Chapter 6

Molten State

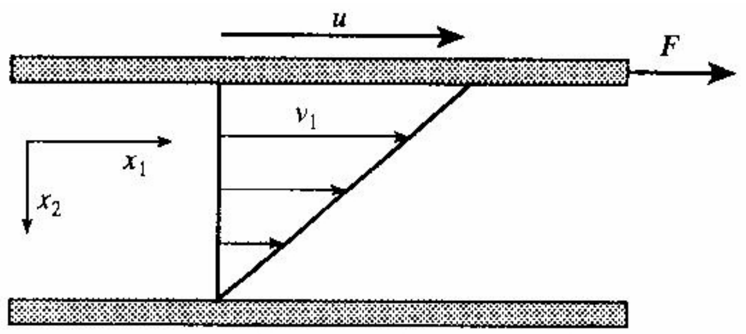
Rheology (流變學)

- study of flow and deformation of (liquid) fluids
- constitutive (stress-strain) relation of fluids

- shear flow
  - shear rate ~ dγ/dt ~ velocity gradient

$$\frac{dv_1}{dx_2} = \dot{\gamma} \qquad (6.6)$$

- $dv_1 = dx_1/dt$
- $\gamma = dx_1/dx_2$



shear flow

- stress state in this flow case

$$\boldsymbol{\sigma} = \begin{Bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ \sigma_{21} & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{Bmatrix} \qquad (6.9)$$

  - simple shear ~ σ_{12} only, all others = 0
  - σ_1, σ_2, σ_3? ~ normal stress by shear flow
- relations in shear flow

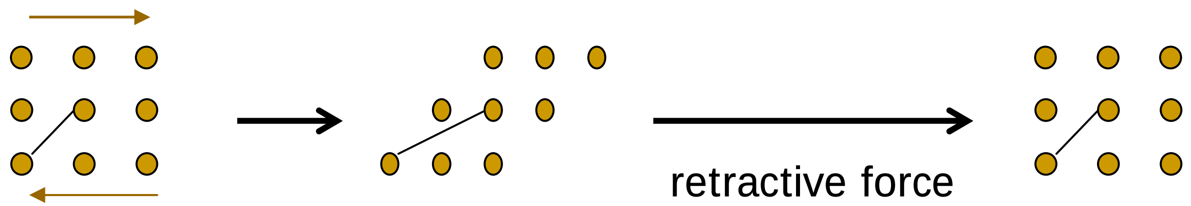
$$\eta = \frac{\sigma_{21}}{\dot{\gamma}}$$ ~ Newton's law

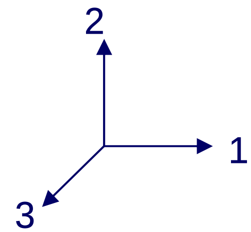
$$\psi_1 = \frac{\sigma_{11} - \sigma_{22}}{\dot{\gamma}^2}$$ ~ 1st normal stress coeff ← N_1

$$\psi_2 = \frac{\sigma_{22} - \sigma_{33}}{\dot{\gamma}^2}$$ ~ 2nd normal stress coeff ← N_2

Normal stress difference

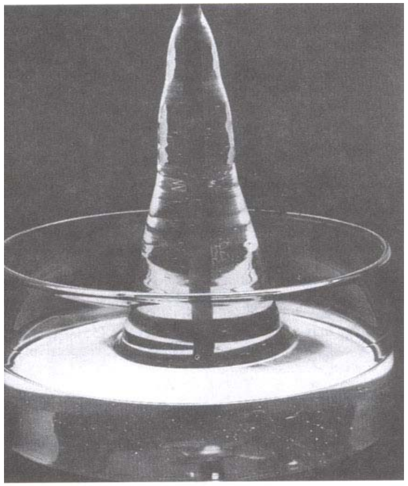
- normal stress caused by shear flow

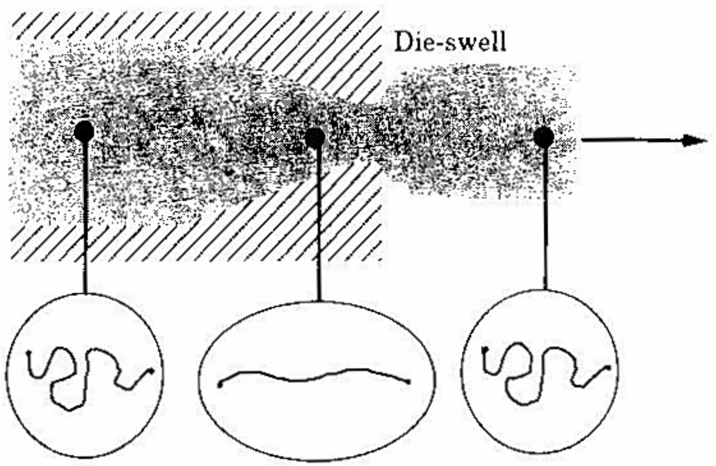




  - $\sigma_1 - \sigma_2 = N_1 > 0$ ~ 1st normal stress difference
  - $\sigma_2 - \sigma_3 = N_2 \approx 0$ ~ 2nd normal stress difference

- results of NSD
  - Weisenberg effect
    - rod-climbing
  - die swell



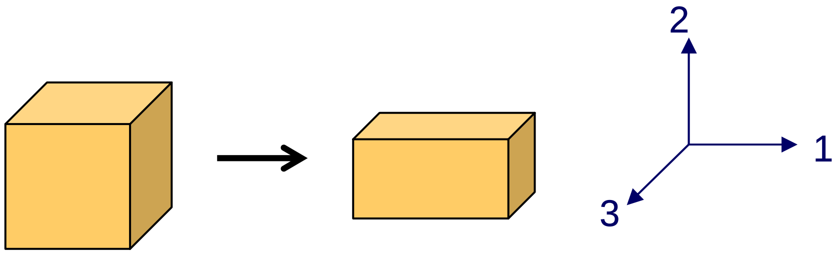


Elongational flow

$$v_i = a_i x_i \qquad (i = 1,\ 2,\ 3) \qquad (6.13)$$

- v = dx/dt, a = dε/dt = dx/xdt

- uniaxial elongational flow
  - σ_1 only, all other stresses = 0



$$a_1 = \dot{\varepsilon} \qquad (6.15)$$

$$a_2 = -\frac{\dot{\varepsilon}}{2} \qquad (6.16)$$

$$a_3 = -\frac{\dot{\varepsilon}}{2} \qquad (6.17)$$

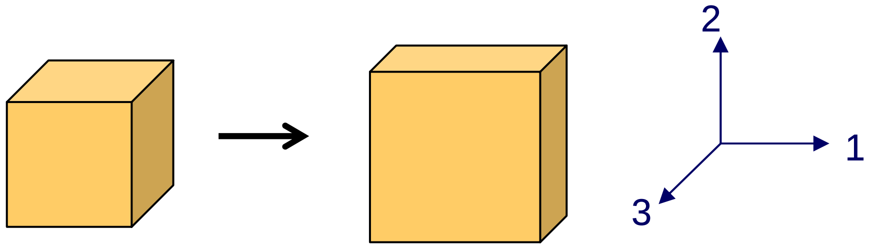
← $\sum_{i=1}^{3} a_i = 0$ for incompressible fluid (ΔV = 0)

  - elongational viscosity, $\bar{\eta} = \frac{\sigma_{11} - \cancelto{0}{\sigma_{22}}}{\dot{\varepsilon}} \qquad (6.18)$ $\eta_E = \sigma/(d\varepsilon/dt)$

  - spinning, contraction flow

- (balanced) biaxial elongation
  - $\sigma_1 = \sigma_2$, all other stresses = 0

$$a_1 = a_2 = \dot{\varepsilon}_B$$
$$a_3 = -2\dot{\varepsilon}_B$$



  - biaxial elongational viscosity

$$\eta_B = \frac{\sigma_{11} - \cancel{\sigma_{33}}^{\,0}}{\dot{\varepsilon}_B} = \frac{\sigma_{22} - \cancel{\sigma_{33}}^{\,0}}{\dot{\varepsilon}_B} \approx 2\,\eta_E$$

  - ballooning, film blowing

Dynamic viscosity

- from dynamic mechanical measurements

$$\gamma = \gamma_0 \cos \omega t \qquad \sigma = \sigma_0 \cos(\omega t + \delta)$$

$$\gamma^* = \gamma_0(\cos \omega t + i \sin \omega t)$$
$$= \gamma_0 \exp(i\omega t) = \gamma' + i\gamma'' \qquad (6.24)$$

$$\sigma^* = \sigma_0(\cos(\omega t + \delta) + i \sin(\omega t + \delta))$$
$$= \sigma_0 \exp[i(\omega t + \delta)] \qquad (6.25)$$

$$G^* = \frac{\sigma^*}{\gamma^*} = \frac{\sigma_0}{\gamma_0} \cos \delta + i \frac{\sigma_0}{\gamma_0} \sin \delta = G' + iG'' \quad (6.26)$$

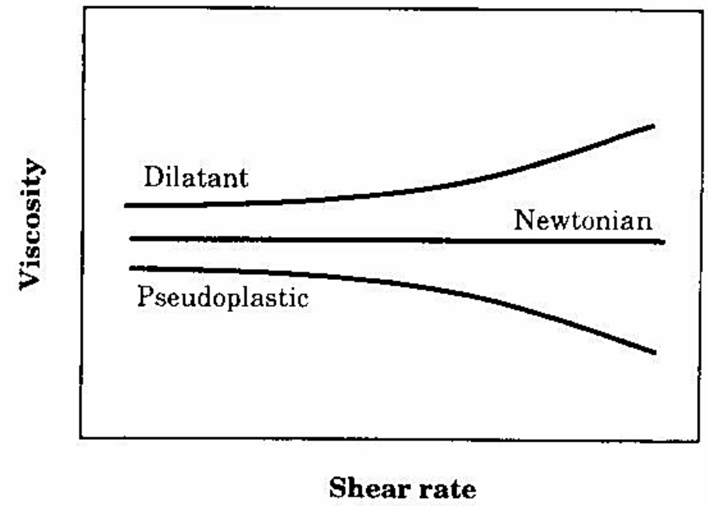
$$\eta^* = \frac{\sigma^*}{\dot{\gamma}^*} = \frac{\sigma^*}{i\omega\gamma^*} = \frac{\sigma_0}{\gamma_0} \cdot \sin \delta \cdot \frac{1}{\omega} - i \frac{\sigma_0}{\gamma_0} \cos \delta \cdot \frac{1}{\omega}$$
$$= \frac{G''}{\omega} - \frac{iG'}{\omega} = \eta' - i\eta'' \qquad (6.27)$$

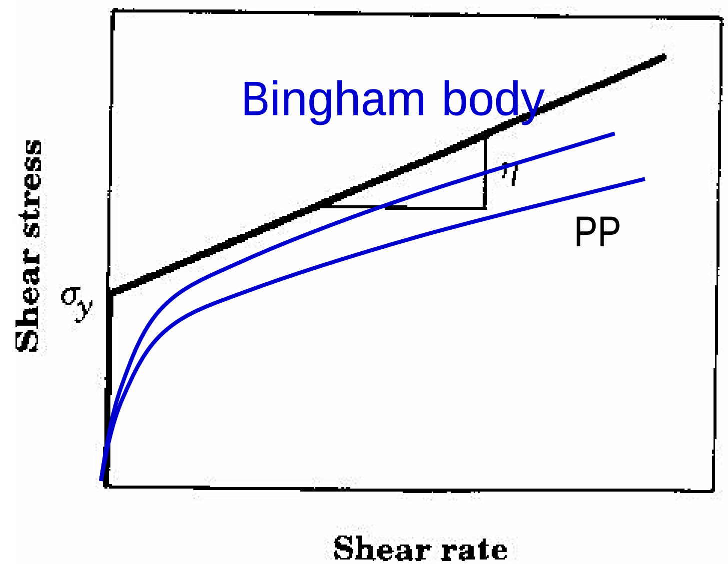
η^* ~ complex viscosity
η' ~ dynamic viscosity

Non-Newtonian behavior

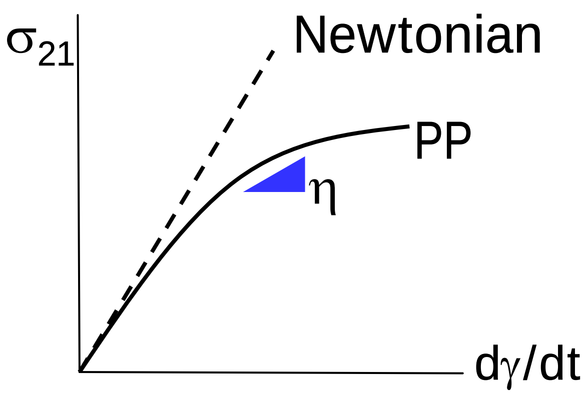
$$\eta = \frac{\sigma_{21}}{\dot{\gamma}}$$

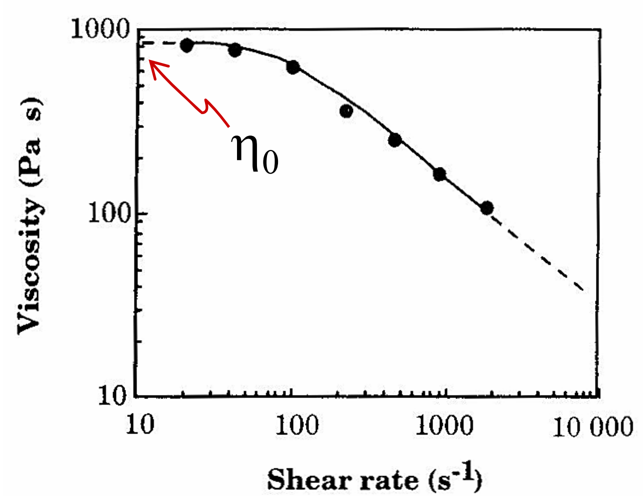
- Newtonian ~ constant viscosity
  - many solutions and melts
- non-Newtonian
  - dilatant ~ shear thickening
    - suspensions
  - pseudoplastic ~ shear-thinning
    - polymer melts
    - chains aligned to shear direction
    - zero-shear-rate viscosity, η_0
    - at $d\gamma/dt = 0$, $N_1 \rightarrow N_{1,0}$
  - Bingham plastic ~ yielding
    - slurries, margarine





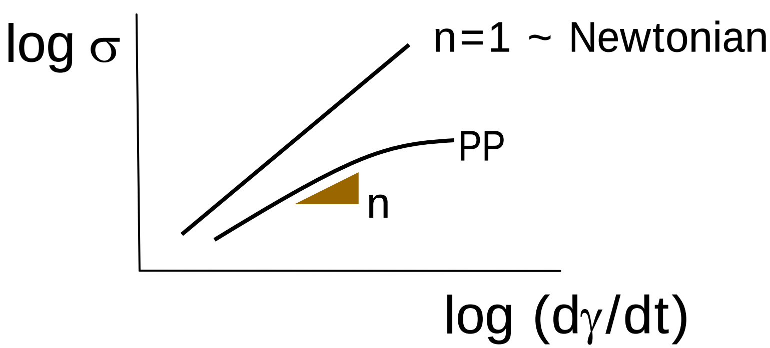
- power-law expression





$$\sigma_{21} = K\dot{\gamma}^{n} \tag{6.28}$$

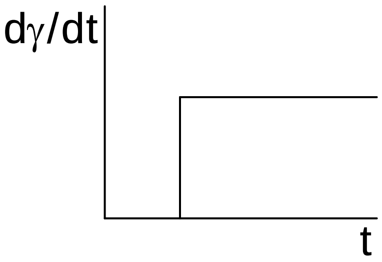
$$\eta = K\dot{\gamma}^{n-1} \tag{6.29}$$

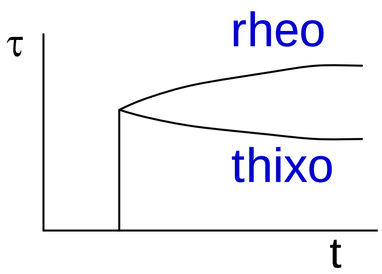


n < 1 and ↓

n const in 1-2 decades only

- time-dependence
  - thixotropic
    - decrease in η with shearing time
    - polymer melts, inks
    - seldom in polymers, more in colloids
    - thixotropic is pseudoplastic; PP is not necessarily thixo
  - rheopectic (anti-thixotropic)
    - gypsum and soils
    - rheopectic is dilatant; dilatant is not necessarily rheo





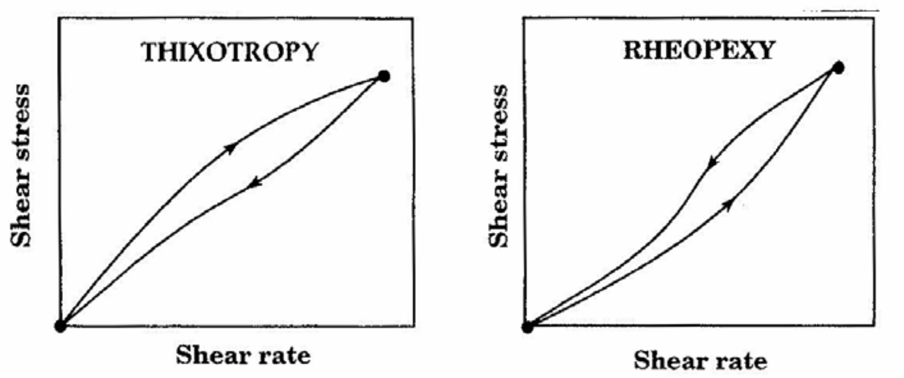
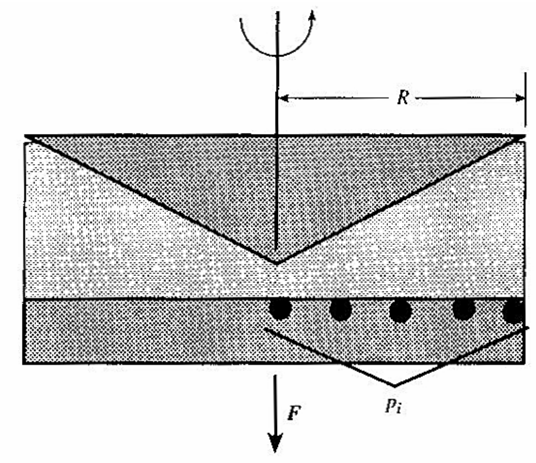


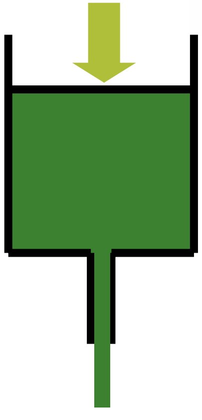
Figure 6.6 Hysteresis loops for time-dependent liquids.

measurement of rheological properties

- shear flow
  - Couette flow
    - parallel-plate, cone-and-plate, two-cylinder
    - η by velocity and torgue
    - N by plate-separating force
    - η* by oscillation

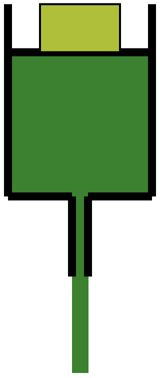


  - Poiseuille flow
    - capillary, slit
    - η by pressure drop and flow rate
    - N by non-zero exit pressure



- elongational flow
  - difficult to perform expt
  - possible only at 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 MW of a polymer

Viscoelastic fluid

- linear viscoelasticity only at small strain and shear rate
  - little use in polymer processing condition
  - useful for comparison of materials and molecular factors (MW, MWD)

- Boltzmann superposition principle

$$\sigma(t) = \sum_{i=1}^{N} G(t - t_i)\delta\gamma(t_i)$$

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\, d\gamma(t')$$ for smooth strain history

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t')\, dt'$$

$$\sigma(t) = \int_{0}^{t} G(t - t')\, d\gamma(t')$$ starting expt at time 0

$$\sigma = \dot{\gamma}\int_{0}^{\infty} G(s)\, ds$$ $t - t' = s$, for steady flow ($d\gamma/dt$ = const)

$$\eta_0 = \int_{0}^{\infty} G(s)\, ds$$ $\eta = \sigma/(d\gamma/dt)$, η_0 at low shear rate limit

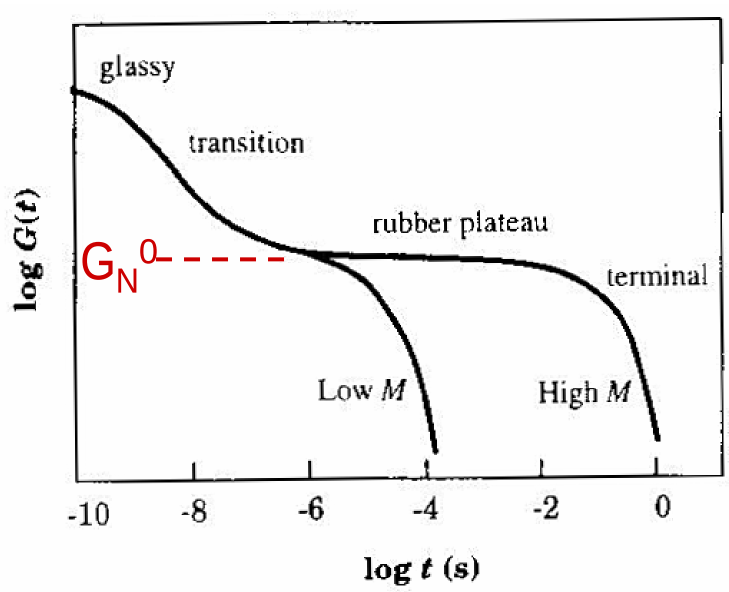
- (stress) relaxation modulus

  $$G(t) = \sigma(t)/\gamma_0$$

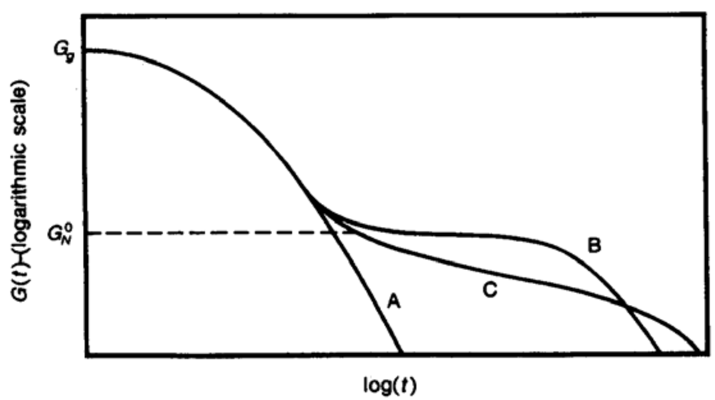
  - glassy ~ solid
  - rubbery plateau region
    - due to entanglement
      - physical crosslink
    - plateau modulus

      $$G_N^0 = \rho RT/M_e$$

    - M_e ~ entanglement mol wt
      - avg mol wt betw entanglements
  - terminal zone ~ flow ~ liquid



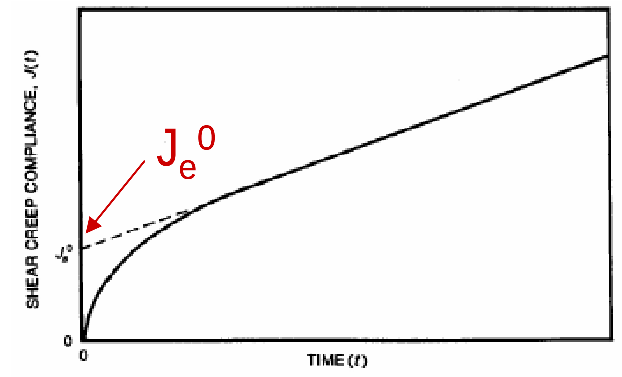
A ~ monodisperse, $M_w < M_C$
B ~ monodisperse, $M_w > M_C$
C ~ polydisperse, $M_w > M_C$
(M_C ~ 2 – 3 M_e)

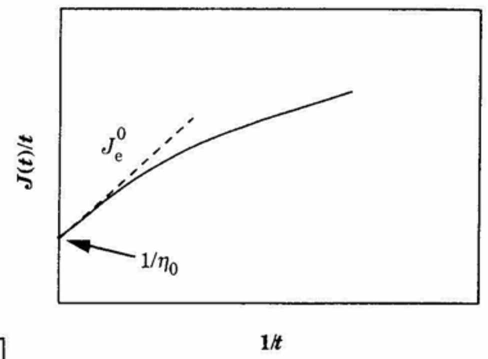


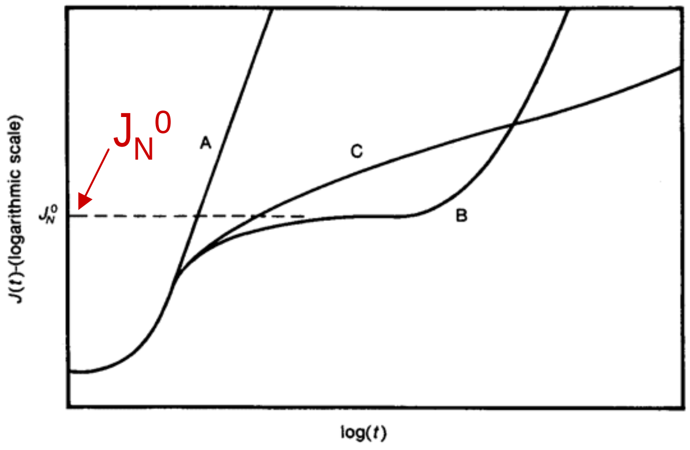
- creep compliance

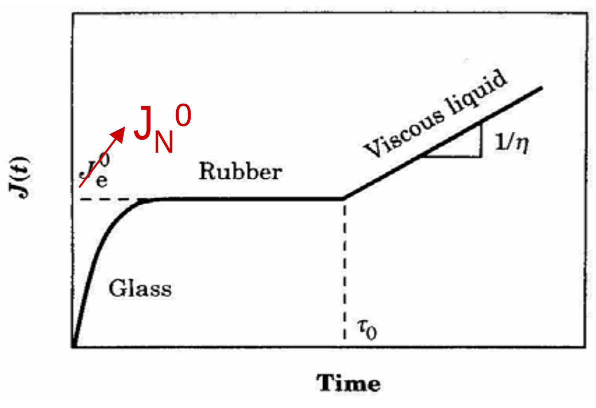
  $J(t) = \gamma(t)/\sigma_0$

  - steady-state compliance, J_e^0
    - constant shear rate at long times
    - $J(t) = J_e^0 + t/\eta_0$

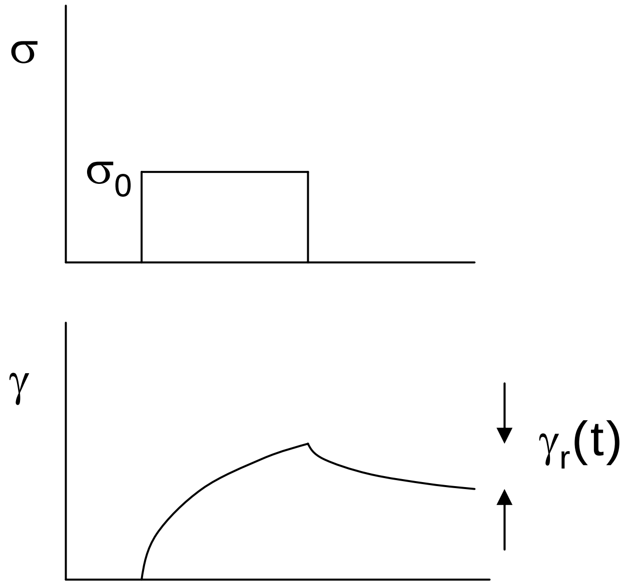


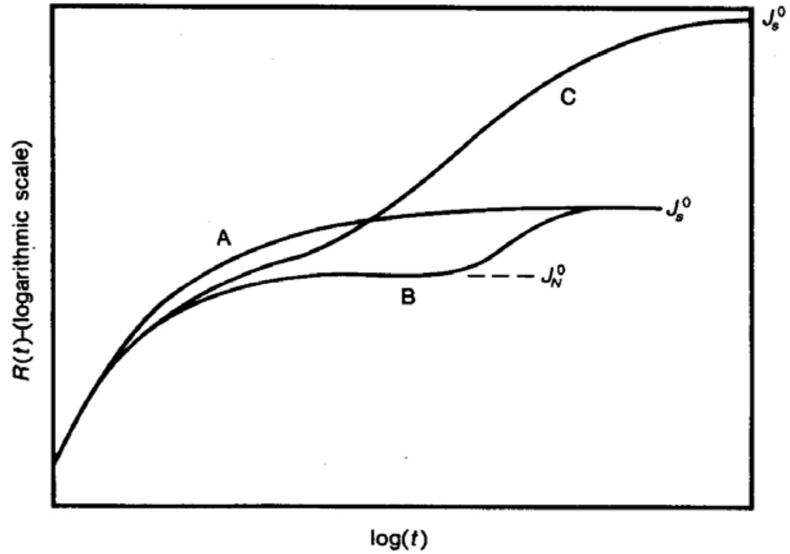






- recovery compliance
  - recovery test



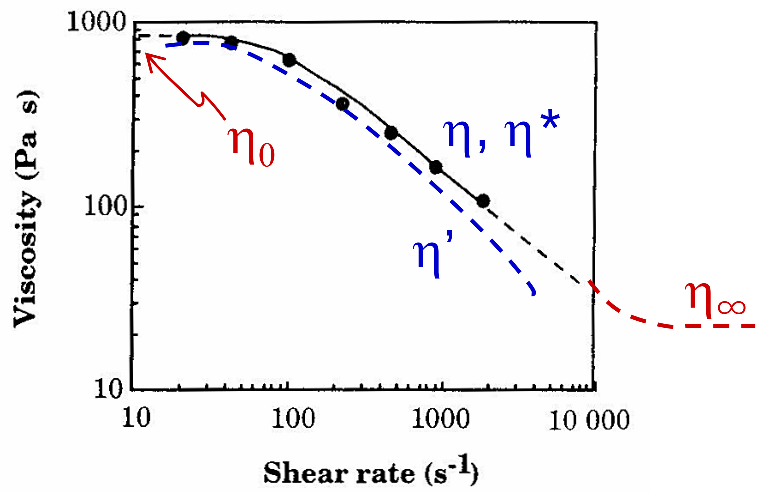


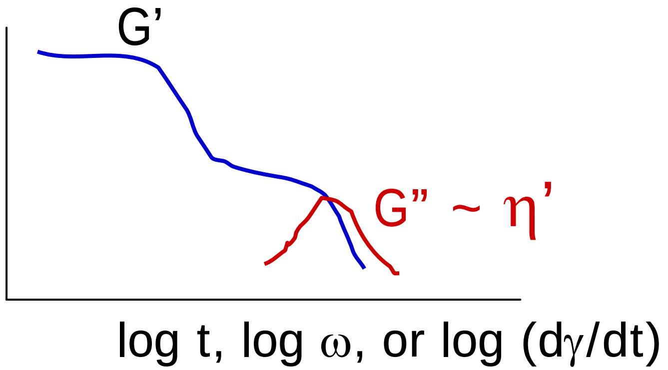
  - recoil function or recovery compliance, $R(t) = \gamma_r(t)/\ \sigma_0$
  - $\lim_{(t=\infty)}$ [R(t)] = J_e^0 ~ steady-state recovery compliance

dynamic η and VE

$$\eta^* = \frac{G''}{\omega} - \frac{iG'}{\omega} = \eta' - i\eta''$$

- as $\omega \rightarrow 0$ (large t, small $d\gamma/dt$)
  - $G' = \omega\eta'' \rightarrow 0$, $G'' = \omega\eta' \rightarrow 0$
  - $\eta' = G''/\omega \rightarrow \eta_0$
  - Newtonian
- as $\omega \rightarrow \infty$ (small t, large $d\gamma/dt$)
  - $\eta' \rightarrow \eta_\infty$
  - $G' \rightarrow \omega\eta_\infty$
  - Hookean





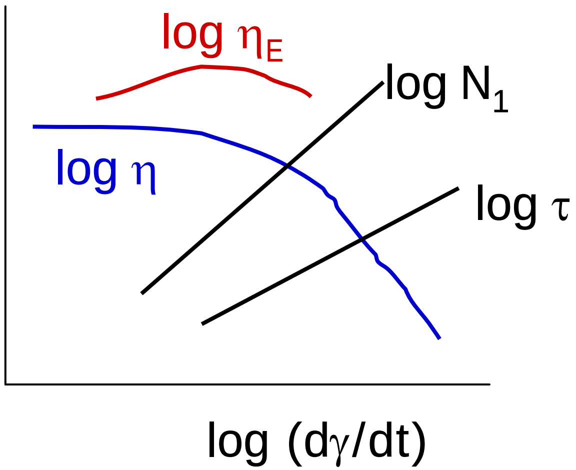
- rheometric and VE functions
  - rheometric ftns
    - η, N_1 (← η_0, $N_{1,0}$)
    - linear (Newtonian) → non-linear (non-Newtonian) as $d\gamma/dt$ ↑
  - viscoelastic ftns
    - η', η^*
    - viscous → elastic as ω ↑

- stress ratio
  - N_1/τ (>1)
  - a measure of elasticity

Behavior of polymeric liquids

- polymeric liquids
  - dilute solution ~ as conc'n → 0, Newtonian
  - concentrated sol'n ~ behaves as melt
  - melt ~ Newtonian as shear rate → 0

- η and N_1
  - shear thinning
    - $\eta = K\,(d\gamma/dt)^{n-1}$ $(n < 1)$
  - $N_1 > 0$
    - $N_1 > \tau$
  - η_E not much dep on $d\varepsilon/dt$
    - at $d\varepsilon/dt \rightarrow 0$, $\eta_E \approx 3\,\eta_0$



- effect of temp
  - at $T_g < T < T_g + 100$ K ~ WLF eqn
    - $\log \eta = \log \eta_{Tg} - C_1(T-T_g)/(C_2+T-T_g)$
  - at $T > T_g + 100$ K ~ Arrhenius relation
    - $\eta = A \exp[E/RT]$

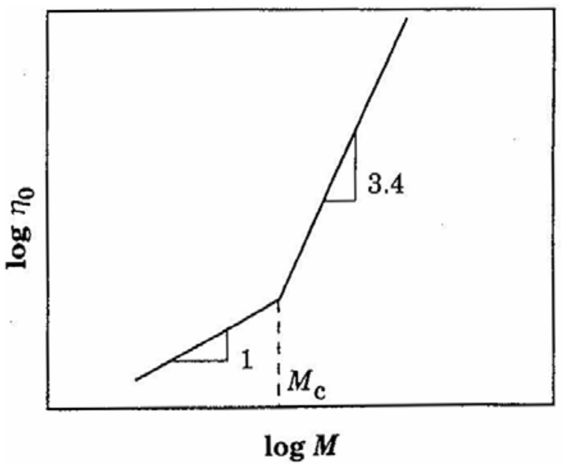
- effect of pressure
  - $\eta = A \exp[BP]$

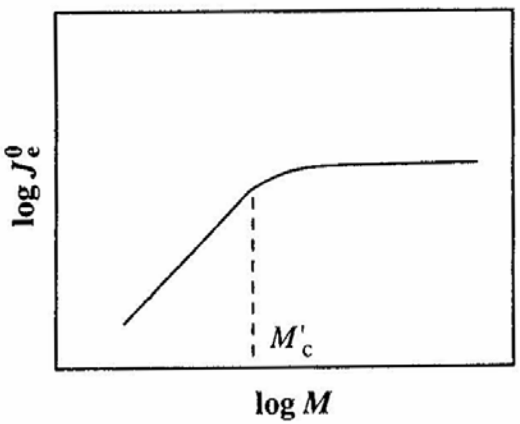
  - conversion factor, $-(\Delta T/\Delta P)_h$
    - example p107

- effect of mol wt
  - η
    - at $M_w < M_c$, $\eta_0 \propto M$
    - at $M_w > M_c$, $\eta_0 \propto M^{3.4}$
    - $M_c \sim 2 - 3\ M_e$

$$M_e = \frac{\rho RT}{G_e^0} \qquad (6.36)$$

    - M_e depends on chemical structure of chain
      - chain stiffness and interactions
      - PE ~1200, PS ~20000, PC ~2500
  - J_e^0
    - at $M_w < M'_c$, $J_e^0 = (0.4)M_w/\rho RT$
    - at $M_w > M'_c$, $J_e^0 = (0.4)M'_c/\rho RT$
    - $M'_c \sim 5 - 10\ M_e$
  - $G_N^0\ J_e^0$ = constant ~ 3

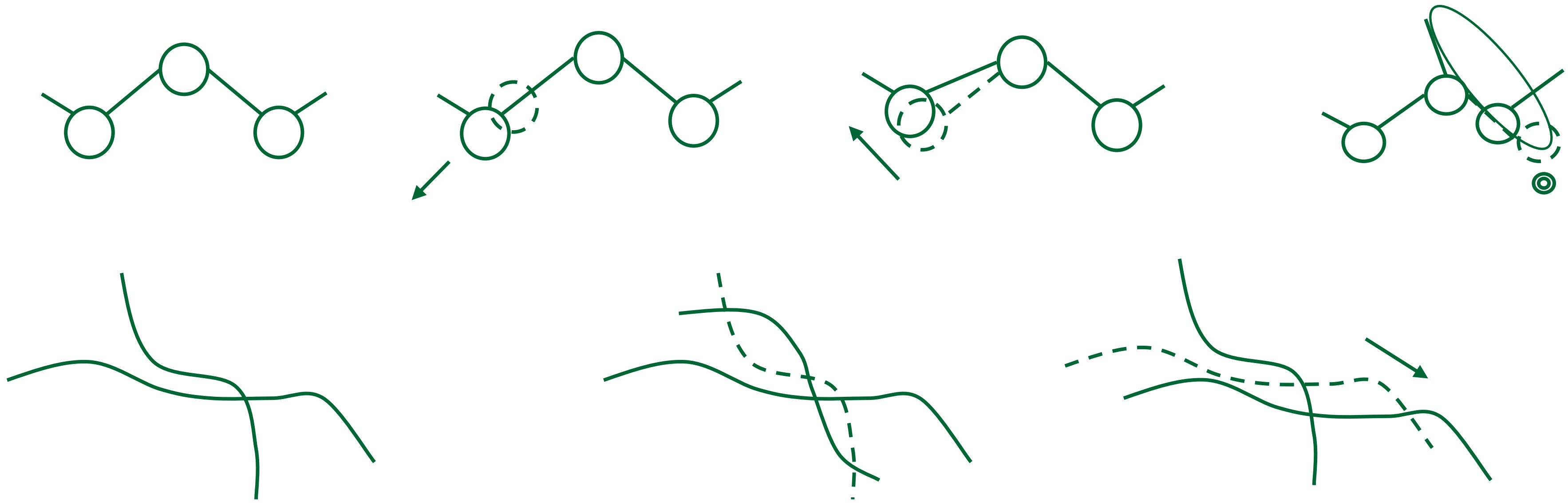




- branching
  - when $M_b < M_c$
    - smaller $<s^2>_0$
    - lower η_0, J_e^0
  - when $M_b > M_c$
    - smaller $<s^2>_0$, but larger reptation time
    - higher η_0, J_e^0
      - $\eta_0 = (M_w)^k$, $k > 6$

Macromolecular Dynamics

- Motions in polymers
  - Defomation in bond angle and length ~ elastic
  - Change in conformation ~ segmental motion ~ viscoelastic
  - Translational motion ~ viscous



Models for macromolecular dynamics

- Rouse (– Bueche – Zimm) model
  - bead (friction) and spring (elastic)
    - single chain with completely flexible repeat units moving in a medium
    - three forces ~ friction, elastic, and Brownian

$$\eta_0 = \left(\frac{\zeta_0 N_A K_\theta \rho}{6M_{rep}}\right) M \qquad (6.41)$$

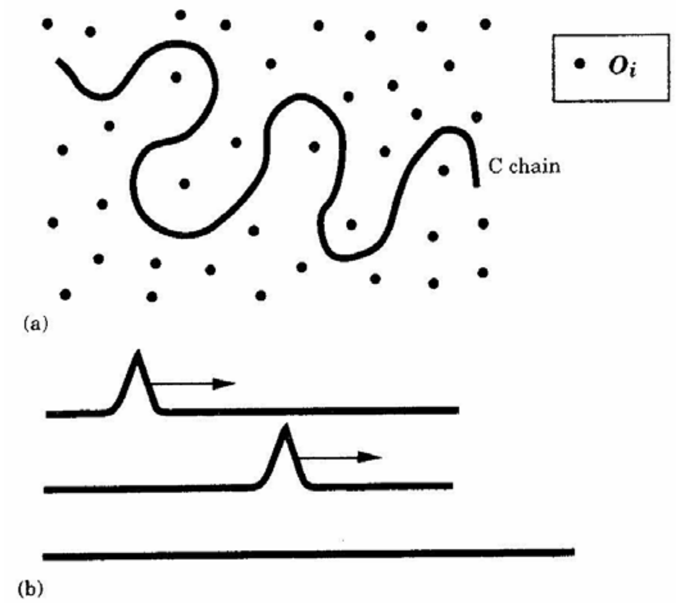
$$J_e^0 = \left(\frac{2}{5\rho RT}\right) M \qquad (6.42)$$

  - not for $M_w > M_c$
  - for $M_w < M_c$
    - correctly describes η_0, J_e^0
    - does not describe shear thinning

- Reptation (de Gennes (– Doi – Edwards)) model
  - chain and obstacles (entanglements)
    - chain reptates between obstacles
    - friction $\propto$ M
  - chain in a tube
    - tube disappears and regenerated
    - diffusion of tube $\propto M^2$

$$\eta_0 \propto M^3 \qquad (6.49)$$

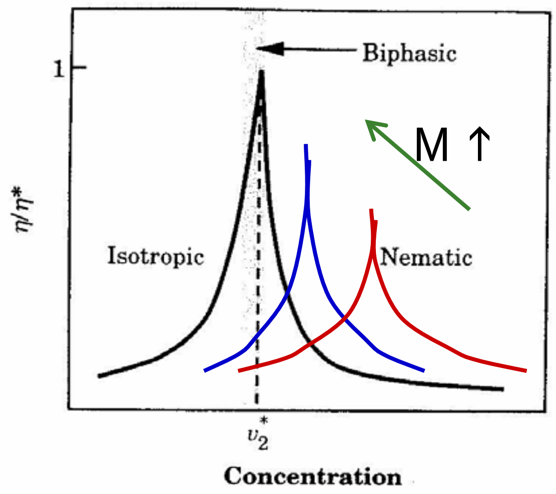
$$J_e^0 \propto M^0 \qquad (6.50)$$



  - successfully describes
    - effect of entanglement
    - effect of branching
  - predicts higher η_0 with lower power (3 instead of 3.4)
    - other mechanism should exist

Rheology of liquid crytals

- solution



- melt