Chapt. 6 Molecular Motions and Transitions of State in Polymers

6.1 Molecular motions of polymers

特点,基本类型

6.2 Glass transition of polymers

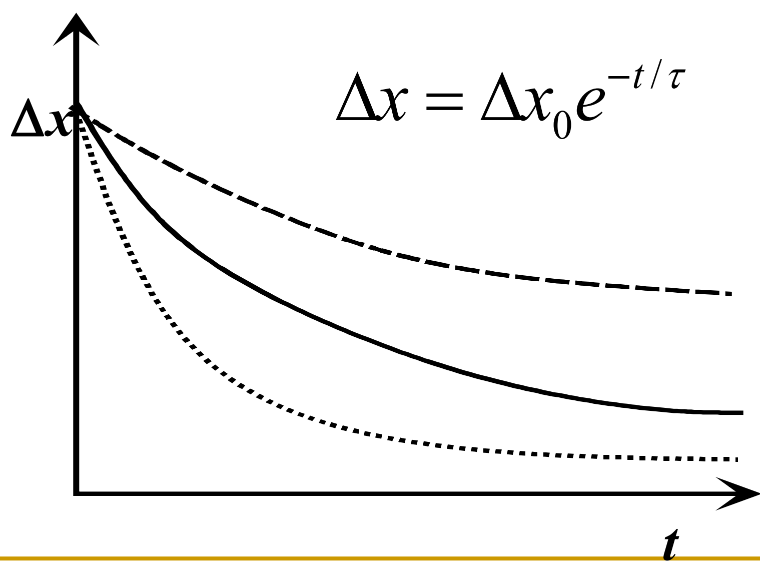
意义,表征,理论

6.3 Viscous flow of polymers

特点,表征,影响因素

6.1 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



$$\Delta x = \Delta x_0 e^{-t/\tau}$$

τ: relaxation time

(1) 与运动单元有关

(2) 与温度有关

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

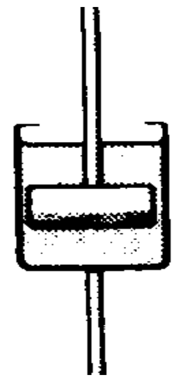
b. WLF 方程

(3) 与观察时的时间标尺有关

Viscoelasticity 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

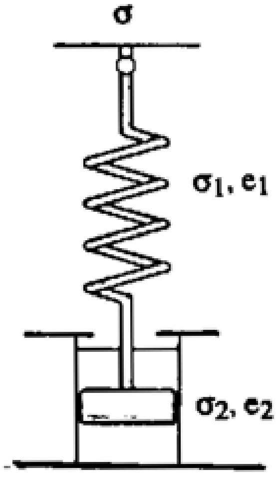


Dashpot as a model:
Viscosity (粘度): η

- Hooke's law: $\sigma = E\varepsilon$
- Newton's law: $\sigma = \eta(\mathrm{d}\varepsilon/\mathrm{d}t)$

σ: stress (应力); ε: strain (应变)

Elasticity + Viscosity = Viscoelasticity ?



Maxwell Model

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

$$\sigma = \sigma_1 = \sigma_2$$

$$\left.\begin{aligned} \frac{d\varepsilon_1}{dt} &= \frac{1}{E_m}\frac{d\sigma}{dt} \\ \frac{d\varepsilon_2}{dt} &= \frac{\sigma}{\eta_m} \end{aligned}\right\}$$

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

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

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

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

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

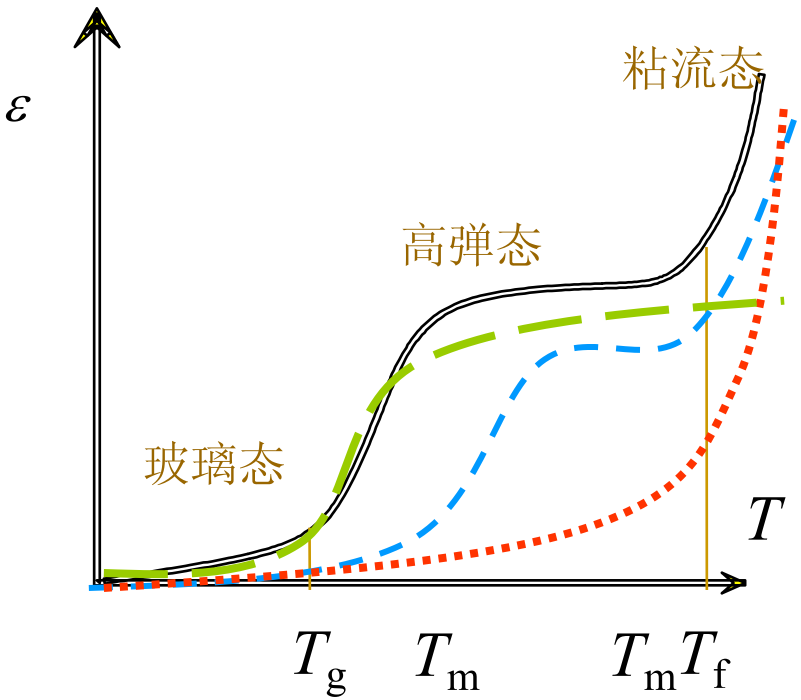
Relaxation time: $\tau = \eta_m/E_m$:

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

粘弹性-力学松弛行为

粘弹性的微观起源-聚合物受到外力作用时，大分子链通过逐渐调整其构象来抵销一部分外力作用；由于聚合物粘度很高，链段运动不可避免受到摩擦和其他阻力，调整构象需一定的时间—故表现出：力学性能随时间而演化发展

2. 力学状态与热转变

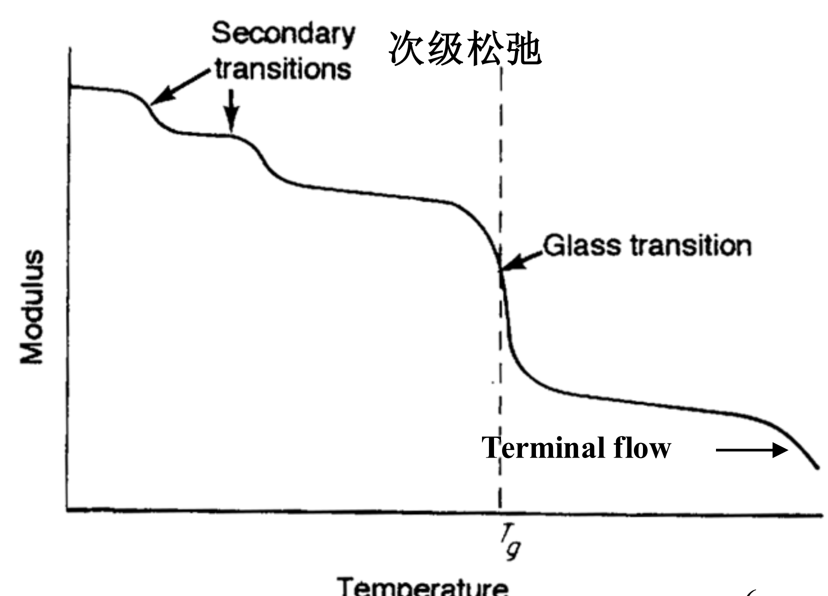


Linear and Cross-link

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



6.2高聚物的玻璃化转变

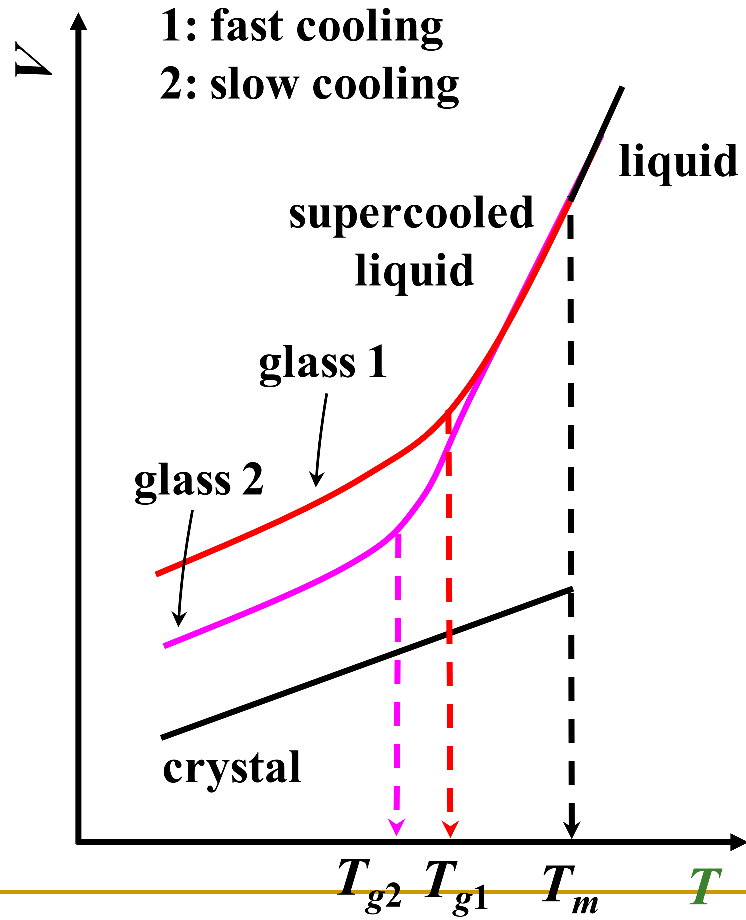
- 1. 定义
- 某些液体在温度迅速下降形成过冷液态(玻璃态)而不发生结晶
- 高聚物从玻璃态(橡胶态)转变为橡胶态(玻璃态)的行为
- 微观：链段运动的解冻或冻结过程
- 主松弛(玻璃化转变-链段)和微松弛(次级松弛-基团)

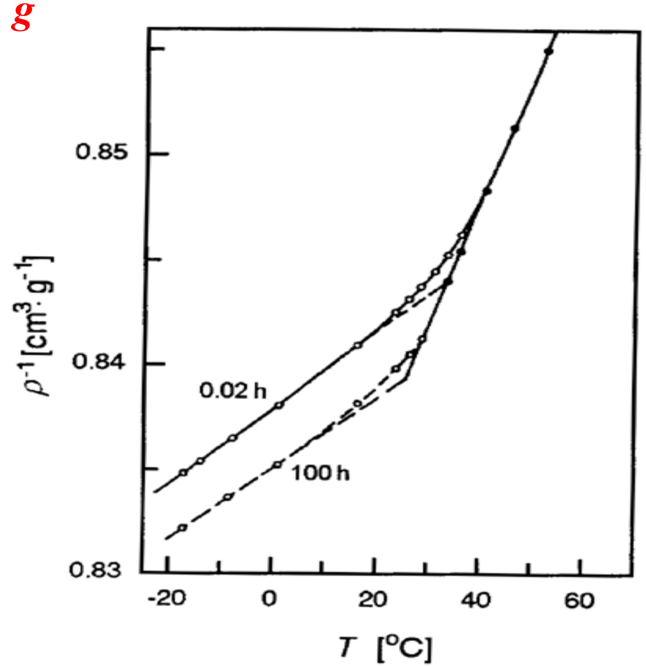
- 2. 工艺意义
- 橡胶的使用下限
- 塑料的使用上限

- 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

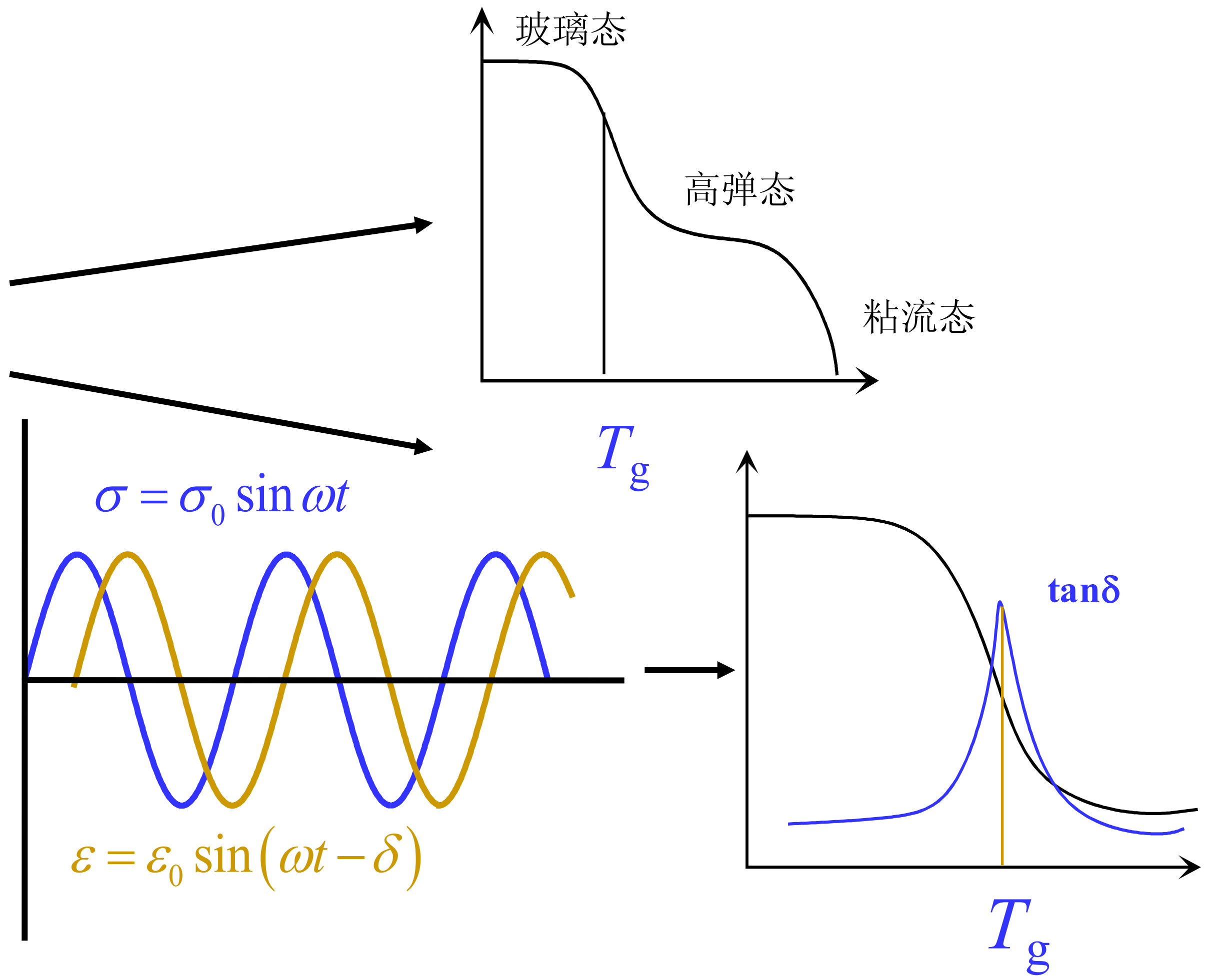




Temperature dependence of the specific volume of PVA, measured during heating. Dilatometric (膨胀计法) results obtained after a quench to –20 °C, followed by 0.02 or 100 h of storage. (Kovacs, A. J. *Fortschr. Hochpolym. Forsch.* **1966**, *3*, 394)

4. 现象和实验表征

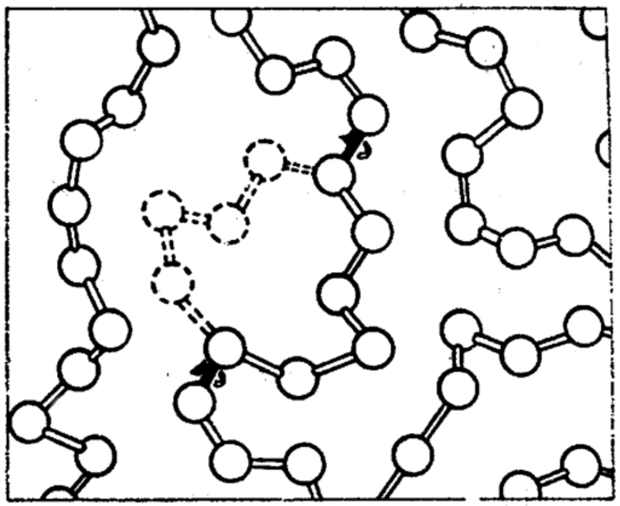
- (1) 体积变化性质
- (2) 热力学性质
- (3) 力学性质
- a. 静态力学
- b. 动态力学



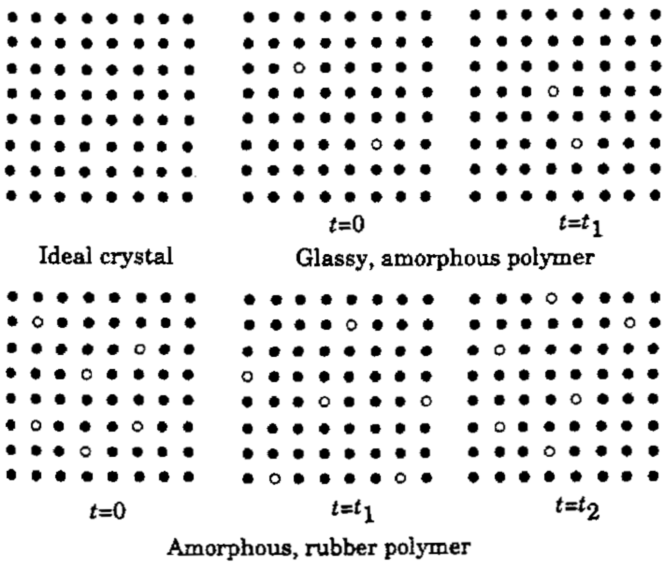
- (4) 光、电、磁性质

5. 理论 - Free Volume Theory

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



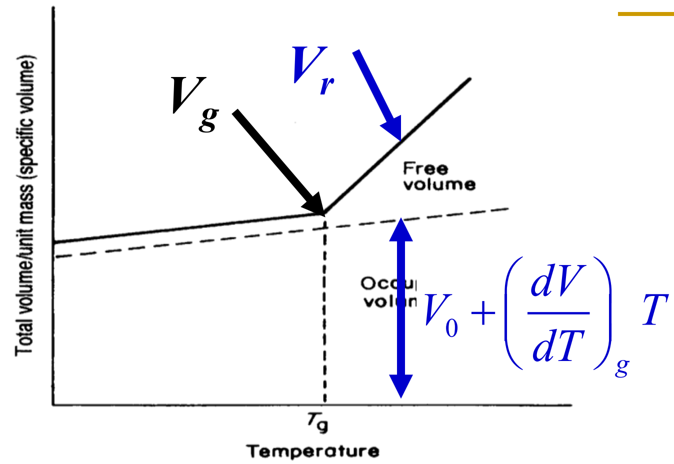
The segmental motion of polymer chain requires more volume



Occupied volume: filled circles; free volume:hole

- **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 volume-temperature relationship for a typical amorphous polymer

- 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

V_f: free volume at $T < T_g$

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

V_t: 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

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

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

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

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

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

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

$$f_T = f_g + \alpha_f (T - T_g) \quad (T \geq T_g)$$

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:** $f_T = \dfrac{V_f(T)}{V_0(T)+V_f(T)} \approx \dfrac{V_f(T)}{V_0(T)}$

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

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

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

$$f_g = 0.025 = 2.5\%$$

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

Appendix: Doolittle equation & Einstein equation

Doolittle equation

$$\eta = A\exp\left(BV_0 / V_f\right)$$

In solution $V_f \gg V_0$ $\quad e^x \approx 1 + x$ and the volume fraction of suspensions $\Phi = V_0 / V_f$

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

Einstein equation

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

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

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影响玻璃化温度的几个因素

- **Chain rigidity:**

  More rigid chain present higher T_g

- **Molecular weight dependence**

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

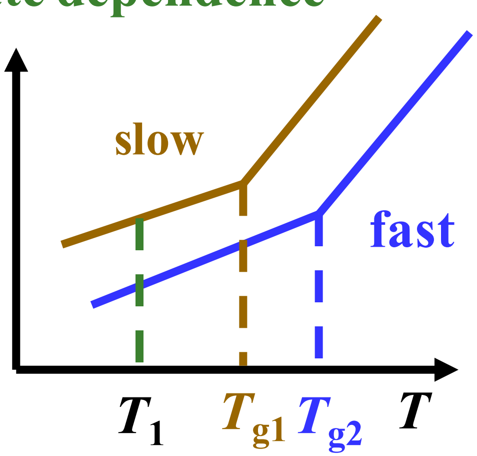
- **Heating rate dependence**

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

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

v 升温速度

t 停留时间



T_1 $\quad t_s \ll \tau_1 \quad t_f \lll \tau_1$

T_{g1} $\quad t_s \sim \tau_{g1} \quad t_f < \tau_{g1}$

T_{g2} $\quad t_f \sim \tau_{g2}$

- **T_m vs. T_g**

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

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

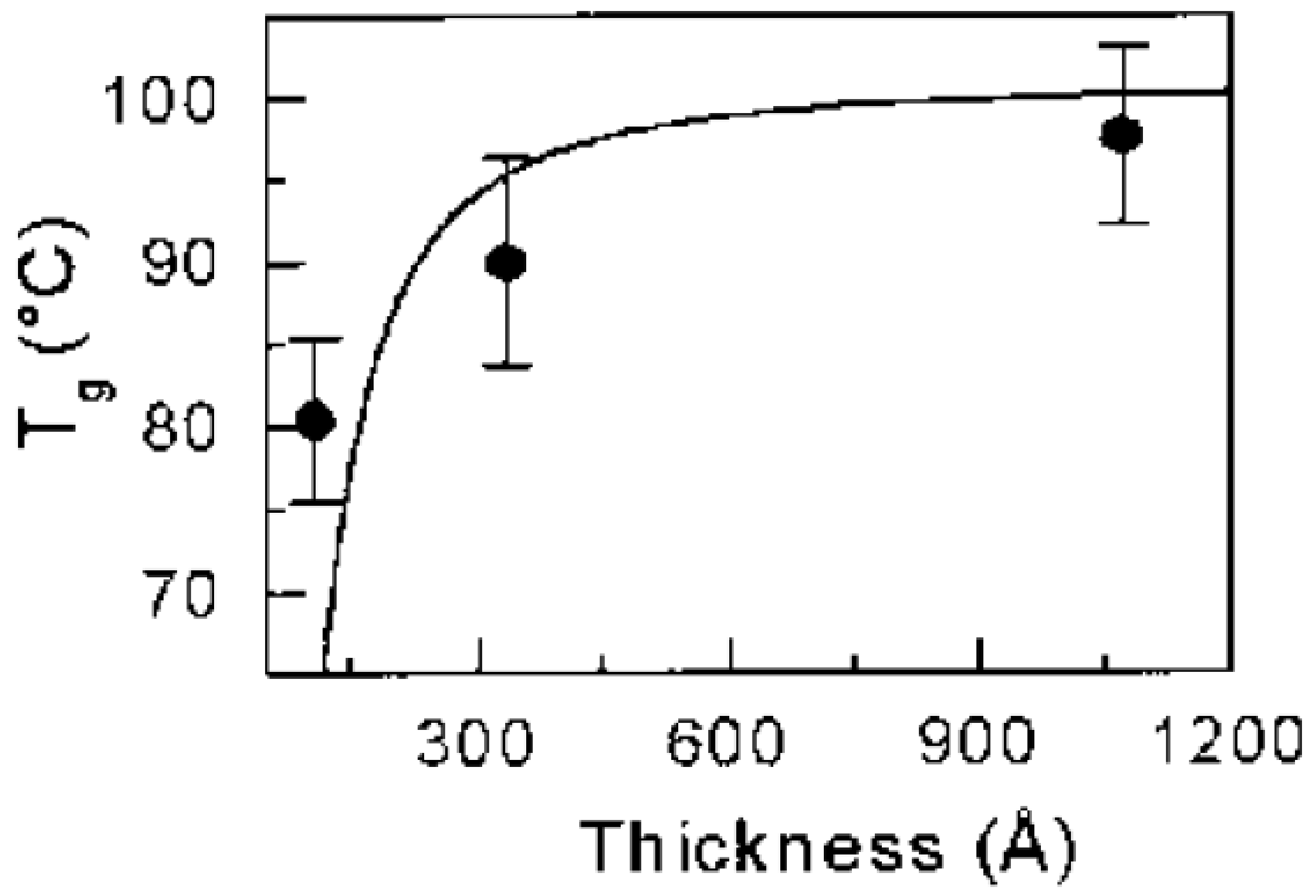
$$T_m = \left| \frac{\Delta H_m}{\Delta S_m} \right|$$

- **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

Effects of film thickness on *Tg*



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

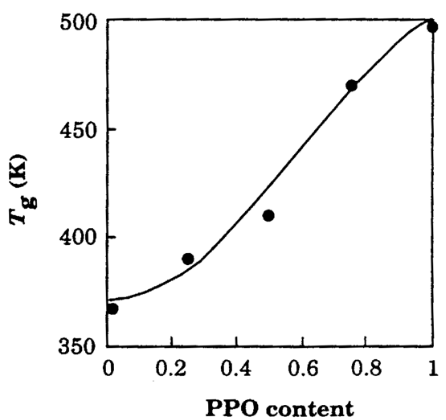
Glass transition of polymer mixtures

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.

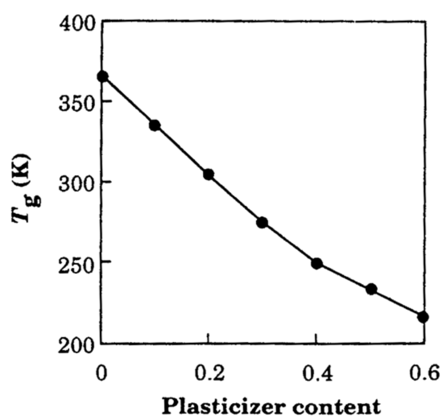
➢ Miscible blend

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

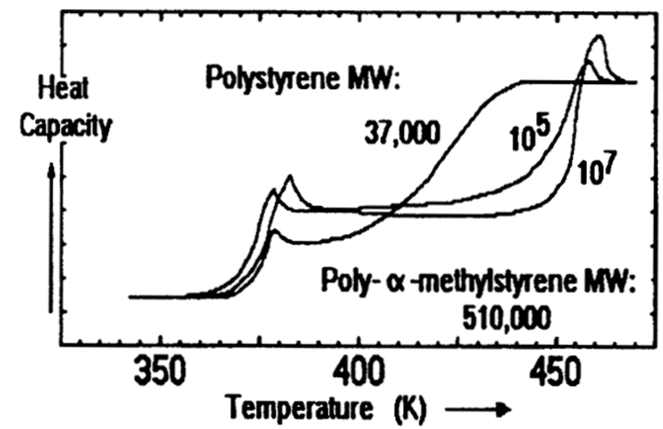
➢ Partial miscible blend



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

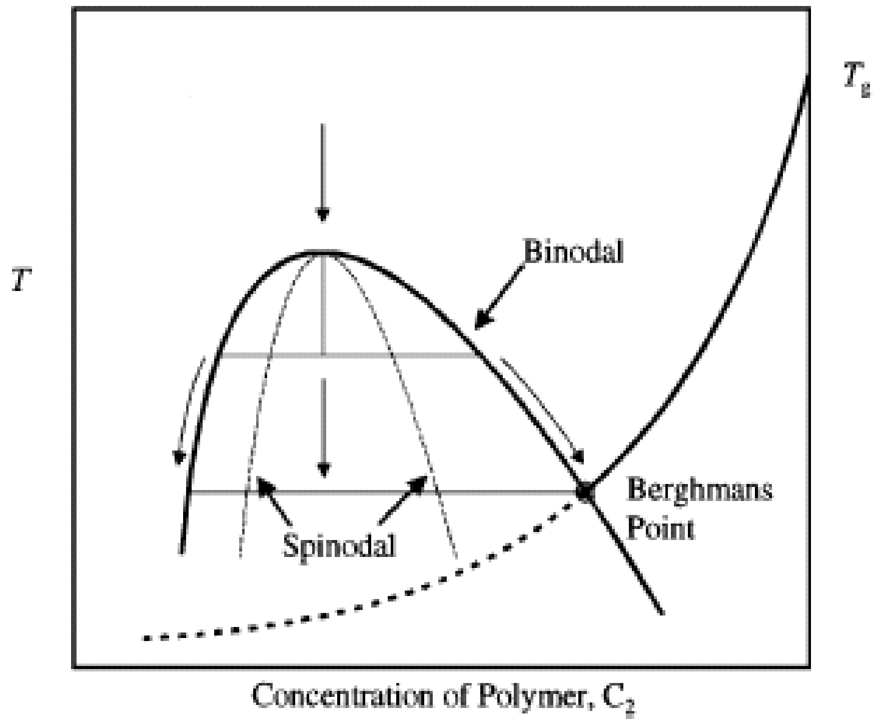


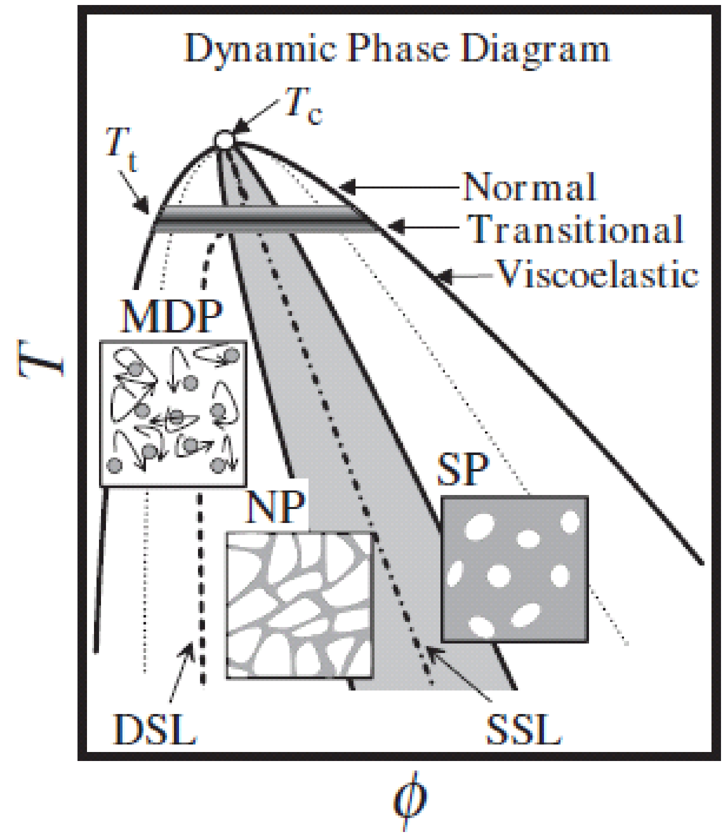
Plasticization of PVC: T_g as function of di(ethylhexyl)-phthalate content. (Wolf, D. *Kunststoffe* **1951**, *41*, 89.)



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





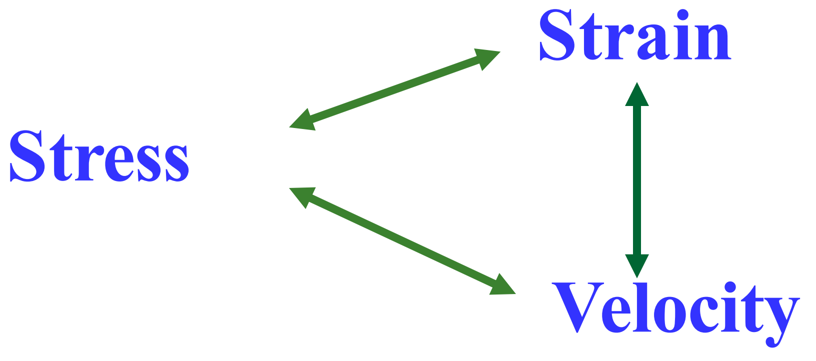
- Cheng SZD, Keller A, ***Ann Rev Mater Sci***, **28**, 533 (1998)

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

6.3 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.



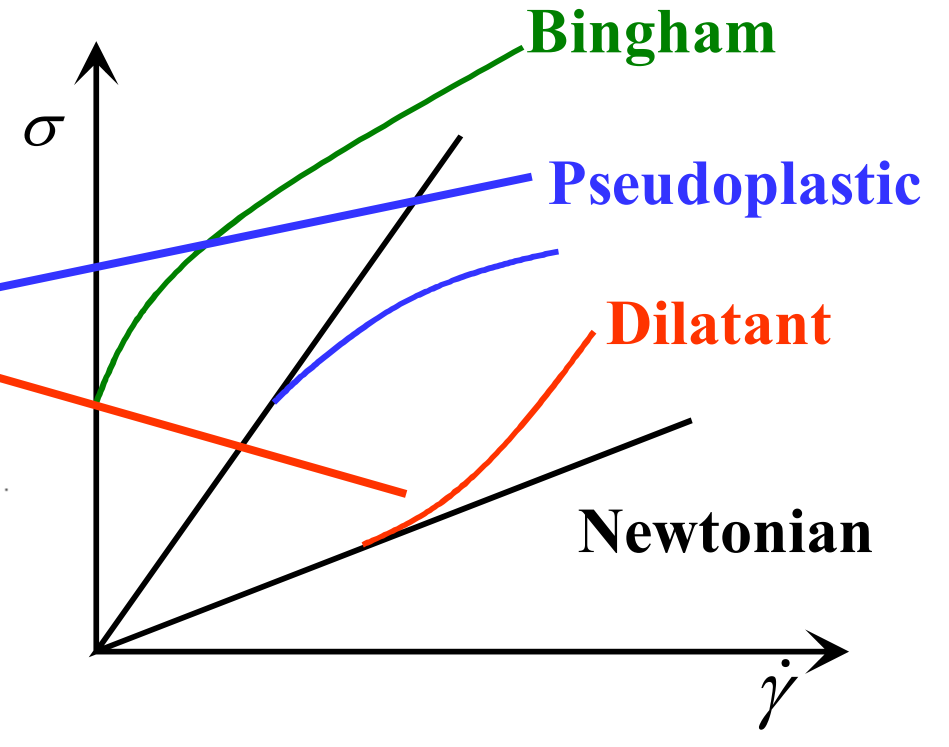
Characteristic of polymer viscous flow

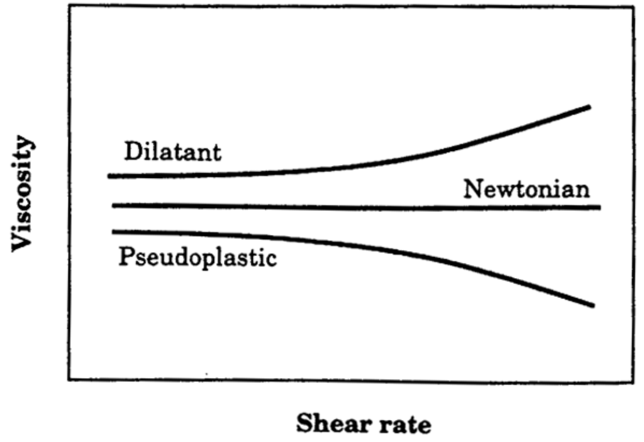
1. 链段的蠕动实现整个分子的迁移

2. 不符合牛顿流体的流动规律

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

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

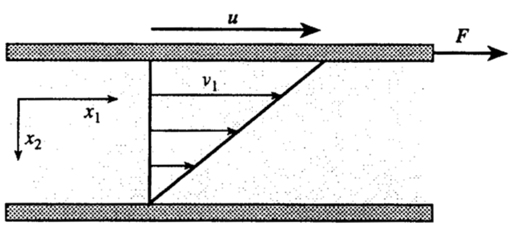


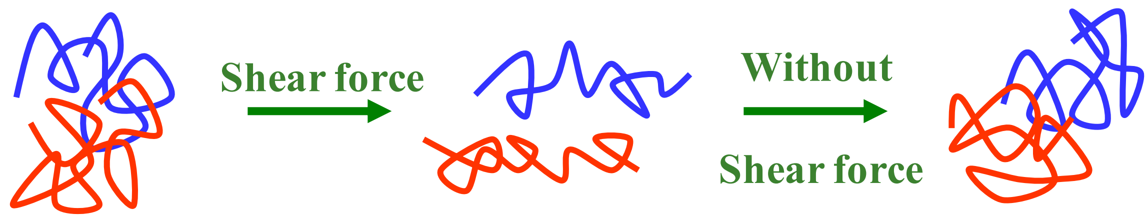


Characteristic of polymer viscous flow

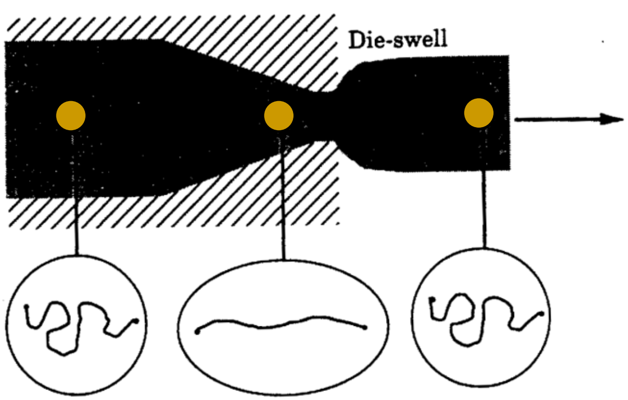
3. 流动时伴有高弹形变

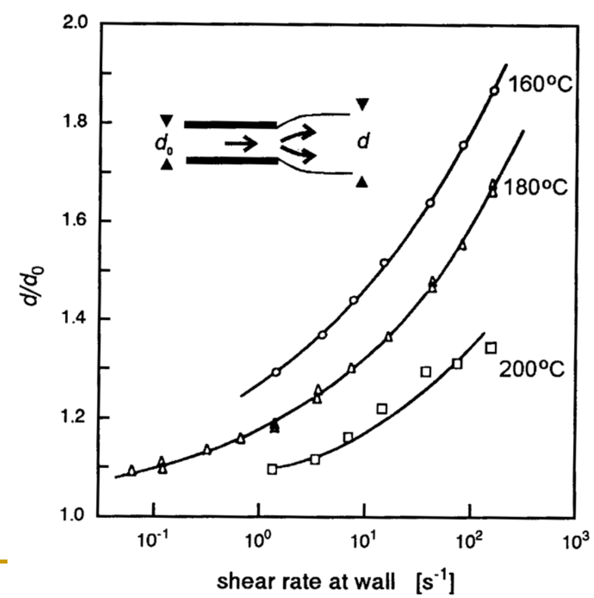
➢ Consider a steady simple shear flow





➢ Die-swell (出口长大)



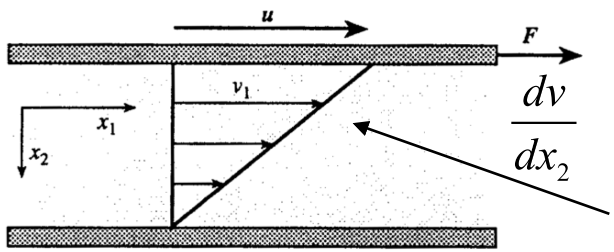


Extrudate swell observed for a melt of PS for various shear rates and temperatures. (Burke, J. J.; etc. *Characterization of Materials in Research*, Syracuse Univ. Press, 1975.)

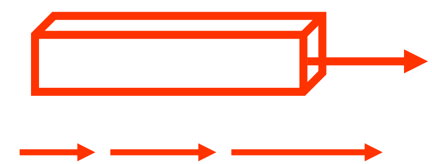
Characterization of viscous flow

三种最基本的流动(变形)方式

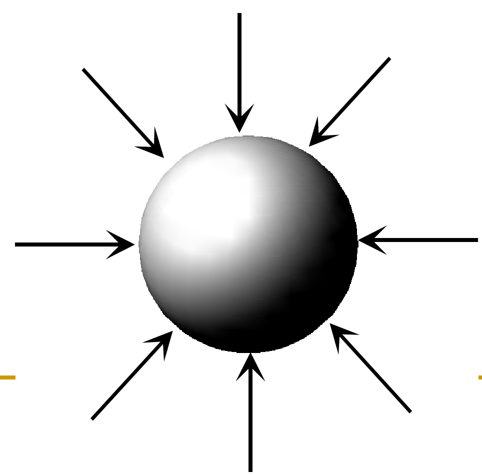
a.剪切流动(形变)-shear viscosity η_s b.拉伸流动(形变)-tensile viscosity η_t



velocity gradient



c. 压缩流动(形变)-bulk viscosity



for incompresible fluids

$\eta_b \to \infty$

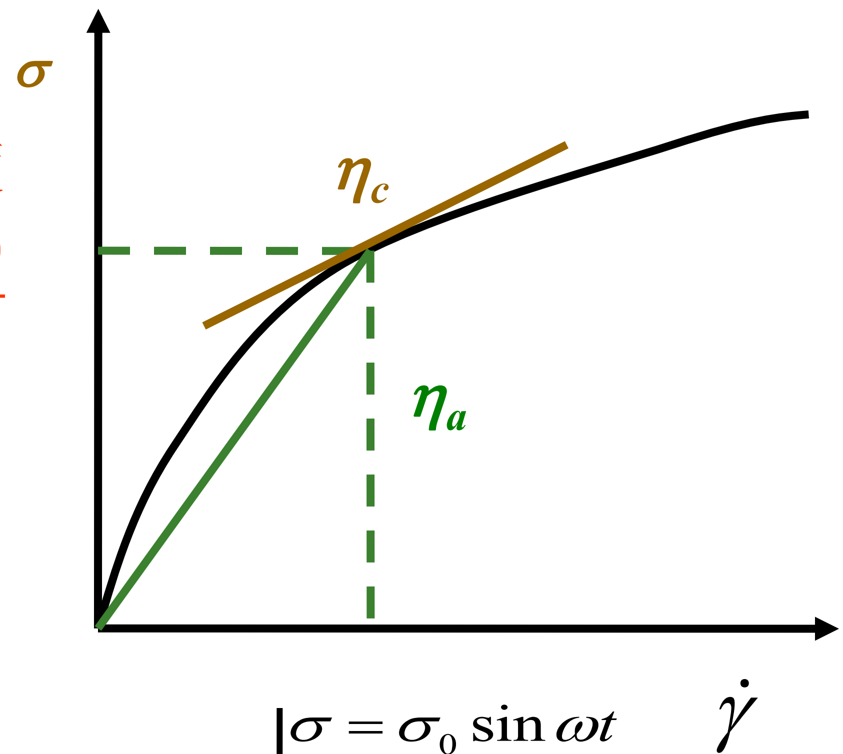
Melt viscosities of polymers

shear viscosity剪切粘度和

extensional viscosity拉伸粘度

$$\eta_s = \frac{\sigma_s(\dot{\gamma})}{\dot{\gamma}} = \sigma_s / \left(\frac{dv}{dh}\right) \qquad \eta_t = \frac{\sigma_t(\dot{\varepsilon})}{\dot{\varepsilon}}$$

1-D **2-D**



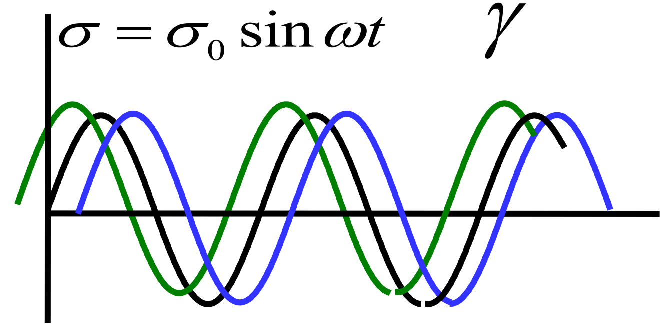
- apparent viscosity表观粘度

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

- 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)



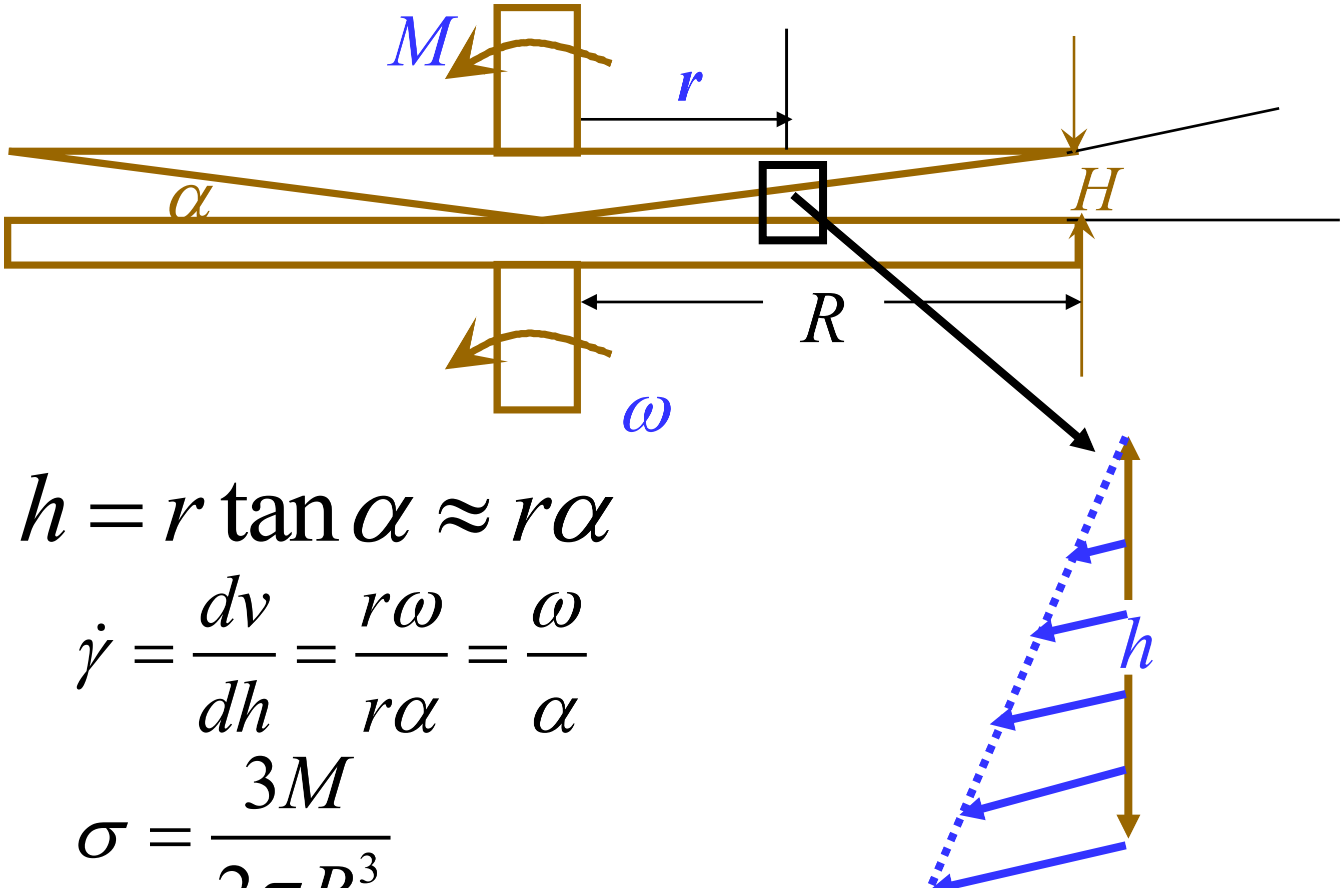
$$\eta^* = \eta' - i\eta''$$

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

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

Measurement of shear viscosity

Cone-plate viscometer - an example



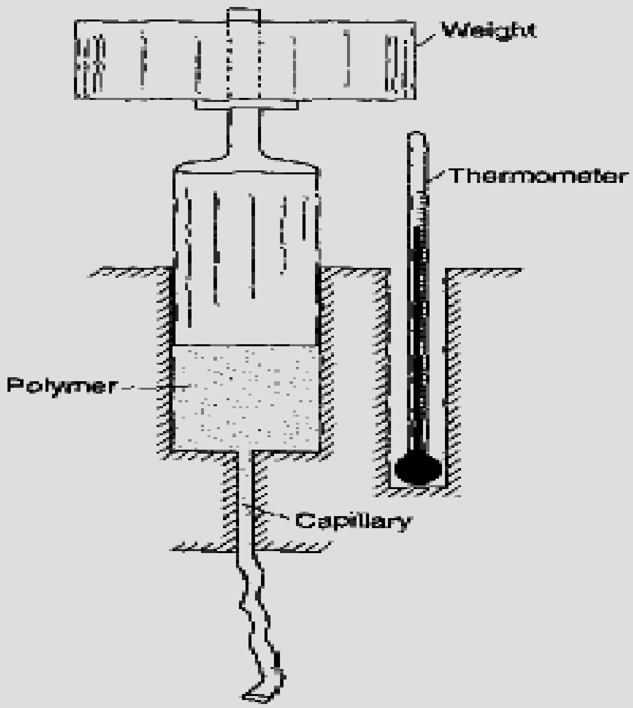
$$h = r\tan\alpha \approx r\alpha$$

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

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

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

Melt flow index (MFI)



ASTM D1238

DIN 53735

Corresponds to simplyfied capillary viscometer (see practical course)

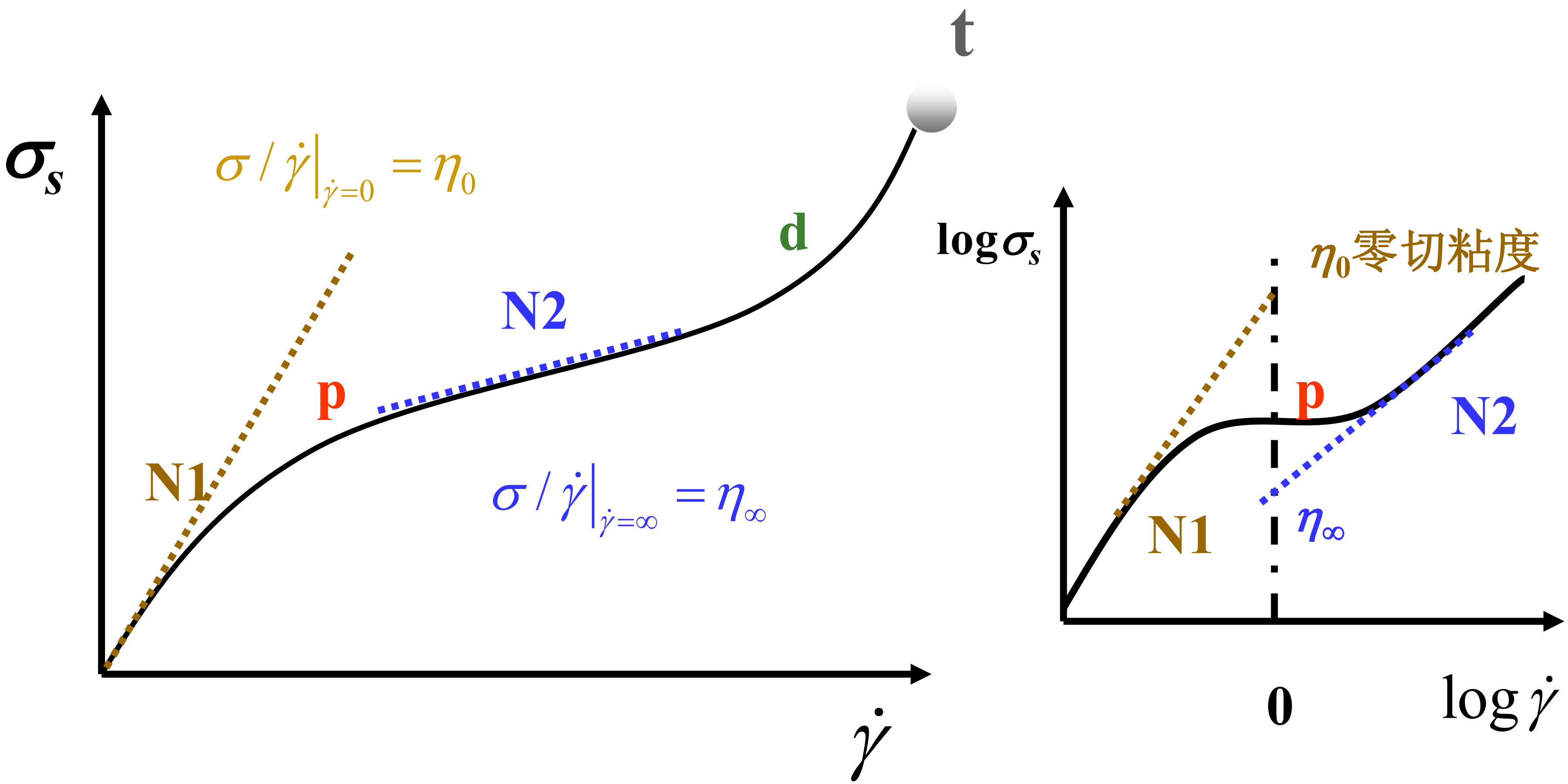
Fig.4.12. Schematic diagram of an extrusion plastometer used to measure melt flow index.

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

The flow curve of polymer melts



turbulence

orientation

disentanglement

entanglement

η_0 dependent of M

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

Exp.

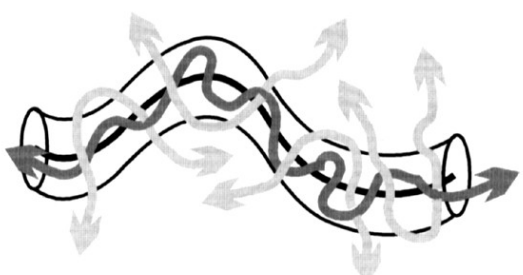
$\eta_0 \sim M_W^1 \quad (M < M_c)$

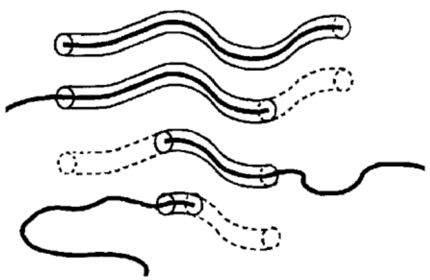
$\eta_0 \sim M_W^{3.3\sim3.4} \quad (M > M_c)$

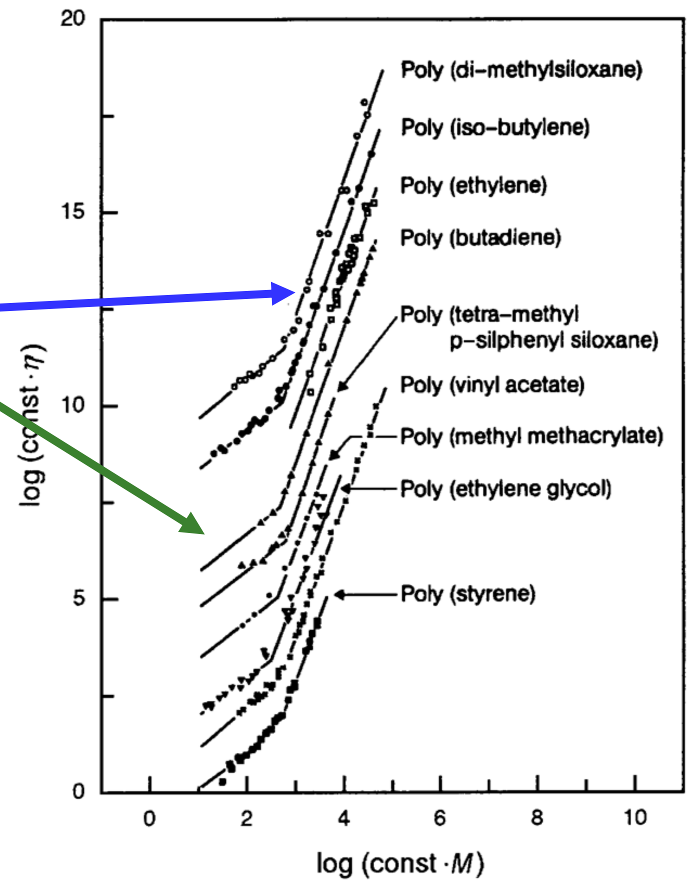
Theory

$\eta_0 \sim M^1$ Rouse Model

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







- **Effects of Temp., Shear Rate and Shear Stress on viscosity**

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

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

$B_{rigid}>B_{flexible}$

3. 剪切应力与剪切速率

4. 链结构-支化

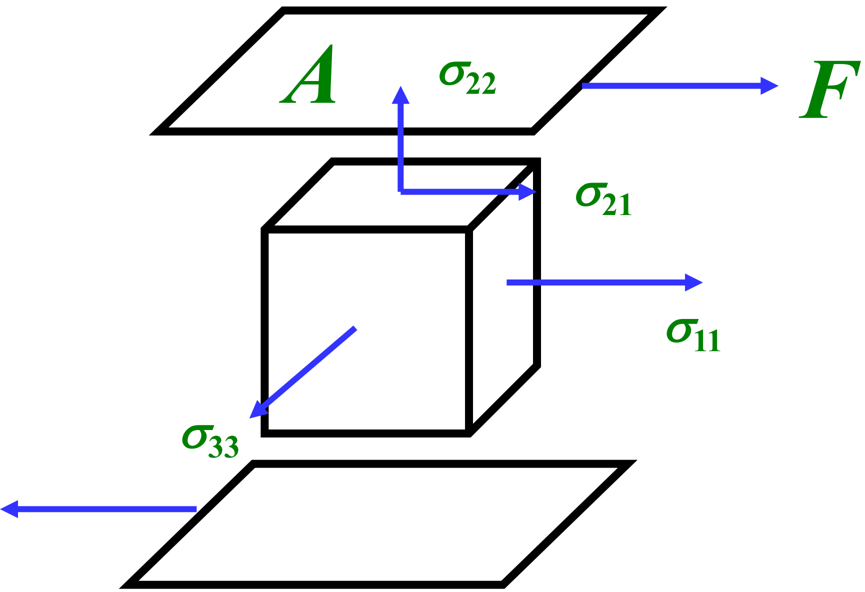
T_f的影响因素

1. 分子结构的柔顺性

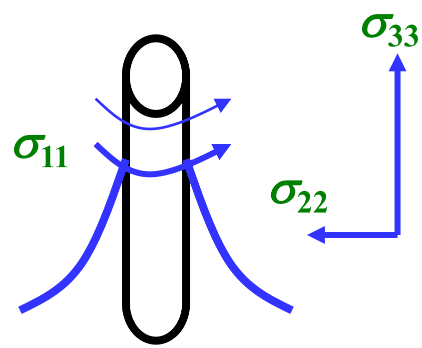
2. 分子量

3. 外力作用

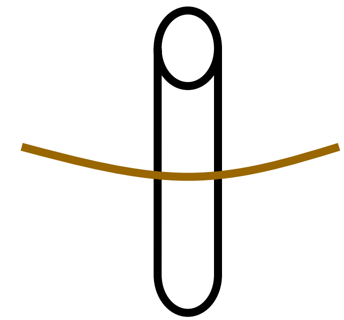
Normal stress difference and Elastic effects on viscous flow of polymers



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



Weissenberg effect



For polymer melts

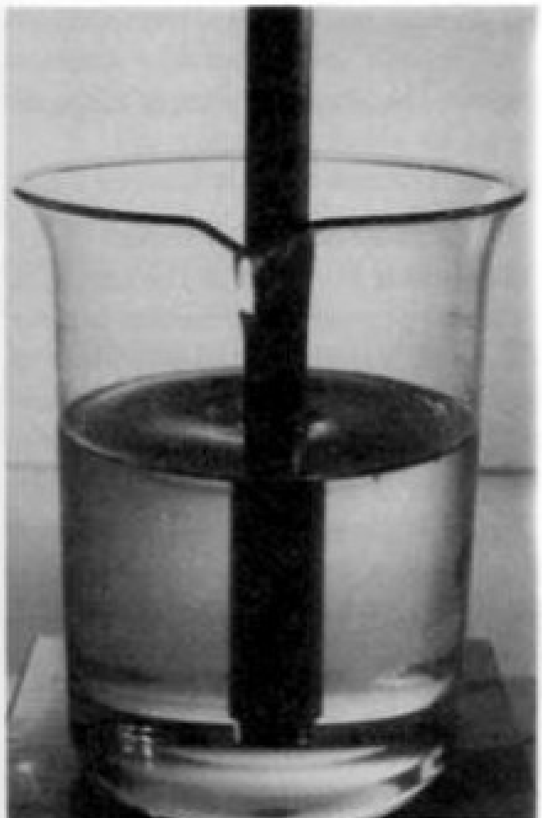
$N_1=\sigma_{11}-\sigma_{22}>0$

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

For low molecular weight liquids

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

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



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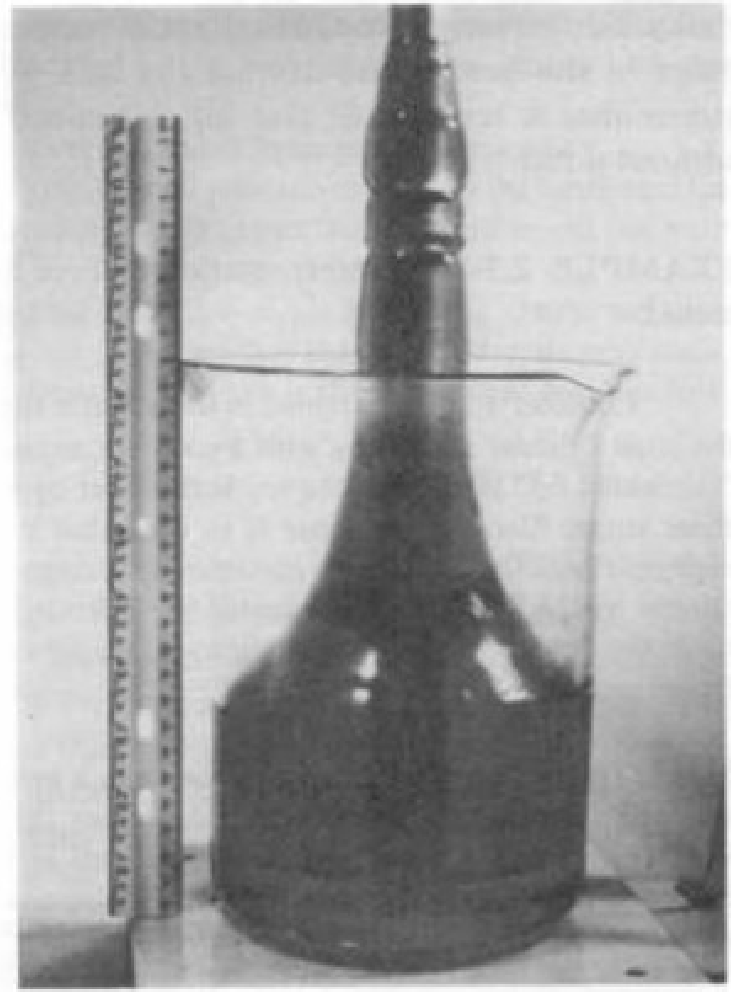

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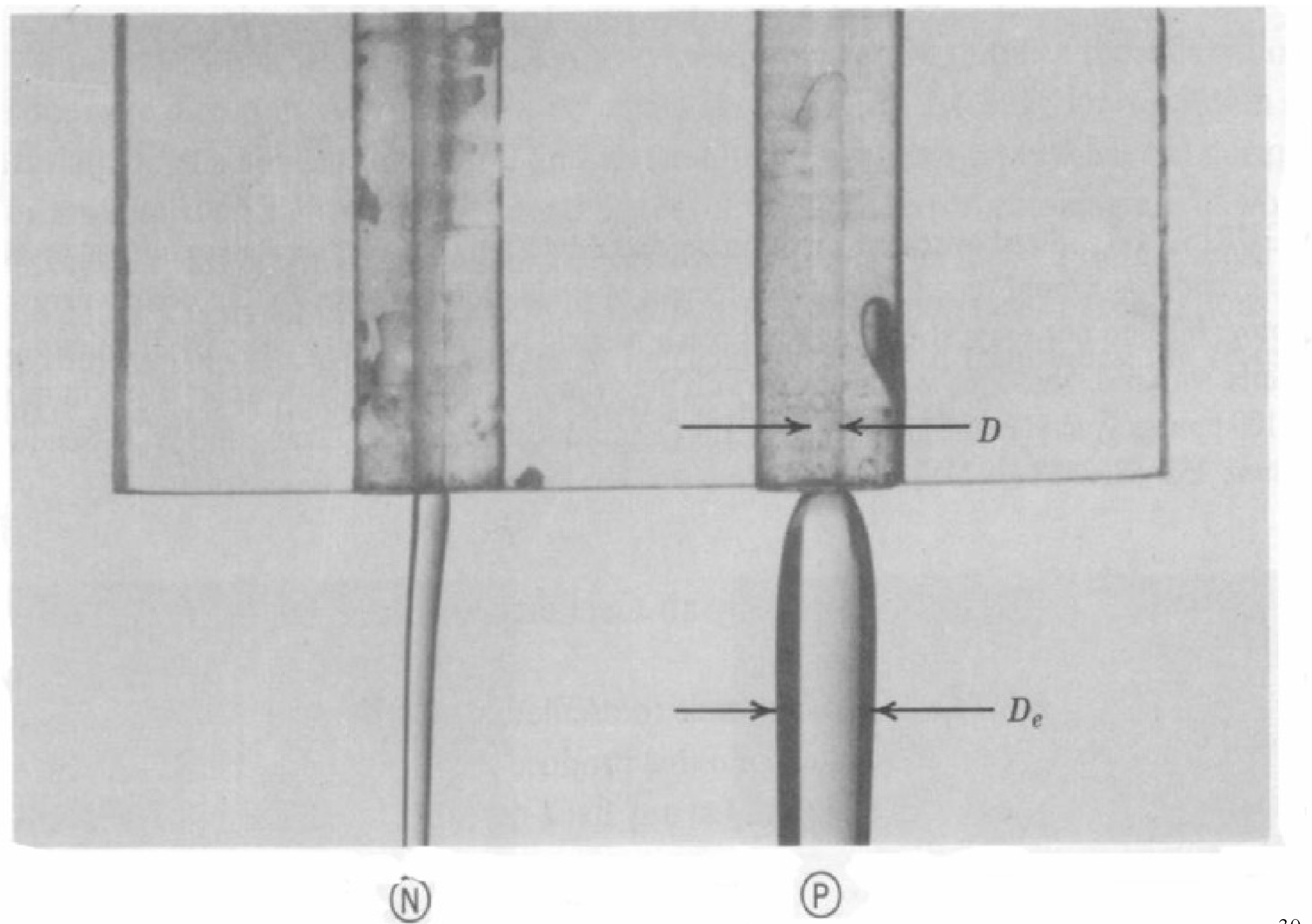
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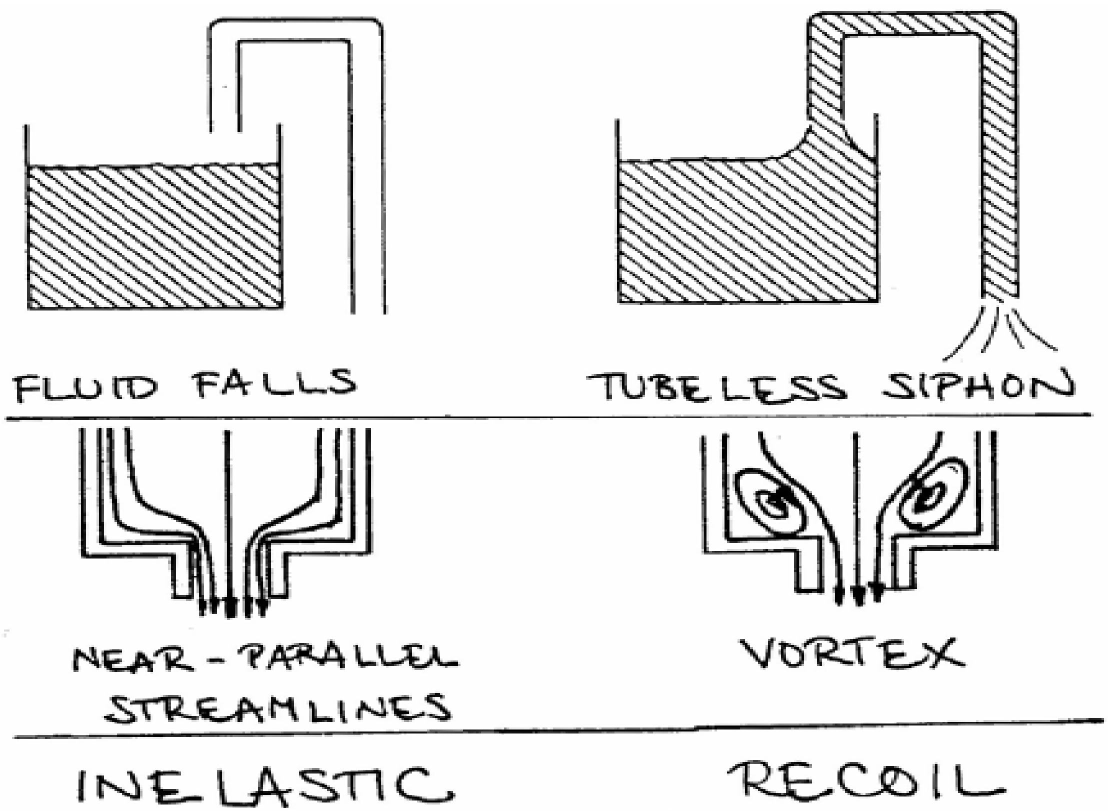
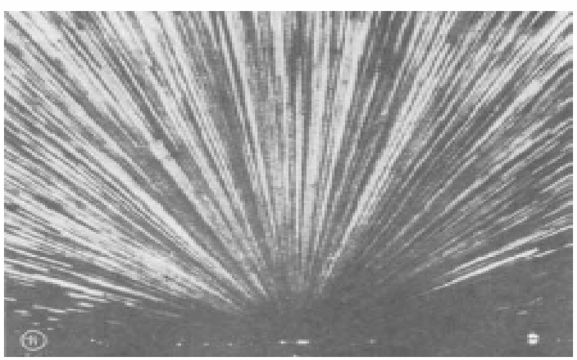
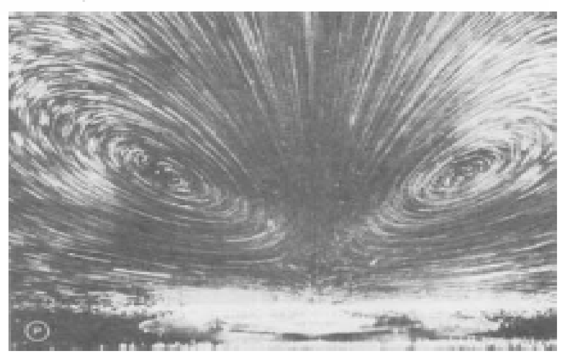






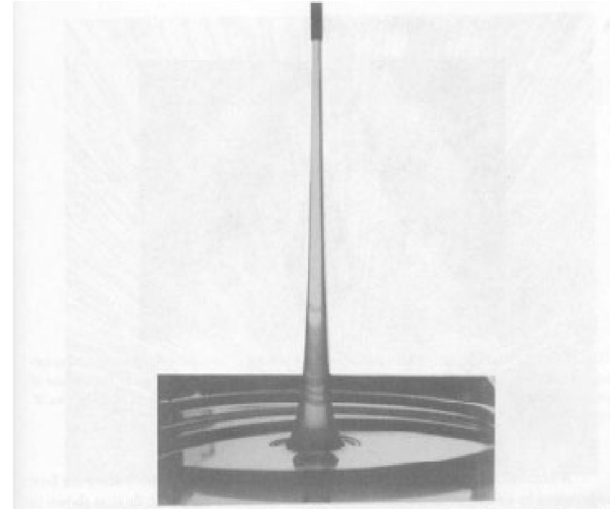
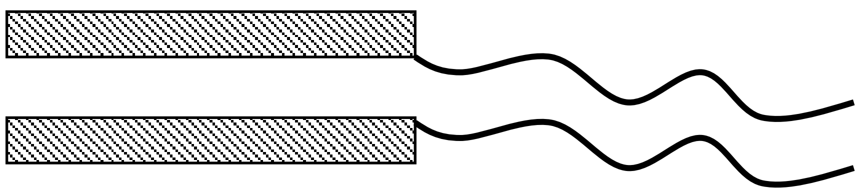


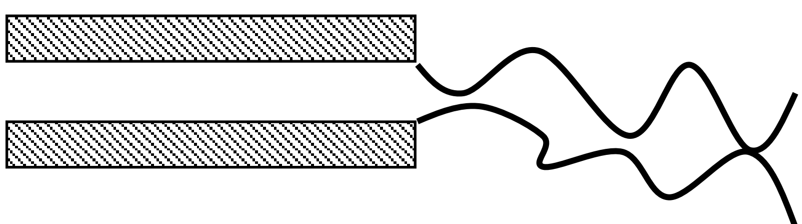
FIGURE 2.5-3. Fluid column in tubeless siphon experiment with a high molecular weight hydrocarbon polymer, AM-1 in JP-8 aviation fuel. [Reproduced from S. T. J. Peng and R. F. Landel, J. Appl. Phys. 47, 4255 (1976)]

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



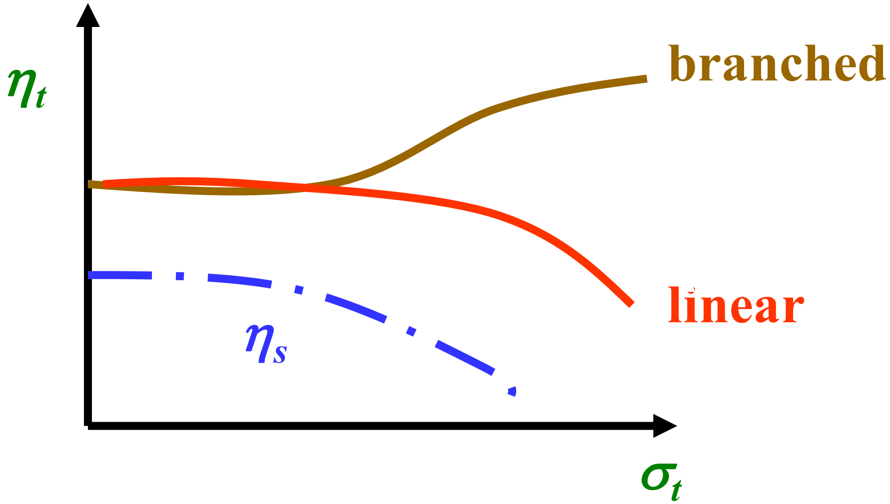
Shark skin



melt fracture

拉伸粘度的性质

- 与拉伸应力的关系



- 与拉伸速率的关系