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 $\sim \frac{dv_1}{dt} \sim$ velocity gradient

\[
\frac{dv_1}{dx_2} = \dot{\gamma} \tag{6.6}
\]

- $dv_1 = dx_1/dt$
- $\gamma = dx_1/dx_2$
stress state in this flow case

\[
\sigma = \begin{pmatrix}
\sigma_{11} & \sigma_{12} & 0 \\
\sigma_{21} & \sigma_{22} & 0 \\
0 & 0 & \sigma_{33}
\end{pmatrix}
\]

- simple shear \(\sim \sigma_{12}\) only, all others = 0
- \(\sigma_1, \sigma_2, \sigma_3?\) \sim normal stress by shear flow

relations in shear flow

\[
\eta = \frac{\sigma_{21}}{\dot{\gamma}} \sim Newton's \ law
\]

\[
\psi_1 = \frac{\sigma_{11} - \sigma_{22}}{\dot{\gamma}^2} \sim 1^{st} \ normal \ stress \ coeff \ \leftrightarrow N_1
\]

\[
\psi_2 = \frac{\sigma_{22} - \sigma_{33}}{\dot{\gamma}^2} \sim 2^{nd} \ normal \ stress \ coeff \ \leftrightarrow N_2
\]
Normal stress difference

- normal stress *caused by* shear flow

\[ \sigma_1 - \sigma_2 = N_1 > 0 \sim \text{1st normal stress difference} \]
\[ \sigma_2 - \sigma_3 = N_2 \approx 0 \sim \text{2nd normal stress difference} \]

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

\[ v_i = a_i x_i \quad (i = 1, 2, 3) \quad (6.13) \]

- \( v = dx/dt, \ a = d\varepsilon/dt = dx/xdt \)

- **uniaxial elongational flow**
  - \( \sigma_1 \) only, all other stresses = 0
  \[
  a_1 = \dot{\varepsilon} \quad (6.15) \\
  a_2 = -\frac{\dot{\varepsilon}}{2} \quad (6.16) \\
  a_3 = -\frac{\dot{\varepsilon}}{2} \quad (6.17)
  \]
  - elongational viscosity,
    \[
    \eta = \frac{\sigma_{11} - \sigma_{22}}{\dot{\varepsilon}} \quad (6.18)
    \]
  - \( \eta_E = \sigma/(d\varepsilon/dt) \)
  - 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

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

- ballooning, film blowing
Dynamic viscosity

from dynamic mechanical measurements

\[ \gamma = \gamma_0 \cos \omega t \quad \sigma = \sigma_0 \cos(\omega t + \delta) \]

\[ \gamma^* = \gamma_0 \exp(i \omega t) = \gamma' + i \gamma'' \quad (6.24) \]

\[ \sigma^* = \sigma_0 \exp[i(\omega t + \delta)] \]

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

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

\[ \eta^* = \frac{\sigma^*}{i \omega \gamma^*} = \frac{\sigma_0}{i \omega \gamma_0} \sin \delta \cdot \frac{1}{\omega} - i \frac{\sigma_0}{\gamma_0} \cos \delta \cdot \frac{1}{\omega} \]

\[ \eta^* \sim \text{complex viscosity} \quad \eta' \sim \text{dynamic viscosity} \]

\[ = \frac{G''}{\omega} - \frac{i G'}{\omega} = \eta' - i \eta'' \quad (6.27) \]
Non-Newtonian behavior

- 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, $\eta_0$
    - at $d\gamma/dt = 0$, $N_1 \rightarrow N_{1,0}$
  - Bingham plastic ~ yielding
    - slurries, margarine
- power-law expression

\[ \sigma_{21} = K \dot{\gamma}^n \quad (6.28) \]

\[ \eta = K \dot{\gamma}^{n-1} \quad (6.29) \]

\[ n < 1 \text{ and } \downarrow \]

n const in 1-2 decades only
- **time-dependence**
  - **thixotropic**
    - decrease in $\eta$ 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
    - rheopecetic is dilatant; dilatant is not necessarily rheo

![Graph showing shear stress vs. shear rate for thixotropy and rheopecty](image)

*Figure 6.6* Hysteresis loops for time-dependent liquids.
measurement of rheological properties

- shear flow
  - Couette flow
    - parallel-plate, cone-and-plate, two-cylinder
    - \( \eta \) by velocity and torque
    - \( N \) by plate-separating force
    - \( \eta^* \) by oscillation
  - Poiseuille flow
    - capillary, slit
    - \( \eta \) 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

- \[ M(F)I = g \text{ of resin/10 min} \]
  - at specified weight and temperature
  - high MI ~ low \( \eta \) ~ 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

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

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

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

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

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

\[
\eta_0 = \int_{0}^{\infty} G(s) \, ds \quad \eta = \sigma/(d\gamma/dt), \ \eta_0 \text{ at low shear rate limit}
\]
(stress) relaxation modulus

\[ G(t) = \frac{\sigma(t)}{\gamma_0} \]

- glassy ~ solid
- rubbery plateau region
  - due to entanglement
    - physical crosslink
  - plateau modulus
    \[ G_N^0 = \frac{\rho RT}{M_e} \]
  - \( M_e \sim \) 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, \( M_w > M_C \)
\( M_C \sim 2 - 3 M_e \)
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, $R(t) = \gamma_r(t)/\sigma_0$
- $\lim_{(t=\infty)} [R(t)] = J_e^0 \sim$ steady-state recovery compliance
dynamic $\eta$ and VE

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

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

- as $\omega \to \infty$ (small $t$, large $d\gamma/dt$)
  - $\eta' \to \eta_\infty$
  - $G' \to \omega \eta_\infty$
  - Hookean

![Graph showing viscosity vs. shear rate with $G'$ and $G''$ as functions of log $t$, log $\omega$, or log $(d\gamma/dt)$]
- rheometric and VE functions
  - rheometric ftns
    - \( \eta, N_1 (\leftrightarrow \eta_0, N_{1,0}) \)
    - linear (Newtonian) \( \rightarrow \) non-linear (non-Newtonian) as \( d\gamma/dt \uparrow \)
  - viscoelastic ftns
    - \( \eta', \eta^* \)
    - viscous \( \rightarrow \) elastic as \( \omega \uparrow \)

- stress ratio
  - \( N_1/\tau (>1) \)
  - a measure of elasticity
Behavior of polymeric liquids

- polymeric liquids
  - dilute solution ~ as conc’n \( \to 0 \), Newtonian
  - concentrated sol’n ~ behaves as melt
  - melt ~ Newtonian as shear rate \( \to 0 \)

- \( \eta \) and \( N_1 \)
  - shear thinning
    - \( \eta = K (d\gamma/dt)^{n-1} \) (\( n < 1 \))
  - \( N_1 > 0 \)
    - \( N_1 > \tau \)
  - \( \eta_E \) not much dep on \( d\varepsilon/dt \)
    - at \( d\varepsilon/dt \to 0 \), \( \eta_E \approx 3 \eta_0 \)
- **effect of temp**
  - at $T_g < T < T_g + 100\ K \sim WLF\ eqn$
    - $\log \eta = \log \eta_{T_g} - C_1(T-T_g)/(C_2+T-T_g)$
  - at $T > T_g + 100\ K \sim Arrhenius\ relation$
    - $\eta = A \exp\left[E/RT\right]$  

- **effect of pressure**
  - $\eta = A \exp[BP]$
    - conversion factor, $-(\Delta T/\Delta P)_h$
      - example p107
effect of mol wt

- \( \eta \)
  - at \( M_w < M_c \), \( \eta_0 \propto M \)
  - at \( M_w > M_c \), \( \eta_0 \propto M^{3.4} \)
  - \( M_c \sim 2 - 3 M_e \)

\[ M_e = \frac{\rho RT}{G_e^0} \quad (6.36) \]

- \( M_e \) depends on chemical structure of chain
  - chain stiffness and interactions
  - PE \( \sim 1200 \), PS \( \sim 20000 \), PC \( \sim 2500 \)

- \( J_e^0 \)
  - at \( M_w < M'_c \), \( J_e^0 = (0.4)M_w/\rho RT \)
  - at \( M_w > M'_c \), \( J_e^0 = (0.4)M'_c/\rho RT \)
  - \( M'_c \sim 5 - 10 M_e \)

- \( G_N^0 J_e^0 = \text{constant} \sim 3 \)
branching

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

\[
\eta_0 = \left( \frac{k_N K_p \rho}{6 M_{\text{rep}}} \right) M \quad (6.41)
\]

\[
J_e^0 = \left( \frac{2}{5 \rho R T} \right) M \quad (6.42)
\]

- not for \( M_w > M_c \)
- for \( M_w < M_c \)
  - correctly describes \( \eta_0, J_e^0 \)
  - 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 $\propto M^2$

\[ \eta_0 \propto M^3 \quad \text{(6.49)} \]
\[ j_e^0 \propto M^0 \quad \text{(6.50)} \]

- successfully describes
  - effect of entanglement
  - effect of branching
- predicts higher $\eta_0$ with lower power (3 instead of 3.4)
  - other mechanism should exist
Rheology of liquid crystals

- solution

- melt