Chapter 6. Molten State

6.1 Introduction

Kinetic energies of molecules	$\approx$	potential energies of interaction	: liquid
"	$\gg$	"	: gas
"	$\ll$	"	: solid (crystal)

Molten state of polymers depends on MW

Flexible-chain polymers - random conformation in molten state
chain entanglements (important)

Liquid-crystalline polymers - orientational order

6.2 Fundamental concepts in rheology

"***Rheology***" : the *study* which deals with the *flow* and *deformation* of fluids.

$\sigma - \gamma$ (or $\sigma - \dot{\gamma}$) relationships : (rheological) constitutive eq'ns

Balance equation : Law of mass conservation (Continuity equation)

Law of momentum conservation (Momentum equation)

Law of energy conservation (Energy or Heat equation)

* Incompressible, steady flow,

$$\nabla \cdot \mathbf{v} = 0 \qquad \text{(mass)}$$

$$\rho \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{g} \qquad \text{(momentum)}$$

$$\rho C_p \mathbf{v} \cdot \nabla T = k \nabla^2 T + \boldsymbol{\sigma} : \nabla \mathbf{v} + \dot{S} \qquad \text{(energy)}$$

• **Steady simple shear flow**

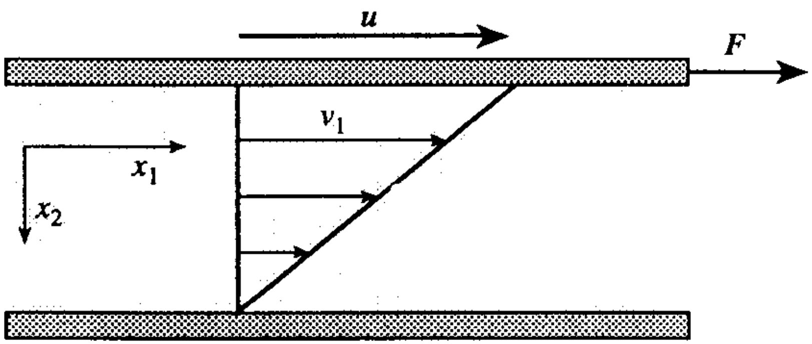


Figure 6.1 Steady simple shear flow.

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

$$\frac{dv_1}{dx_2} = \dot{\gamma}, \quad v_2 = 0, \quad v_3 = 0$$

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

$\sigma_{12} = \sigma_{21}$ (symmetric),

$\sigma_{11}, \sigma_{22}, \sigma_{33}$: normal stresses

* ***Material parameters***

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

$$\Psi_1 = \frac{\sigma_{11} - \sigma_{22}}{\dot{\gamma}^2}$$: first (or primary) normal stress coefficient

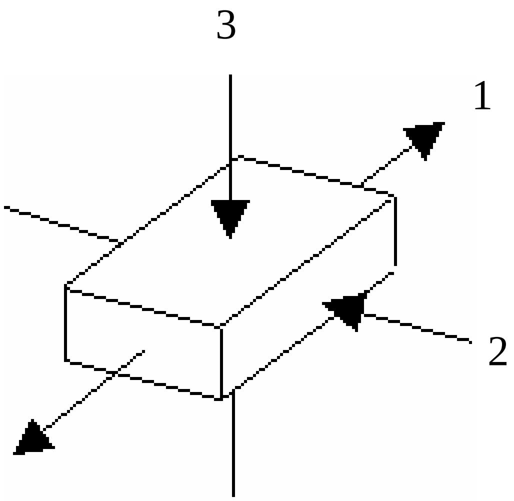
$$\Psi_2 = \frac{\sigma_{22} - \sigma_{33}}{\dot{\gamma}^2}$$: second (or secondary) normal stress coefficient

- **Elongational flow**

* ***Uniaxial elongational flow***

$$v_1 = \dot{\varepsilon}\, x_1,\ \ v_2 = -\frac{\dot{\varepsilon}}{2} x_2,\ \ v_3 = -\frac{\dot{\varepsilon}}{2} x_3$$

for an incompressible fluid



$\dot{\varepsilon}$: elongational (or extensional) strain rate

$\overline{\eta} = \dfrac{\sigma_{11} - \sigma_{22}}{\dot{\varepsilon}}$: elongational viscosity

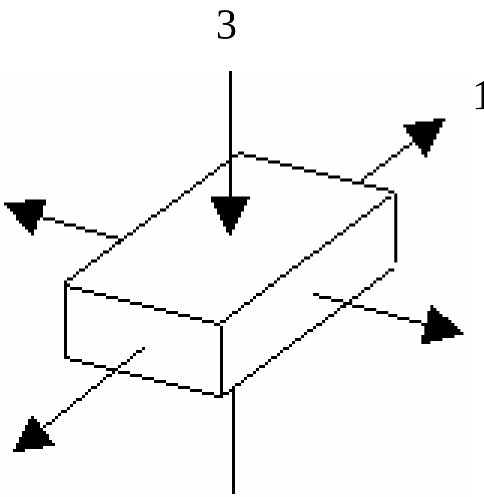
(fiber spinning)

* ***Biaxial elongational flow***

$$v_1 = \dot{\varepsilon}\, x_1,\ v_2 = \dot{\varepsilon}\, x_2,\ v_3 = -2\dot{\varepsilon}\, x_3$$

$$\eta_B = \frac{\sigma_{11} - \sigma_{33}}{\dot{\varepsilon}} = \frac{\sigma_{22} - \sigma_{33}}{\dot{\varepsilon}}$$

(film blowing)

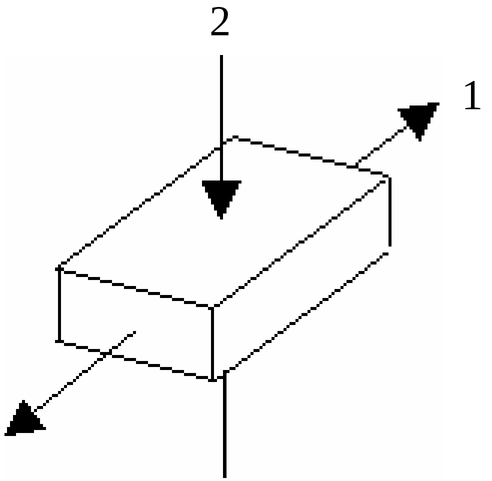


* ***Planar extensional flow***

$$v_1 = \dot{\varepsilon}\, x_1,\ \ v_2 = -\dot{\varepsilon}\, x_2,\ \ v_3 = 0$$

$$\eta_{EP} = \frac{\sigma_{11} - \sigma_{22}}{\dot{\varepsilon}}$$

(sheet casting)



- **Dynamic flow**

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

$$\sigma^* = \sigma_0 \exp(i(\omega t + \delta)) \qquad \delta : \text{phase angle}$$

- Complex shear modulus

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

G' : storage modulus (elastic modulus, or in-phase modulus)

G'' : loss modulus (out-of-phase modulus)

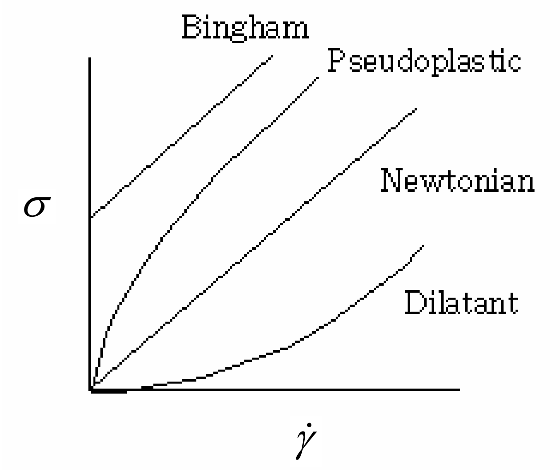
- Complex viscosity

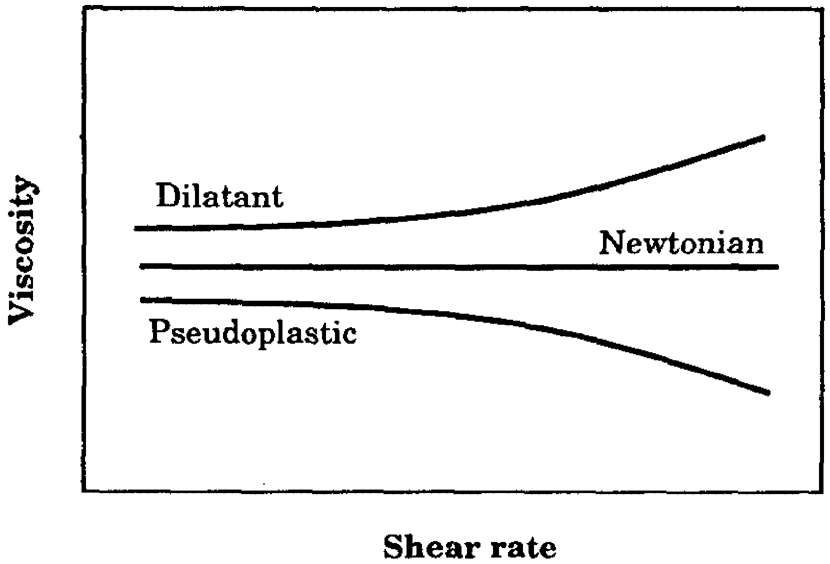
$$\eta^* = \frac{\sigma^*}{\dot{\gamma}^*} = \frac{G''}{\omega} - i\frac{G'}{\omega} = \eta' - i\eta''$$

η' : dynamic viscosity (energy dissipation)

η'' : elastic part of complex viscosity (energy storage)

- Rheological behaviors of simple shear





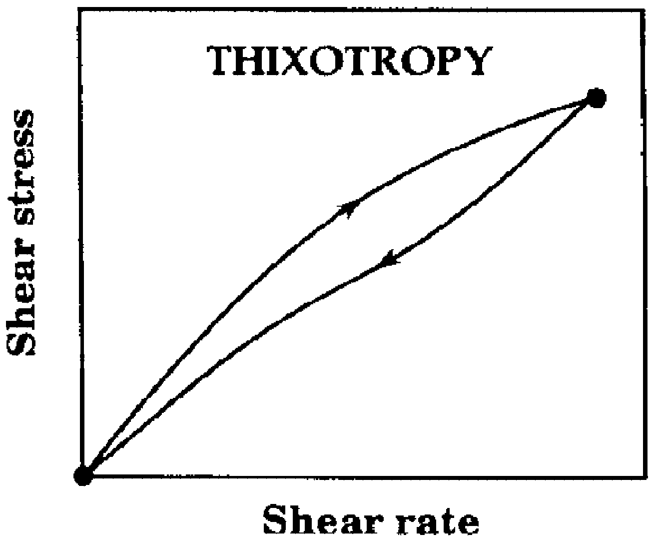
most polymer melts (pseudoplastic)
wet beach sand (dilatant)
oils, cement slurries, margarine (Bingham)

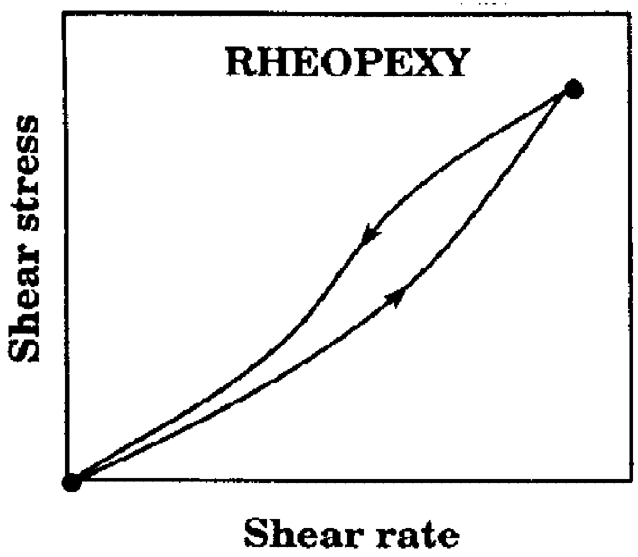
$$\sigma_{21} = \eta \dot{\gamma} \quad \text{(Newtonian)}$$

$$\sigma_{21} = K \left| \dot{\gamma} \right|^{n-1} \dot{\gamma} \quad \text{(power-law) Ostwald-de Waele equation}$$

K : consistency factor, n : power-law index

- Time dependence of a non-Newtonian liquid





6.3 Measurement of rheological properties

: η, N_1 & N_2

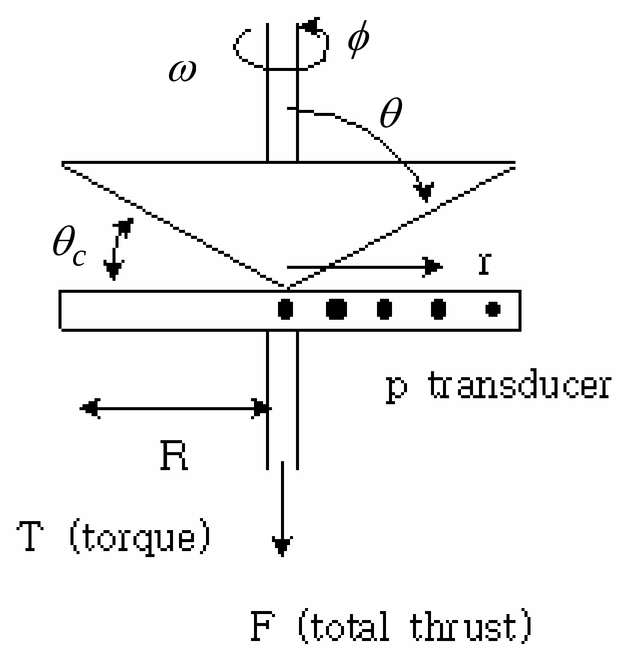
Couette viscometer, capillary viscometer, parallel-plate viscometer, cone-and-plate viscometer

N_1 (first normal stress difference) $= \sigma_{11} - \sigma_{22}$

N_2 (second normal stress difference) $= \sigma_{22} - \sigma_{33}$

Ψ_1 (first normal stress coefficient) $= \dfrac{N_1}{\dot{\gamma}^2}$

Ψ_2 (second normal stress coefficient) $= \dfrac{N_2}{\dot{\gamma}^2}$



Spherical coordinates (1: ϕ, 2: θ, 3: r)

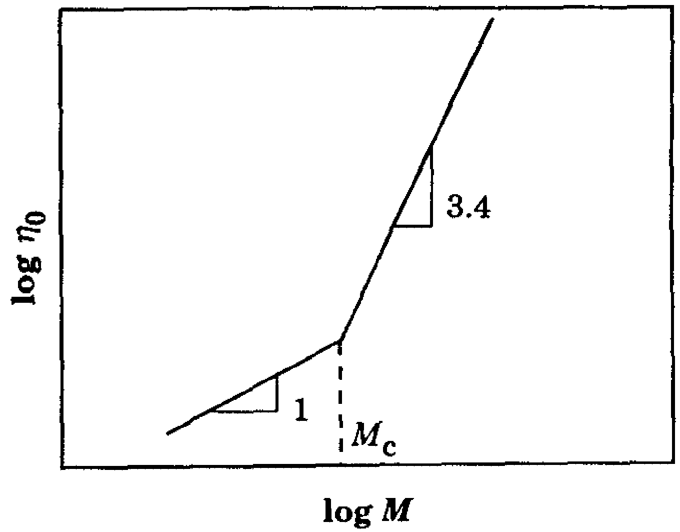
$$N_1 = \sigma_{11} - \sigma_{22} = \frac{2F}{\pi R^2}$$

$$\frac{\partial \sigma_{\theta\theta}}{\partial \ln r} = \frac{r\partial p}{\partial r} = N_1 + 2N_2 = \sigma_{11} + \sigma_{22} - 2\sigma_{33}$$

$$\sigma_{12}\,(=\eta\dot{\gamma}) = \frac{3T}{2\pi R^3}, \quad \dot{\gamma} = \frac{\omega}{\theta_c}$$

6.4 Flexible-chain polymers

Flow properties ~ function of MW & chain branching



$\eta_0 \propto M$ for $M < M_c$

$\eta_0 \propto M^{3.4}$ for $M > M_c$

M_c : critical molar mass

(starting point of chain entanglement)

$$\eta_0 = A\exp\left(\frac{B}{\alpha(T-T_0)}\right) = A\exp\left(\frac{\Delta E}{R(T-T_0)}\right)$$

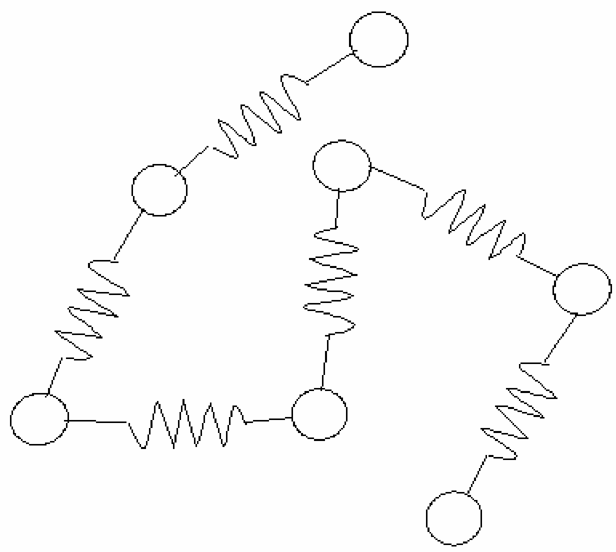
일반적으로 온도 $\uparrow \rightarrow \eta \downarrow$

압력 $\uparrow\uparrow \rightarrow \eta \uparrow$

- Rouse model

flexible repeating units in viscous surroundings

long enough to obey Gauss distribution



Forces acting on each repeating unit

i) drag force w.r.t. surrounding medium

$\propto$ relative velocity of the repeating unit

ii) force from the adjacent repeating units

iii) force from Brownian motion

Not applicable to polymer melts of $MW > M_c$

$\therefore$ Model for dilute solution

• Reptation model

coiled chain trapped in a network

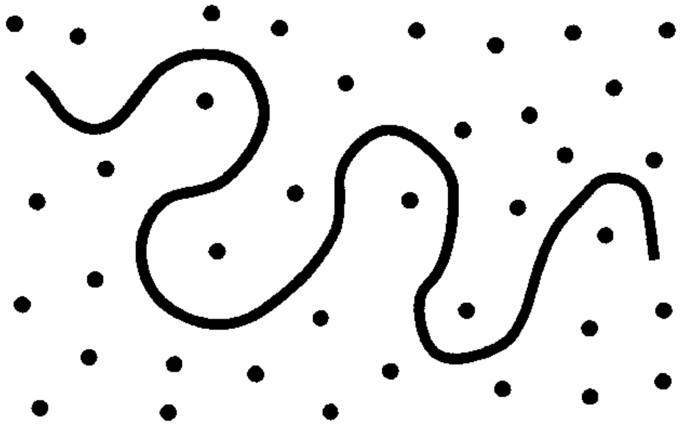
du Gennes : theory of reptation of polymer chains

Doi & Edwards : the relationship of the dynamics of repeating chains to mechanical properties

$G_p \propto M^0$ (rubbery plateau shear modulus)

$\eta_0 \propto M^3$ (zero-shear rate viscosity)

experimental data : $\eta_0 \propto M^{3.4}$



$\therefore$ Model for entangled polymer chains in the absence of a permanent network