

Chapt. 7 Mechanics Properties of Polymers

7.1 Basic physical quantities

Stress, strain, modulus

7.2 Mechanics properties of rubber elasticity

Theory of rubber elasticity

7.3 Fracture Mechanics of Brittle Materials

Griffith Theory

7.4 Fracture properties of polymer in glassy and crystalline state

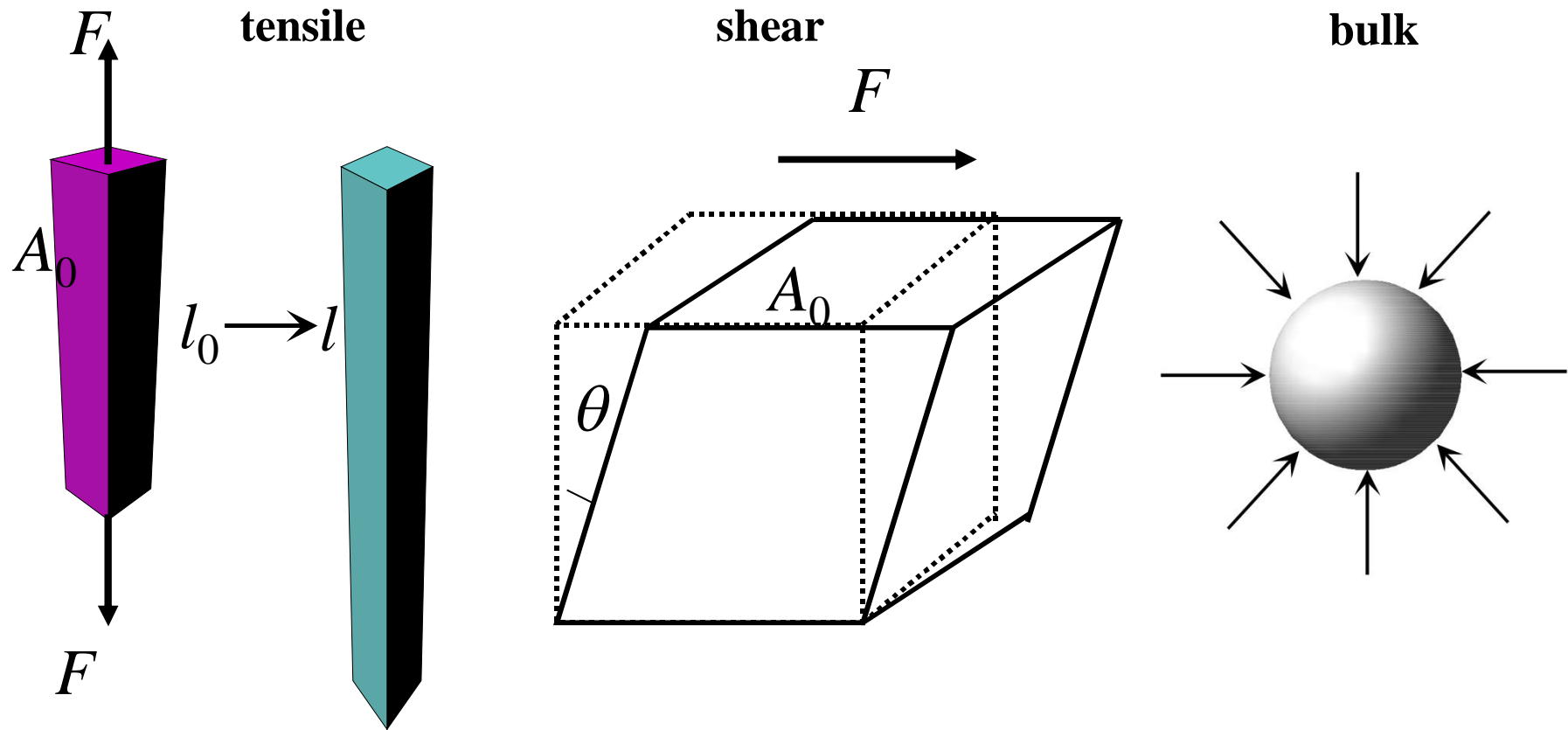
Yield(屈服), Craze(银纹), Fracture(断裂)

Mechanical properties of polymer:

Bulk polymers combine elastic and viscous properties in both the fluid and the solid state. Therefore, they are generally addressed as “viscoelastic” (粘弾) and, in fact, polymers are the main representatives of this special class of materials.

- **Different fields of polymer application are concerned and they all need their own approaches:**
 - **the properties under moderate loads, where deformations and velocities of viscous flow remain small**
 - **the case of large reversible deformations realized in rubbers and the rheological properties of polymer melts at higher strain rates, both representing non-linear behavior**
 - **and finally, of special importance for applications, yielding (屈服) and fracture (断裂)。**
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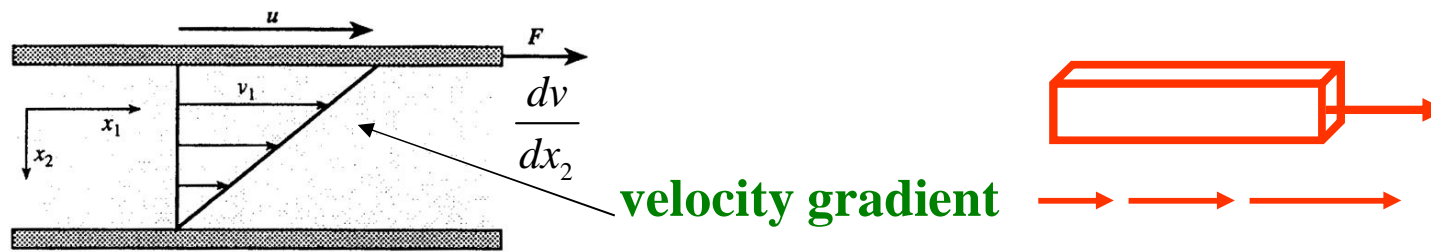
7.1 Stress, strain and Modulus



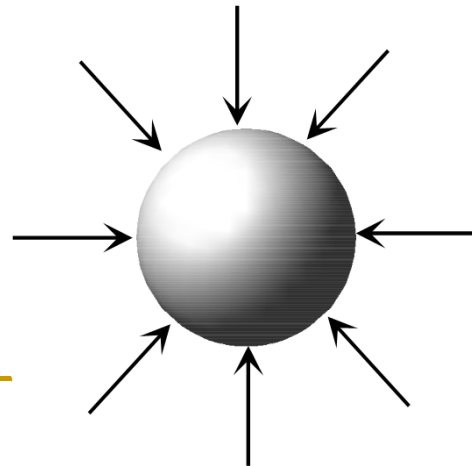
Characterization of viscous flow

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

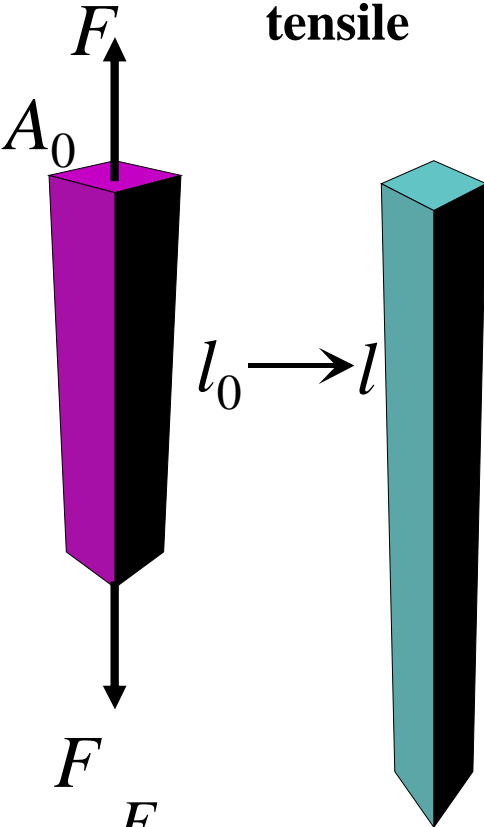
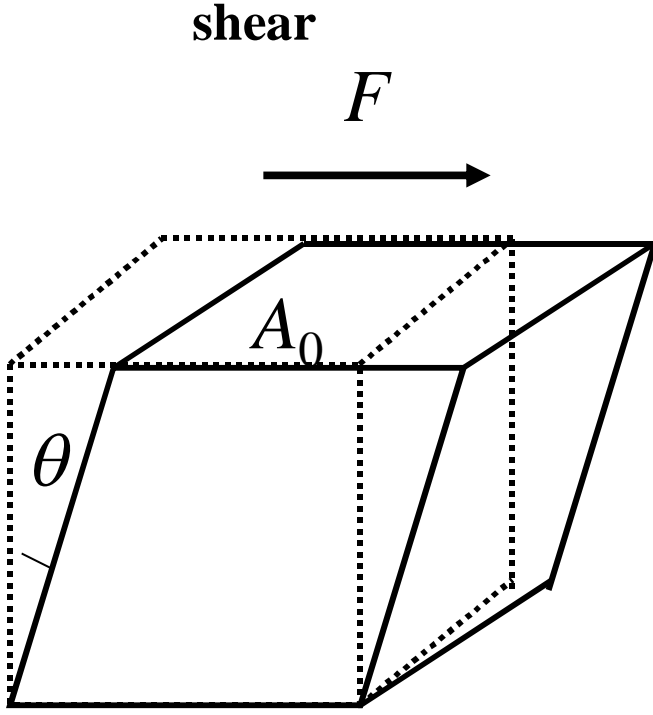
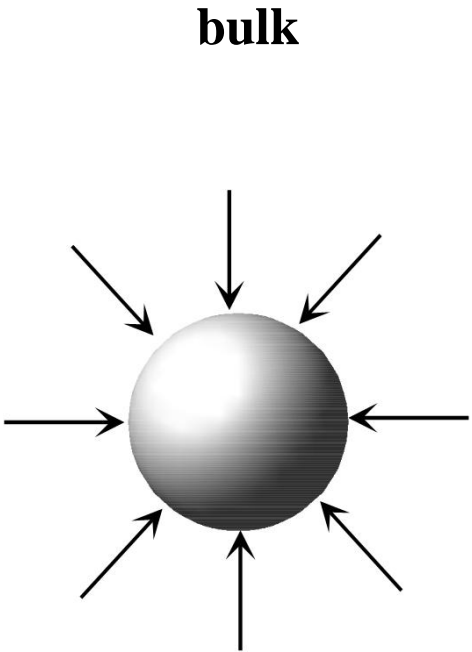


c. 压缩流动(形变)-bulk viscosity

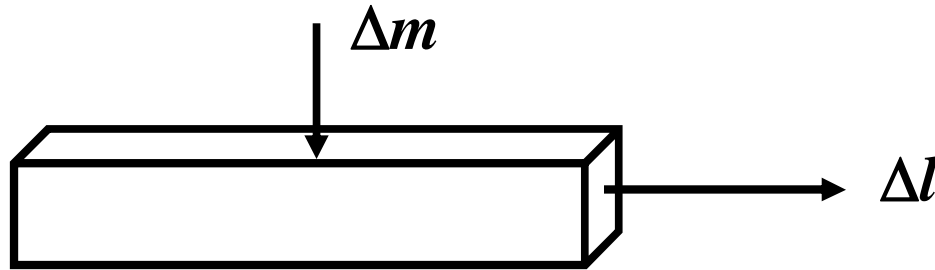


for incompressible fluids $\eta_b \rightarrow \infty$

7.1 Stress, strain and Modulus

 <p style="text-align: center;">tensile</p>	 <p style="text-align: center;">shear</p>	 <p style="text-align: center;">bulk</p>
$\sigma_{t,N} = \frac{F}{A_0}$	$\sigma_{t,t} = \frac{F}{A}$	$\sigma_s = \frac{F}{A_0}$
$\varepsilon = \frac{l - l_0}{l_0} = \lambda - 1$	$\varepsilon = \int_{l_0}^l \frac{dl}{l} = \ln \frac{l}{l_0}$	$\gamma = \frac{\Delta l}{l} = \tan \theta \approx \theta$
$E = \sigma_t / \varepsilon$	$G = \sigma_s / \gamma$	$B = \sigma_b / \Delta$
Young's Modulus	Shear Modulus	Bulk Modulus

isotropic ideal solids



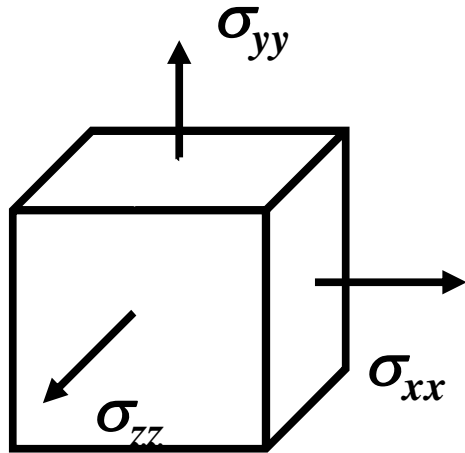
ν : Poisson ratio
$$\nu = -\frac{\Delta m / m_0}{\Delta l / l_0} = -\frac{\varepsilon_t}{\varepsilon}$$

$$E = 2G(1 + \nu) = 3B(1 - 2\nu)$$

Incompressible solids $\nu=0.5$

$$E=3G$$

anisotropic ideal solids



$$\sigma_{xx} = a_{xx} \varepsilon_{xx} + a_{xy} \varepsilon_{xy} + a_{xz} \varepsilon_{xz} + \dots$$

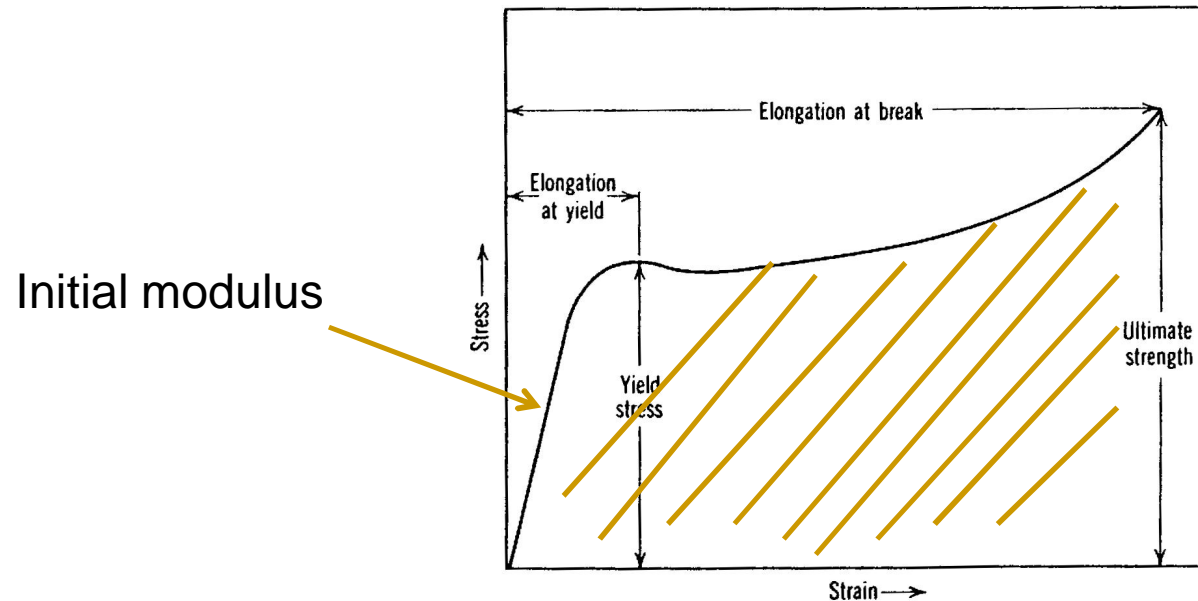
$$\varepsilon_{xx} = a'_{xx} \sigma_{xx} + a'_{xy} \sigma_{xy} + a'_{xz} \sigma_{xz} + \dots$$

$$[\sigma_{ij}] = [a_{ij}] [\varepsilon_{ij}]$$

$$[\varepsilon_{ij}] = [a'_{ij}] [\sigma_{ij}]$$

generalized hook's law (广义虎克定律)

Nonlinear Behaviors of Materials Property



Strength

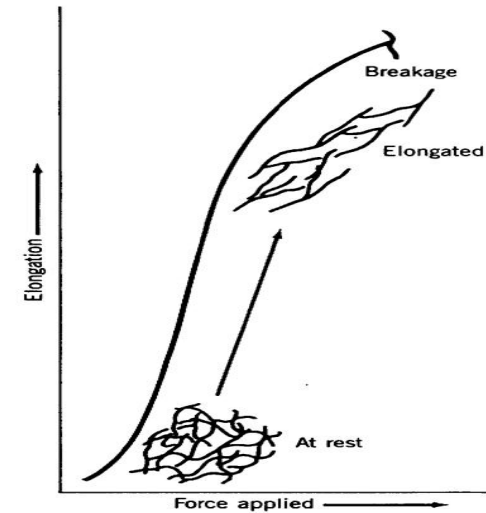
$$\sigma \varepsilon = \frac{f}{A_0} \frac{\Delta l}{l_0} = f \Delta l / V_0$$

$$\int \sigma d\varepsilon = \int f dl / V_0 = W / V_0$$

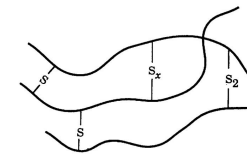
Work(功) of Unit Volume

7.2 Rubber (Elastomers) and Rubber Elasticity

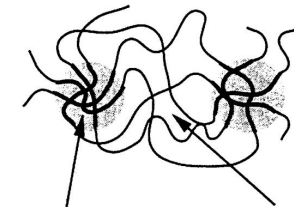
- **General properties of elastomers**
- The individual polymer chains of elastomers are held together by weak intermolecular bonding forces, which allow rapid chain slippage when a moderate pulling force is employed.
- **Cross-links**, which are introduced during vulcanization (硫化), permit rapid elongation of the principal sections, to a point where the chains are stretched to their elastic limit. Any additional elongation causes primary bond breakage. **The cross-links, which are the boundaries for the principal sections, permit the rubber to “remember” its original shape, that is, the original orientation of the particular chains.**



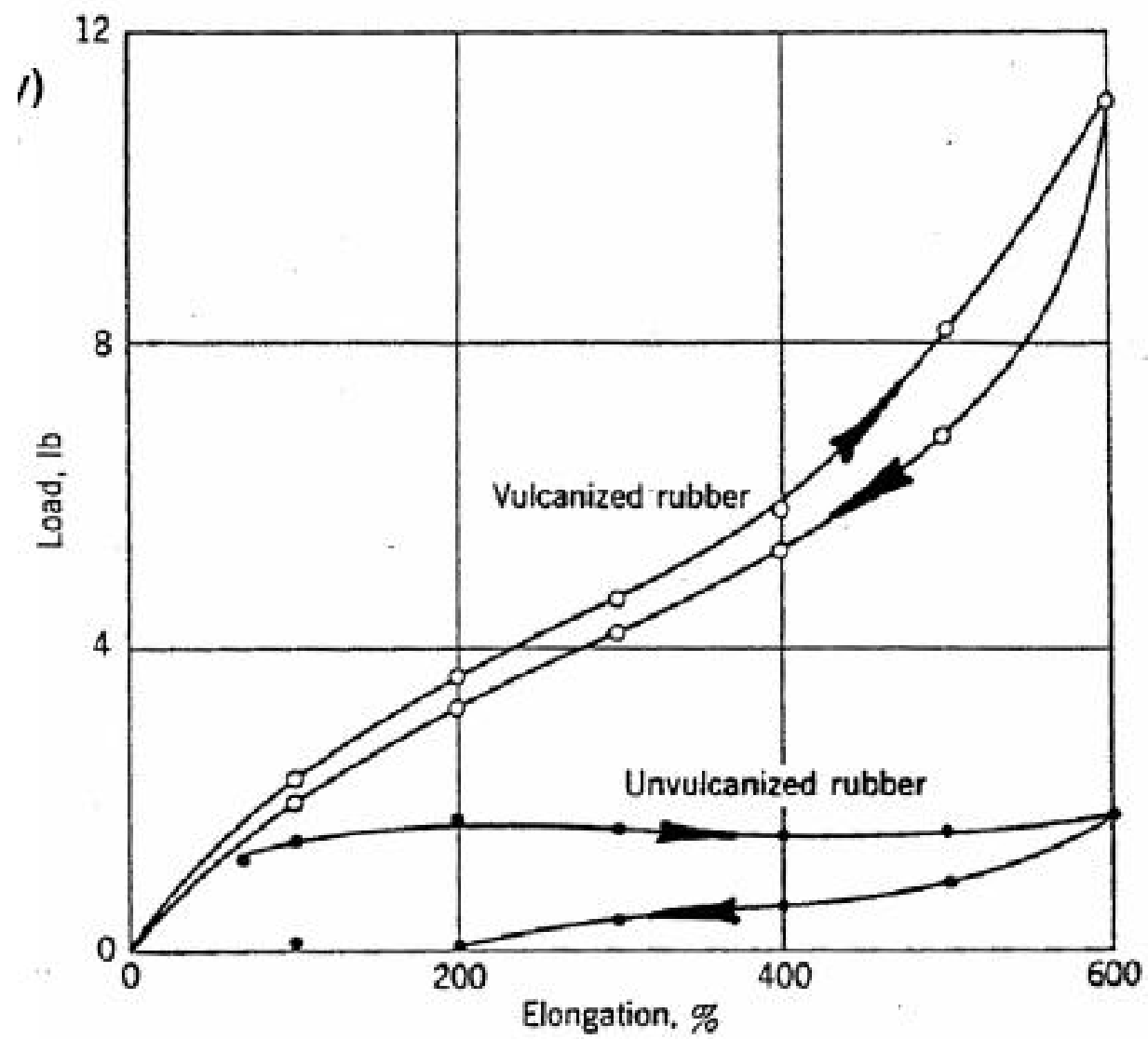
Typical applied-force-elongation behavior of rubber



Sulphur bridges linking *cis*-1,4-polyisoprene



Structure of thermoplastic elastomers



Goodyear's Invention of Vulcanization

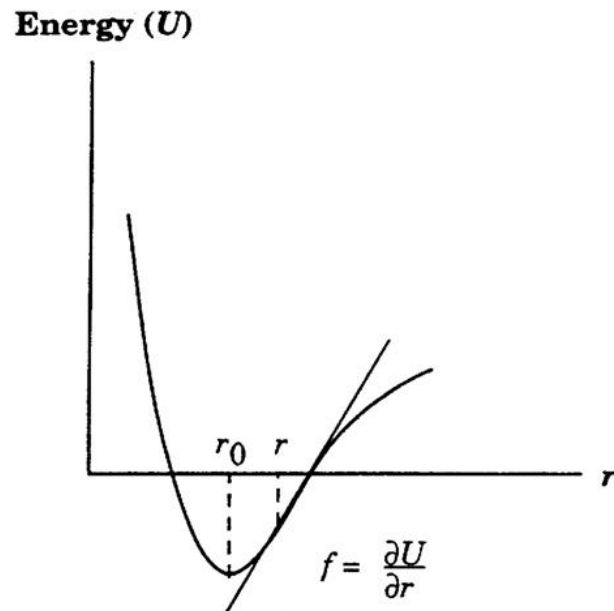
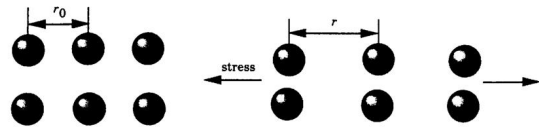


- Rendition of Charles Goodyear's 1839 invention of vulcanization (*Rubber and Plastics News*, August 1984)

Rubber Elasticity

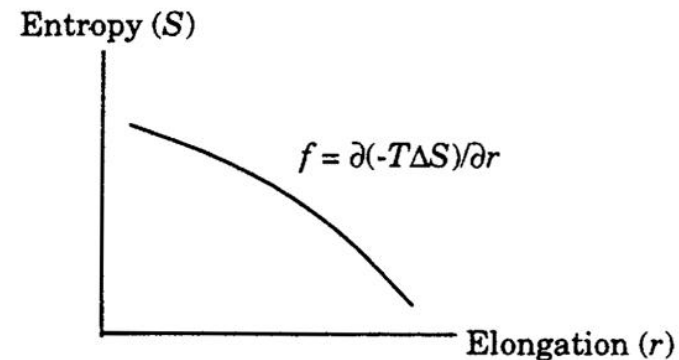
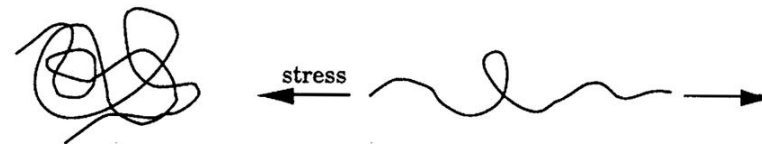
➤ **Energy-driven** vs **entropy-driven elasticity**

➤ **Energy-driven elasticity**
typical of crystalline solids



➤ **Entropy-driven elasticity** of rubber materials

- A stretched rubber sample subjected to a constant uniaxial load contracts reversibly on heating
- A rubber sample gives out heat reversible when stretched



Thermodynamics of Rubber Elasticity

$$du = \delta Q - \delta W, \quad \delta W = pdV - fdl$$

$$\delta Q = TdS$$

$$du = TdS - pdV + fdl$$

$$G = H - TS = u + pV - TS \quad dG = fdl + Vdp - SdT$$

$$\left(\frac{\partial G}{\partial l}\right)_{p,T} = f, \quad \left(\frac{\partial G}{\partial T}\right)_{l,p} = -S, \quad \left(\frac{\partial G}{\partial l}\right)_{p,T} = f = \left(\frac{\partial H}{\partial l}\right)_{p,T} - T\left(\frac{\partial S}{\partial l}\right)_{p,T}$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial l}\right)_{p,T}\right)_{p,l} = \left(\frac{\partial}{\partial l}\left(\frac{\partial G}{\partial T}\right)_{l,p}\right)_{p,T} \quad \left(\frac{\partial f}{\partial T}\right)_{l,p} = -\left(\frac{\partial S}{\partial l}\right)_{p,T}$$

$$f = \underbrace{\left(\frac{\partial H}{\partial l}\right)_{p,T}}_{\text{intercept}} + T \underbrace{\left(\frac{\partial f}{\partial T}\right)_{p,l}}_{\text{slope}} \quad \text{or} \quad f = \left(\frac{\partial u}{\partial l}\right)_{T,v} + T \left(\frac{\partial f}{\partial T}\right)_{l,v}$$

$$\left(\frac{\partial u}{\partial l}\right)_{T,v} \approx 0$$

$$\delta Q = TdS < 0$$

Thermoelastic effects

Thermoelastic inversion (热弹转变)

$$\left(\frac{\partial f}{\partial T}\right)_{p,l} = \frac{f - \left(\frac{\partial H}{\partial l}\right)_{p,T}}{T}$$

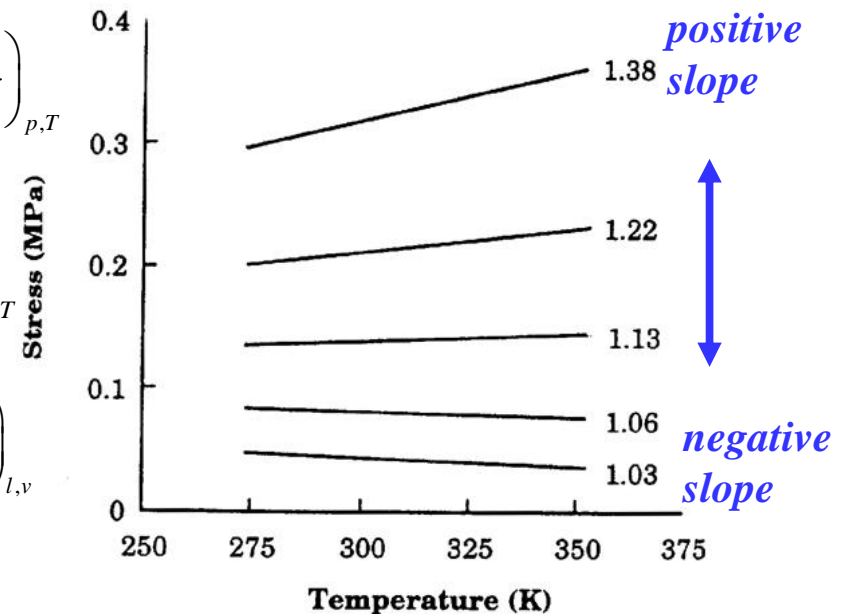
$$f < \left(\frac{\partial H}{\partial l}\right)_{p,T}$$

for small elongation

$$f > \left(\frac{\partial H}{\partial l}\right)_{p,T}$$

for large elongation (>10 %),
but not for very large elongation

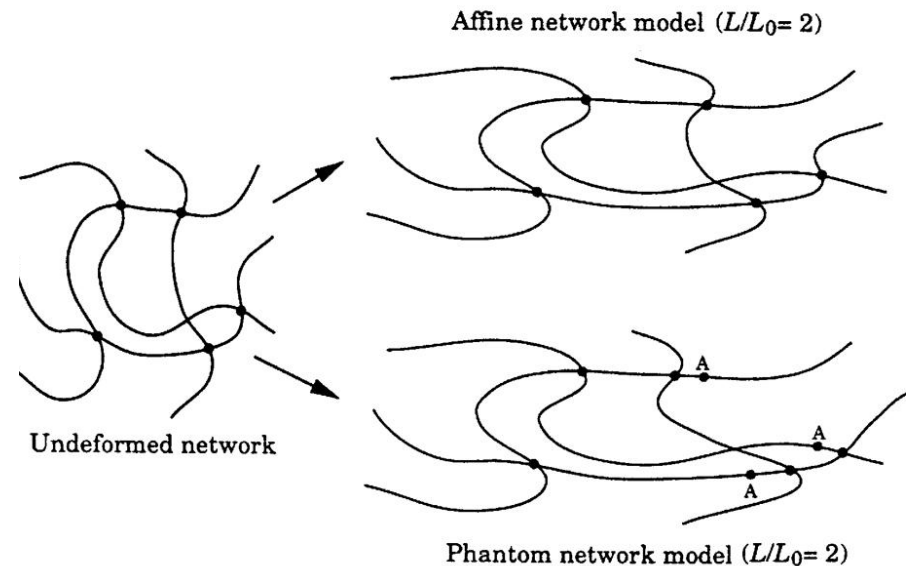
➤ Thermo-elastic behavior
Measured at constant pressure



The statistical mechanics of rubber elasticity

Affine network (仿射网络)

- The chain segments between crosslinks can be represented by Gaussian statistics of unperturbed chains.
- The network consists of N -chains per unit volume. The entropy of the network is the sum of the entropies of the individual chains.
- All different conformational states have the same energy.
- The deformation on the molecular level is the same as that on the macroscopic level, i.e. deformation is affine.
- The unstressed network is isotropic.
- The volume remains constant during deformation.



Stretching of an Ideal Chain



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

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

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

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

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

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

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

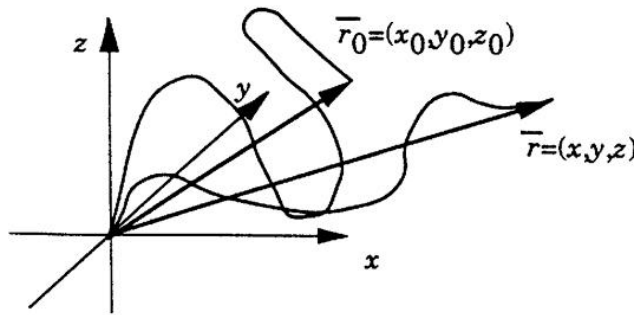
$$G(\mathbf{h}, N_g) = U - TS = \frac{3}{2} k_B T \frac{\mathbf{h}^2}{N_g l^2} + G(N_g)$$

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

$$f = kx$$

相当于拉一根弹簧，弹性系数=???

The statistical mechanics of rubber elasticity



N_c : Number of segment
between Crosslink

$$\sum_{i=1}^n G_i(\mathbf{h}_i, N_c) = \frac{3}{2} k_B T \sum_{i=1}^n \frac{\mathbf{h}_i^2}{N_c l^2} + \sum_{i=1}^n G_i(N_c)$$

$$\sum_{i=1}^n \Delta G_i(\mathbf{h}_i, N_c) = \frac{3}{2} k_B T \sum_{i=1}^n \frac{\Delta \mathbf{h}_i^2}{N_c l^2}$$

$$\Delta \mathbf{h}_i^2 = x_i^2 + y_i^2 + z_i^2 - (x_{i0}^2 + y_{i0}^2 + z_{i0}^2)$$

$$= \lambda_x^2 x_{i0}^2 + \lambda_y^2 y_{i0}^2 + \lambda_z^2 z_{i0}^2 - (x_{i0}^2 + y_{i0}^2 + z_{i0}^2)$$

$$= (\lambda_x^2 - 1) x_{i0}^2 + (\lambda_y^2 - 1) y_{i0}^2 + (\lambda_z^2 - 1) z_{i0}^2$$

$$\sum_1^n x_{i0}^2 + \sum_1^n y_{i0}^2 + \sum_1^n z_{i0}^2 = \sum_1^n \mathbf{h}_{i0}^2 \quad \sum_{i=1}^n \Delta \mathbf{h}_i^2 = [(\lambda_x^2 - 1) + (\lambda_y^2 - 1) + (\lambda_z^2 - 1)] \left(\frac{1}{3} n \mathbf{h}_0^2 \right)$$

$$\sum_1^n x_{i0}^2 = \sum_1^n y_{i0}^2 = \sum_1^n z_{i0}^2$$

$$\mathbf{h}_0^2 = N_c l^2$$

$$\sum_1^n x_{i0}^2 = \sum_1^n y_{i0}^2 = \sum_1^n z_{i0}^2 = \frac{1}{3} \sum_1^n \mathbf{h}_{i0}^2 = \frac{n \mathbf{h}_0^2}{3}$$

The equations of state of rubber elasticity

$$\Delta G = \sum_{i=1}^n \Delta G_i(\mathbf{h}_i, N_c) = -\frac{1}{2}nk_B(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

For uniaxial stress, $\lambda_x = \lambda$, $\lambda_y = \lambda_z = \lambda_t$, $\lambda = \frac{l}{l_0}$

$$\lambda_x \lambda_y \lambda_z = 1, \quad \lambda \lambda_t^2 = 1, \quad \lambda_t = \frac{1}{\sqrt{\lambda}} \quad (\text{volume remains constant})$$

$$f = \left(\frac{\partial(\Delta G)}{\partial l} \right)_{T,V} = \left(\frac{\partial(\Delta G)}{\partial \lambda} \right)_{T,V} \left(\frac{\partial \lambda}{\partial l} \right)_{T,V}$$

$$f = \frac{\partial}{\partial \lambda} \left(\frac{1}{2}nk_B T \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \right) \frac{\partial}{\partial l} \left(\frac{l}{l_0} \right) = \frac{nk_B T}{l_0} \left(\lambda - \frac{1}{\lambda^2} \right)$$

True stress

$$\sigma = f / \left(\frac{A_0}{\lambda} \right) = \frac{nk_B T}{l_0} \left(\lambda - \frac{1}{\lambda^2} \right) / (A_0 / \lambda) \longrightarrow \sigma = \frac{nk_B T}{V_0} \left(\lambda^2 - \frac{1}{\lambda} \right)$$

↑
True stress
↑

“Modulus” increase in a linear manner with increasing temperature. This is a typical entropy-elastic.

A_0 : cross section area of the unstrained rubber

V_0 : the volume of the rubber

The equations of state of rubber elasticity

True stress (真应力)

$$\frac{n}{V_0} = \left(\frac{n_{mole} M_c N_a}{V_0} \right) \left(\frac{1}{M_c} \right) = \left(\frac{m_0}{V_0} \right) \left(\frac{1}{M_c} \right) N_a = \frac{\rho}{M_c} N_a \rightarrow \sigma = \frac{\rho RT}{M_c} \left(\lambda^2 - \frac{1}{\lambda} \right)$$

↑

Nominal stress (习用应力)

Rubber with high crosslinking density, i.e. low M_c , behave stiff

$$f = \frac{\partial}{\partial \lambda} \left(\frac{1}{2} n k_B T \left(\lambda^2 + \frac{2}{\lambda} - 3 \right) \right) \frac{\partial}{\partial l} \left(\frac{l}{l_0} \right) = \frac{n k_B T}{l_0} \left(\lambda - \frac{1}{\lambda^2} \right)$$

$$\sigma = \frac{f}{A_0} \rightarrow \sigma = \frac{\rho RT}{M_c} \left(\lambda - \frac{1}{\lambda^2} \right)$$

Small strain limit: $\lambda \rightarrow 1$ Note: $\lambda = l/l_0 = 1 + \varepsilon$

$$\sigma_{\varepsilon \rightarrow 0} = 3 \frac{\rho RT}{M_c} (\lambda - 1) \quad \sim \quad \sigma_{\text{solids}} = E \varepsilon = E \frac{l - l_0}{l_0} = E (\lambda - 1) \quad E = 3 \frac{\rho RT}{M_c}$$

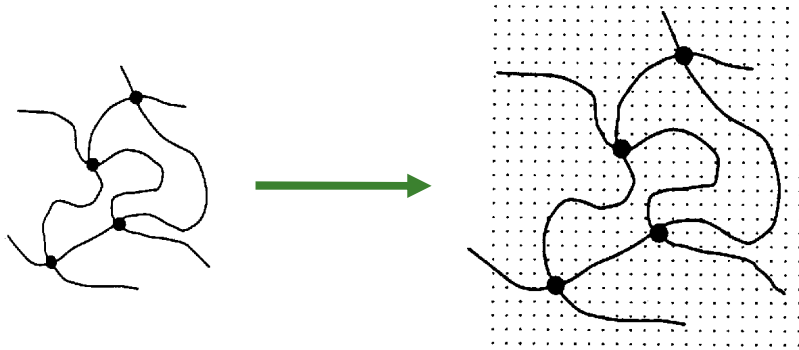
Gel Swelling

➤ Swelling of rubbers in solvents

$$\lambda_x \lambda_y \lambda_z = \frac{V}{V_0} = \lambda_v = \frac{1}{\phi_2} \quad \lambda = \phi_2^{-1/3}$$

$$\lambda_x = \lambda_y = \lambda_z = \lambda = \sqrt[3]{\lambda_v}$$

(ϕ_2 : volume fraction of polymer component in swollen gel)



Isotropic swelling of a network polymer

$$\Delta F_{el} = \frac{1}{2} NkT (3\lambda^2 - 3) = \frac{3\rho RTV_0}{2M_c} (\phi_2^{-2/3} - 1)$$

$$\Delta\mu_1 = \frac{\partial\Delta F}{\partial n_1} = \frac{\partial\Delta F_m}{\partial n_1} + \frac{\partial\Delta F_{el}}{\partial\phi_2} \frac{\partial\phi_2}{\partial n_1} = 0$$

$$\phi_2 = \frac{V_0}{V_0 + n_1 V_1} \longrightarrow \Delta\mu_{1,el} = \frac{\rho RT}{M_c} V_1 \phi_2^{1/3}$$

➤ Flory-Huggins solution theory:

$$\Delta\mu_{1,mix} = RT \left(\ln(1 - \phi_2) + \left(1 - \frac{1}{x}\right) \phi_2 + \chi \phi_2^2 \right)$$

$$\approx RT (\ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2)$$

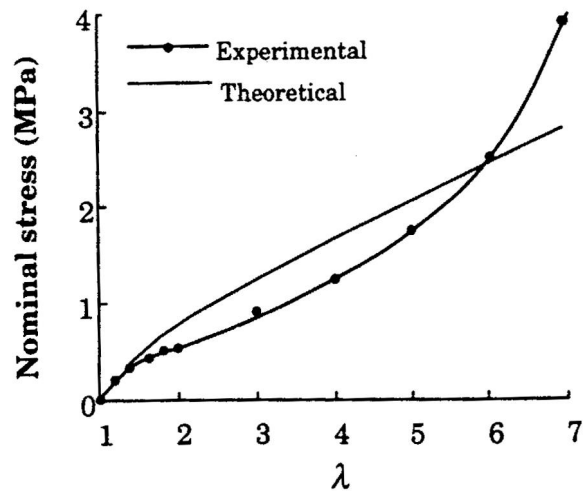
➤ At swelling equilibrium

$$\Delta\mu_1 = \Delta\mu_{1,el} + \Delta\mu_{1,m} = 0$$

$$\ln(1 - \phi_2^*) + \phi_2^* + \chi \phi_2^{*2} + \frac{\rho V_1}{M_c} \phi_2^{*1/3} = 0$$

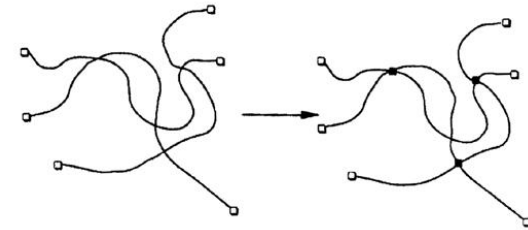
(Flory-Rehner equation)

Deviations from classical statistical theories

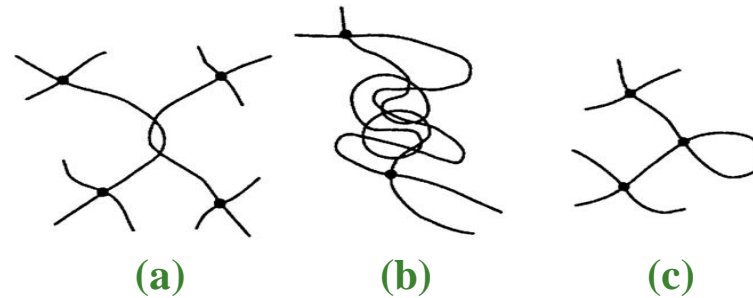


$$\lambda = l/l_0$$

- **Crosslinking of a polymer with finite MW indicating the formation of loose chain ends.**

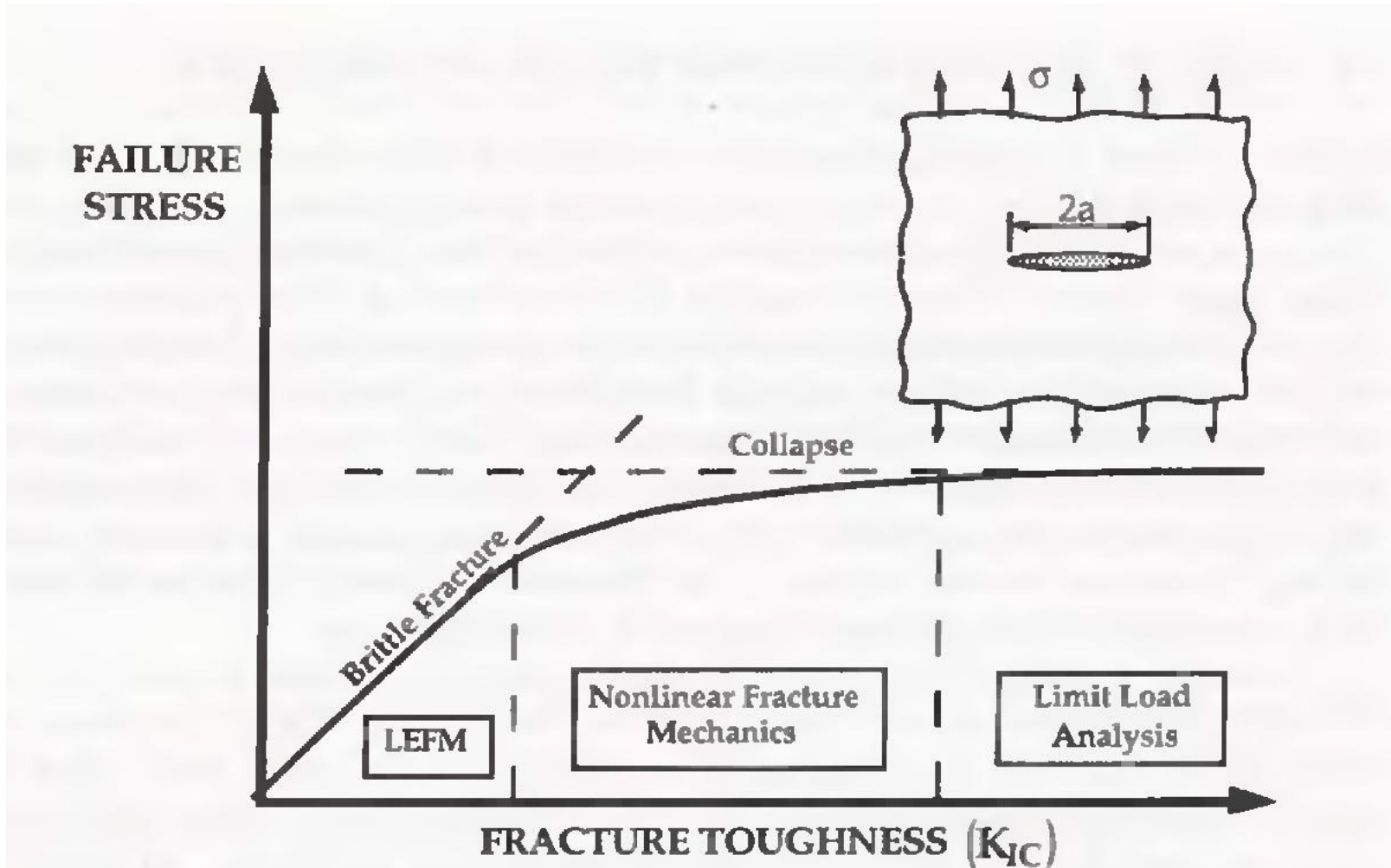


- **“Chain defects” in network: (a) permanent physical crosslink; (b) temporary physical crosslink; (c) intramolecular crosslink.**

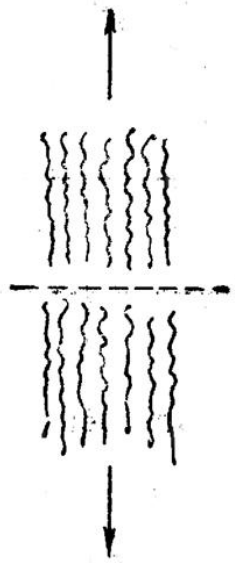


- **Segment vectors do not follow Gaussian statistics when rubbers are highly stretched.**
- **At high extension ratio, crystallization may occur in rubbers.**

Fracture Mechanics



Theoretical limits of strength (強度)



Chain scission:

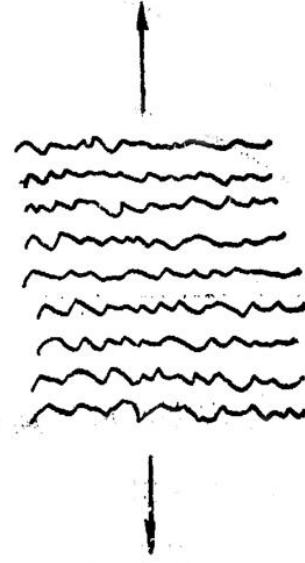
$$\sigma \sim 2 \times 10^{10} \text{ N/m}^2$$

Much higher the value measured



Chain slippage

Cohesive energy
 $\sim 10^3 \text{ KJ/mol}$

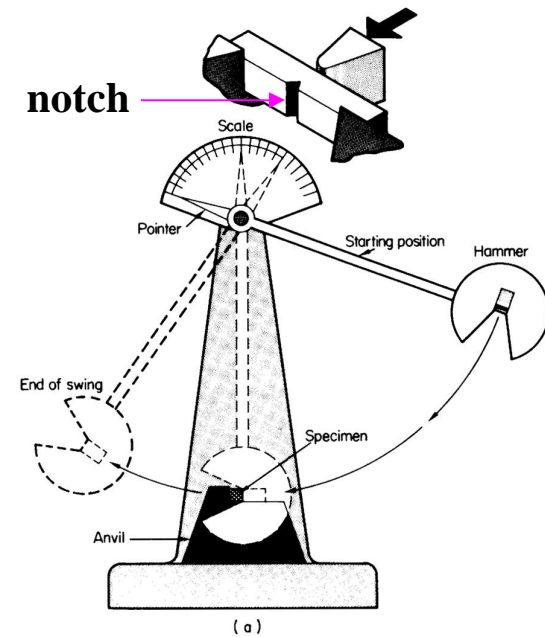


Breaking of interchain interactions

$$\sigma \sim 10^8 \text{ N/m}^2$$

close to the value measured

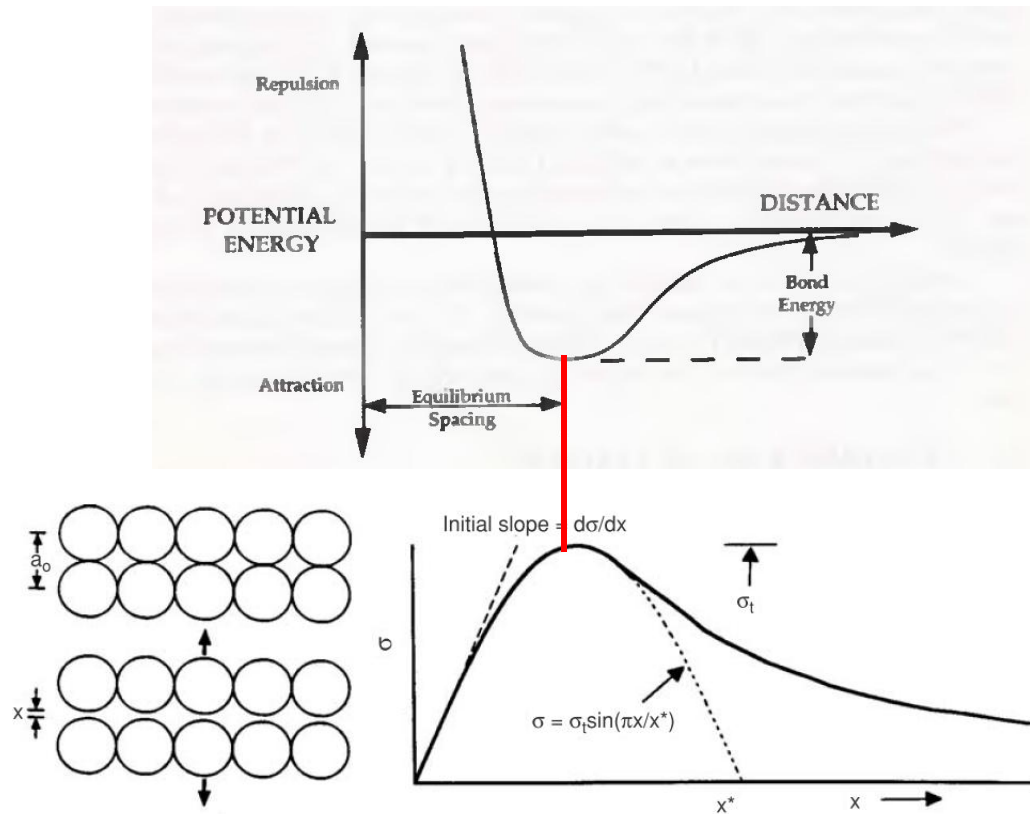
➤ Impact strength measurement



Schematic drawing of a Charpy impact tester

7.3 Fracture Mechanics of Brittle Materials

Theoretical Fracture Strength



$$\sigma \approx \sigma_t \sin(\pi x / x^*)$$

$$\varepsilon = (a - a_0) / a_0 = x / a_0$$

E : Young's modulus

$$E = \frac{d\sigma}{d\varepsilon} = a_0 \frac{d\sigma}{dx} = a_0 \frac{\pi}{x^*} \sigma_t \cos\left(\frac{\pi x}{x^*}\right)$$

$$\approx \frac{a_0 \pi}{x^*} \sigma_t$$

$$\sigma_t = E x^* / \pi a_0$$

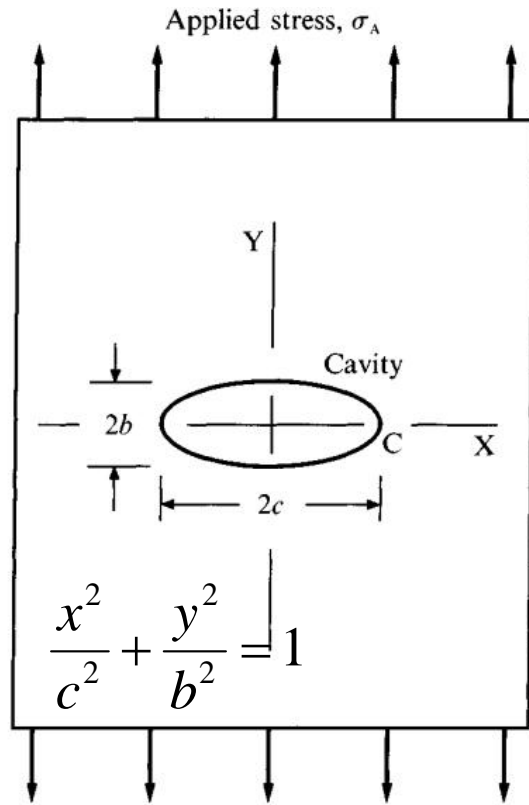
$$2\gamma = \int_0^{x^*} \sigma dx = (2x^* / \pi) \sigma_t$$

$$x^* = \pi \gamma / \sigma_t$$

$$x^* \approx a_0$$

$$\sigma_c = \sigma_t = \sqrt{E\gamma / a_0}$$

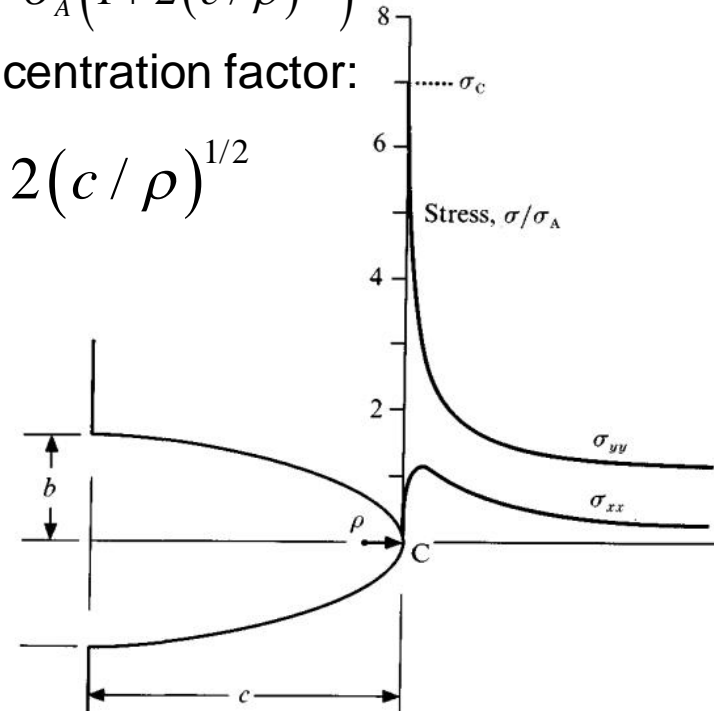
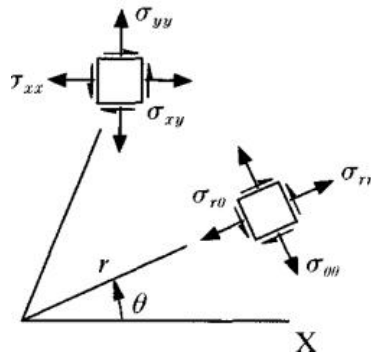
Stress Concentration Effect



$$\sigma_C = \sigma_A \left(1 + 2c/b\right) = \sigma_A \left(1 + 2(c/\rho)^{1/2}\right)$$

$b \ll c$ stress-concentration factor:

$$\sigma_C / \sigma_A \approx 2c/b = 2(c/\rho)^{1/2}$$



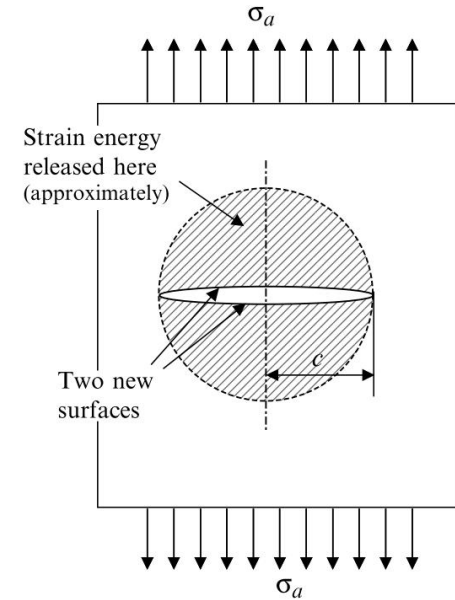
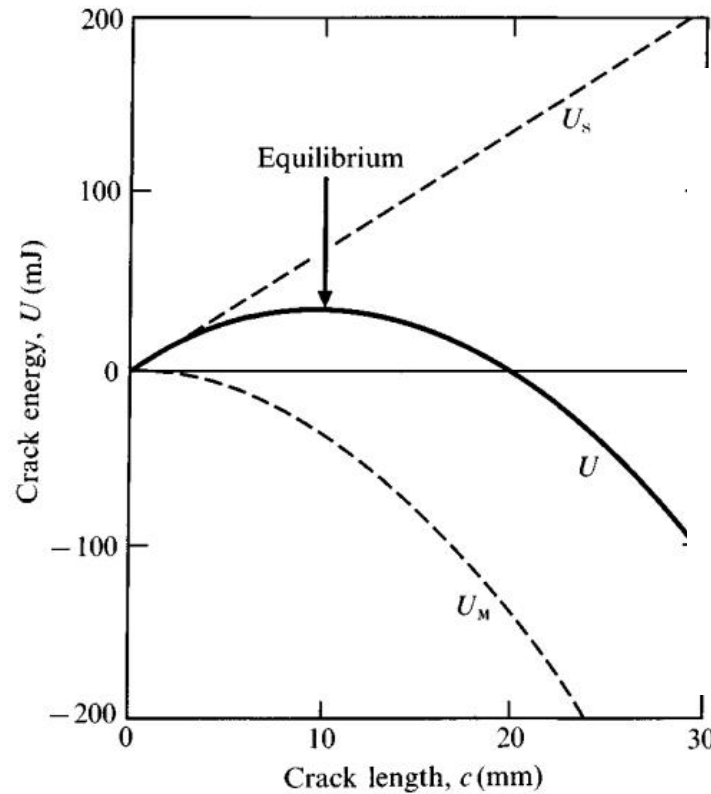
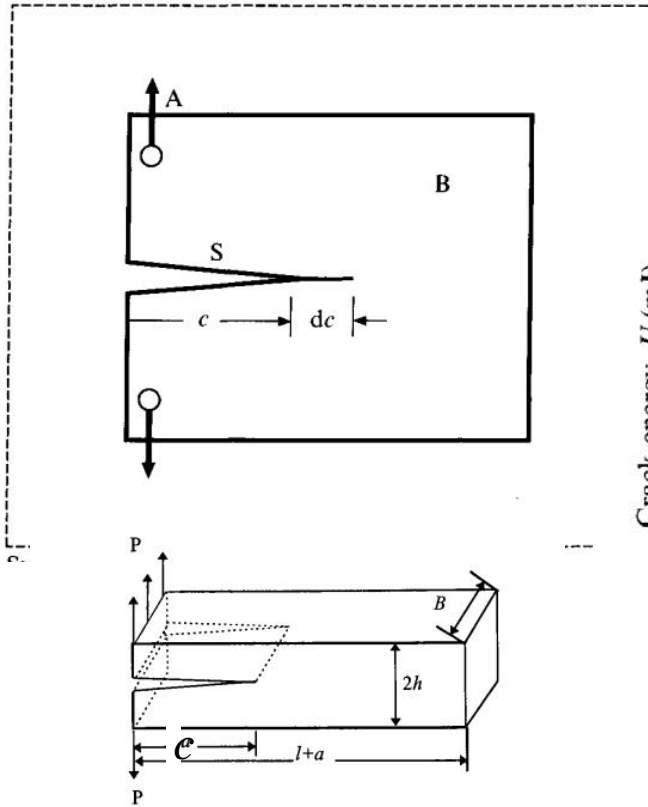
minimum radius of curvature at C: $\rho = \frac{b^2}{c} \approx a_0$???

$$\sigma_C = 2\sigma_A \sqrt{c/a_0} = \sqrt{E\gamma/a_0}$$

$$\sigma_A = \sqrt{\frac{E\gamma}{4c}}$$

Note: $\sigma_c = \sqrt{E\gamma/a_0}$

Griffith Theory for Brittle Materials



B: Thickness of plate

$$\sigma = E\varepsilon$$

E: Young's modulus

$$U = U_E + U_S \quad U_E = -\sigma_A \varepsilon \pi c^2 B = -\pi c^2 B \sigma_A^2 / E = -\frac{\pi c^2 \sigma_A^2 B}{E}$$

U_E : Elastic potential

$$U_S = 4cB\gamma \quad \gamma: \text{surface energy density of the material}$$

U_S : Surface Energy

Griffith Criterion

$$\frac{\partial U}{\partial c} = 0 \quad \sigma_f = \sigma_A$$

Griffith Criterion

$$\sigma_f = \sqrt{\frac{2E\gamma}{\pi c}} \quad \gamma = 1J / m^2$$

Irwin's modification – Plastic Modification

$$\sigma_f = \sqrt{\frac{E(2\gamma + G_p)}{\pi c}}$$

Plastic Energy: $G_p \approx 1000J / m^2$

Other modifications – Fracture Mode

Stress Intensity Factor: K

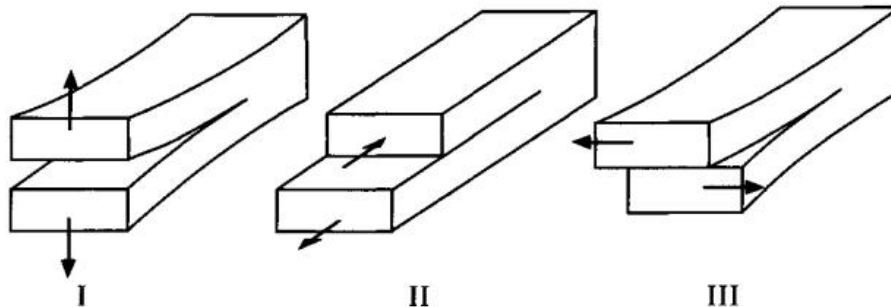
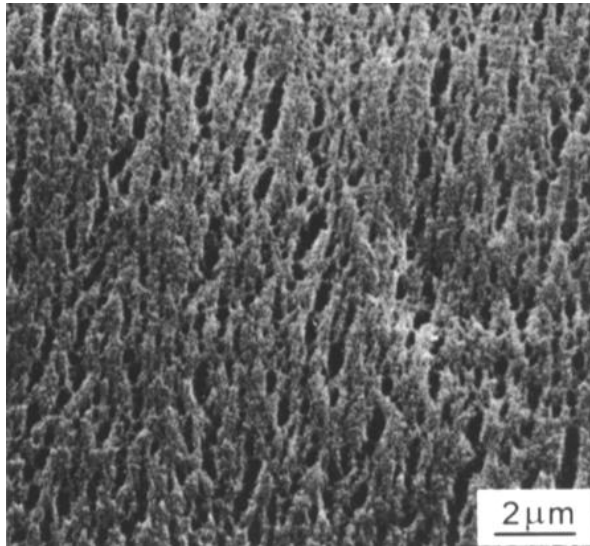


Fig. 2.3. The three modes of fracture: I, opening mode; II, sliding mode; III, tearing mode.

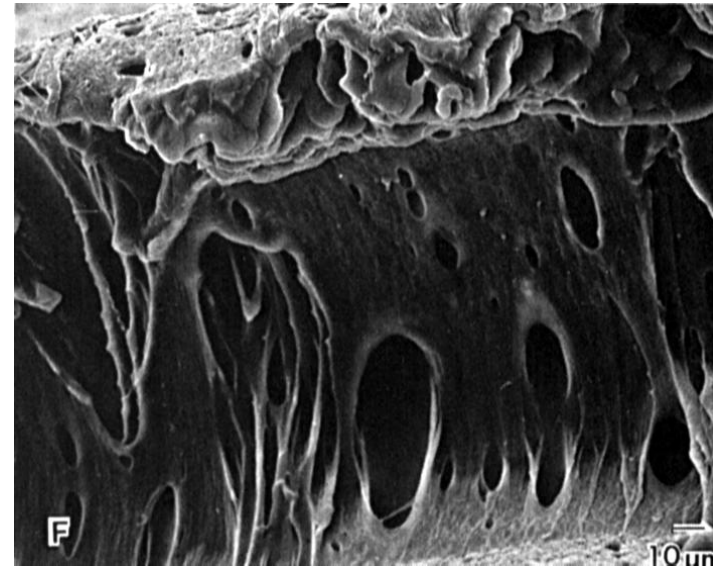
Energy Release Rate: G

7.4 Fracture Properties of Polymers

➤ Fracture surface



Fracture surface of PMMA as observed in a scanning electron microscope. The structure originates from collapsed crazed matter. (Doll, W. in *Fractography and failure Mechanism of Polymers and Composites*, page 405, Elsevier, 1989.)



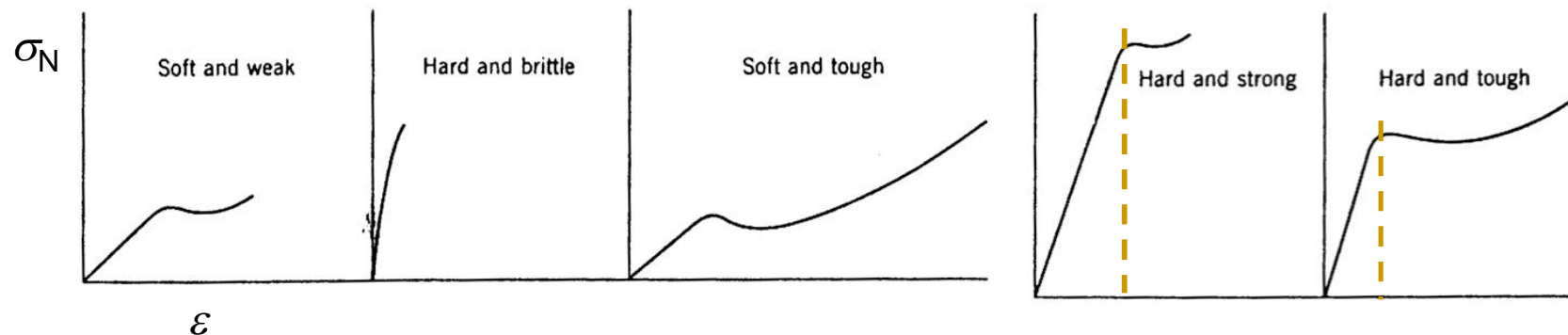
SEM picture of a Nylon fracture surface. The specimen with high elongation properties exhibited ductile failure. (Sawyer, L.C.; Grubb, D. T. *Polymer Microscopy*, Chapman & Hall, London, 1996, page 150.)

- Microscopically smooth fracture surfaces, which would result for a cleavage in a truly brittle fracture, are not observed in polymers.

Tensile stress-strain curves for several types of polymeric materials

$$\frac{d\sigma_N}{d\varepsilon} = 0$$

Yield point:
屈服点



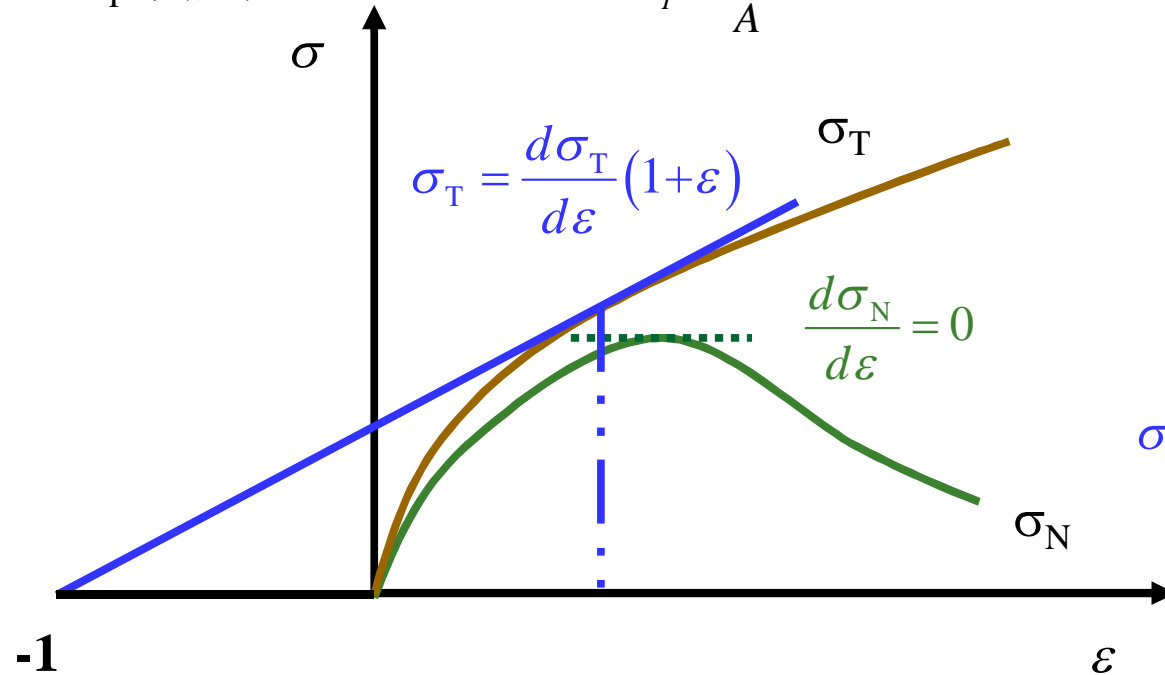
Characteristic features of stress-strain curves as related to polymer properties

Description of Polymer	Characteristics of Stress-Strain Curve			
	Modulus	Yield Stress	Ultimate Strength	Elongation at Break
Soft, weak	Low	Low	Low	Moderate
Soft, tough	Low	Low	Yield stress	High
Hard, brittle	High	None	Moderate	Low
Hard, strong	High	High	High	Moderate
Hard, tough	High	High	High	High

Yield criterion for nominal stress and true stress

σ_N : 习用应力(工程应力) $\sigma_N = \frac{F}{A_0}$

σ_T : 真应力 $\sigma_T = \frac{F}{A}$



Consideres' plot

$$\frac{d\sigma_N}{d\epsilon} = 0$$

$$Al = A_0 l_0 \quad A = \frac{A_0 l_0}{l}$$

$$\epsilon = \frac{l - l_0}{l_0} \quad \frac{l}{l_0} = 1 + \epsilon$$

$$\sigma_T = \frac{F}{A} = \frac{F}{(A_0 l_0 / l)} = (1 + \epsilon) \sigma_N$$

$$\sigma_N = \frac{\sigma_T}{1 + \epsilon}$$

$$\frac{d\sigma_N}{d\epsilon} = \frac{1}{(1 + \epsilon)^2} \left[(1 + \epsilon) \frac{d\sigma_T}{d\epsilon} - \sigma_T \right] = 0$$

$$\sigma_T = \frac{d\sigma_T}{d\epsilon} (1 + \epsilon) = k (\epsilon + 1)$$

7.4 Fracture properties of amorphous and crystalline or semi-crystalline polymers

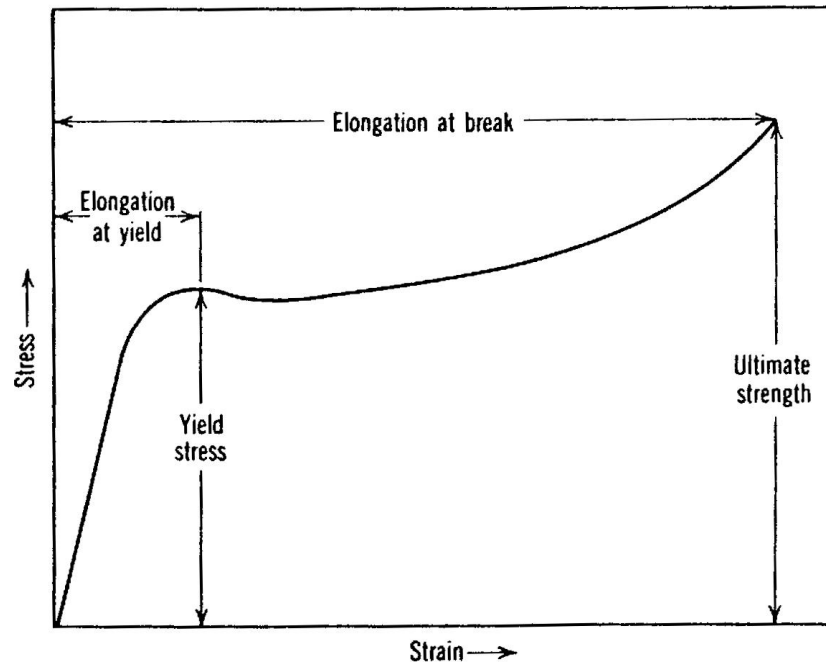
➤ Mechanical Strength of polymers

tensile modulus (拉伸模量) – 刚性

bending strength (弯曲强度)

impact strength (抗冲强度) – 韧性

➤ General tensile stress-strain (load-extension) curve for plastics



(1) Very small strain

Linear, follows Hooks law

(2) Strain at yield

Neck, Shear band, Craze

(3) Strain after yield

Cold-drawing

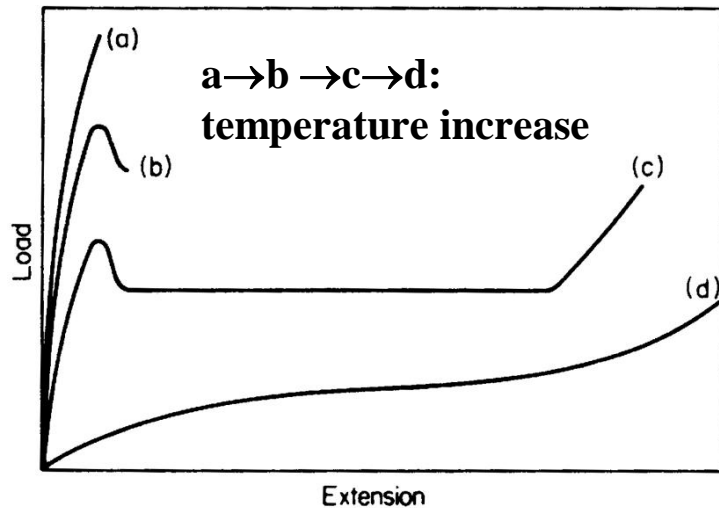
Craze and Crack

(4) Strain at break

Ultimate strength and stress

7.4.1 Yield Process and Fracture of Polymers

➤ Temperature dependence of the stress-strain curves



Load-extension curves for a typical polymer tested at four temperatures showing different regions of mechanical behavior.

(a) brittle (脆性) fracture, (b) ductile failure (韧性) (冷拉) and (d) homogeneous deformation (quasi-rubber-like behavior)

- At low temperature ($T < T_b$) the load rises approximately linearly with increasing elongation up to the breaking-point.
- At higher temperatures ($T > T_b$) a yield point is observed and the load falls before failure. Sometimes with the appearance of a neck: i.e. ductile failure, but still at low strain (typically 10-20 %).
- At still higher temperatures ($T_b < T < T_g$), under certain conditions, strain hardening occurs, the neck stabilizes and cold-draw ensures. The extensions in this case are generally very large, up to 1000 %. – **Forced high elastic deformation**
- At even higher temperatures ($T > T_g$), homogeneous deformation is observed, with a very large extension at break.

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: $T_g = T_g(\infty) - \frac{K}{M_n}$

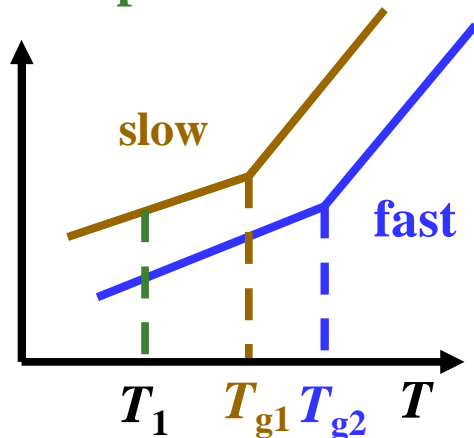
➤ Heating rate dependence

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

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

ν 升温速度

t 停留时间



T_1	$t_s \ll \tau_1$	$t_f \ll \tau_1$
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, $T_g/T_m \approx 1/2$

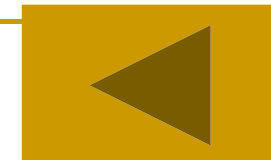
For asymmetrical backbone, $T_g/T_m \approx 2/3$

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

➤ T_g vs. T_b

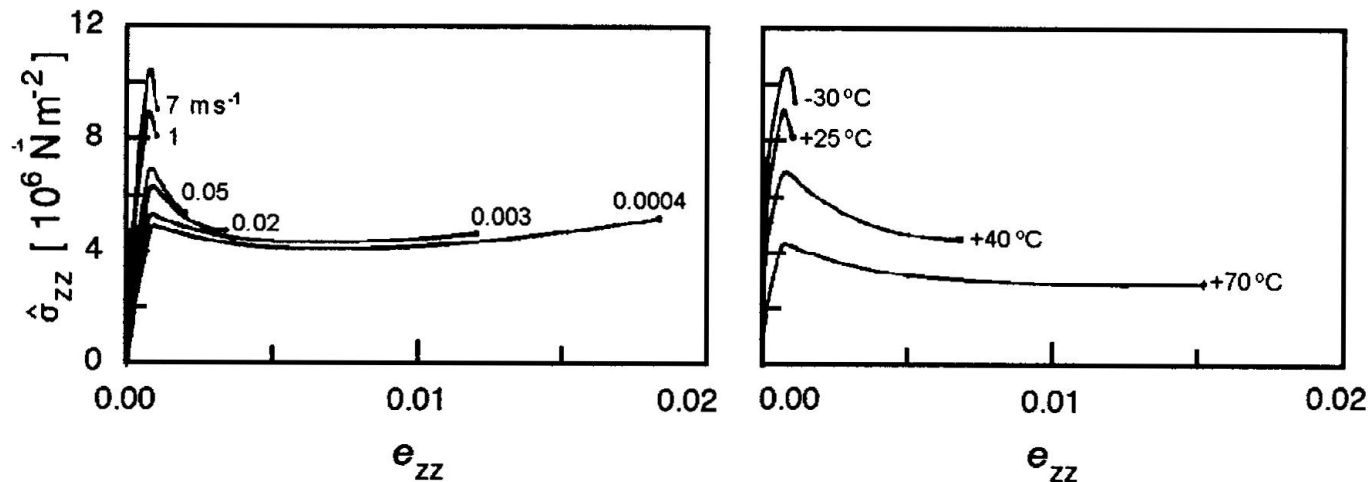
$T_g - T_b \approx 0$ 高度柔性和刚性链

$T_g - T_b \neq 0$ 中度刚性链 强迫高弹形变



Yield Process of Polymers

➤ Strain rate dependence of the stress-strain curves



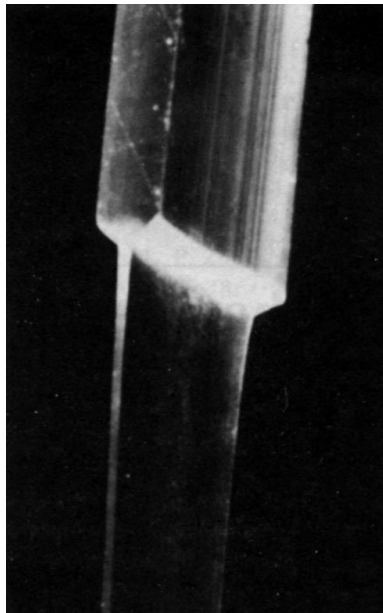
Load-extension curves of PVC measured at room temperature or indicated strain rates (*left*) and at different temperatures for a constant strain rate (1 ms⁻¹) (*right*). (Retting, W. *Rheol. Acta* 1969, 8, 259.)

- Yielding is based on specific relaxation processes and thus depends on the ratio of strain rates to respective relaxation rates.
- The large deformation occurred after yield is irreversible at low temperature, but can be recovered at T_g . Yielding is related to plastic flow (塑性流动).

Yield Process and Fracture of Polymers

➤ Shear yielding (剪切屈服)

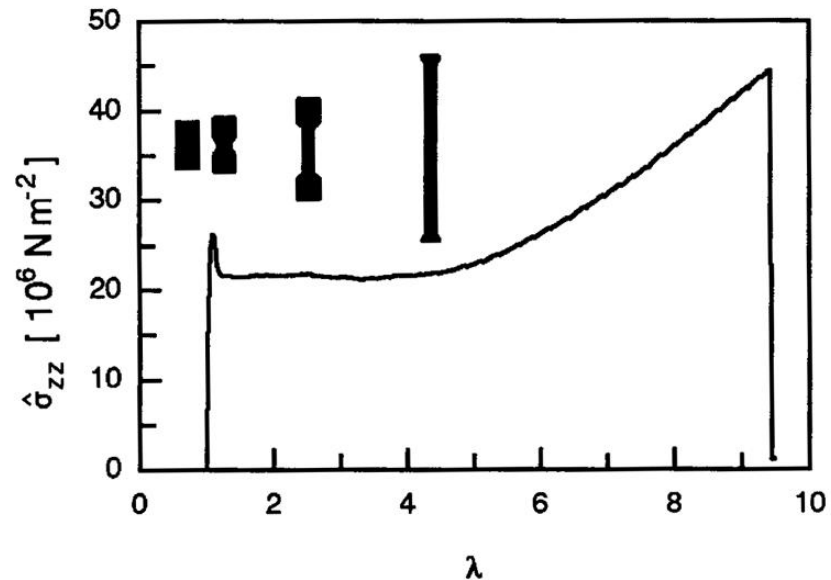
Typical for semicrystalline polymers and also several amorphous polymers



Photograph of a neck formed in the redrawing of oriented polyethylene



Schematic drawing of a cross section through a neck region of drawn polymers

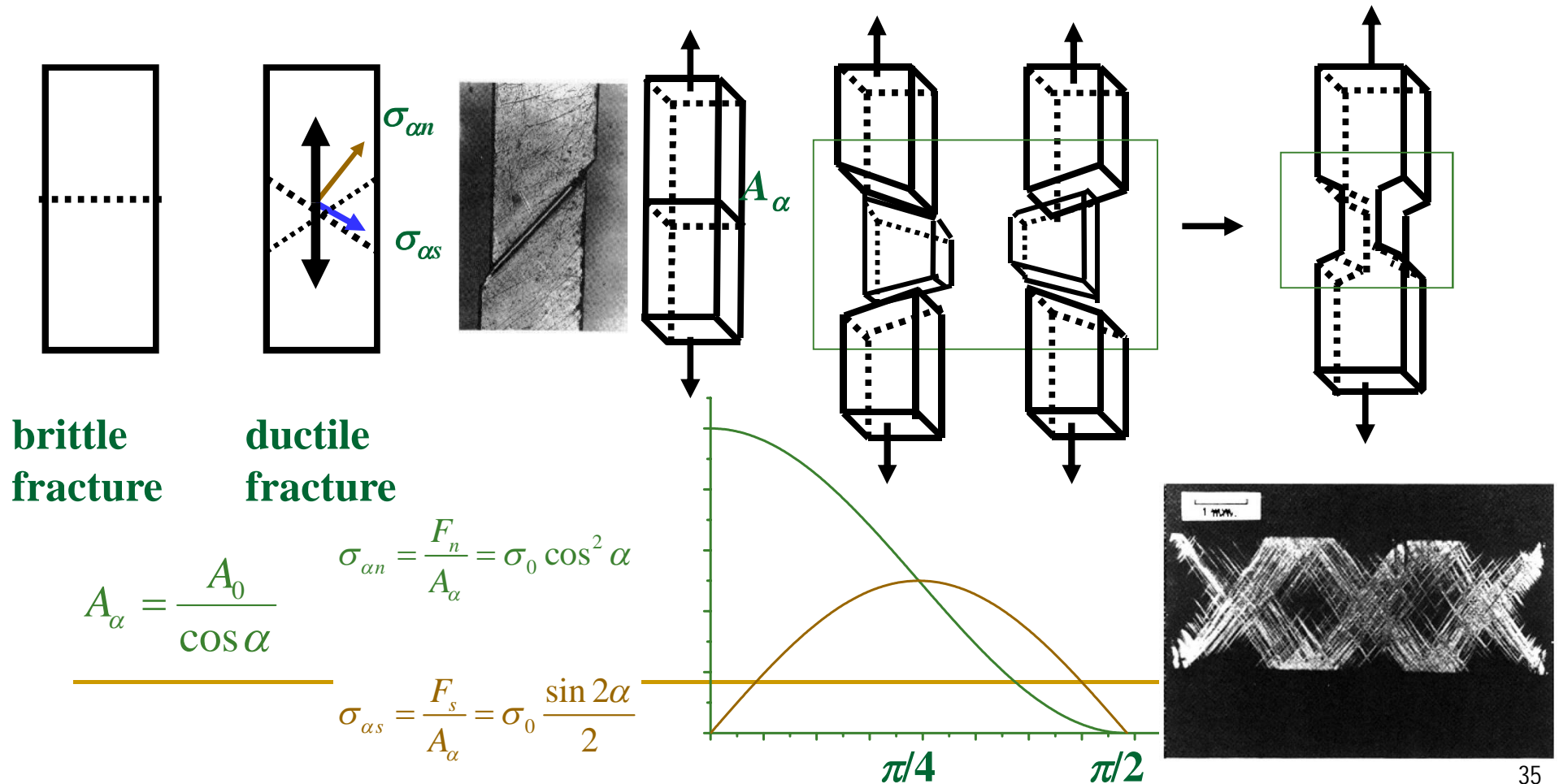


Load (nominal tensile stress)-extension (extension ratio) curve of a sample of PE (M of 3.6×10^5 , drawing velocity $d\lambda/dt = 2.4 \times 10^{-2} \text{ s}^{-1}$). The changes in shape of the sample are schematically indicated.

Shear Yielding Process

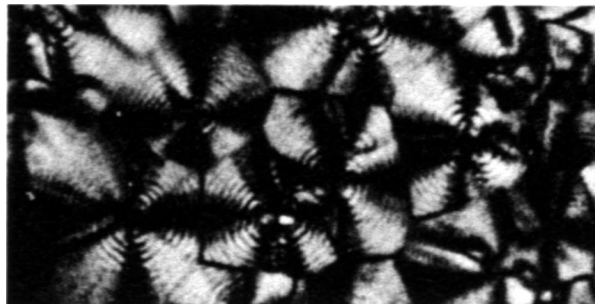
➤ Structure changes on cold-drawing

■ (1) Macroscopic Structure changes - Shear band (剪切带)

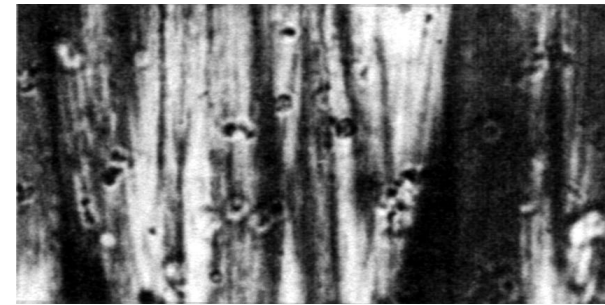


Shear Yielding Process

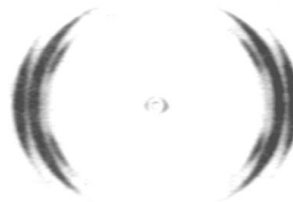
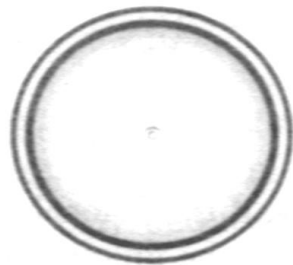
(2) Microscopic structure changes of crystalline polymers



Cold-drawing



Morphological changes on cold-drawing, observed for a film of PE in a POM. Hay, I. L.; Keller, A. Z. *Kolloid Polym.* 1965, 204, 43.

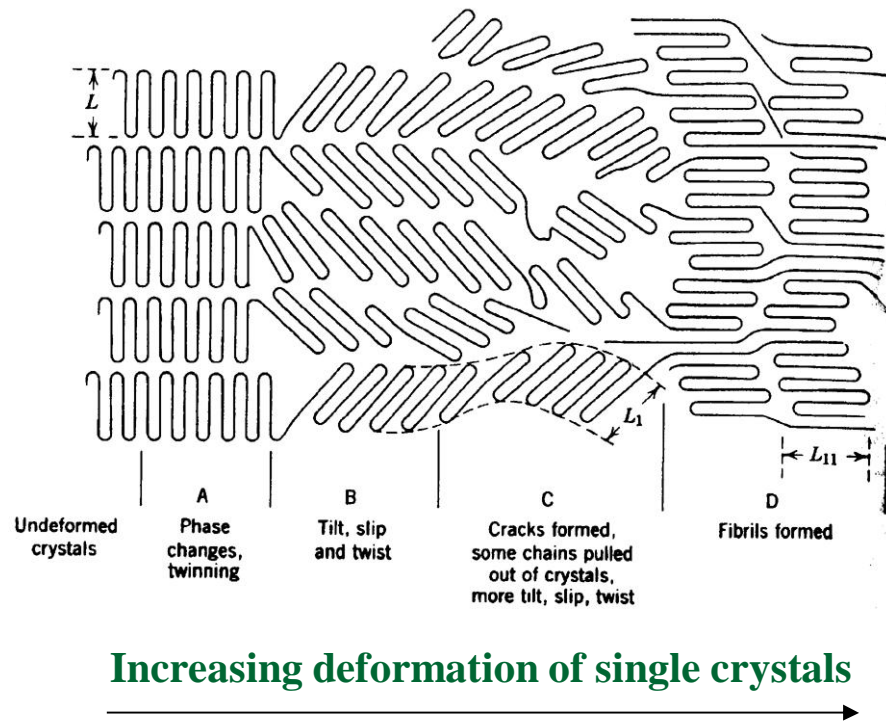


X-ray diffraction patterns of PE, as registered for the isotropic part (*left*), the center of shoulder (*center*) and the neck (*right*) of a cold-drawn sample. The two reflections in the isotropic pattern are to be assigned to (110) and (200) planes of orthorhombic PE. The third reflection with a larger lattice plane spacing emerging in the textured patterns is due to another metastable crystalline phase which forms during drawing

Shear Yielding Process

(2) Microscopic structure changes of crystalline polymers

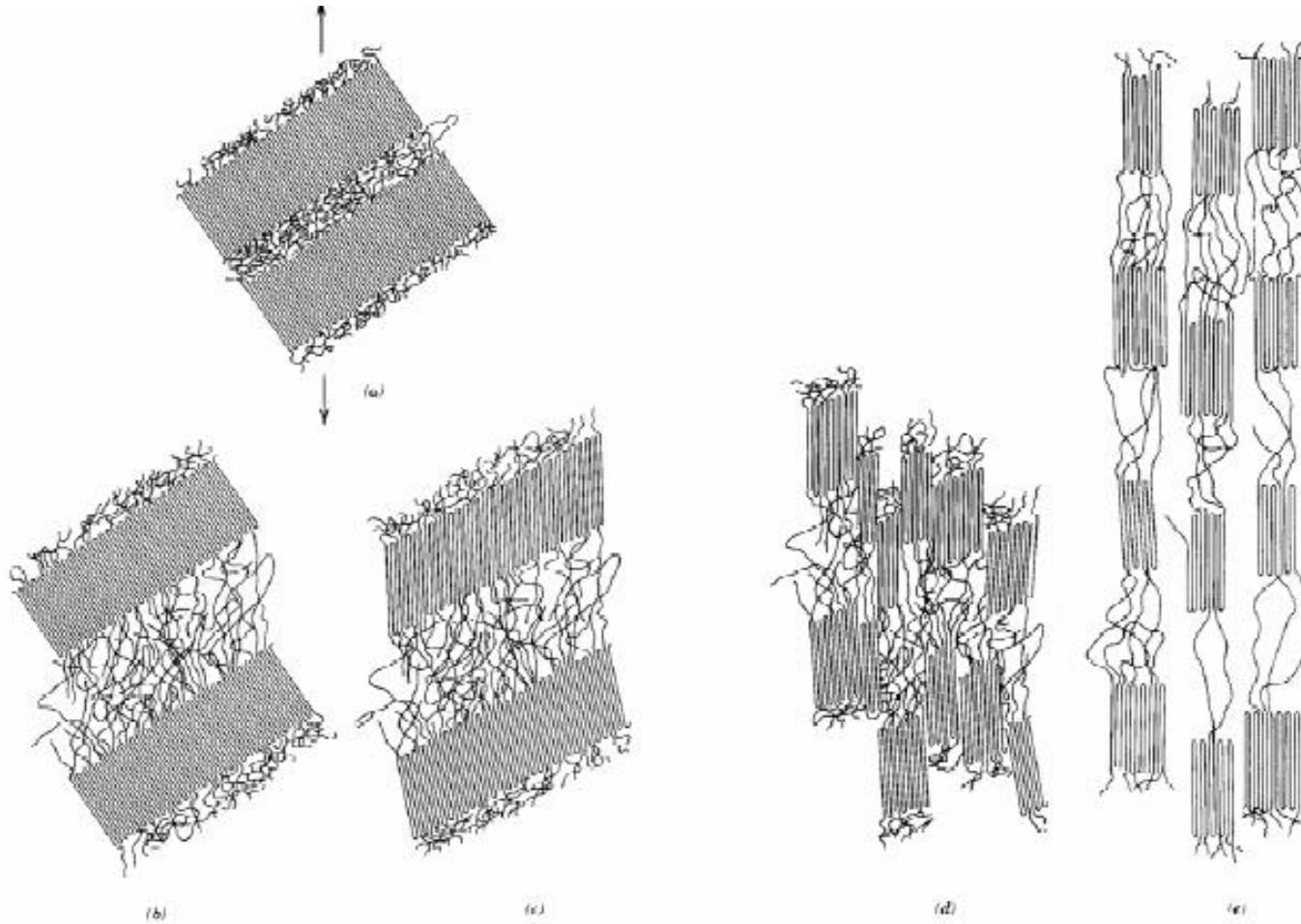
Molecular processes during yield



- affine deformation region, small;
- slip and rotation between lamellae;
- deformation of lamellae along slip planes, twinning and phase transformation;
- Change to fibrillar superstructure;
- Rearrangement within the fibrils (tie molecules between blocks of folded chains with the fibril and between the fibril).

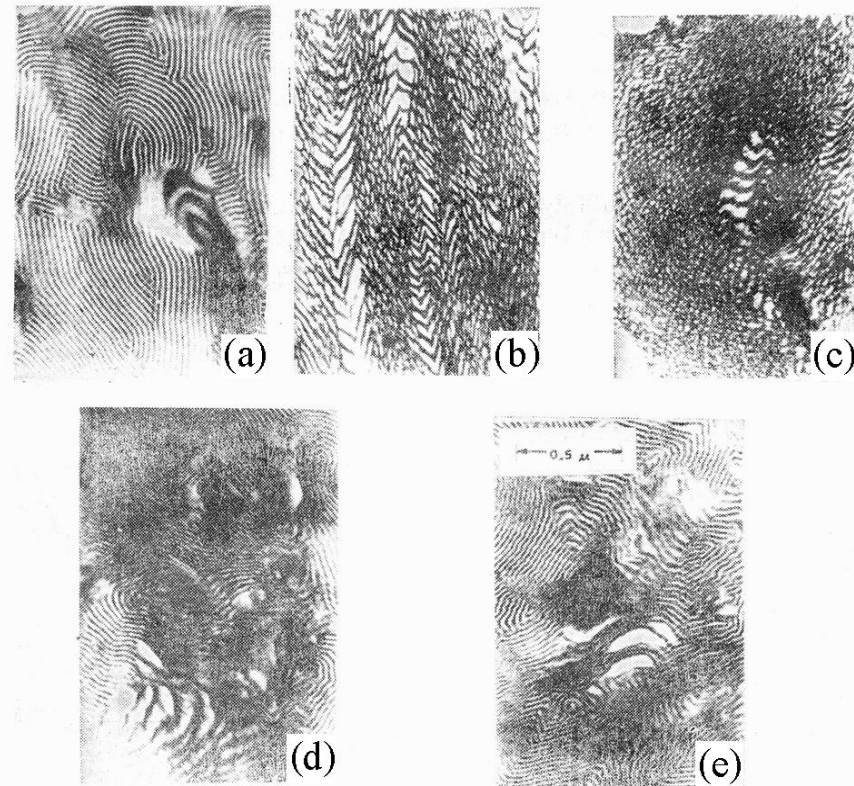
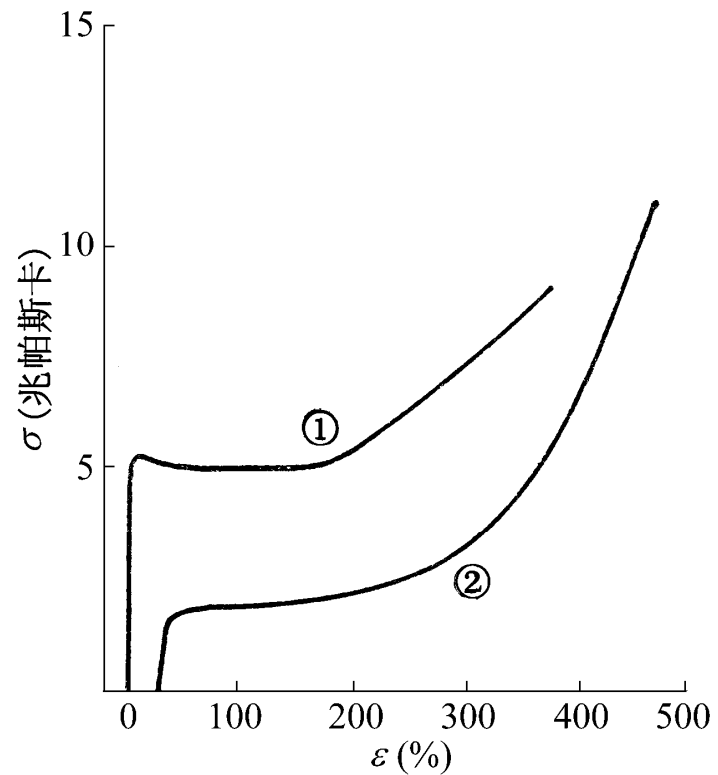
Schematic drawing of the deformation stages on drawing of folded chain lamellae

(2) Microscopic structure changes of crystalline polymers



Shear Yielding Process

(3) Microscopic structure changes of block copolymers



SBS triblock copolymer

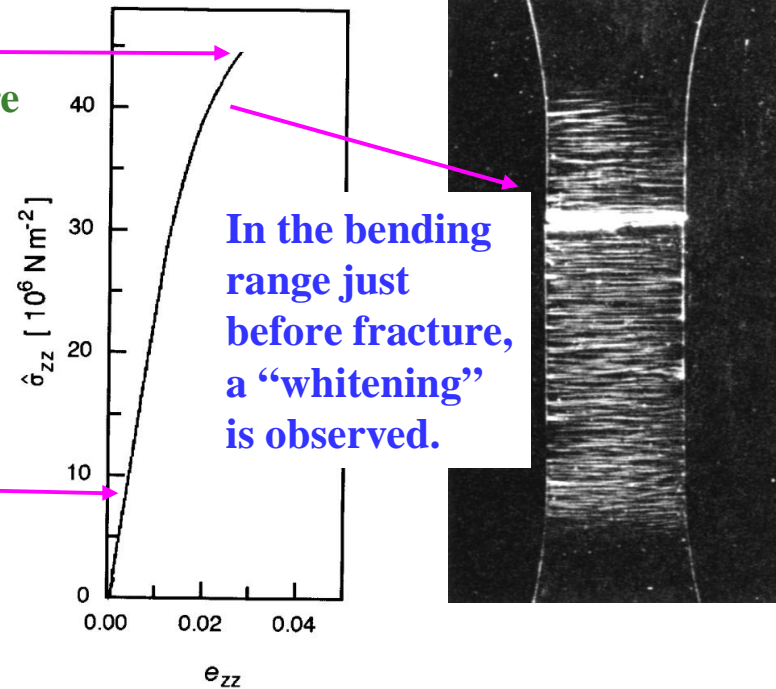
Strain Induced Plastic-to-Rubber Transition

7.4.2 Crazeing and Fracture of Polymers

➤ Stress whitening (应力发白)

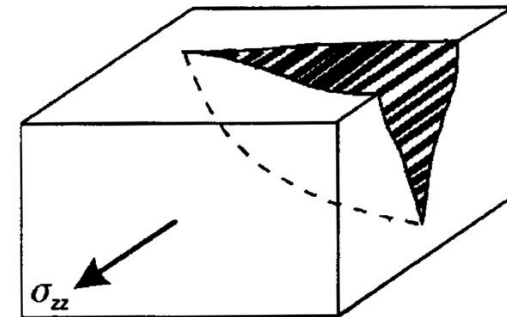
The sample breaks before the force reaches the maximum

The force increases at first linearly



Tensile stress-strain curve of a sample of PS and photograph showing crazes

- Craze (银纹): contains fibrils in void matrix. The fibrils have diameters in the order of 10 nm and fill the craze volume to about 50 %.

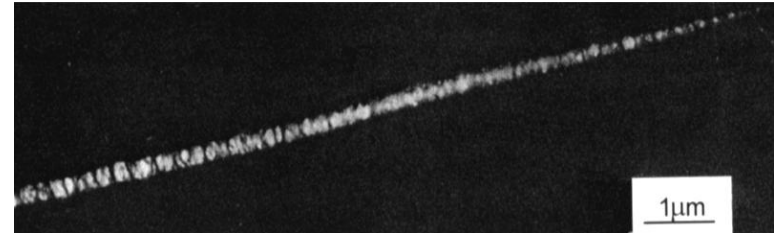


Schematic of an edge-located craze. The surfaces of the deformation zone are connected by fibrils which fill the craze only partially.

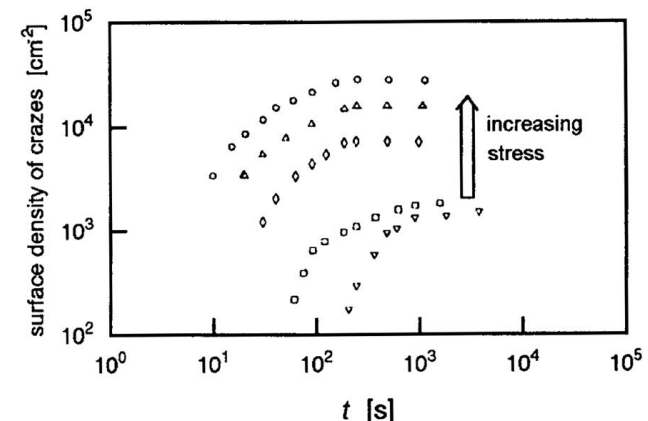
Crazing of Polymers

➤ Craze: localized zones of plastic flow

- Crazes form primarily in amorphous polymers, for MWs above the entanglement limit. There is no craze formation under compression or under pure shear.
- The typical situation leading to craze initiation is the imposition of an uniaxial (单轴) or biaxial (双轴) stress. If such stress are applied and fulfill certain threshold condition, crazes form statistically, preferentially at first at the sample surface.
- Removing the stress, the crazes close their openings somewhat, but survive. They disappear only if the sample is annealed at temperature above T_g .



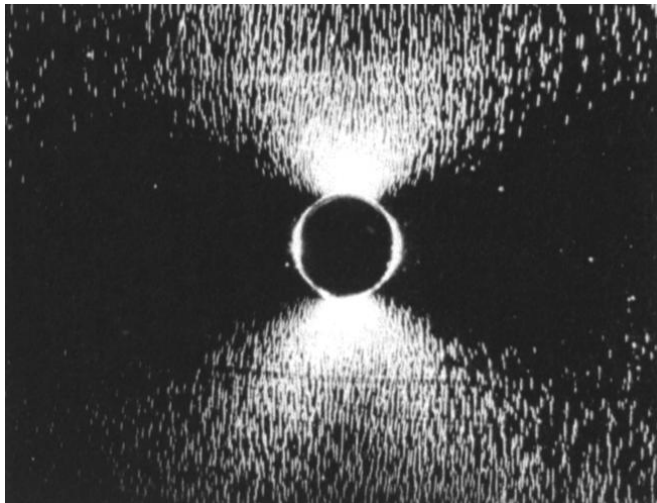
TEM image of a microtomed ultrathin slice which cuts through a craze in PS. (Kambour, R. P. *Macromol. Rev.* **1973**, 7, 1.)



Increasing of the number of crazes with time, observed for a PS subjected to various states of tensile stress. (Argon, A. S.; etc. *Phil. Mag.* **1977**, 36, 1195)

Crazing of Polymers

- **Craze: localized zones of plastic flow**

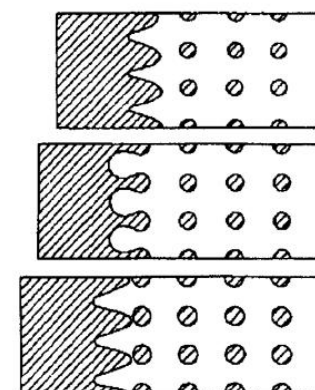
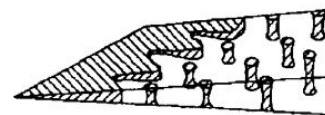
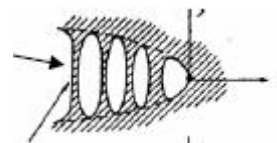


Craze pattern in the vicinity of a hole in the plate of PMMA subjected to a tensile stress in horizontal direction

- **The local heterogeneities may result in a stress intensification, which initiate crazing**

- **Argon's model of lateral craze growth based on the phenomenon known as "meniscus instability". Side view on the corrugated polymer-air interface (left). Advances of the craze front by a repeated break-up of the interface (view in fibril direction, right).**

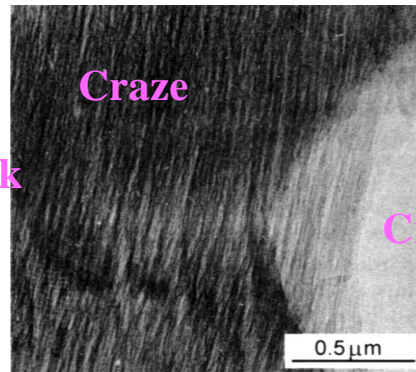
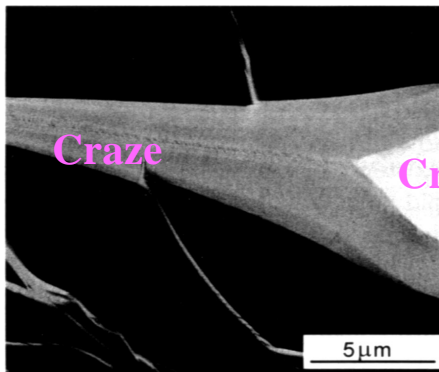
(Argon, A. S.; etc. *Phil. Mag.* **1977**, 36, 1195)



Crazing and Fracture of Polymers

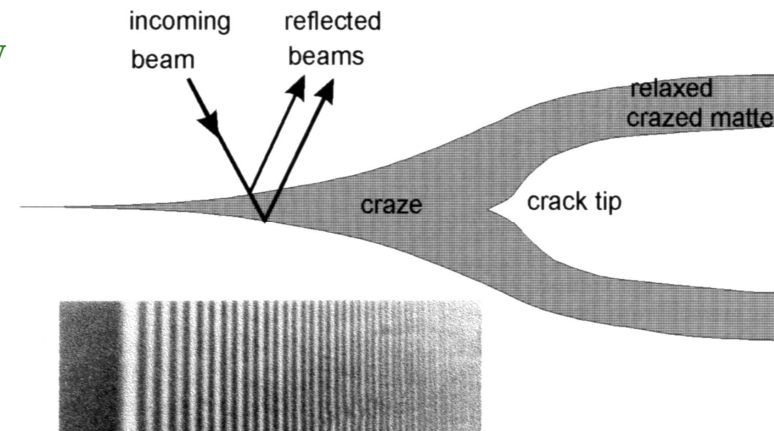
➤ Crack (裂缝) and fracture

For polymers, the work required for the formation of surface during fracture is obviously dominated by a preceding plastic flow.



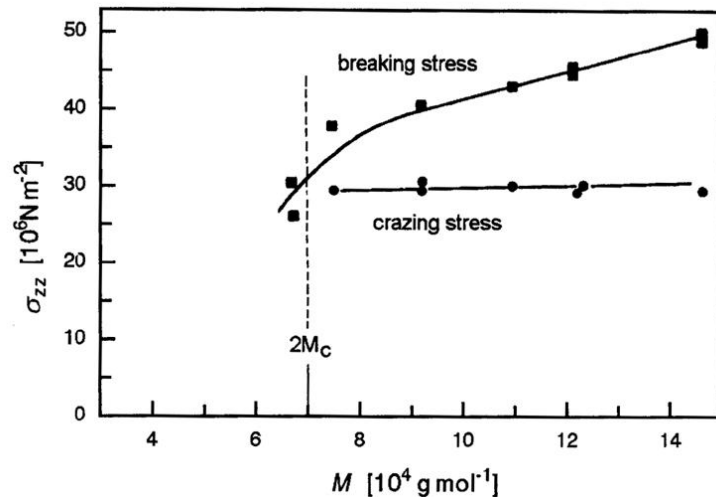
Crack tip (bright sections on the right in both pictures) within a craze in PS. (Michler, G. H. *Kunststoff-Mikromechanik*, page 100, CARL Hanser Verlag, 1992.)

Crack propagation behind a simultaneously moving zone with crazed matter. The profile of the preceding craze tip can be derived from the interference pattern produced by the two reflected beams. The fringe pattern presented here was obtained for PMMA. (Doyle, M. J. *J. Polym. Sci. Polym. Phys. Ed.* **1975**, *13*, 2429.)



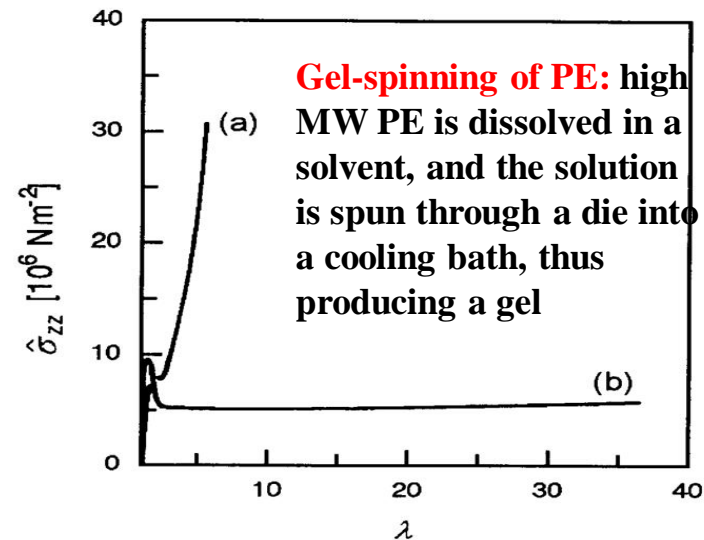
Structure Dependence of Fracture Properties I

➤ Molecular weight and entanglement effect



Crazing and fracture of fractions of PS, subject to uniaxial stress. (Fellers, J. F.; Kee, B. F. *J. Appl. Polym. Sci.* **1974**, *18*, 2355)

- **Stability of the fibrils against rupture increases with the MW**
- **The minimum stresses for crazes are MW independent, indicating that craze initiation is a local event, depending primarily on the interaction between neighboring chain sequences.**

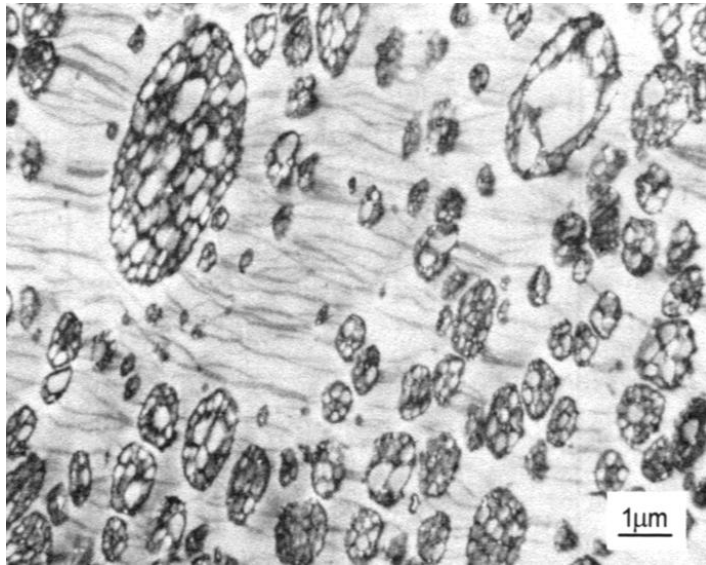


Load-extension curves observed on drawing at room temperature a melt crystallized PE (a) and gel-spun PE fiber. (Lemstra, P. J.; etc. in *Developments in Oriented Polymers-2*, Elsevier Applied Science, 1987, page 39.)

- **A reduction in entanglement density greatly increases the drawability of samples.**

Structure Dependence of Fracture Properties II

➤ High impact polystyrene (HIPS)



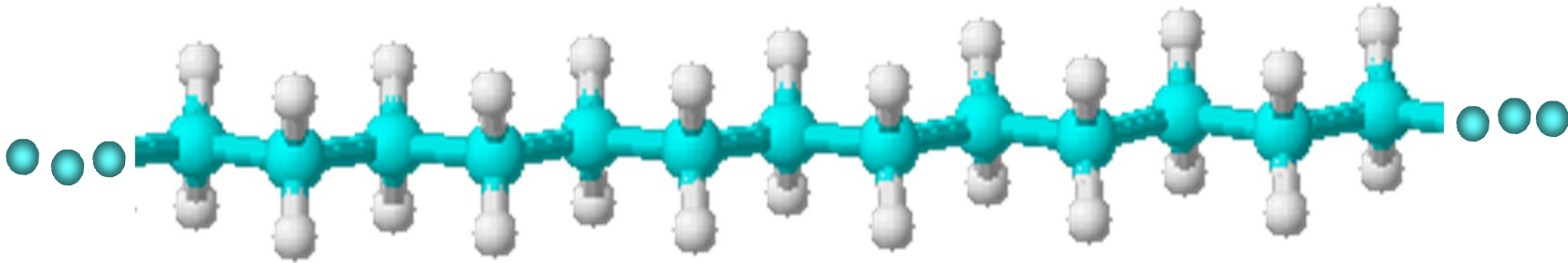
Electron micrograph of a stained microtomed section of HIPS, showing crazes running between the elastomeric precipitates. (Kambour, R. *P. Macromol. Rev.* 1973, 7, 1.)

➤ HIPS: “rubber toughened” thermoplastics.

- mixing polystyrene with an elastomer like polybutadiene results in a two-phase structure.
- Embedded in the PS matrix are spherical inclusions of PB, and there are PS inclusions within the inclusion.
- The tough material is due to the initiation of crazes in large numbers. If the stress is applied, crazes are generated at the surface of the inclusions, which produce a stress intensification.
- Each craze runs only to an adjacent rubber particle and there becomes arrested.

Unique Features of Polymers

(1) Large Spatial Extent

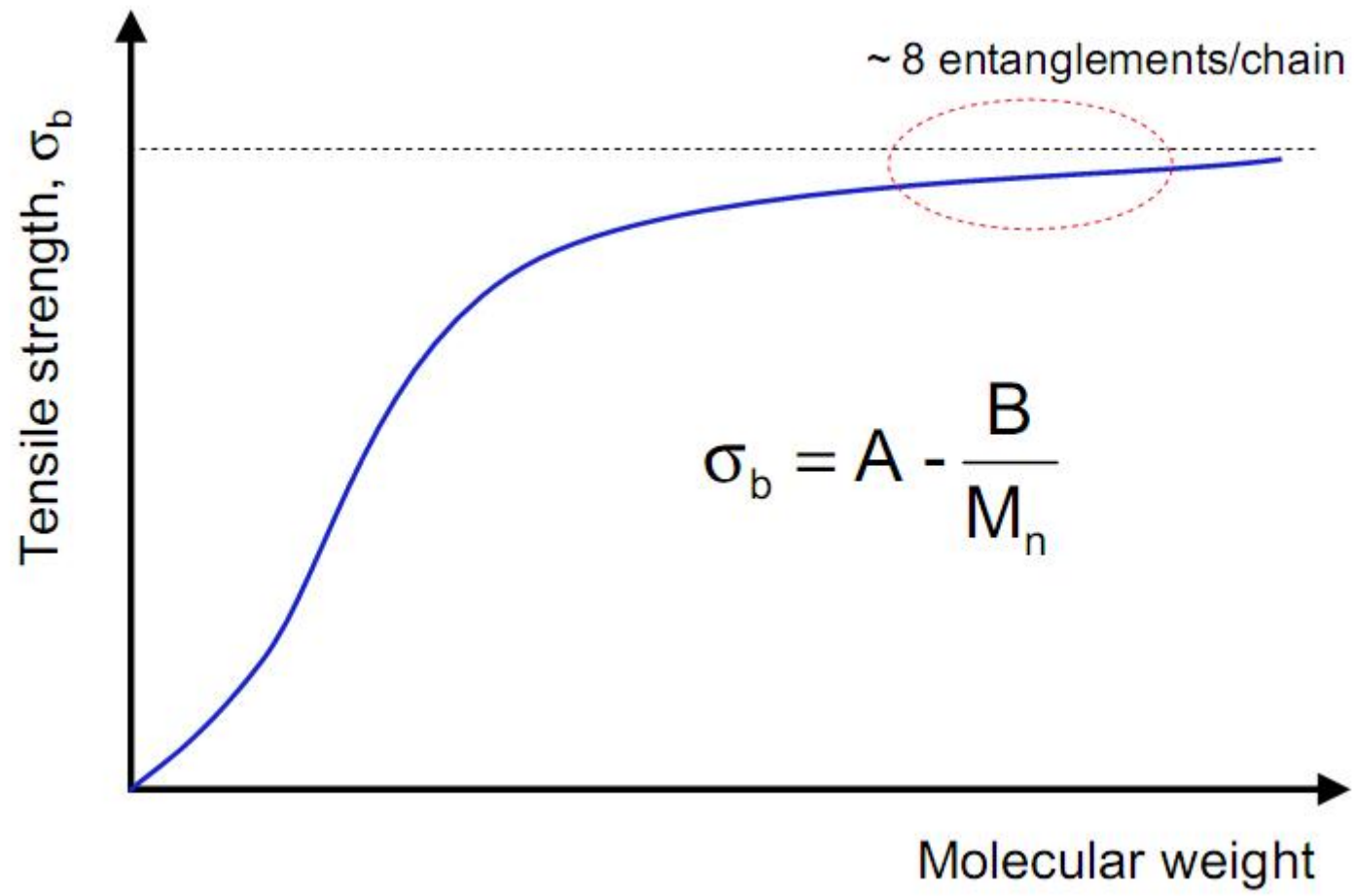


$N \gg 1$

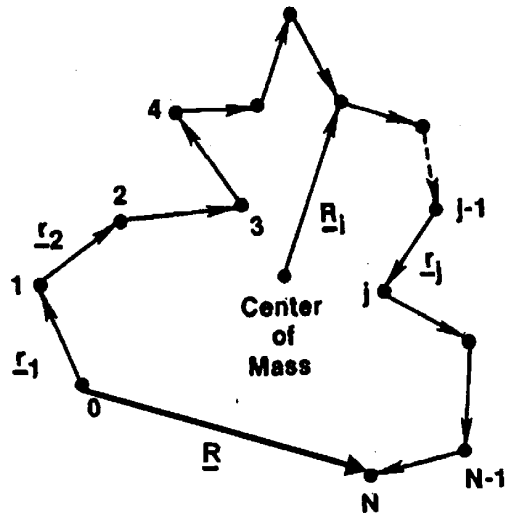
合成高分子 $N \sim 10^2 - 10^4$

天然高分子 $N \sim 10^9 - 10^{10}$ DNA、RNA, Protein,...

Polydispersity



The Mean Size of a Polymer Chain



Radius of gyration

$$\bar{R} \sim \bar{h} \approx CN^\nu l$$

Root Mean Square of end-to-end Distance

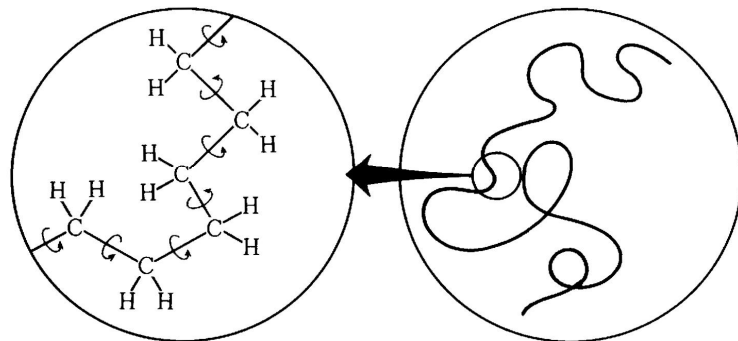
$$\langle h^2 \rangle = Nl^2 + 2 \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathbf{r}_i \cdot \mathbf{r}_j \right\rangle = Nl^2$$

$$\bar{h} \approx \sqrt{\langle h^2 \rangle} = N^{1/2} l$$

$\nu=0.5$ Ideal Chain — Random Walk Chain

$\nu=0.6$ Real Chain — Self-avoiding Chain

Unperturbed Chain:



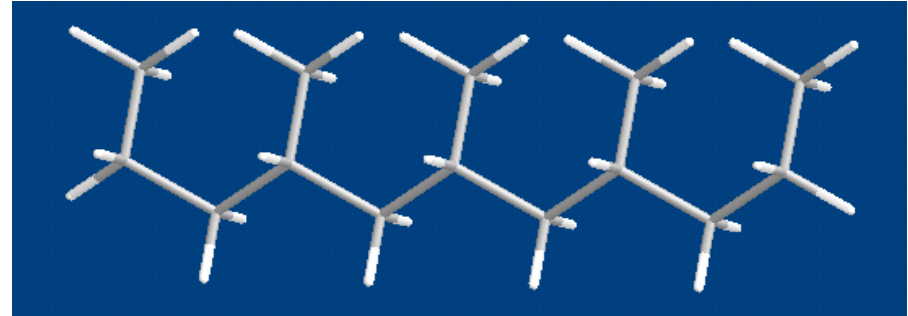
Freely Jointed Chain
and Kuhn Segment l_e

$$\langle R^2 \rangle_0 = \langle h^2 \rangle_0 / 6 = L \cdot l_e / 6$$

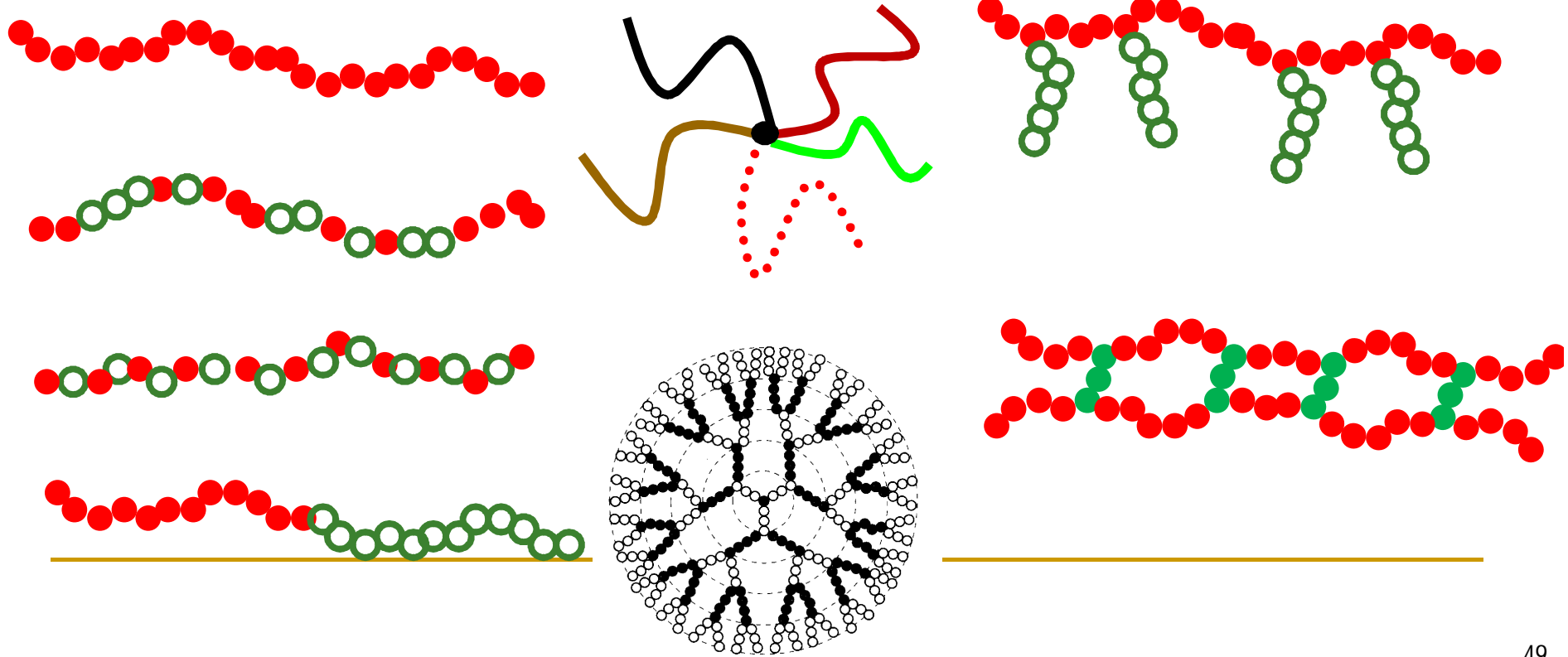
L : Contour Length of a Chain

(2) Connectivity

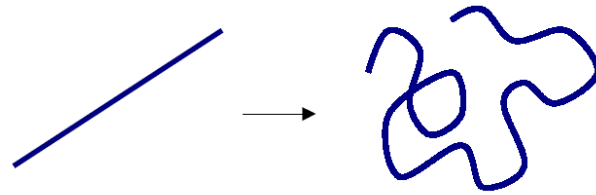
a. Tacticity – 立构性



b. Polymer Topology – Homo, Hetero, Copolymers



c. Flexible vs. Rigid Polymers

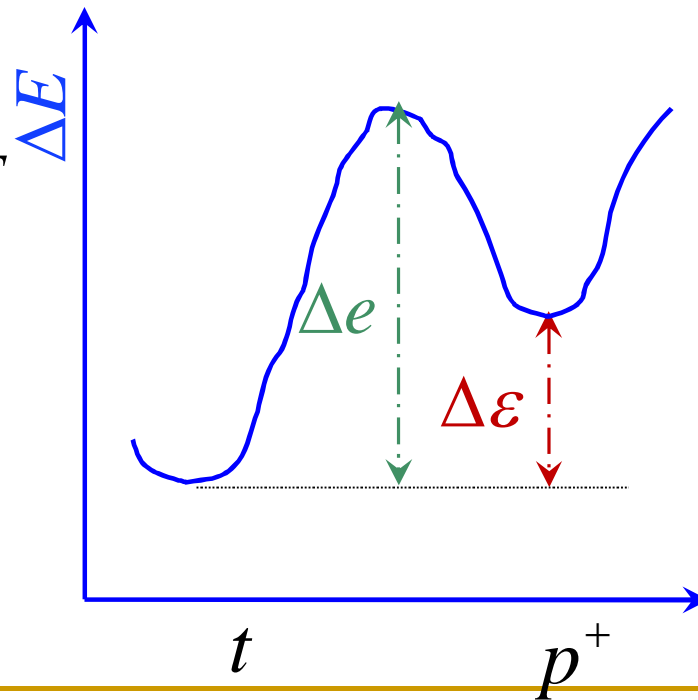


Static Flexibility

Dynamical Flexibility

$$t / p^+ \propto e^{\Delta \epsilon / kT}$$

Persistence Length
 $l_p = l \exp(\Delta \epsilon / kT)$



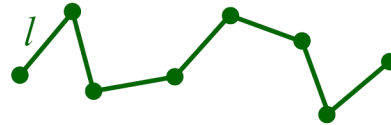
$$r = \omega e^{-\Delta e / kT}$$

$$\omega \sim \text{time}^{-1} \sim (10 \text{ ps})^{-1}$$

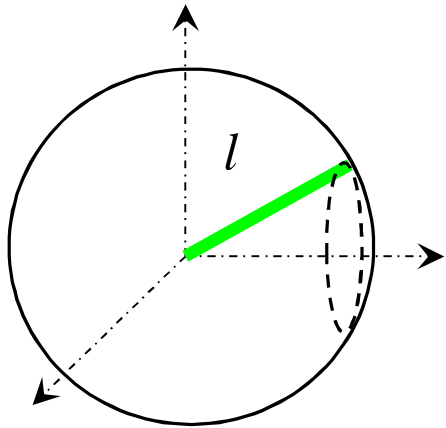
Persistence Time
 $\tau_p = \omega^{-1} \exp(\Delta e / kT)$

d. Multiple Configurations(Confirmations)

$$S = k \ln \Omega$$

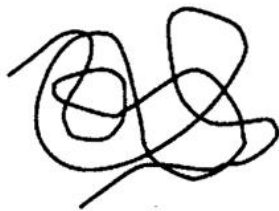


Entropy of Chain Conformations



$$\Omega \propto (4\pi)^N$$

Total number of chain conformations



Ω'

stress

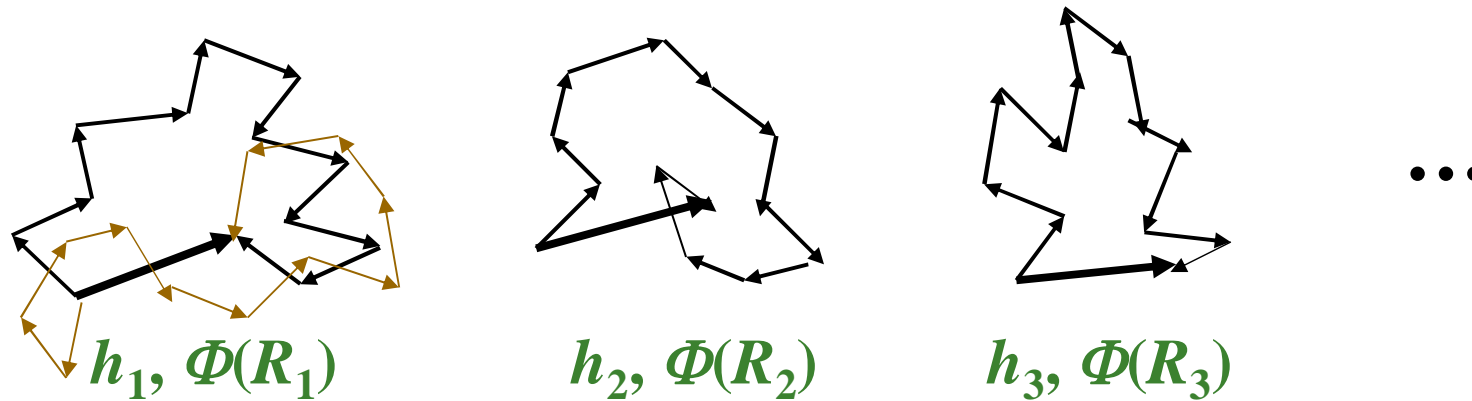


Ω

The number of chain conformations in a state

$$\Delta S \propto k \ln \Omega / \Omega'$$

The Probability Distribution Function of Conformations $\Phi(R)$

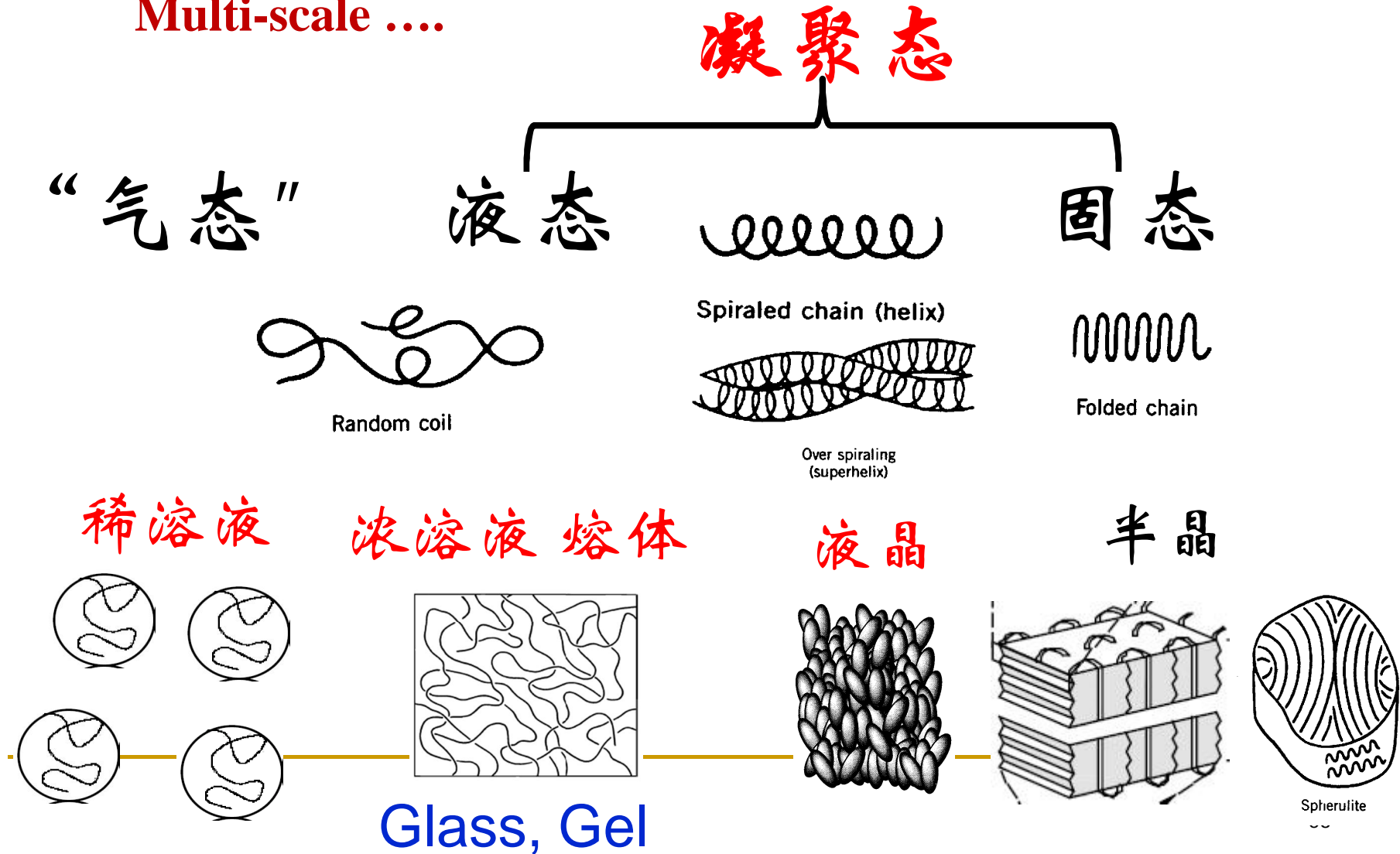


$$\Phi(R) = \left(\frac{\beta}{\pi}\right)^3 \exp\left[-\beta^2 R^2\right] \quad \beta^2 = \frac{3}{2N_e l_e^2}$$

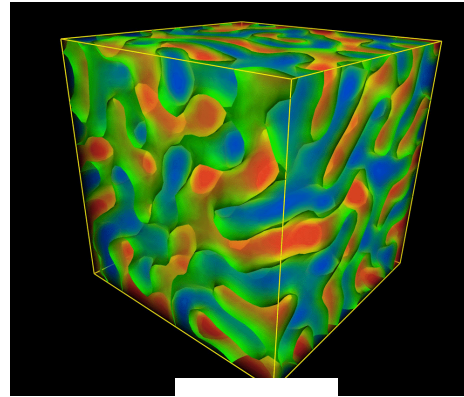
$$\Delta S \propto k \ln \Phi / \Phi'$$

(3) Multiple Interactions

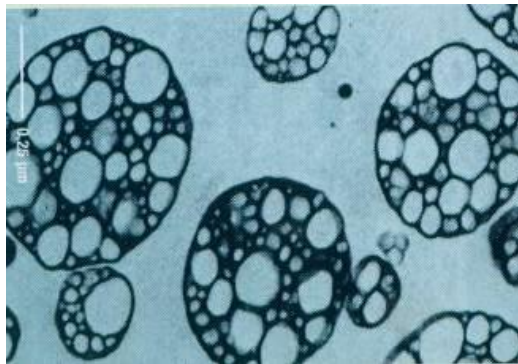
Van der Waals, Hydrogen bond, Electrostatic
Multi-scale



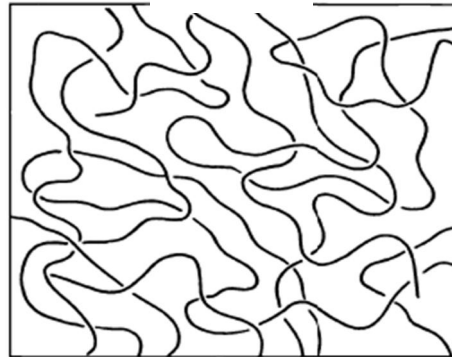
Condensed Matters



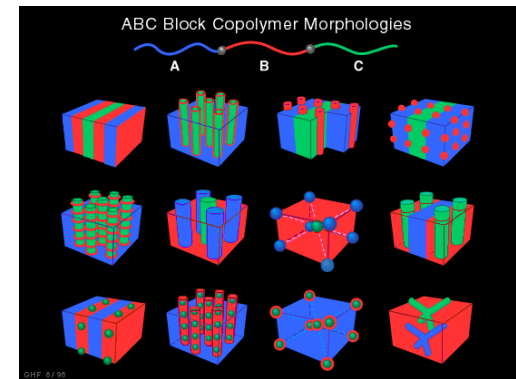
Blend



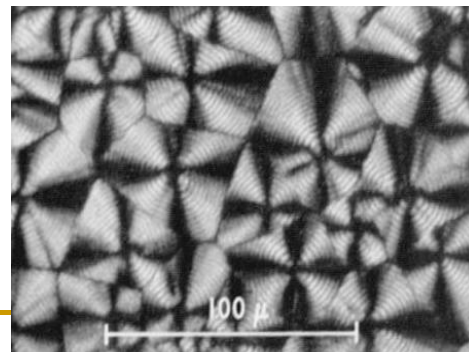
HIPS & ABS



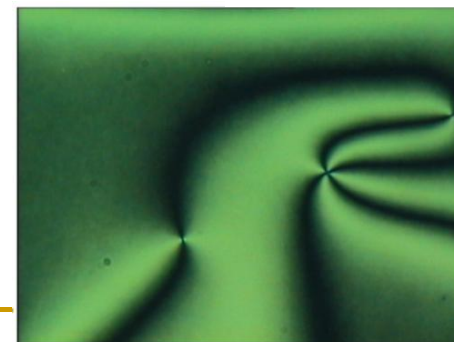
Amorphous & Melt



Triblock Copolymer

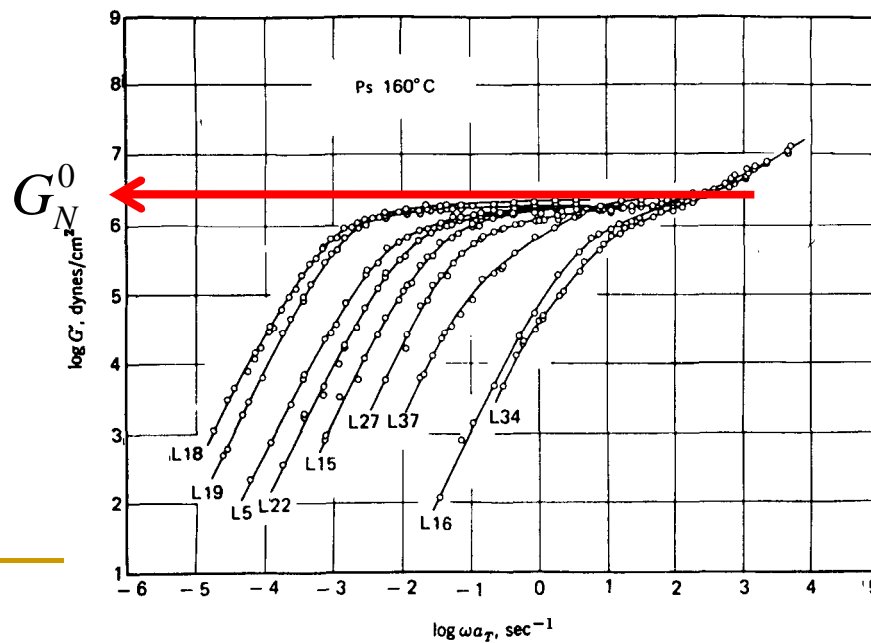
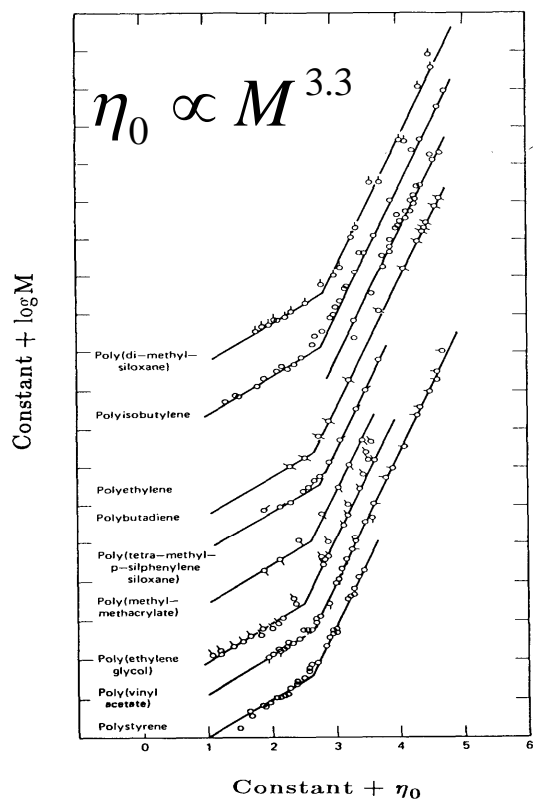
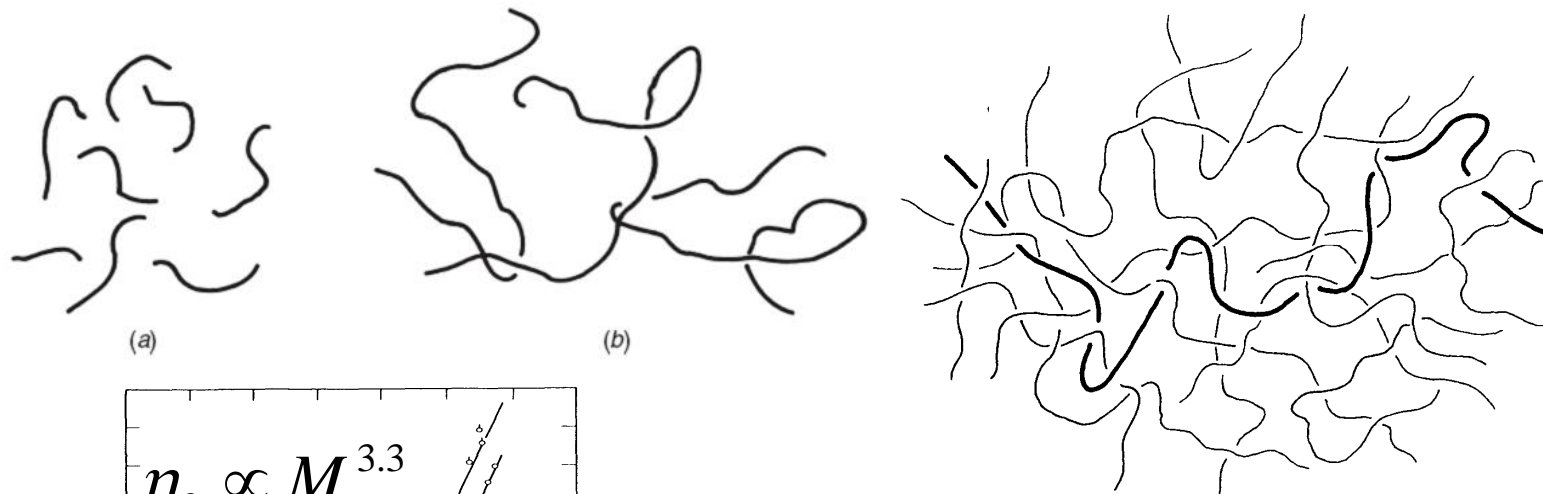


Crystal



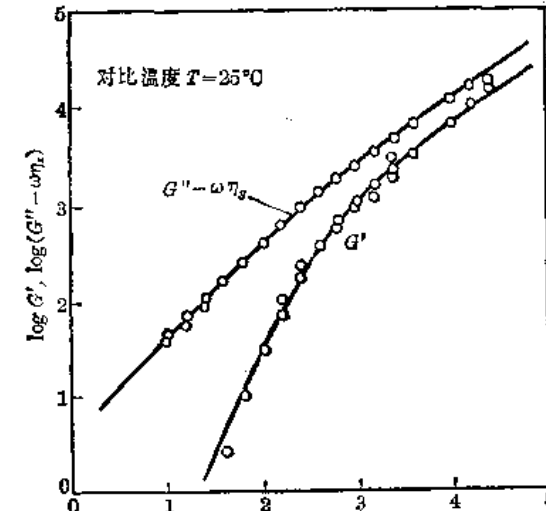
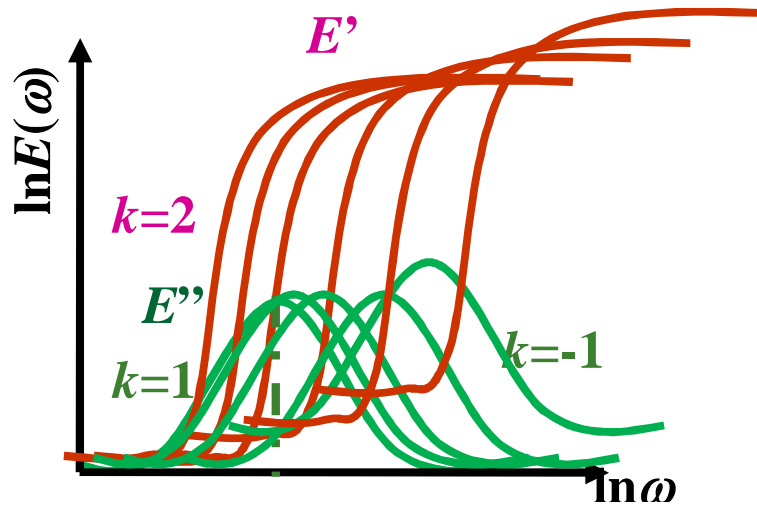
Liquid Crystal

(4) Uncrossibility, Entanglement

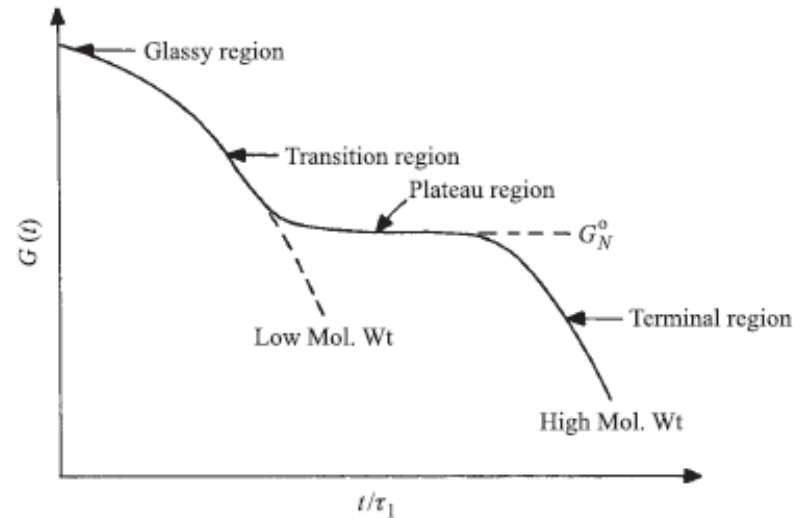
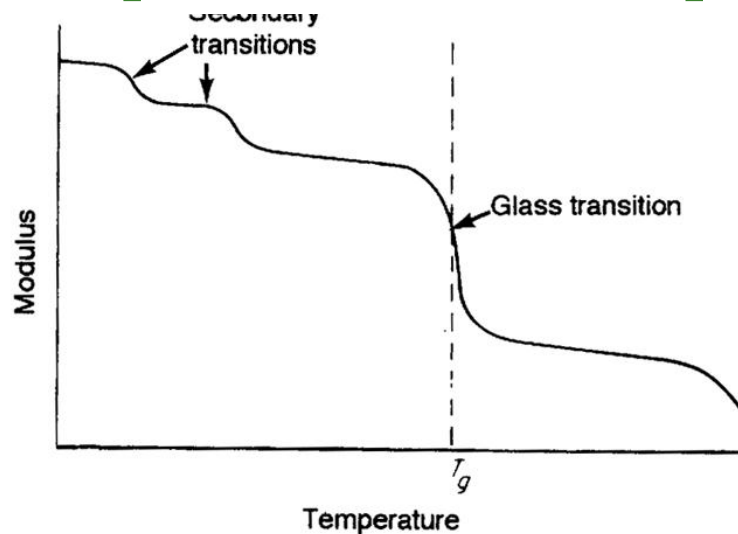


(5) Responsive Molecules - Viscoelasticity

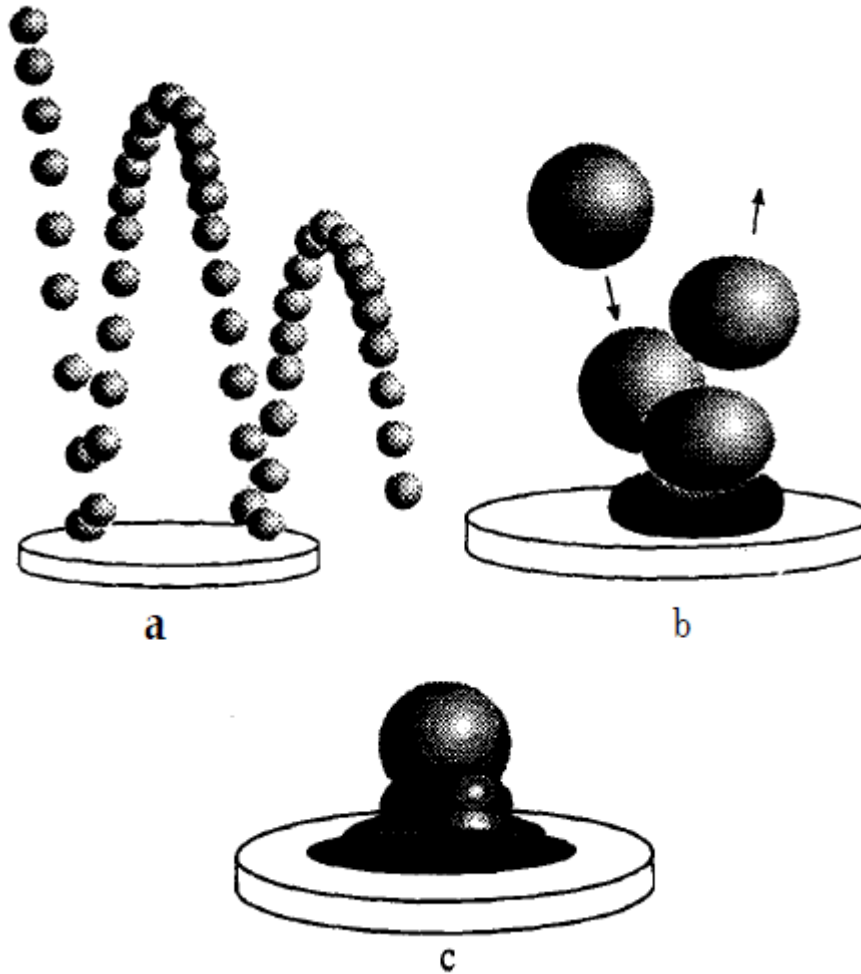
a. Large-scale Relaxation Time Spectrum



b. Temp, Rate and Time Dependent Behavior



b. Temp, Rate and Time Dependent Behavior An Example: Silly Putty



2 Unique Features of Polymers

Thermodynamics:

(1) Large Spatial Extent

(2) Connectivity

a. Tacticity – 立构性

c. Flexible vs. Rigid

b. Polymer Topology

d. Multiple Conformations (Entropy)

(3) Multiple Interactions (Enthalpy)

Dynamics:

(4) Entanglement

(5) Responsive Molecules

a. Large-scale Relaxation Time Spectrum

b & c . Temp, Rate and Time Dependent Behavior

高分子物理中重要的分子理论总结

热力学

链构象统计理论与橡胶弹性理论

Flory-Huggins溶液理论和Flory稀溶液理论(共混物、嵌段共聚物)

突破平均场的标度概念和串滴模型

动力学

经典成核理论及Hoffman二次成核结晶理论

无缠结的Rouse-Zimm链动力学理论

链缠结下的reptation运动和管道模型

几个重要的唯像模型和经验方程

Mark-Houwink方程

粘弹性的几种唯像模型

WLF方程与高分子的松弛时间、时温等效原理

高分子结晶的熔点下降理论

结晶动力学的Avrami方程