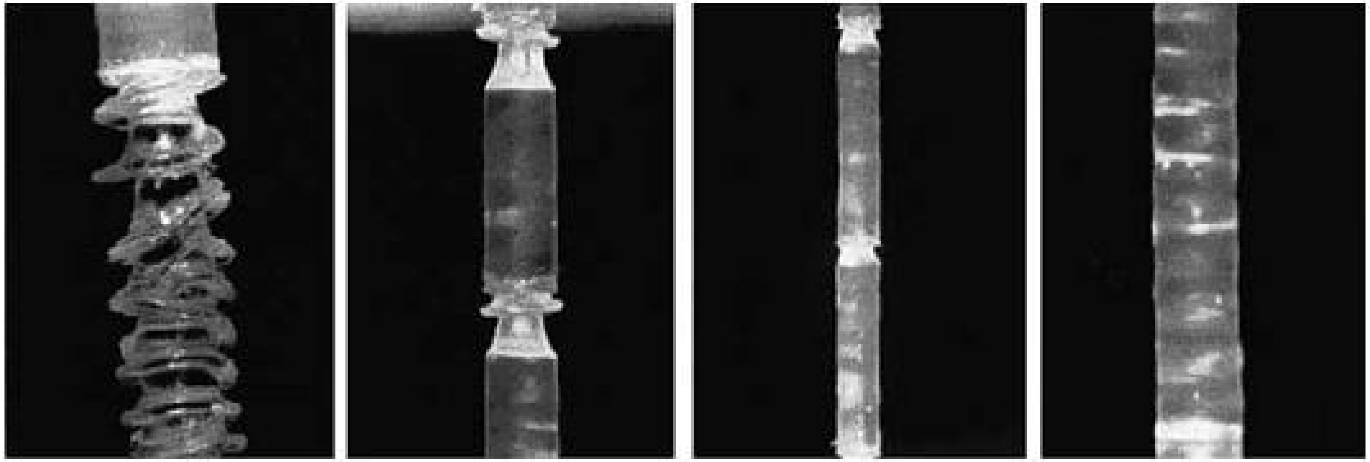
Sharkskin





Stick-slip

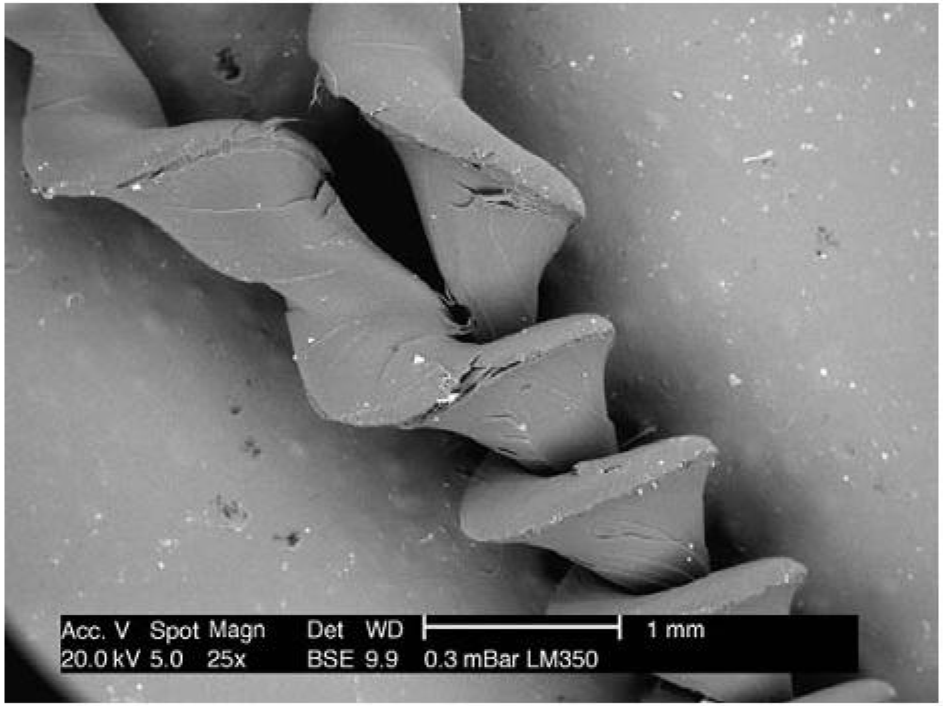




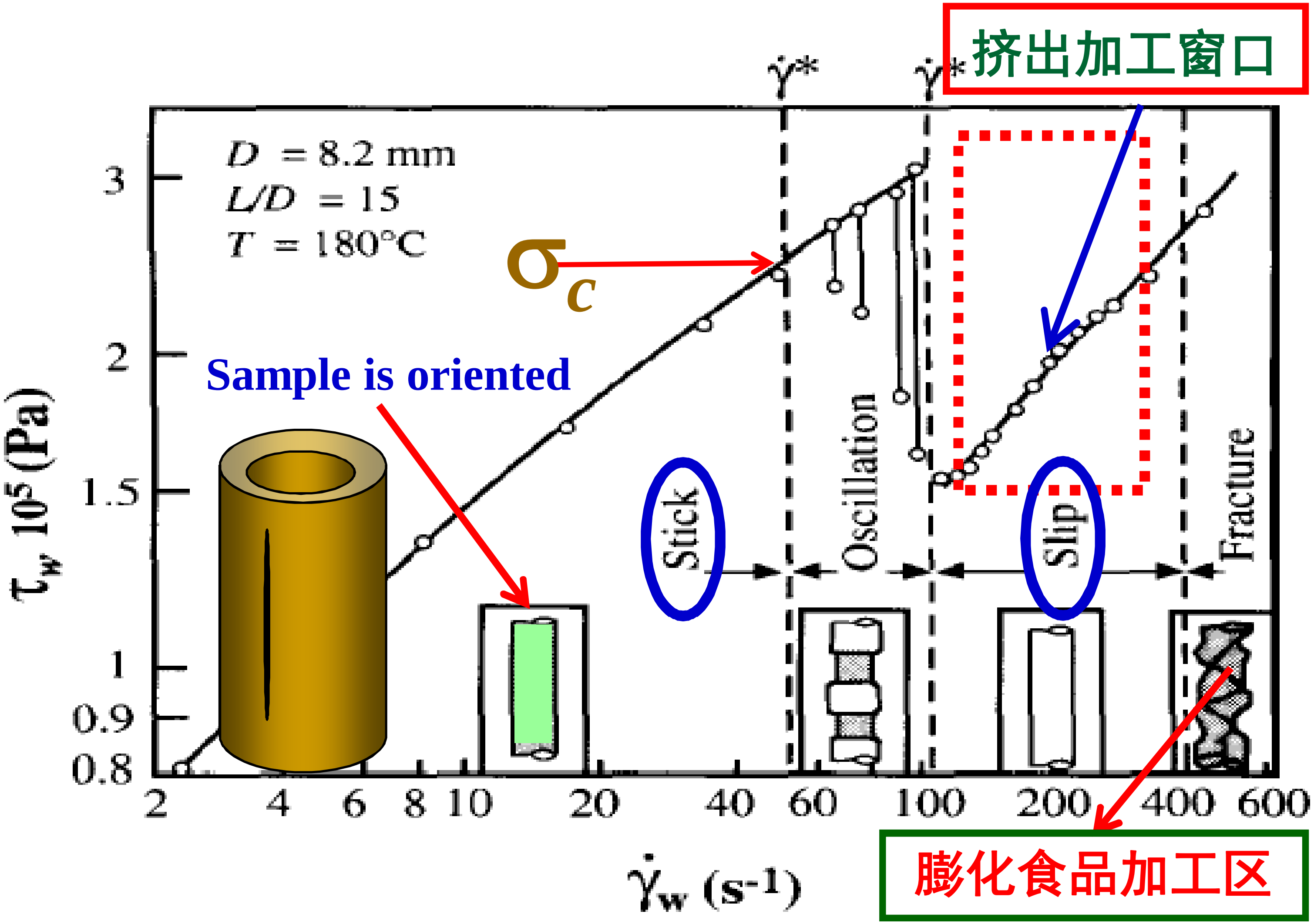
0.45 mg/s 1.15 mg/s 1.70 mg/s 2.26 mg/s

(a) (b) (c) (d)

GMF

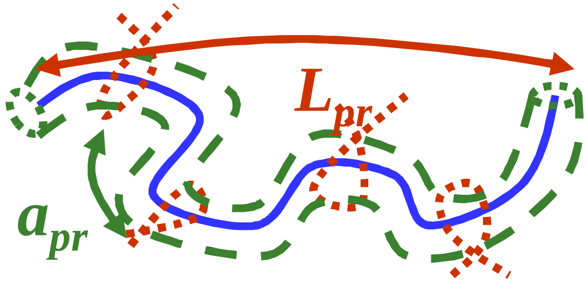


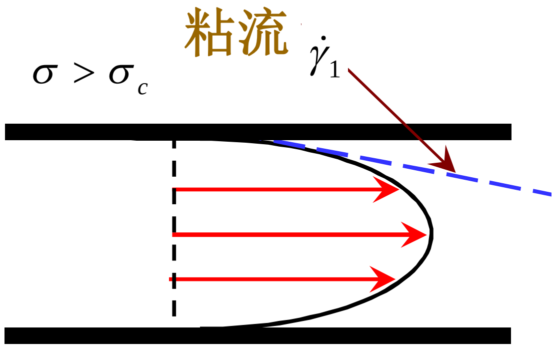
Stick-Slip Transition

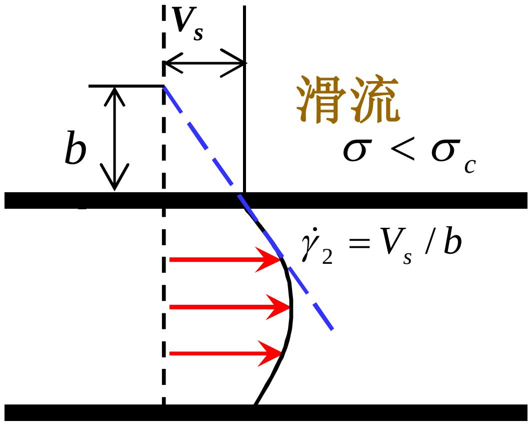


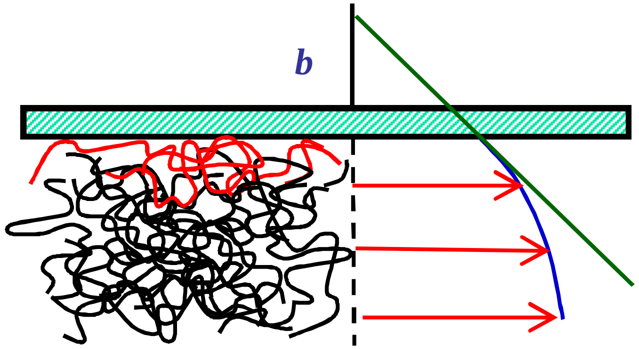
Stick-Slip Transition

$$\sigma_c = nF_e \qquad F_e \propto \frac{k_B T}{a_{pr}} \propto \frac{k_B T}{N_e^{1/2} l_e}$$



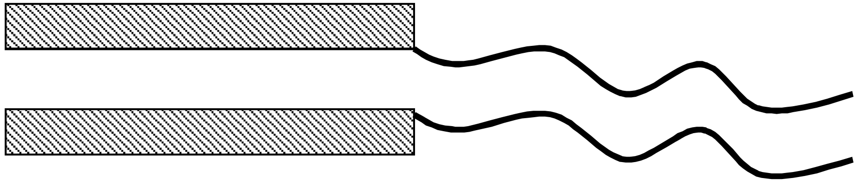




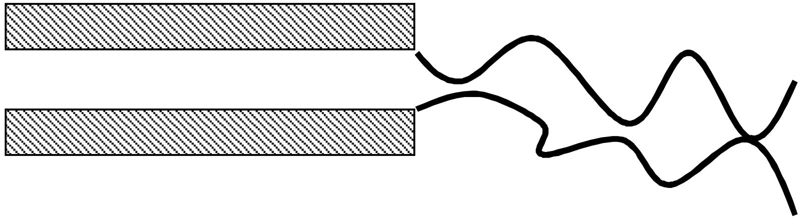


Flow instability and melt fracture

当剪切速率超过临界值后，随着剪切速率的增大，挤出物的外观依次出现表面粗糙（鲨鱼皮状）、尺寸周期性起伏（波纹、竹节或螺旋状），直至破裂成碎块等畸变现象

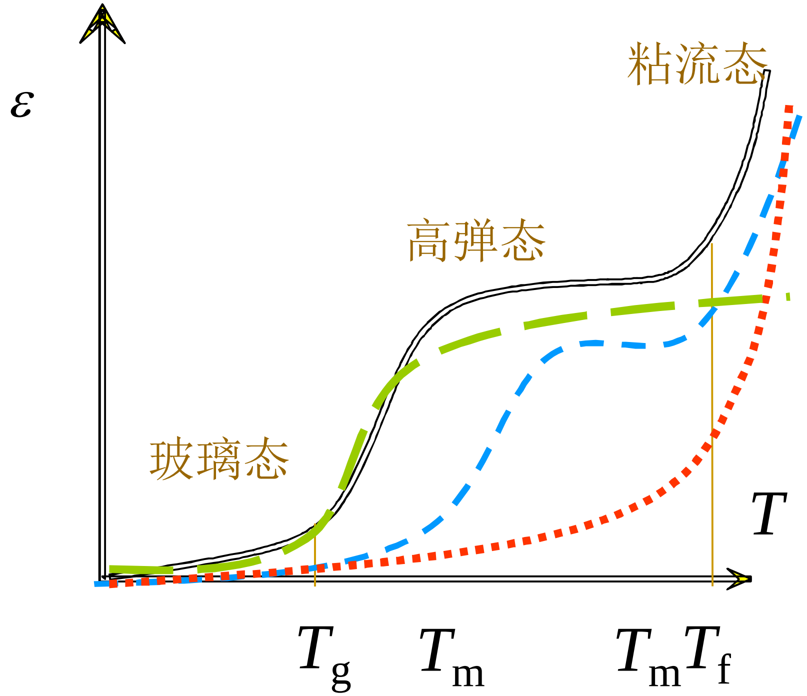


Shark skin



melt fracture

5.3 力学状态与热转变

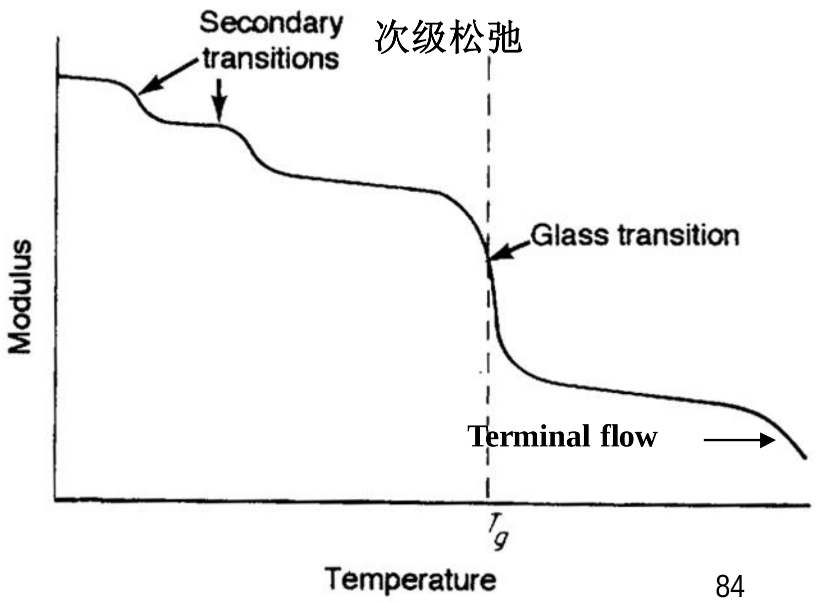


Linear and Cross-link

Semi-crystalline or crystalline $T_m<T_f$

Crystalline $T_m>T_f$

力学性质	普弹性	高弹性	形变不可回复
运动单元	< 链段	~ 链段	>链段 ~分子
松弛时间	实验不可测范围	实验可测	实验可测



5.2高聚物的玻璃化转变

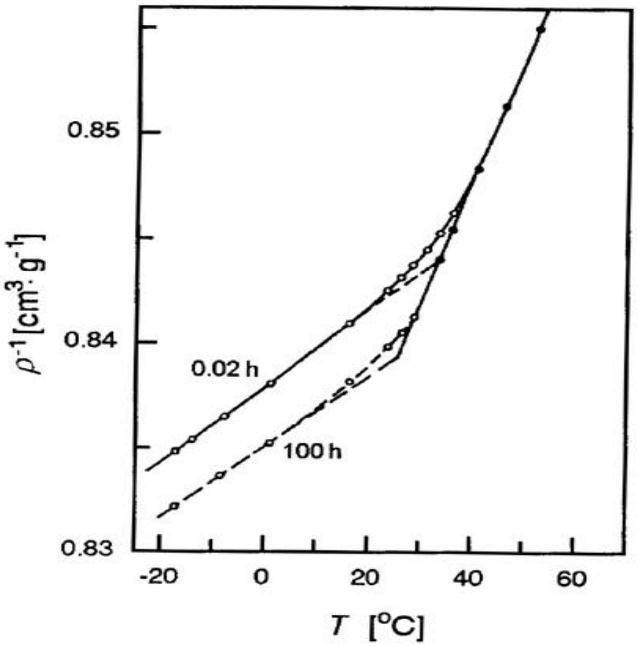
- 1. 定义
- 某些液体在温度迅速下降形成过冷液态(玻璃态)而不发生结晶
- 高聚物从玻璃态(橡胶态)转变为橡胶态(玻璃态)的行为
- 微观：链段运动的解冻或冻结过程
- 主松弛(玻璃化转变-链段)和微松弛(次级松弛-基团)

- 2. 工艺意义
- 橡胶的使用下限温度
- 塑料的使用上限温度

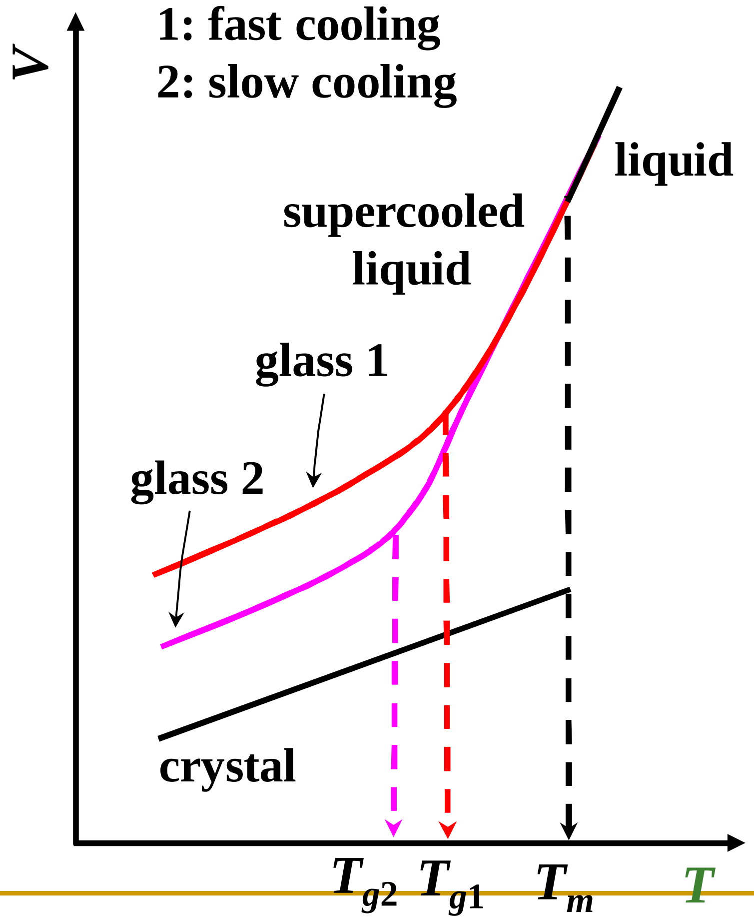
- 3. 学术意义
- 高聚物的特征指标，基本参数

Glass Transition as a Relaxation Process

- **Thermal history dependence of T_g**

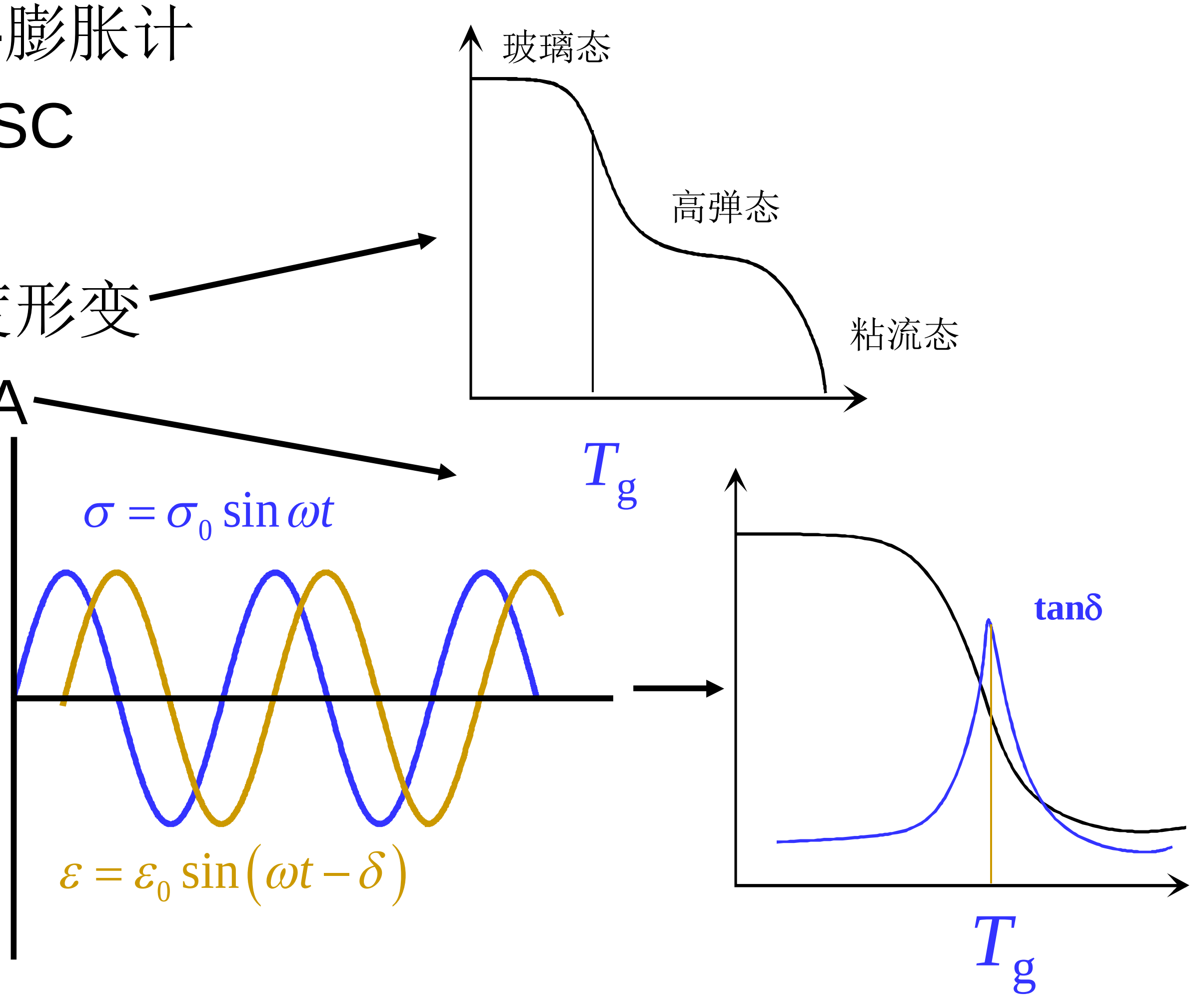


Temperature dependence of the specific volume of PVA, measured during heating. Dilatometric (膨胀计法) results obtained after a quench to –20 °C, followed by 0.02 or 100 h of storage. (Kovacs, A. J. *Fortschr. Hochpolym. Forsch.* **1966**, *3*, 394)



4. 现象和实验表征

- (1) 体积变化性质-膨胀计
- (2) 热力学性质-DSC
- (3) 力学性质
- a. 静态力学-温度形变
- b. 动态力学-DMA

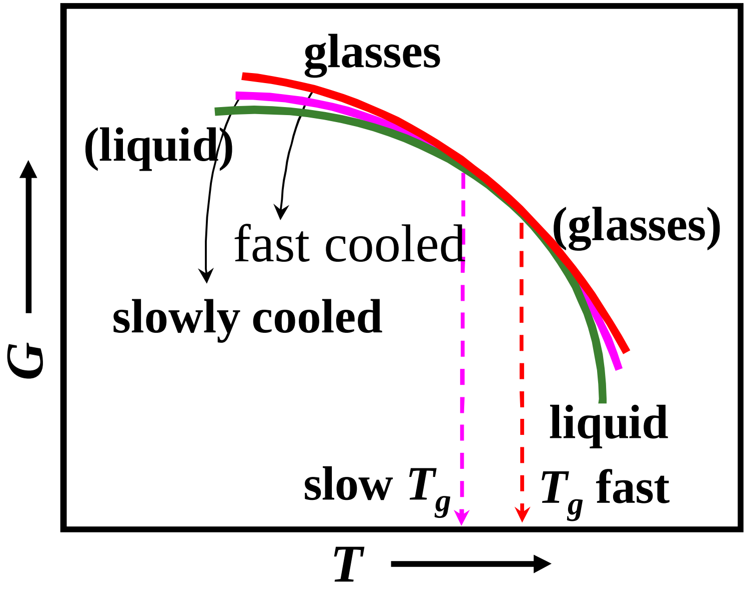


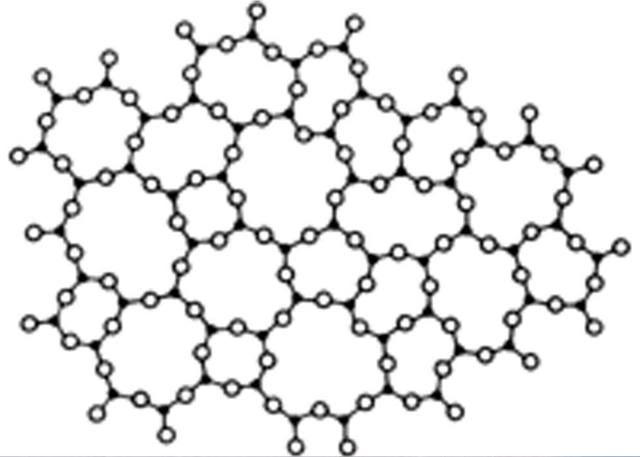
- (4) 光、电、磁性质-NMR, 介电松弛，折光指数

Polymer Melts and Glasses

- **The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition.** (Anderson, P.W. *Science* **1995**, *267*, 1615.)

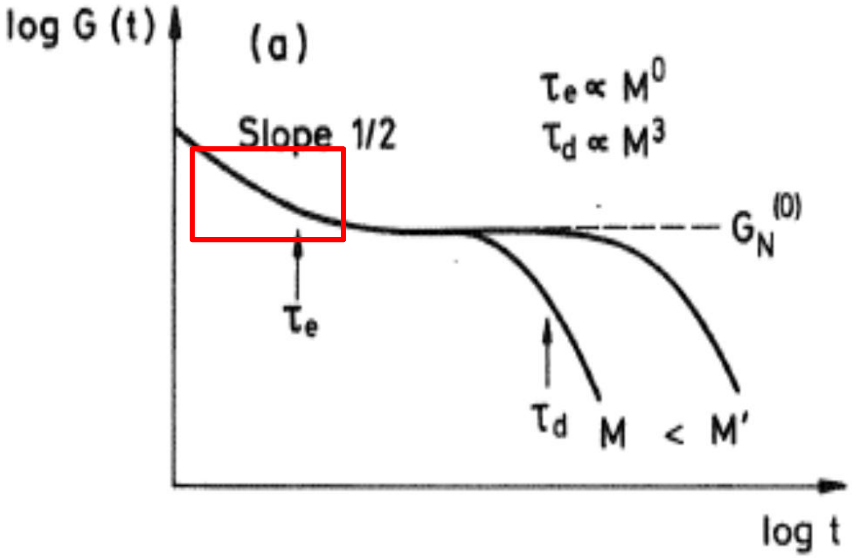
- **The transition from melt to glass is called glass transition (玻璃化转变)**





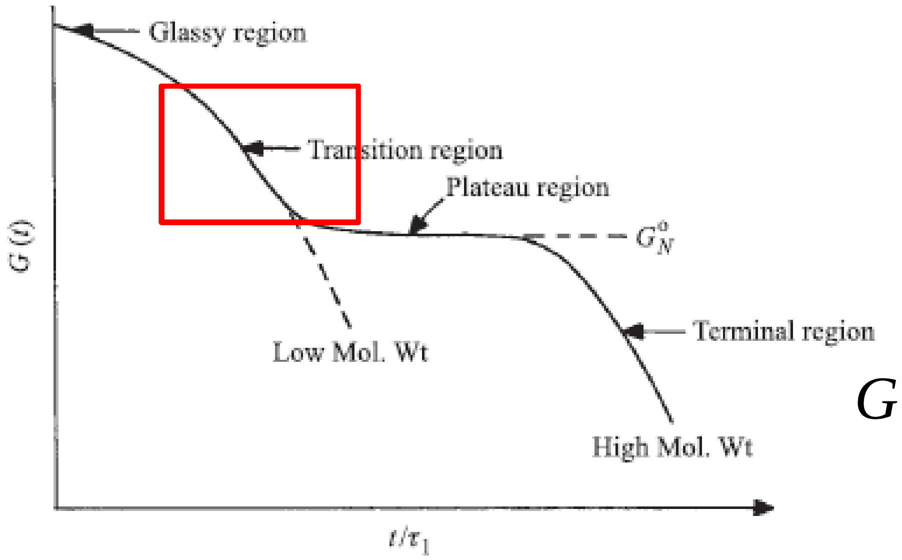
- **T_g: glass transition temperature (玻璃化转变温度)**

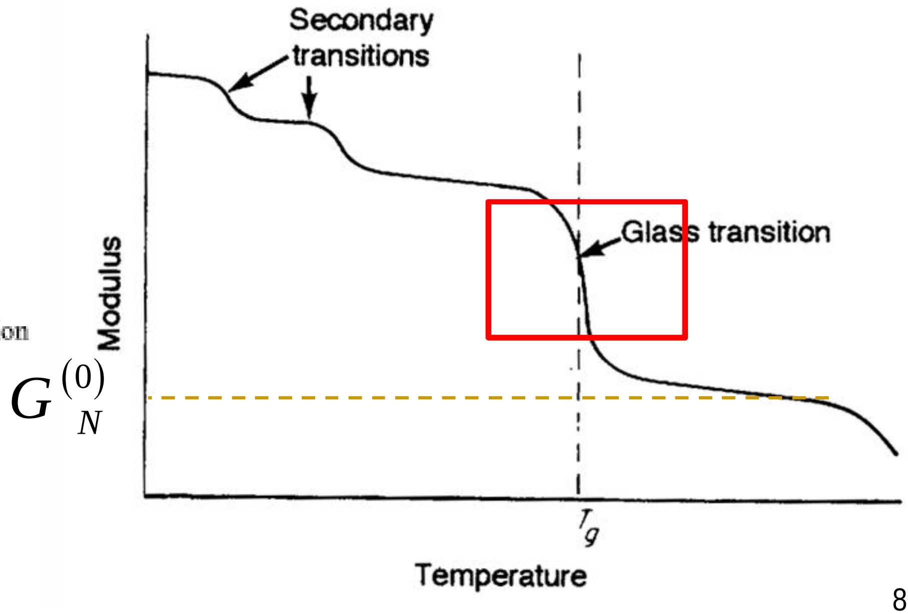
Why Glass Transition belongs to Segment Relaxation?



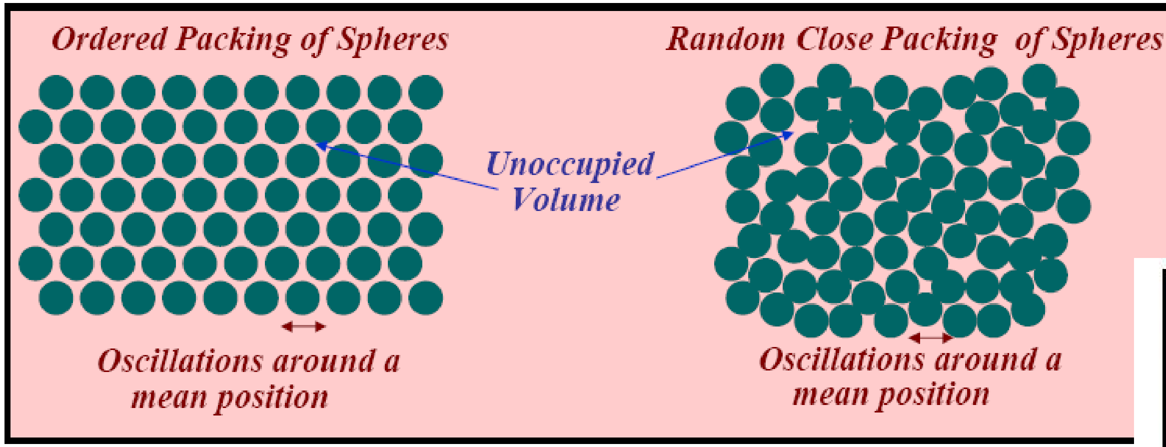
$$\tau_{\text{secondary}} < \tau_g < \tau_e$$

$$length_{\text{secondary}} < length_g < length_e$$



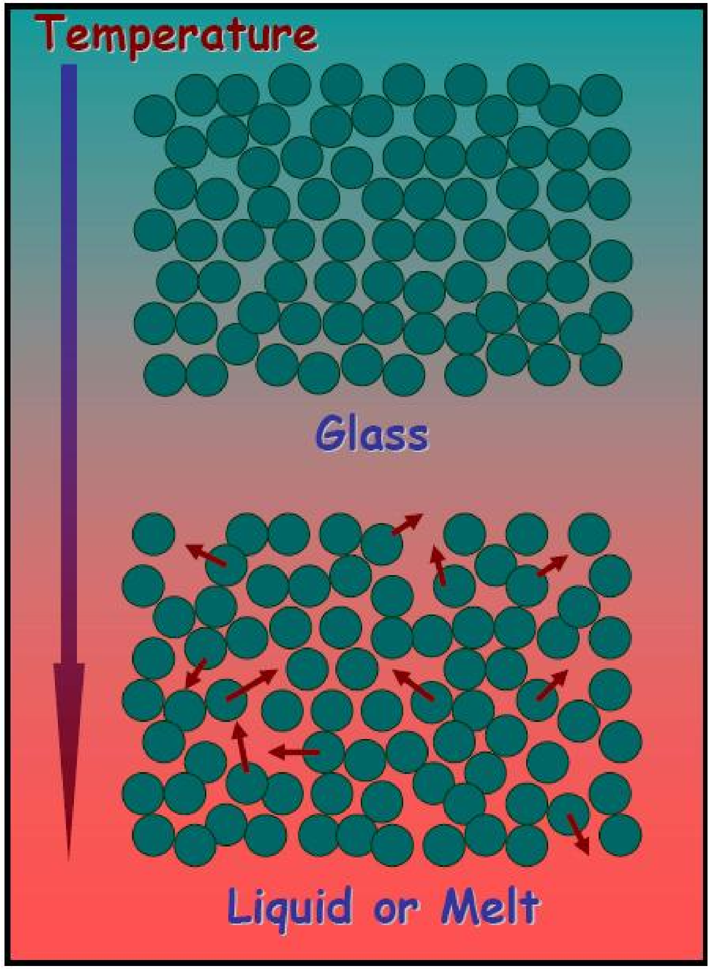


Free Volume



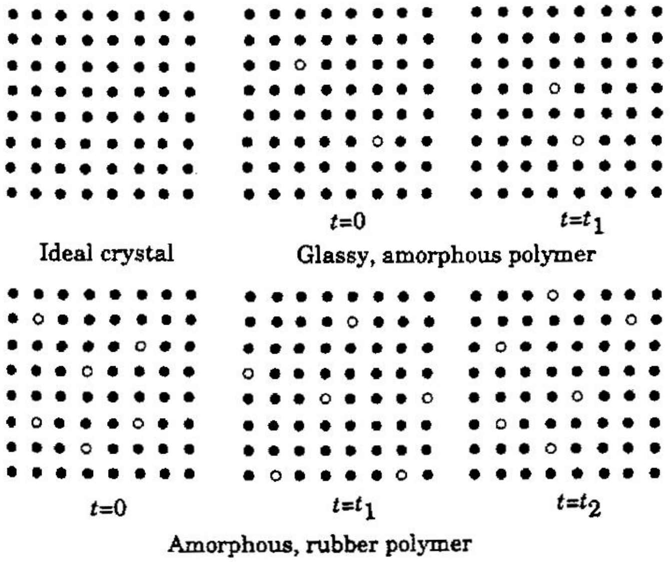
Solid vs Glass

Liquid vs Glass

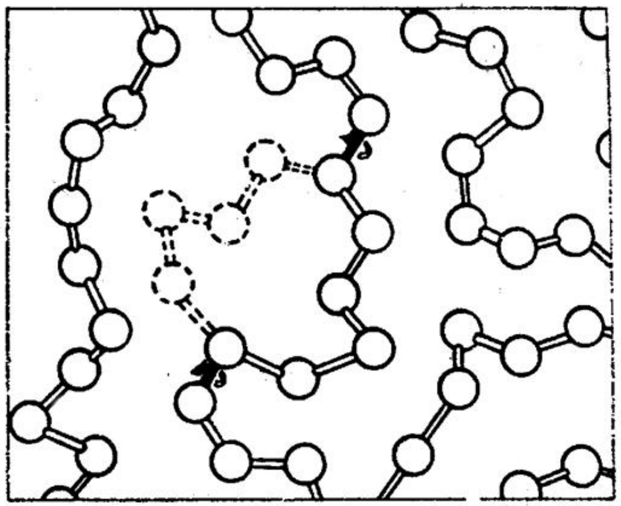


5. 理论 - Free Volume Theory

- **Free volume: a concept useful in discussing transport properties such as viscosity and diffusion in liquids.**



Occupied volume: filled circles; free volume:hole

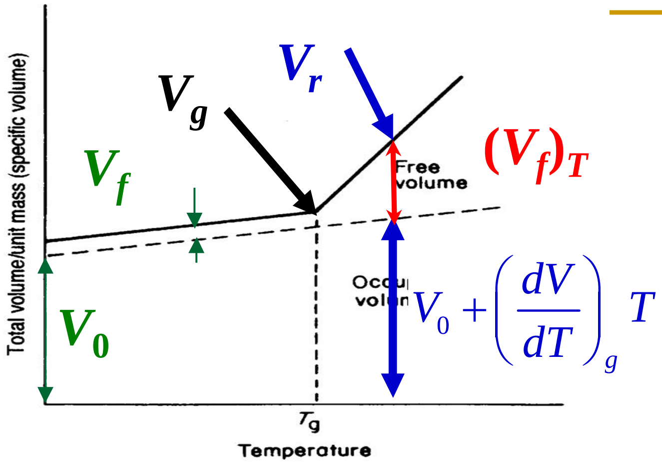


The segmental motion of polymer chain requires more volume

- **Hole theory of liquid:** the liquid consists of matter and holes. The larger volume of liquid when compared to the crystal is represented by a number of holes of a fixed volume. The holes represent a quantized free volume, which can be redistributed by movement or collapse in one place and creation in another.

Free Volume Theory

- The coefficient of thermal expansion (CTE, 热膨胀系数) is constant for the occupied volume for both temperature below and above T_g
- Assume that at the temperature below T_g, the free volume is constant; and the free volume will increase with temperature when temperature exceed T_g



The volume-temperature relationship for a typical amorphous polymer

V_f: free volume at $T < T_g$

$(V_f)_T$: free volume at $T \geq T_g$

V_r: total volume at $T \geq T_g$

V_0: occupied volume (determined by van der Waals interaction + vibration)

(dV/dT): CTE of the glass- and rubber-state

$$V_g = V_f + V_0 + \left(\frac{dV}{dT}\right)_g T_g$$

$$V_r = V_g + \left(\frac{dV}{dT}\right)_r (T - T_g)$$

$$(V_f)_T = V_r - V_0 - \left(\frac{dV}{dT}\right)_g T = V_f + \left(\frac{dV}{dT}\right)_r (T - T_g) + \left(\frac{dV}{dT}\right)_g T_g - \left(\frac{dV}{dT}\right)_g T$$

$$= V_f + (T - T_g)\left[\left(\frac{dV}{dT}\right)_r - \left(\frac{dV}{dT}\right)_g\right]$$

$$f_T = \frac{(V_f)_T}{V_g} \qquad (T \geq T_g)$$

$$f_g = \frac{V_f}{V_g} \qquad (T < T_g)$$

$$\alpha_f = \Delta\alpha = \frac{1}{V_g}\left(\frac{dV}{dT}\right)_r - \frac{1}{V_g}\left(\frac{dV}{dT}\right)_g$$

$$\underline{f_T = f_g + \alpha_f (T - T_g)} \qquad (T \geq T_g)$$

Free Volume Theory (cont.)

- **Relation of the molecular mobility to free volume: Doolittle equation** $\eta = A\exp\left(BV_0/V_f\right)$

$$\left.\begin{aligned}\ln\eta(T) &= \ln A + BV_0(T)/V_f(T)\\ \ln\eta(T_g) &= \ln A + BV_0(T_g)/V_f(T_g)\end{aligned}\right\} \longrightarrow \ln\frac{\eta(T)}{\eta(T_g)} = B\left[\frac{V_0(T)}{V_f(T)} - \frac{V_0(T_g)}{V_f(T_g)}\right]$$

- **Normalized free volume:** $f_T = \frac{V_f(T)}{V_0(T)+V_f(T)} \approx \frac{V_f(T)}{V_0(T)}$

$$f_T = f_g + \alpha_f\left(T - T_g\right)$$

$$\log\frac{\eta(T)}{\eta(T_g)} = \frac{B}{2.303}\left(\frac{1}{f_T} - \frac{1}{f_g}\right) = -\frac{B}{2.303\, f_g}\frac{T-T_g}{f_g/\alpha_f + \left(T-T_g\right)}$$

- **WLF equation:** $\log\frac{\eta(T)}{\eta(T_g)} = -\frac{17.44(T-T_g)}{51.6+(T-T_g)} = \log\frac{\tau(T)}{\tau(T_g)}$

Nearly equal to 1 $\rightarrow$ $\frac{B}{2.303\, f_g} = 17.44$ $\quad \frac{f_g}{\alpha_f} = 51.6$ $\longrightarrow$

$$f_g = 0.025 = 2.5\%$$

$$\alpha_f = 4.8\times10^{-4}/K$$

Appendix: Doolittle equation & Einstein equation

Doolittle equation

In glass or melt $\eta = A\exp\left(BV_0/V_f\right)$ $V_f \ll V_0$

In solution $V_f \gg V_0$

and the volume fraction of suspensions

$$\Phi = V_0/\left(V_f + V_0\right) \approx V_0/V_f$$

$$e^x \approx 1 + x$$

$$\eta = A\exp\left(BV_0/V_f\right) \approx A\left(1 + BV_0/V_f\right) = A\left(1 + B\Phi\right)$$

Einstein equation

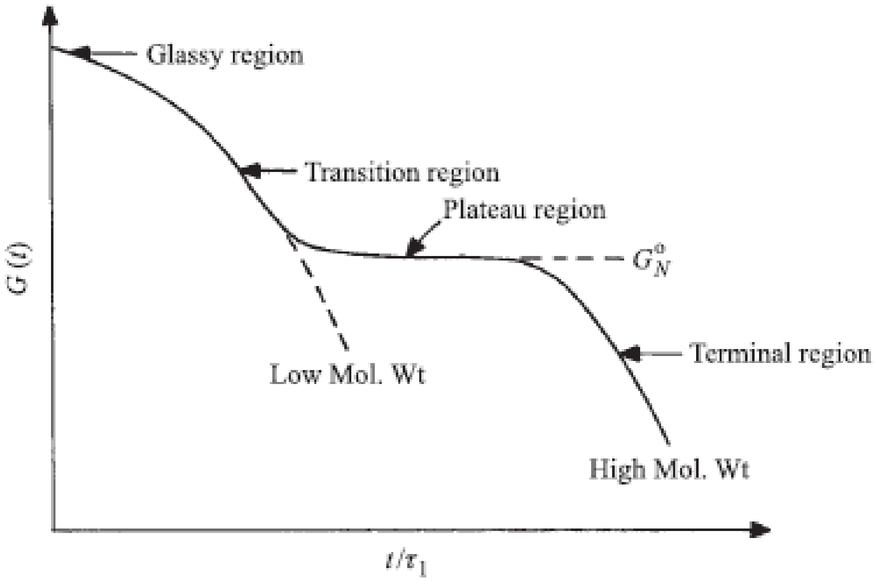
For the solution of impenetrable spheres of radius ***R*****,** Einstein derived the Effective viscosity of suspensions

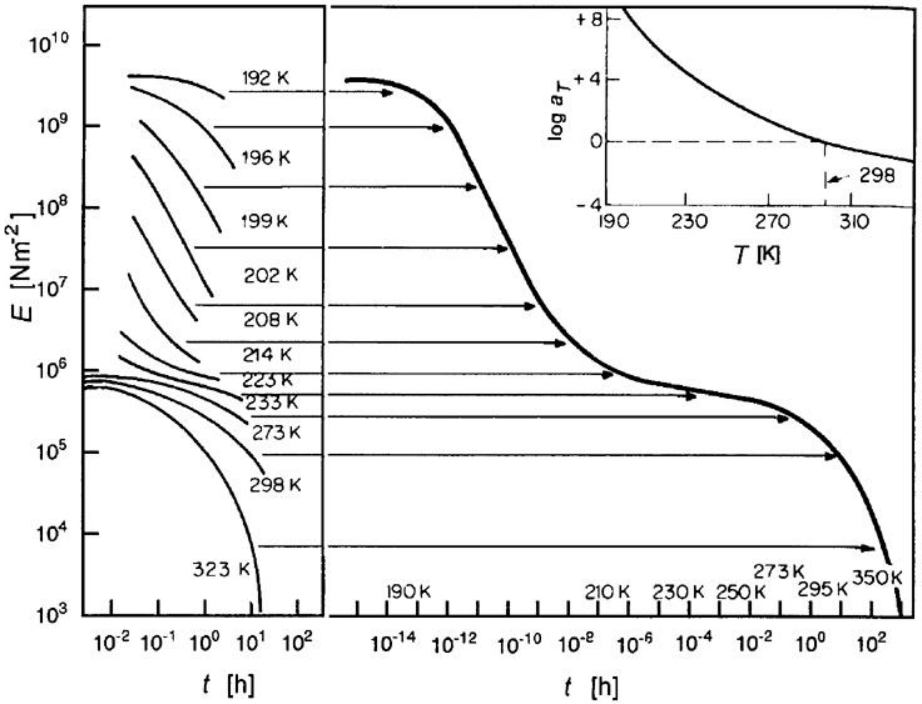
$$\eta = \eta_0\left(1 + 2.5\Phi\right)$$

Applications of WLF Eq.

$$\tau \propto \eta$$

$$\lg \frac{\tau}{\tau_s} = \lg a_T = \frac{-C_1\left(T - T_s\right)}{C_2 + \left(T - T_s\right)}$$



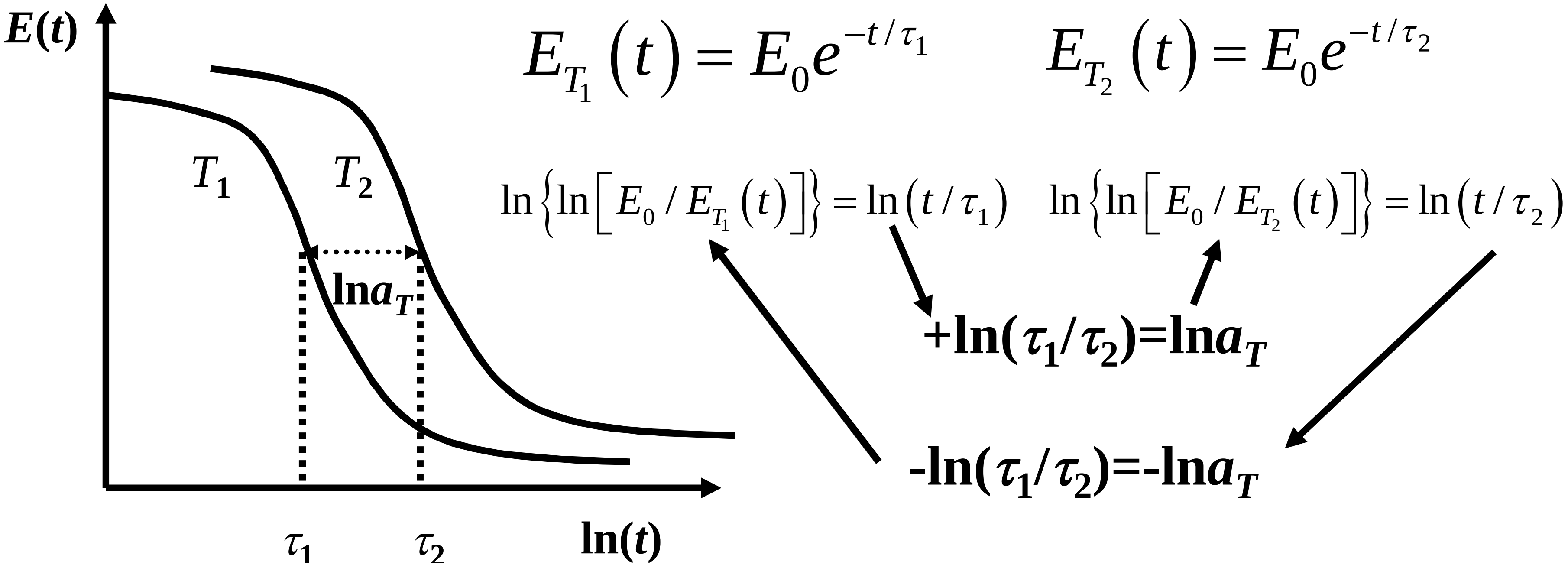


Two principles for linear viscoelasticity

(1) Time-Temperature Equivalence and Superposition

➢**Time-temperature equivalence (时温等效) in its simplest form implies that the viscoelastic behavior at one temperature can be related to that at another temperature by a change in the time-scale only.**

$$\tau = \tau_0 e^{\Delta E / RT}$$



$$E_{T_1}(t) = E_0 e^{-t/\tau_1} \qquad E_{T_2}(t) = E_0 e^{-t/\tau_2}$$

$$\ln\left\{\ln\left[E_0 / E_{T_1}(t)\right]\right\} = \ln\left(t/\tau_1\right) \qquad \ln\left\{\ln\left[E_0 / E_{T_2}(t)\right]\right\} = \ln\left(t/\tau_2\right)$$

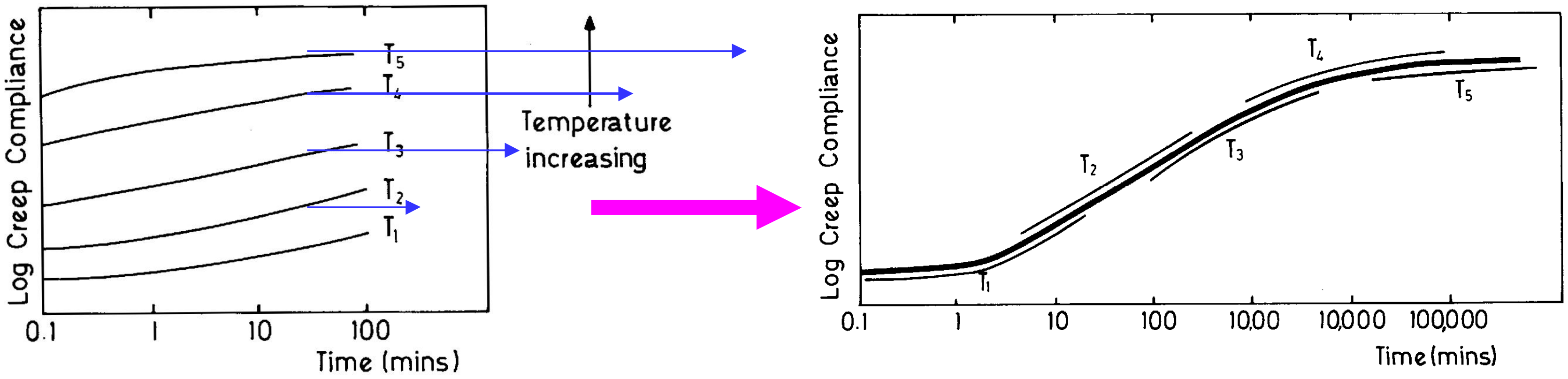
$$\mathbf{+\ln(\tau_1/\tau_2) = \ln a_T}$$

$$\mathbf{-\ln(\tau_1/\tau_2) = -\ln a_T}$$

$T_1 \quad T_2 \quad T_3 \quad \ldots..$

$\tau_1 \quad \tau_2 \quad \tau_3 \quad \ldots..$

Synthesized master-curve (叠合曲线)

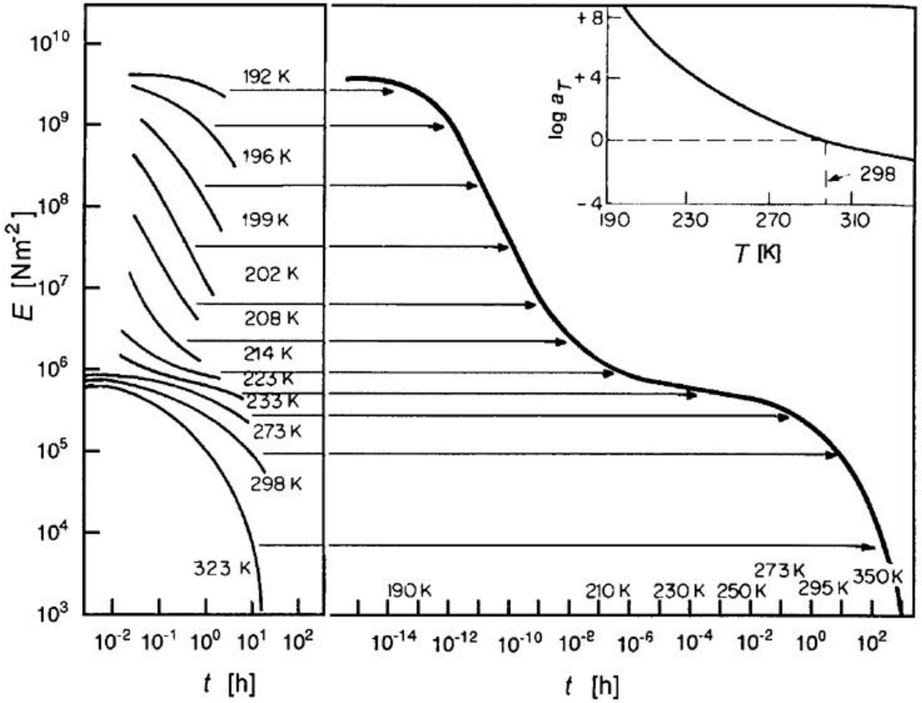


Superpose

Schematic creep plots at different temperatures

Master curve of creep from superposing plots of the left figure

Synthesized master-curve

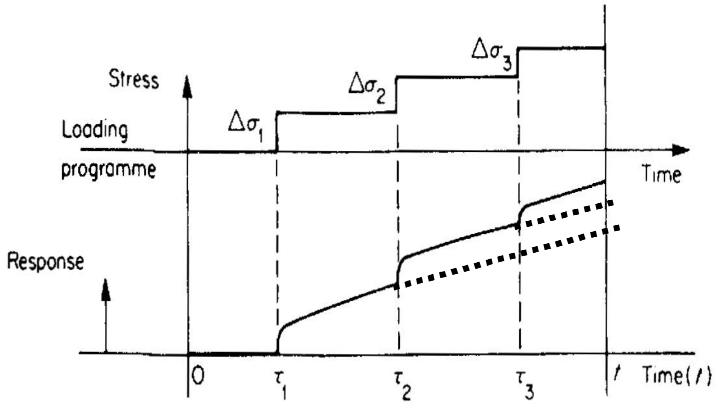


$$\lg \frac{\tau}{\tau_s} = \lg a_T = \frac{-C_1\left(T - T_s\right)}{C_2 + \left(T - T_s\right)}$$

- **In both the glass-transition range and terminal flow region, the modes of motions vary greatly in their spatial extensions, which begin with the length of a Kuhn segment and go up to the size of the whole chain, and vary also in character, as they include intramolecular motions and diffusive movements of the whole chain. Nevertheless, all modes behave uniformly.**

(2) The Boltzmann Superposition Principle

- **The Boltzmann superposition principle (叠加原理)**
- **In 1876, Boltzmann proposed:**
  1. **The creep is a function of the entire past loading history of the specimen;**
  2. **Each loading step makes an independent contribution to the final deformation, so that the total deformation can be obtained by the addition of all the contribution.**
- **Creep**



$$\varepsilon(t)=\Delta\sigma_1 J(t-\tau_1)+\Delta\sigma_2 J(t-\tau_2)+\Delta\sigma_3 J(t-\tau_3)+\dots$$

$$\varepsilon(t)=\int_{-\infty}^{t} J(t-\tau)d\sigma(t) \quad \varepsilon(t)=\int_{-\infty}^{t} J(t-\tau)\frac{\partial\sigma(\tau)}{\partial\tau}d\tau$$

- **Stress relaxation** $\sigma(t)=\Delta\varepsilon_1 G(t-\tau_1)+\Delta\varepsilon_2 G(t-\tau_2)+\Delta\varepsilon_3 G(t-\tau_3)+\dots$ $\quad \sigma(t)=\int_{-\infty}^{t} G(t-\tau)\frac{\partial\varepsilon(\tau)}{\partial\tau}d\tau$

In steady shear:

$$t-\tau\equiv s$$

$$-d\tau = ds$$

$$\sigma(t)=\frac{d\varepsilon}{d\tau}\int_0^\infty G(s)ds$$

$$\boxed{\eta=\int_0^\infty G(s)\,ds}$$

Viscosity & Relaxation Modulus

$$E_i(t) = E_i e^{-t/\tau_i} \qquad \eta_i = \tau_i E_i$$

$$E(t) = \sum_i E_i e^{-t/\tau_i}$$

$$\int_0^\infty E_i(t)dt = \int_0^\infty E_i e^{-t/\tau_i} dt = E_i \int_0^\infty e^{-t/\tau_i} dt = E_i \tau_i = \eta_i$$

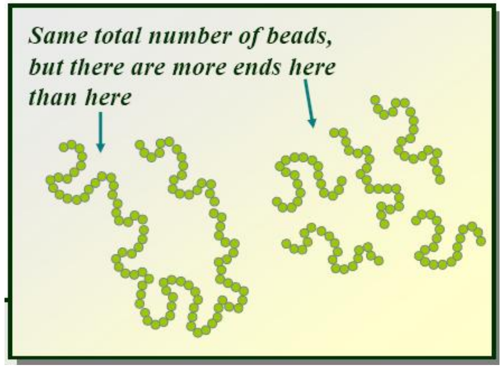
$$\eta = \sum_i \eta_i = \sum_i \int_0^\infty E_i(t)\, dt = \int_0^\infty \sum_i E_i(t)\, dt = \int_0^\infty E(t)\, dt$$

$$\boxed{\eta(T) = \int_0^\infty E(T,t)\, dt}$$

影响玻璃化温度的几个物理因素

- **Molecular weight dependence T_g vs. M_n**

Fox equation: $T_g = T_g(\infty) - \dfrac{K}{M_n}$



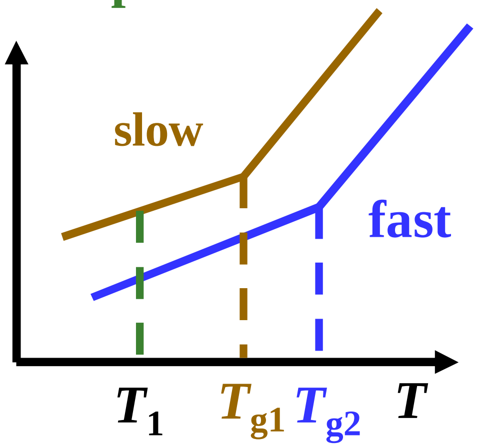
- **Heating rate dependence**

$\tau = \tau_0 e^{\Delta E/RT}$

$t \sim 1/v$ $t_s > t_f$

v 升温速度

t 停留时间



T_1	$t_s \ll \tau_1$	$t_f \lll \tau_1$
T_{g1}	$t_s \sim \tau_{g1}$	$t_f < \tau_{g1}$
T_{g2}		$t_f \sim \tau_{g2}$

- **T_m vs. T_g**

For symmetrical backbone, $T_g / T_m \approx 1/2$

For asymmetrical backbone, $T_g / T_m \approx 2/3$

$$T_m = \left| \frac{\Delta H_m}{\Delta S_m} \right|$$

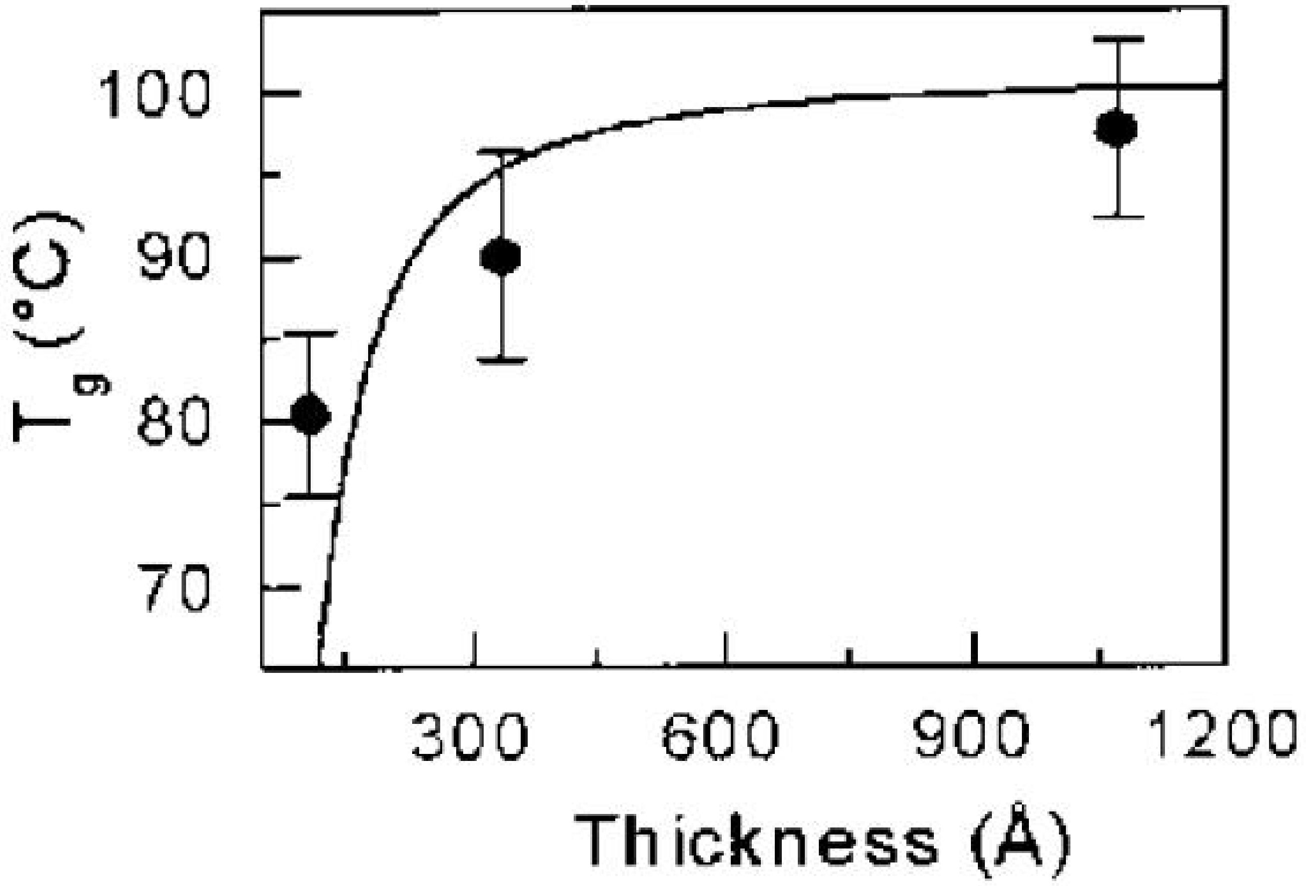
- **T_g vs. T_b**

$T_g - T_b \approx 0$ 高度柔性和刚性链

$T_g - T_b \neq 0$ 中度刚性链 强迫高弹形变

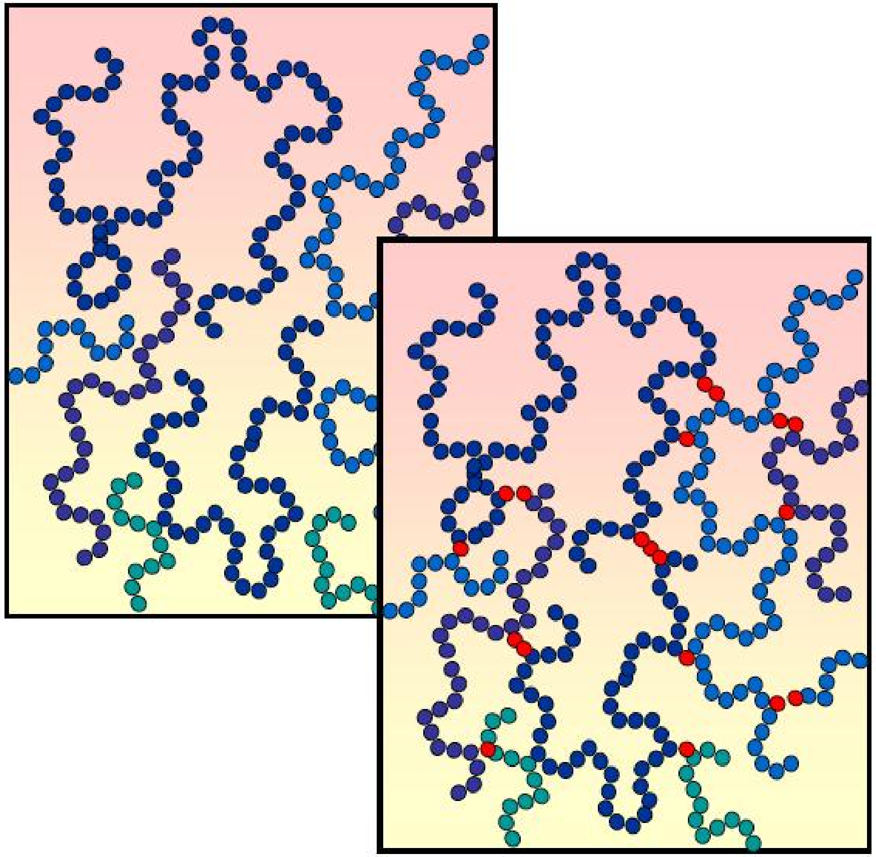
- **Chain rigidity:** **More rigid chain present higher T_g**

Effects of film thickness on *Tg*

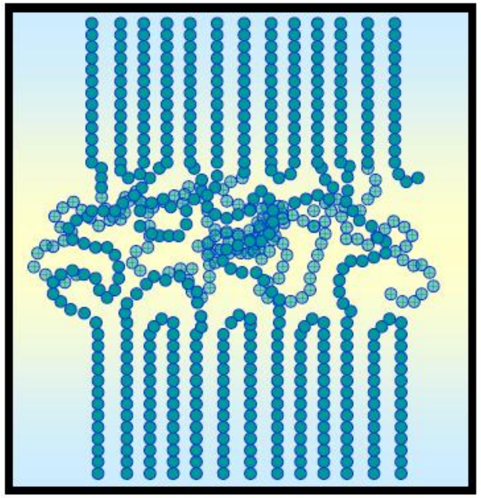


Tsui, OKC, Macromolecules, 34, 5535 (2001)

The Effect of Cross - Linking

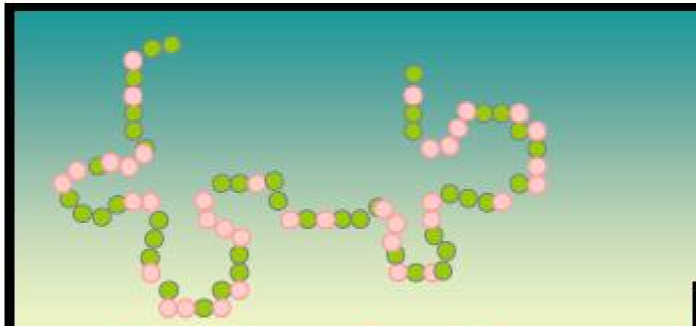


The Effect of Crystallization

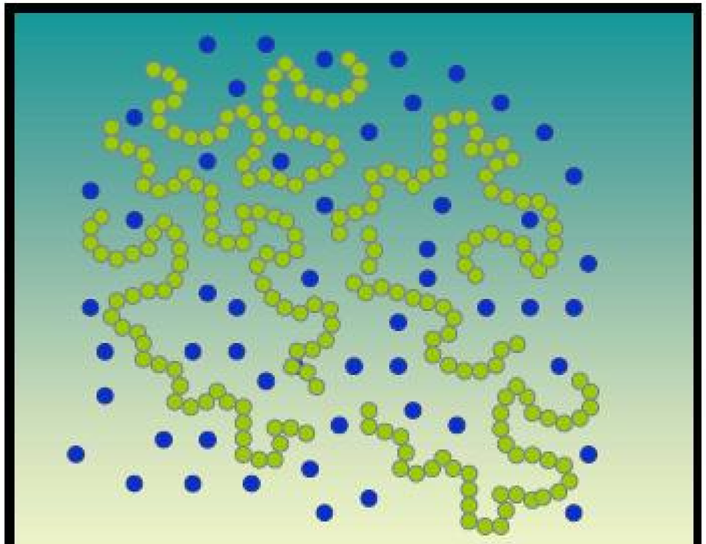


Glass transition of polymer mixtures

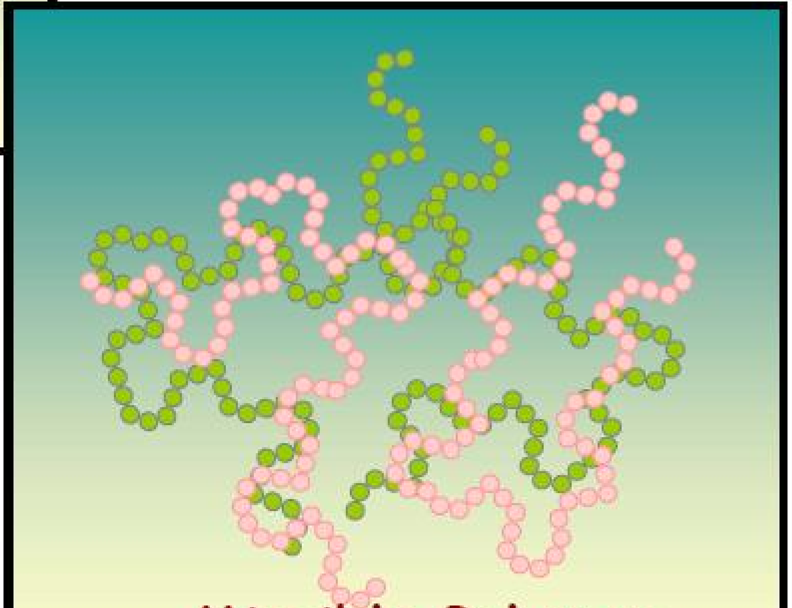
$$\frac{1}{Tg} = \frac{W_1}{Tg_1} + \frac{W_2}{Tg_2}$$



Random Copolymer



Polymer + Solvent or Plasticizer



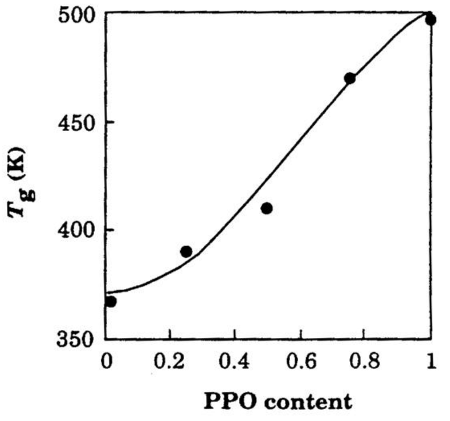
Miscible Polymer Blend

Glass transition of polymer mixtures

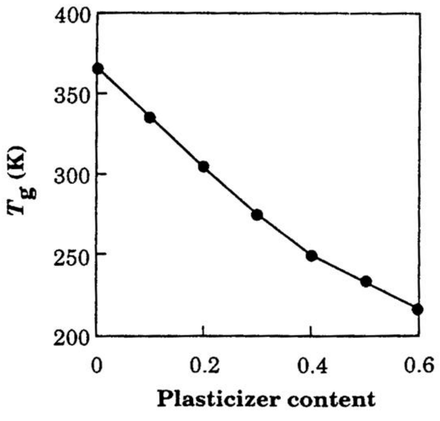
Some polymer blends exhibit partial miscibility. They have a mutual, limited solubility indicated by a shift in the two T_g's accompanying a change in the phase composition of the blend. More uncommon is the type of miscibility indicated by the presence of only single T_g.

- **Miscible blend**
- **Partial miscible blend**

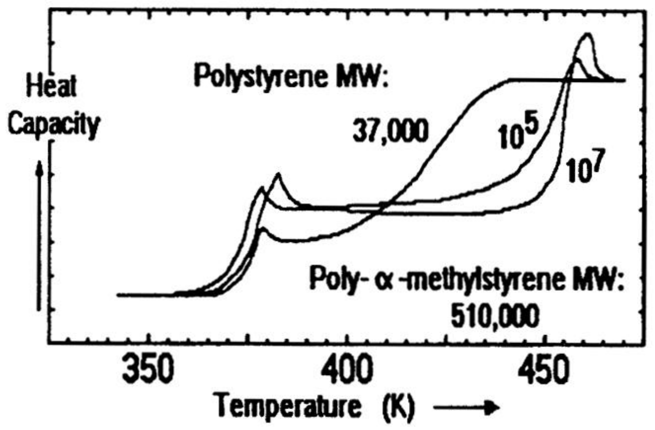
- **Fox-Flory equation:** $$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$



T_g of compatible blend PPO and PS as a function of PPO content. (Bair, H. E. *Polym. Eng. Sci.* **1970**, *10*, 247.)

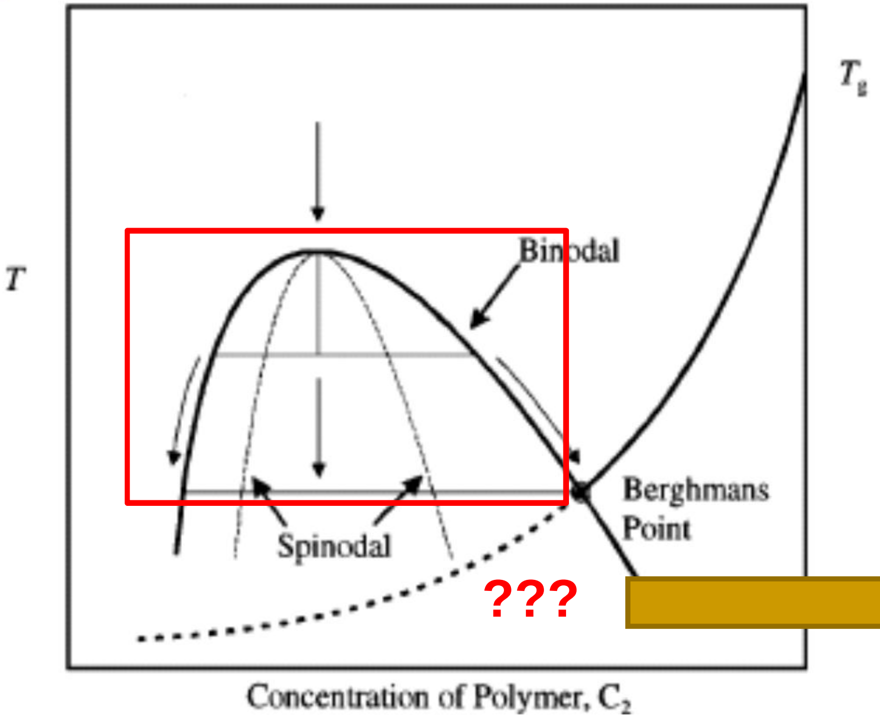


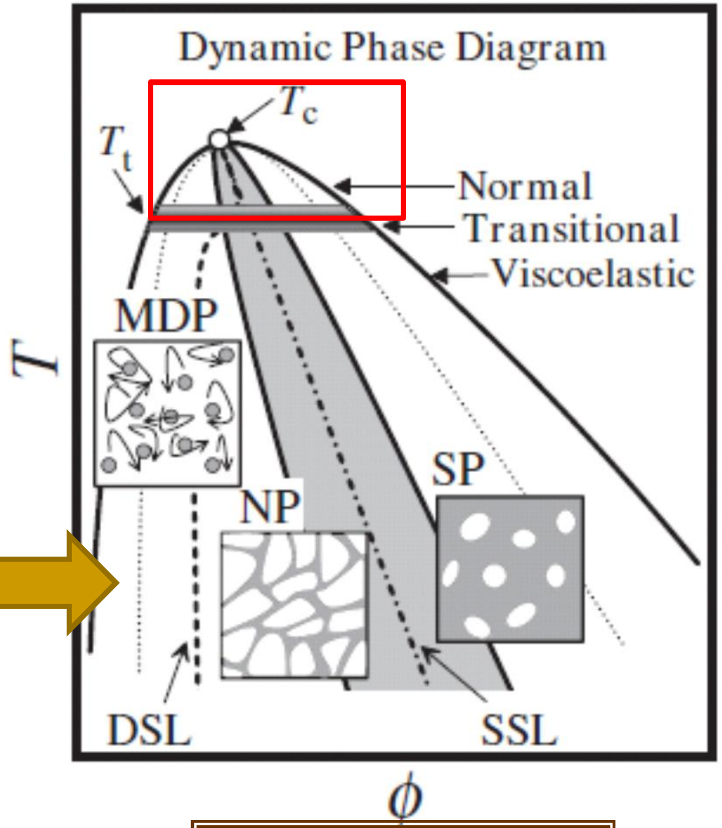
Plasticization of PVC: T_g as function of di(ethylhexyl)-phthalate content. (Wolf, D. *Kunststoffe* **1951**, *41*, 89.)

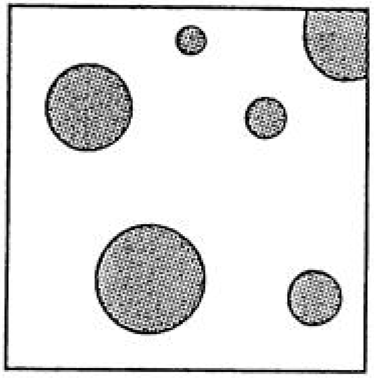


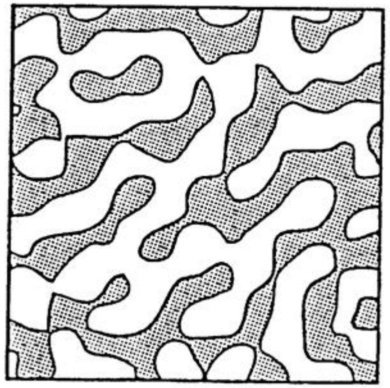
DSC curves of 50 mass-% blends of PS and poly(α-methyl styrene) at a heating rate of 10 K/min. (Lau, S. F.; etc. *Macromolecules* **1982**, *15*, 1278.)

Effects of *Tg* on Morphology of Polymer Blends









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- Cheng SZD, Keller A, ***Ann Rev Mater Sci***, **28**, 533 (1998)

Tanaka H, ***J Phys Condens Matter***, **12**, R207 (2000)