Chapter 21

Elastomers

Structure

Thermodynamics

Statistical approach

Mechanical behavior

Elastomer

- rubber (← eraser), ｺﾞﾑ (← gum), elastomer [彈性體]
- Requirements for rubber
  - (1) stretch to > 100% and (2) retract to original dimension instantly
    - flexible chain — T_g < room temp
    - <u>no</u> crystalline phase — EPR vs PE or PP
    - (lightly) crosslinked — how lightly? segmental motion
      - chemically ~ vulcanization [加黃] by sulfur or peroxide
      - physically ~ TPE

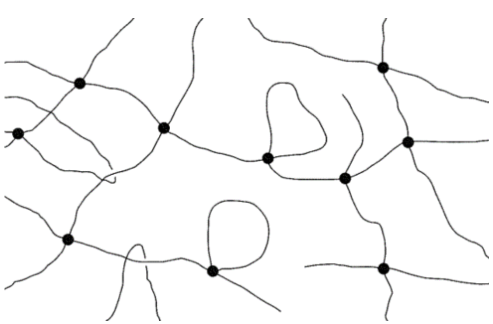
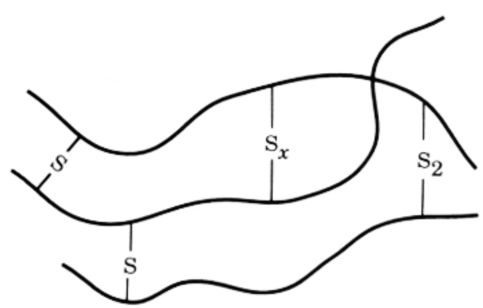
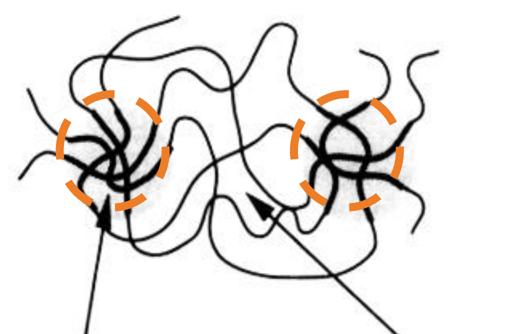


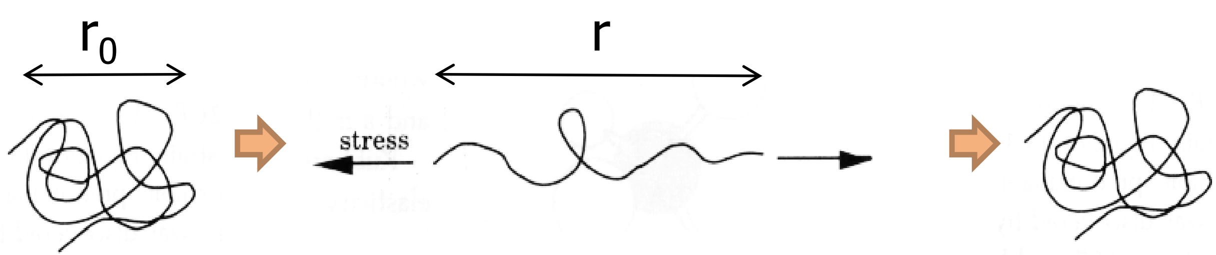
Fig 21.1 p513

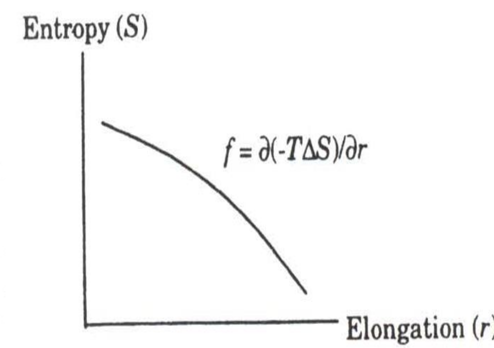




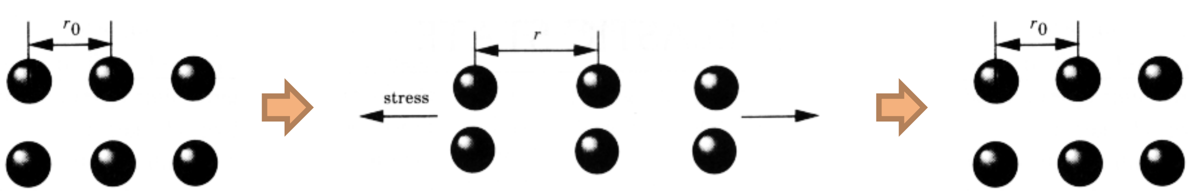
Rubber is an entropy spring.

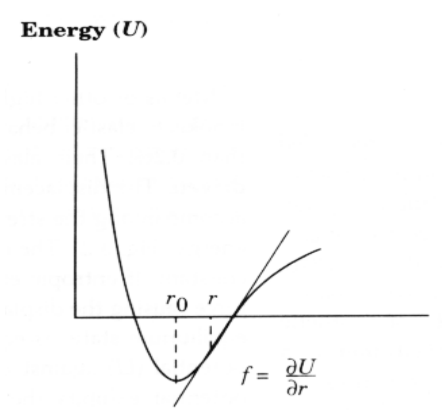
- thermoelastic effect
  - Rubbers contract when heated, and
  - give out heat [get warm] when stretched.
- rubber spring ~ entropy-driven elasticity





  - metal? energy-driven elasticity





(Classical) thermodynamics

- internal energy U

$$dU = đQ - đW \xrightarrow[đW = -f\,dl]{đQ = T\,dS} f\,dl = dU - T\,dS$$

- Helmoltz free energy ← constant volume ← ν = 0.5 for rubbers

$$A = U - TS \longrightarrow dA = dU - T\,dS \longrightarrow f\,dl = dA \text{ (at constant } T\text{)}$$

- retractive force f

$$f = \left(\frac{\partial A}{\partial l}\right)_T = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T$$

energetic [f_e] 0 or small

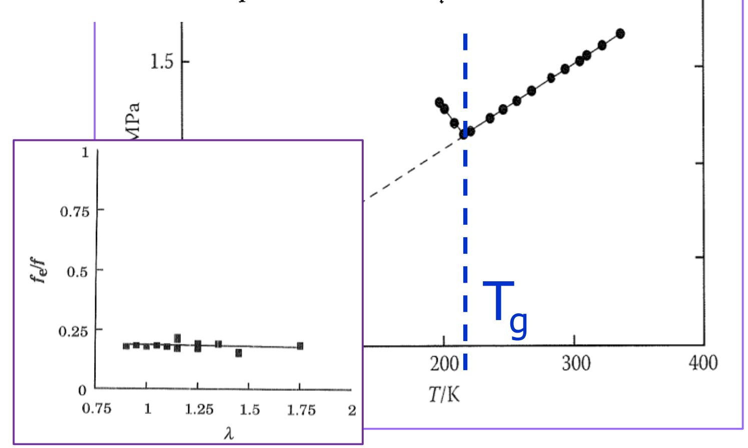
entropic [f_s] dominant

eqn (21.9-14)

$$f = \left(\frac{\partial U}{\partial l}\right)_T + T\left(\frac{\partial f}{\partial T}\right)_l$$

thermodynamic 'eqn of state' for rubber elasticity

Fig 21.3



dU ≈ 0 → dW = dQ
adiabatic stretching → get warm

Statistical theory

- ΔS with deformation
  of one chain from (x,y,z) to (x′,y′,z′)

$$W(x,y,z) = \left(\frac{\beta}{\pi^{1/2}}\right)^3 \exp\left(-\beta^2 r^2\right)$$

$$\beta = (3/(2nl^2))^{1/2}$$

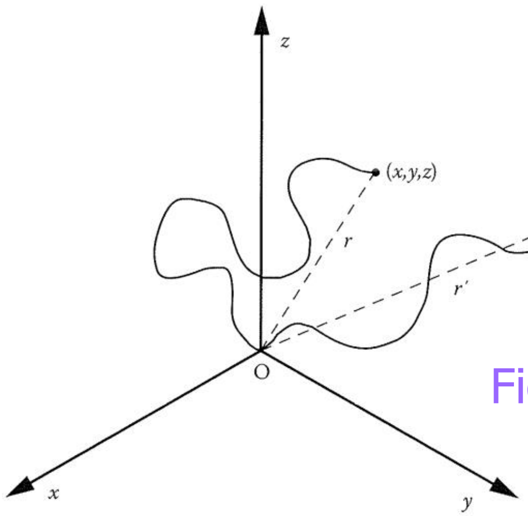


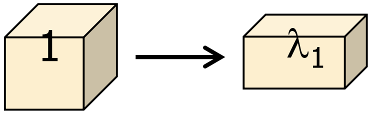
Fig 21.5

$$S = \mathbf{k} \ln \Omega$$

$$S = c - \mathbf{k}\beta^2 r^2$$

$$S = c - \mathbf{k}\beta^2 (x^2 + y^2 + z^2)$$

$$x' = \lambda_1 x, \quad y' = \lambda_2 y, \quad z' = \lambda_3 z$$



λ = extension ratio = L/L_0

$$S' = c - \mathbf{k}\beta^2 (\lambda_1^2 x^2 + \lambda_2^2 y^2 + \lambda_3^2 z^2)$$

$$\Delta S_i = S' - S = -\mathbf{k}\beta^2 [(\lambda_1^2 - 1)x^2 + (\lambda_2^2 - 1)y^2 + (\lambda_3^2 - 1)z^2]$$

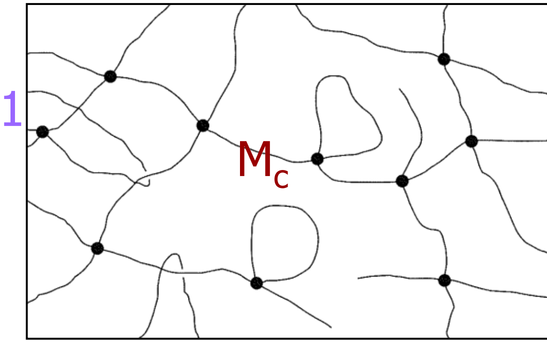
- ΔS of N chains (per unit volume)

$$dN = NW(x,y,z)\,dx\,dy\,dz$$

$$dN = N\left(\frac{\beta}{\pi^{1/2}}\right)^3 \exp[-\beta^2(x^2+y^2+z^2)]\,dx\,dy\,dz$$

$$\Delta S = \int \Delta S_i\,dN \;= -\frac{1}{2}N\mathbf{k}(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)$$

Fig 21.1

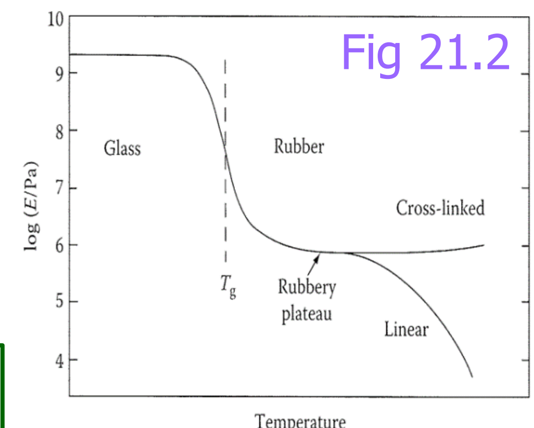


- work of deformation $w = \frac{1}{2}G(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)$

$$dU = đQ - đW \xrightarrow{dU = 0} dw = (-)T\Delta S$$

$$\rho = \frac{NM_c}{\mathbf{N}_A} \longrightarrow N = \frac{\rho\mathbf{N}_A}{M_c} = \frac{\rho\mathbf{R}}{M_c\mathbf{k}}$$

$$G = \frac{\rho\mathbf{R}T}{M_c}$$



- T ↑ → modulus ↑ ~ another characteristic of elastomer
- for linear polymers, $M_e = \frac{\rho\mathbf{R}T}{G_N^o}$

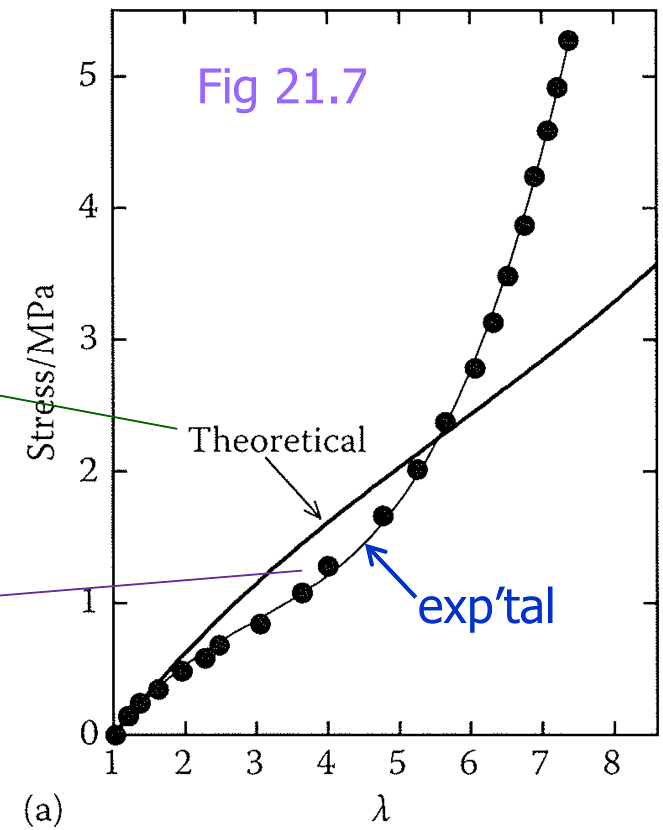
Stress-strain behavior

$$w = \frac{1}{2}G(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) = \frac{1}{2}G\left(\lambda^2 + \frac{2}{\lambda} - 3\right)$$

$\lambda_1 = \lambda$ and $\lambda_1\lambda_2\lambda_3 = 1$

$$\sigma_n = \frac{dw}{d\lambda} = G\left(\lambda - \frac{1}{\lambda^2}\right)$$

statistical mechanical equation for rubber elasticity



- comparison with exp't
  - at low λ, σ(theo) > σ(exp't)
    - affine deformation vs phantom network
  - at high λ, σ(theo) < σ(exp't)
    - Gaussian to non-Gaussian chain segments
      - stressed, extended, fewer conformations
    - strain-induced crystallization

Chapter Extra 1-1

Polymer Rheology

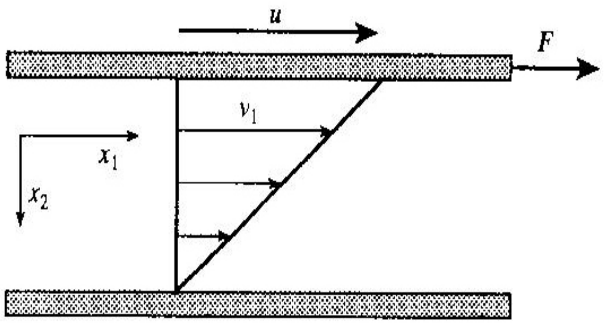
Shear and elongational viscosity

Normal stress difference

Rheometry

Rheology

- rheology [流變學]
  - study of flow and deformation of fluids [liquids]
  - constitutive [stress-strain] relation of fluids
- shear flow
  - shear stress τ = F/A [N/m^2 = Pa]
  - shear strain $\gamma = dx_1/dx_2$
  - shear (strain) rate $d\gamma/dt$ [s^{-1}]
    - $dv_1 = dx_1/dt$
    - $d\gamma/dt = dv_1/dx_2$ ~ velocity gradient



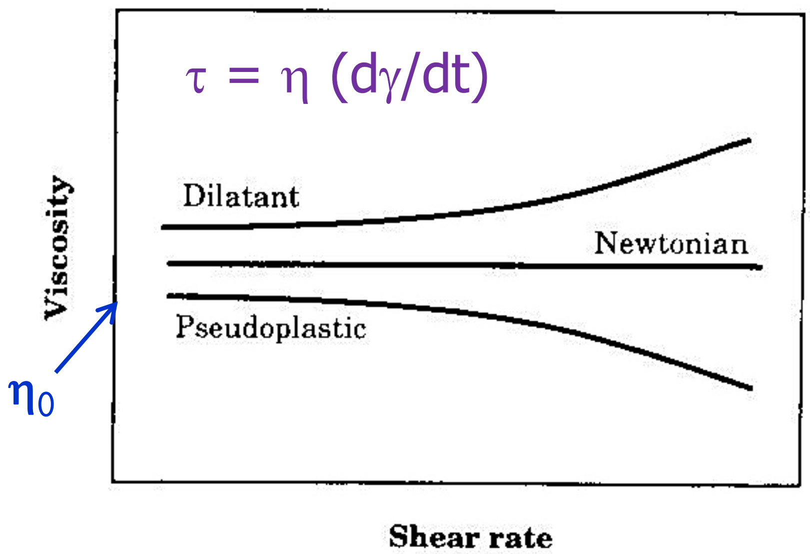
- constitutive eqn: Newton's law: $\tau = \eta_{(s)} (d\gamma/dt)$
  - (shear) viscosity $\eta_{(s)}$
    - η of water ~ 10^{-3} Pa s = 1 cP
    - η of polymer melt ~ 10^{3} Pa s

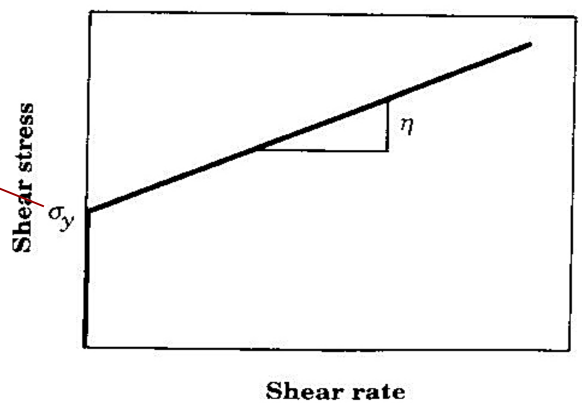
1 Pa s = 10 P(oise)

Shear viscosity

- Temperature dependence of η
  - WLF eqn ~ for $T_g - 50 < T < T_g + 100$ K
  - Arrhenius-type relation ~ for $T > T_g + 100$ K
    - $\eta = A \exp[-B/T]$
    - $T \uparrow \rightarrow \eta \downarrow$
    - not for large ΔT (> 20 K)
- Pressure dependence of η
  - $\eta = A \exp[B/P]$
  - $p \uparrow \rightarrow \eta \uparrow$
  - inter-particle distance
- increasing P and decreasing T the same effect
  - 100 atm is equiv to 30–50 K

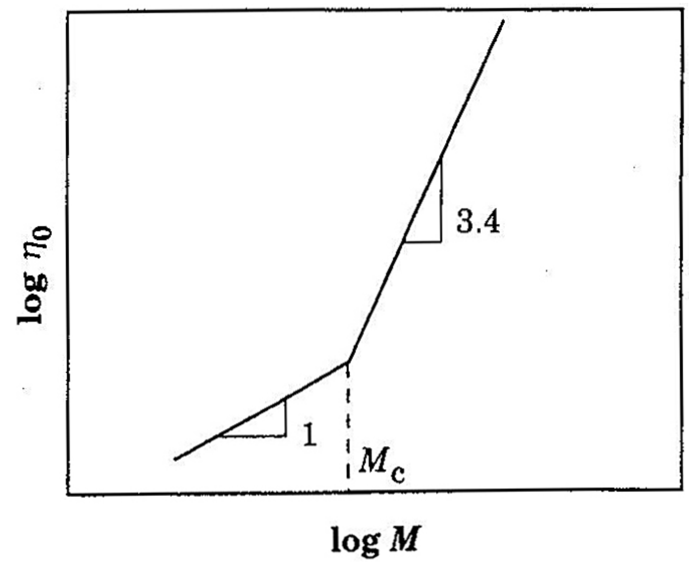
- Shear rate dependence of η
  - Newtonian ~ constant viscosity
    - many solutions and melts
  - non-Newtonian
    - dilatant = shear-thickening
      - suspensions
    - pseudoplastic = shear-thinning
      - polymer melts
      - chains aligned to shear direction
      - zero-shear(-rate) viscosity η_0
    - Bingham plastic ~ yielding
      - slurries, margarine

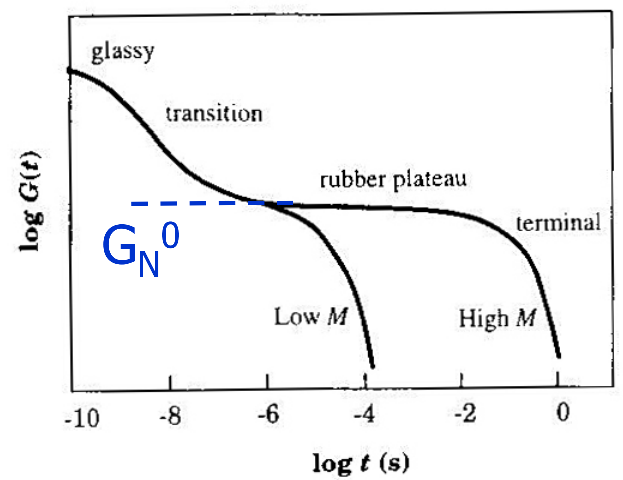




- molecular weight dependence of η
  - $\eta = K M_w^{1.0}$ for $M < M_c$

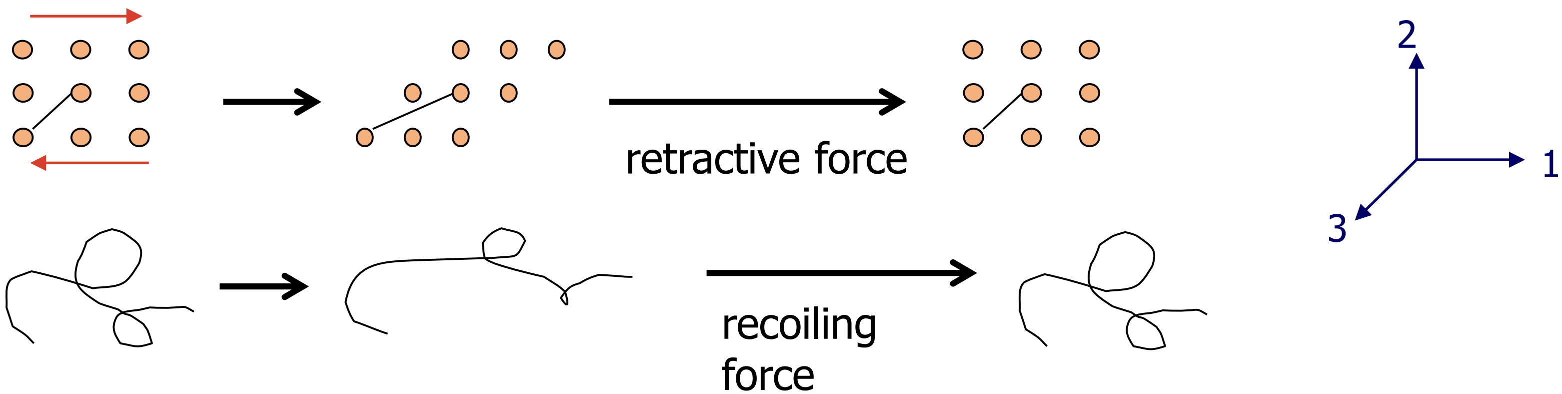
    $\eta = K M_w^{3.4}$ for $M > M_c$
  - $M_c = 2 - 3 M_e$
  - $M_e \sim$ entanglement MM
    - $M_e = \rho RT / G_N^0$
    - M_e depends on structure of chain
      - chain stiffness and interactions
      - PE ~1200, PS ~20000, PC ~2500
      - M_e(step polymers) < M_e(chain polymers)



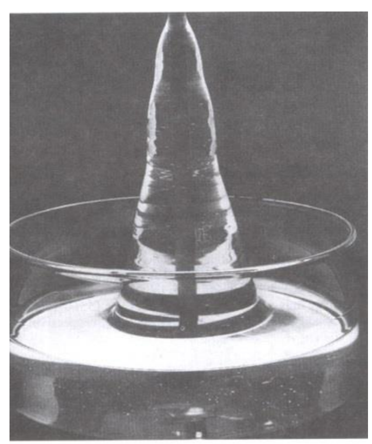


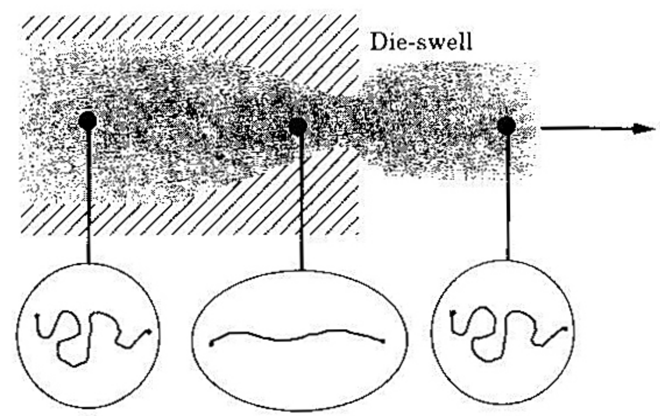
Normal stress difference

- normal stress caused by shear flow



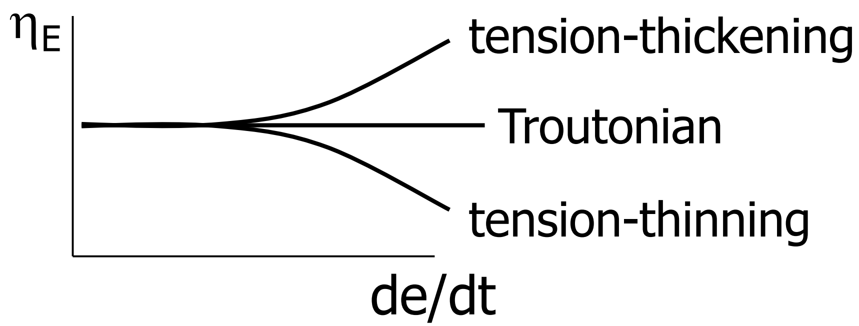
  - $\sigma_1 - \sigma_2 = N_1 > 0$ ~ 1st normal stress difference
  - $\sigma_2 - \sigma_3 = N_2 \approx 0$ ~ 2nd normal stress difference
- results of NSD
  - Weisenberg effect
    - rod-climbing
  - die swell



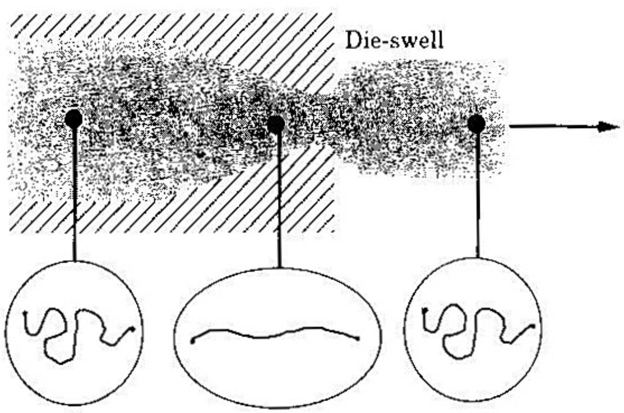


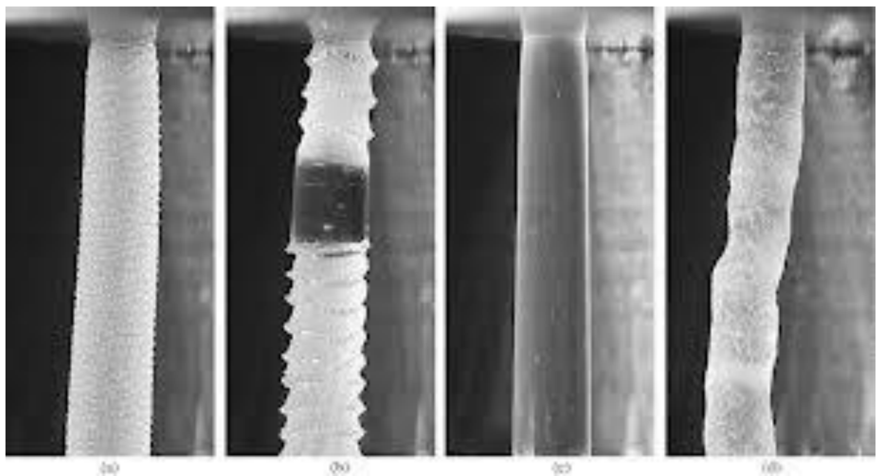
Elongational viscosity

- $\sigma = \eta_E$ (de/dt)
  - η_E ~ elongational [tensile] viscosity



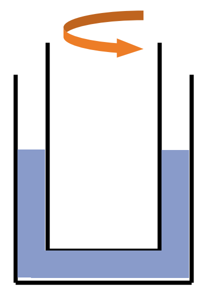
- η_E determines melt strength [stability of melt]

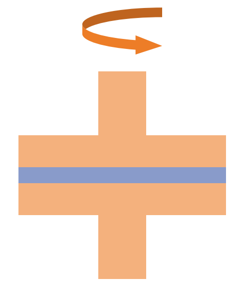


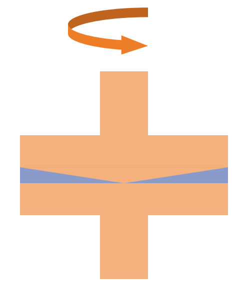


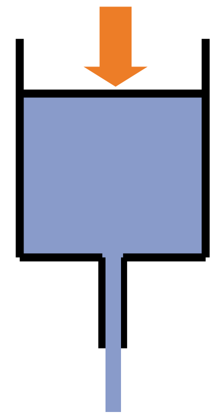
Rheometry

- Shear flow
  - rotational rheometers ~ drag
    - cylinder, Brookfield
    - parallel-plate rheometer
    - cone-and-plate rheometer
  - capillary or slit rheometer ~ pressure drop
  - dynamic rheometry
    - $\eta' = G''/\omega$ ~ dynamic viscosity
    - $\eta'' = G'/\omega$
    - $\eta^* = \eta' - i\eta''$ ~ complex viscosity
- elongational flow
  - difficult to perform expt
  - possible only for very small strain rate

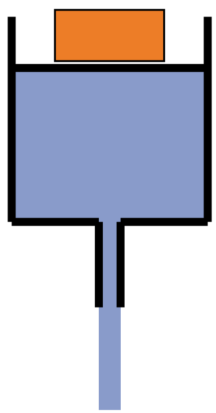








- melt index (MI) or melt flow index (MFI)
  - melt indexer ~ a simple capillary viscometer



  - M(F)I = g of resin/10 min
    - at specified weight and temperature
    - high MI = low η = low MM of a polymer