Chapter 10

Viscoelasticity & Rheology

Viscoelasticity [粘彈性論]

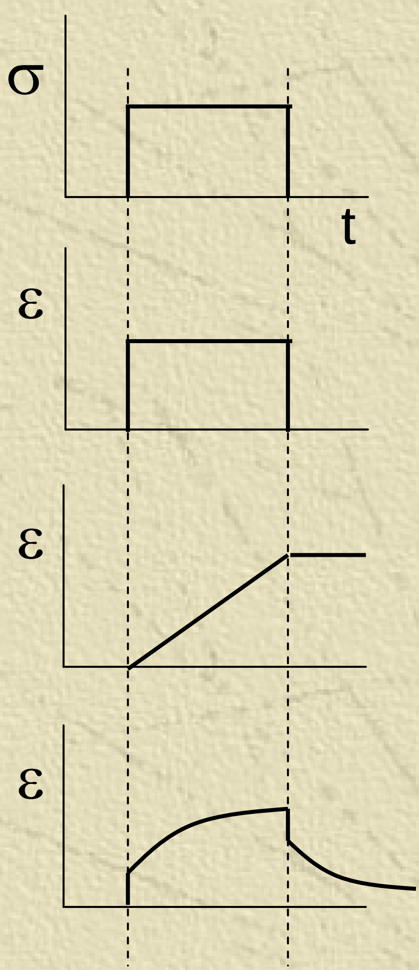
study of time-dependent deformation

Rheology [流變學]

study of flow and deformation

Viscoelasticity

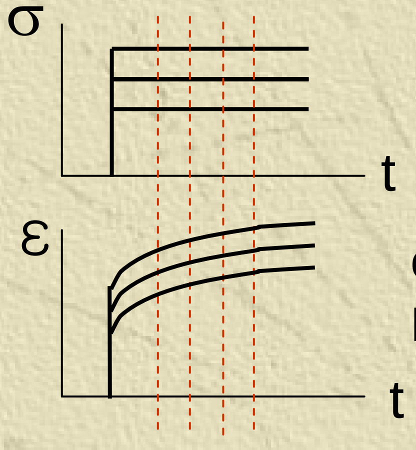
- VE ~ time-dependent $\sigma-\varepsilon$ behavior



tensile	shear
$\varepsilon = \sigma/E = D\sigma$	$\gamma = \tau/G = J\tau$
$d\varepsilon/dt = \sigma/\eta_E$	$d\gamma/dt = \tau/\eta_{(s)}$
$\varepsilon(t) = \sigma/E(t) = D(t)\sigma$	$\gamma(t) = \tau/G(t) = J(t)\tau$

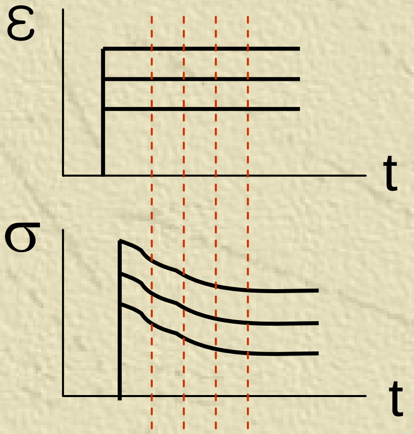
$1/E(t) = D(t)$?

Creep & stress relaxation



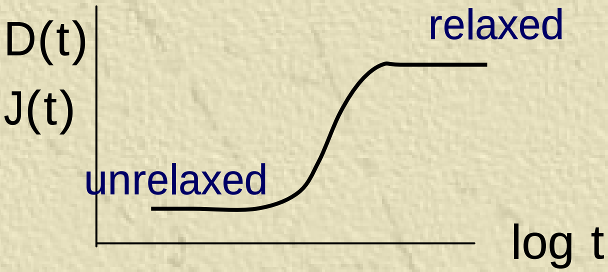
creep compliance

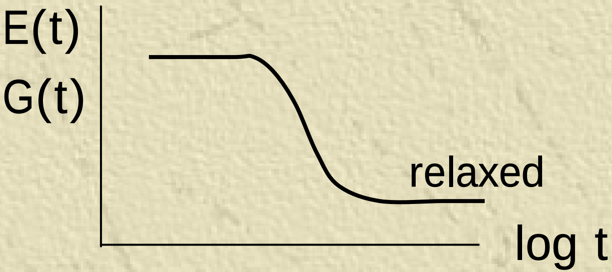
$D(t) = \varepsilon(t)/\sigma_0$

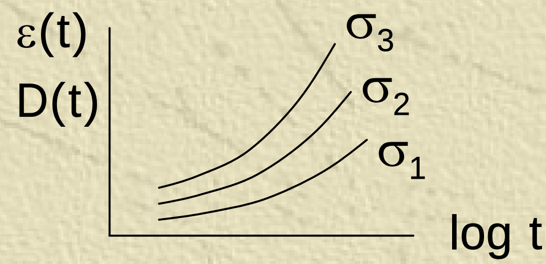


SR modulus

$E(t) = \sigma(t)/\varepsilon_0$



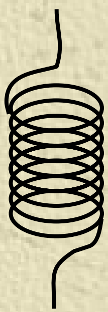




$1/E(t) \neq D(t)$

Mechanical models

- elements



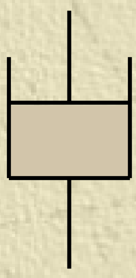
spring

elastic (Hookean)

$\sigma = E \varepsilon$

$d\sigma/dt = E\, d\varepsilon/dt$

p510



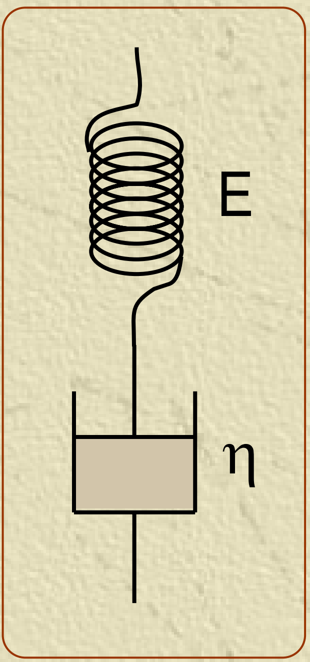
dashpot

viscous (Newtonian)

$\sigma = \eta\, d\varepsilon/dt$

Mechanical models 2

Maxwell model ~ serial



Stress the same

$d\varepsilon/dt = (1/E)\, d\sigma/dt + \sigma/\eta$

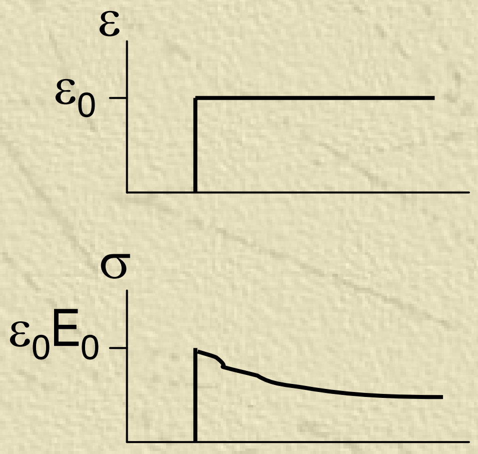
Fig 10.4

creep ~ $d\sigma/dt = 0 \rightarrow d\varepsilon/dt = \sigma/\eta$ ~ viscous only

SR ~ $d\varepsilon/dt = 0 \rightarrow d\sigma/\sigma = d\ln\sigma = -(E/\eta)\,dt$

$\sigma(t) = \sigma_0 \exp[-(E/\eta)t]$

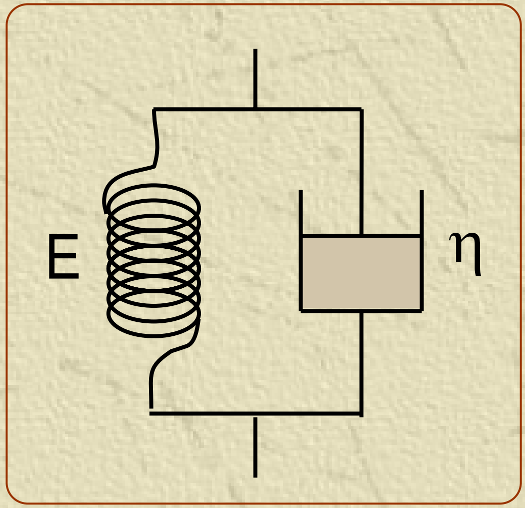
$= \varepsilon_0 E_0 \exp[-t/\tau]$



$\tau = \eta/E$ ~ relaxation time

Mechanical models 3

- Voight [Kelvin] model ~ parallel



Strain the same

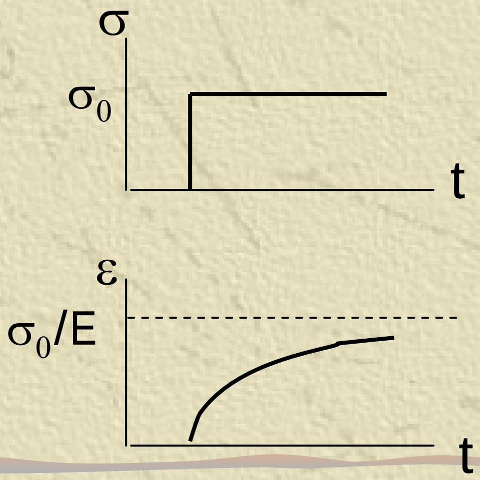
$\sigma = \eta\ (d\varepsilon/dt) + E\ \varepsilon$

SR ~ $d\varepsilon/dt = 0 \rightarrow \sigma = E\ \varepsilon$ ~ elastic only

creep ~ $d\sigma/dt = 0\ (\sigma = \sigma_0)$

$\varepsilon(t) = (\sigma_0/E)\ (1 - \exp[-t/\tau])$

$\tau = \eta/E$ ~ retardation time

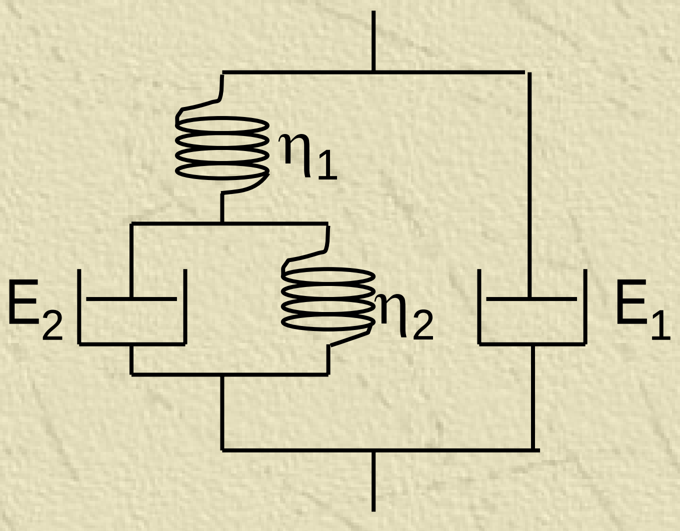


📖Fig 10.4

Mechanical models 4

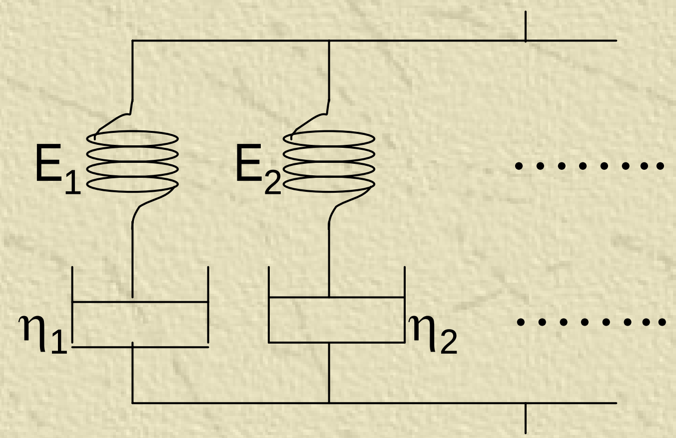
- Composite models
  - 3-element model, 4-element model
  - Zener model, standard linear solid (SLS) model
  - Takayanagi model, etc

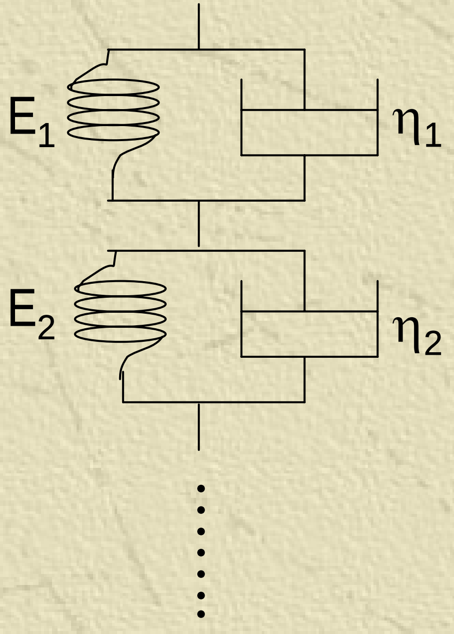
✓ math improved, not physics



Mechanical models 5

- Generalized Maxwell model
  Generalized Voight model





$\tau_1 = \eta_1/E_1$

$\tau_2 = \eta_2/E_2$

⋮

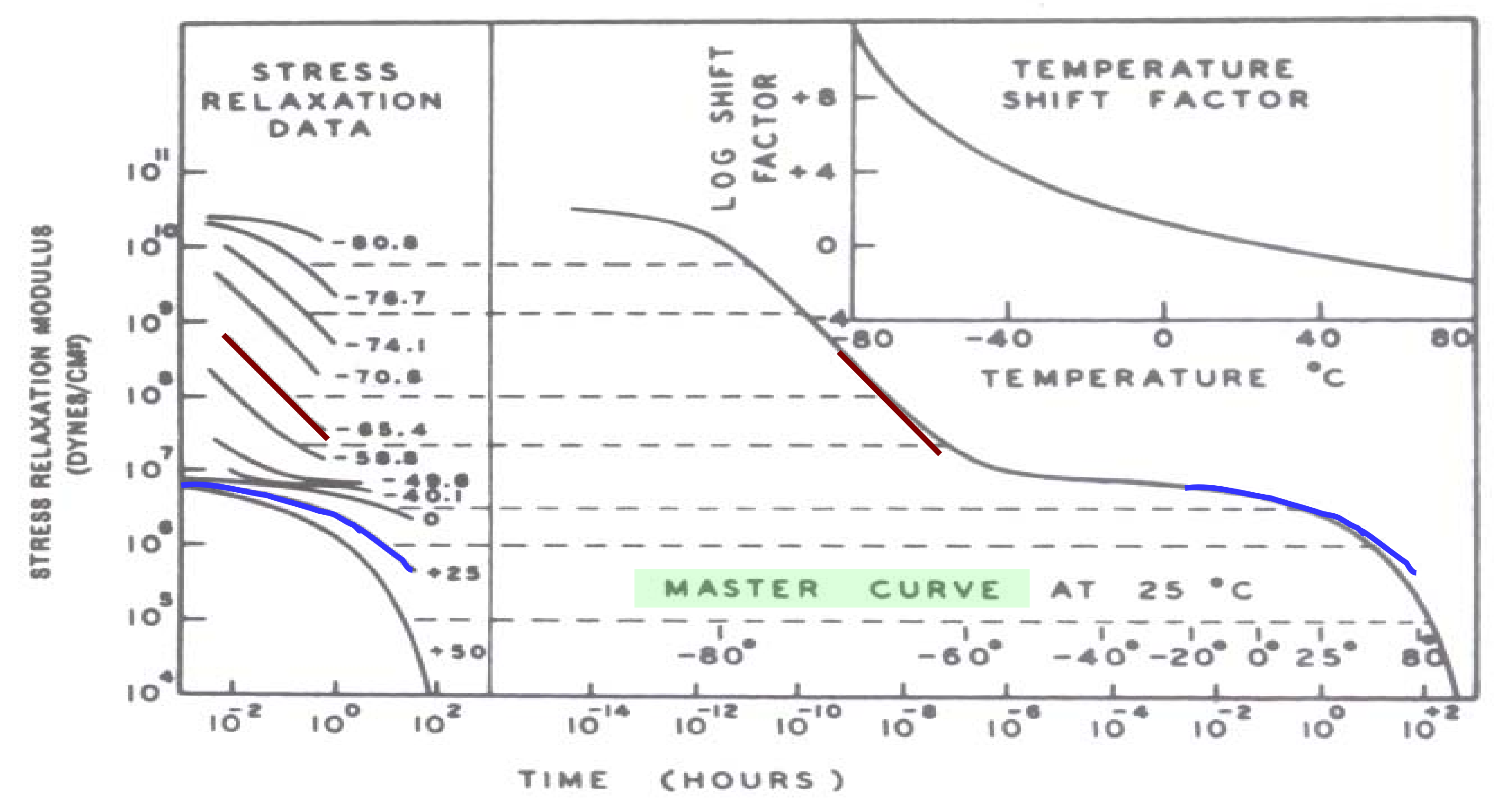
τ_i ~ spectrum of relaxation times

✓physics improved,
but <u>not</u> real.

Time-Temperature Superposition

- High temperature & long time is equivalent in viscoelasticity
  - for chain motion
  - Data can be superimposed (T & log t)

📖Fig10.14 p531



Time-Temperature Superposition 2

- shifting

$$\frac{E(T_1,\ t)}{\rho(T_1)\ T_1} = \frac{E(T_2,\ t/a_T)}{\rho(T_2)\ T_2}$$

~ horizontal shift

~ vertical shift ~ negligible

$E \propto \rho RT/M$

- when T_2 [T_{ref}] is T_g → WLF eqn

$$\log a_T = \frac{-C_1\ (T - T_g)}{C_2 + T - T_g}$$

- $T > T_{ref}\ (T_g)$ ~ $a_T < 1$ ~ $t > t/a_T$ ~ shift to longer time

  $T < T_{ref}\ (T_g)$ ~ $a_T > 1$ ~ $t < t/a_T$ ~ shift to shorter time

Rheology (流變學)

- rheology ~ study of flow and deformation
- Shear viscosity ~ processability
  - $\tau = \eta_{(s)}\,\dot{\gamma} = \eta\,(d\gamma/dt)$
    - τ ~ shear stress [N/m^2] = [Pa]
    - γ ~ shear (strain) rate [s^{-1}]
    - η ~ (shear) viscosity [N/m^2 s] = [Pa s]
  - 🕮 Table 10.5 p538
    - η of water ~ 10^{-3} Pa s = 1 cP

      1 Pa s = 10 P(oise)
    - η of polymer melt ~ 10^{3} Pa s

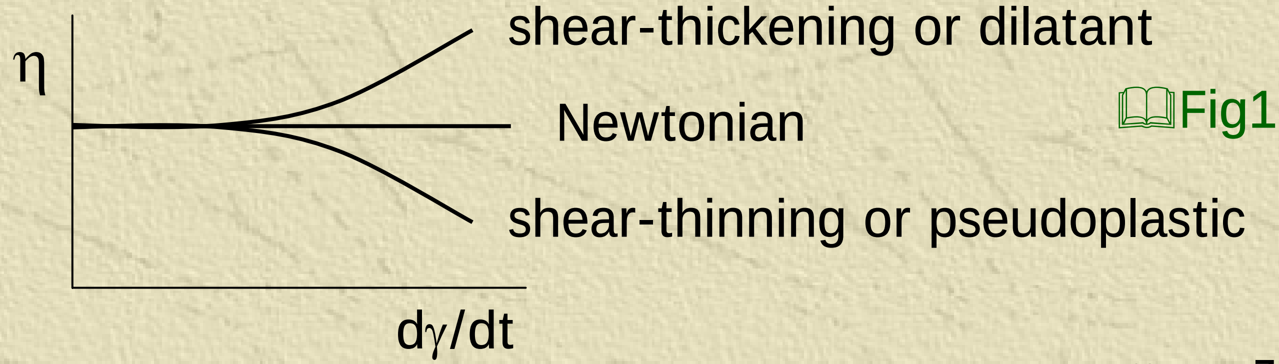
Shear viscosity 2

- Temperature dependence
  - WLF eqn ~ for $T_g - 50 < T < T_g + 100$ K
  - Arrhenius relation ~ for $T > T_g + 100$ K
    - $\eta = A \exp[-B/T]$
      - $B < 0$ ~ T↑ → η ↓
    - for narrow temp region only

- Pressure dependence
  - $\eta = A \exp[B/P]$
    - P ↑ → η ↑
    - interparticle distance

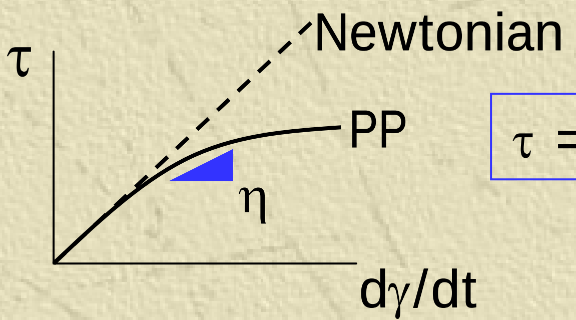
Shear viscosity 3

- Shear rate dependence

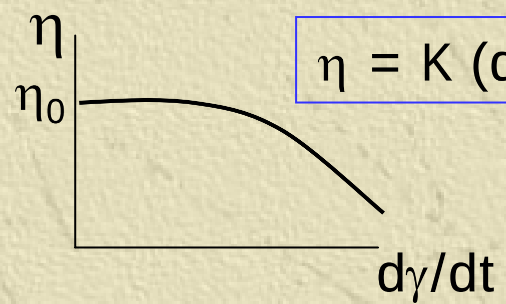


📖Fig10.23 p546

η_0 ~ zero shear viscosity

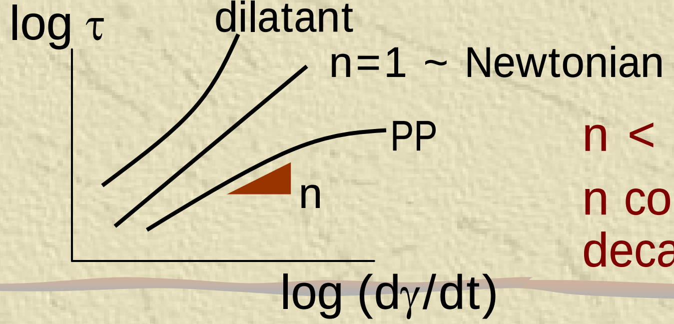


$\boxed{\tau = K\,(d\gamma/dt)^n}$



$\boxed{\eta = K\,(d\gamma/dt)^{n-1}}$

- power-law expression
  - n ~ power-law index
  - K ~ consistency



n < 1 and ↓

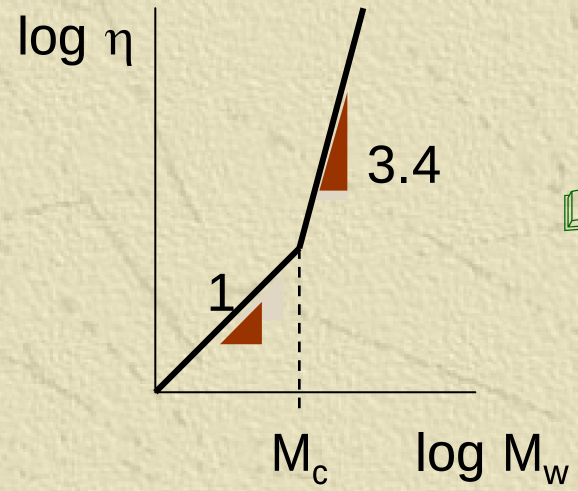
n const at 1-2 decades

Shear viscosity 4

- Mol wt dependence
  - $\eta = K\, M_w^{1.0}$ for $M < M_c$
    $\eta = K\, M_w^{3.4}$ for $M > M_c$
  - $M_c \sim$ 2-3 $M_e \sim$ entanglement mol wt 🕮Table 10.4 p537
    $M_e = \rho RT / G_N^0$

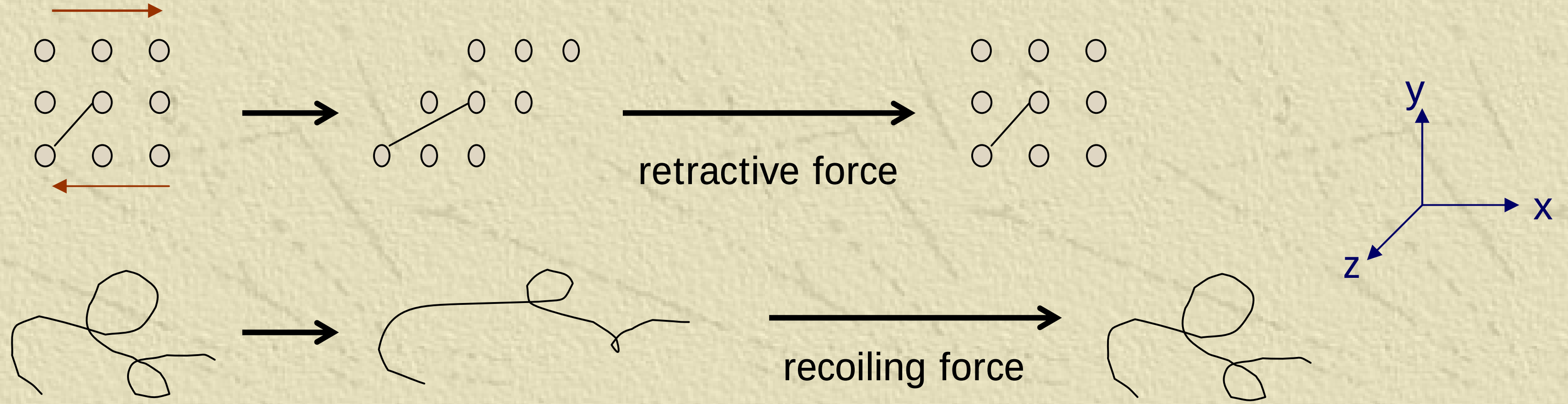
M_c(step polymers) < M_c(chain polymers)

results of intermol interactions



🕮Fig10.16 p534

Normal stress difference

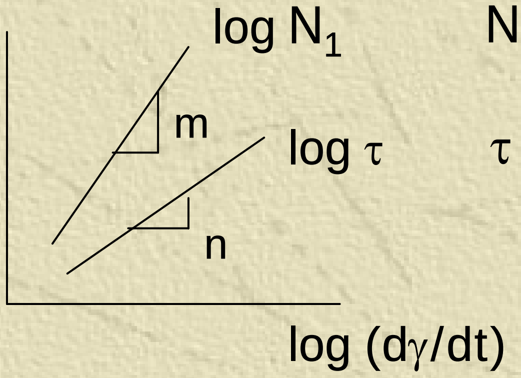


retractive force

recoiling force

- $\sigma_{xx} - \sigma_{yy} = N_1 > 0$ ~ 1st normal stress difference
- $\sigma_{yy} - \sigma_{zz} = N_2 \approx 0$ ~ 2nd normal stress difference
- $N_1/(d\gamma/dt)^2$ ~ 1st NS coeff
- $N_2/(d\gamma/dt)^2$ ~ 2nd NS coeff

Normal stress difference 2

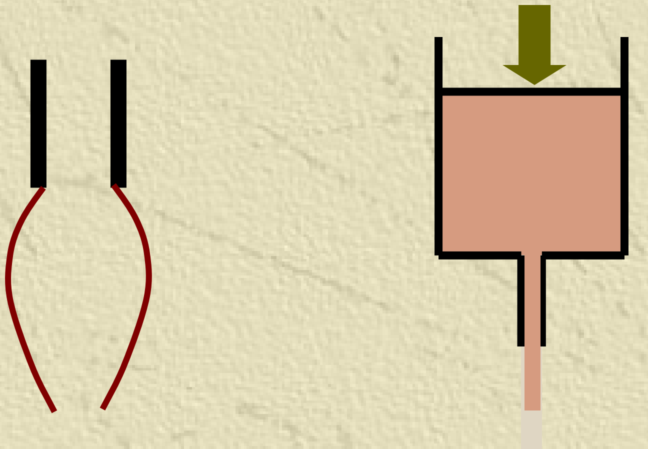


$N_1 = A\,(d\gamma/dt)^m$ $(1<m<2)$

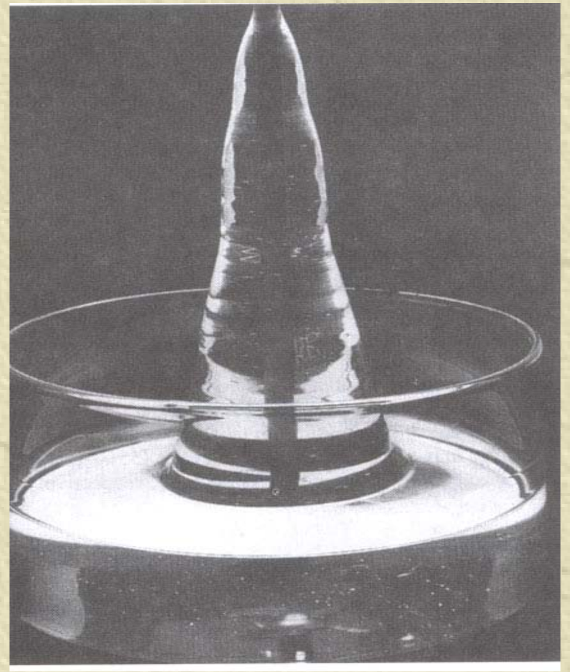
$\tau = K\,(d\gamma/dt)^n$ $(0<n<1)$

- Results of NSD
  - Weisenberg effect (rod-climbing)
  - die swell

📖Fig10.21 p543



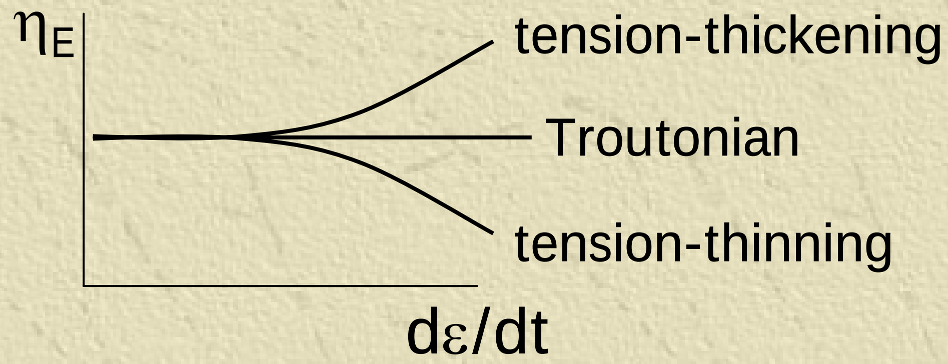
📖Fig10.19 p542



Elongational viscosity

$$\sigma = \eta_E \, (d\varepsilon/dt)$$

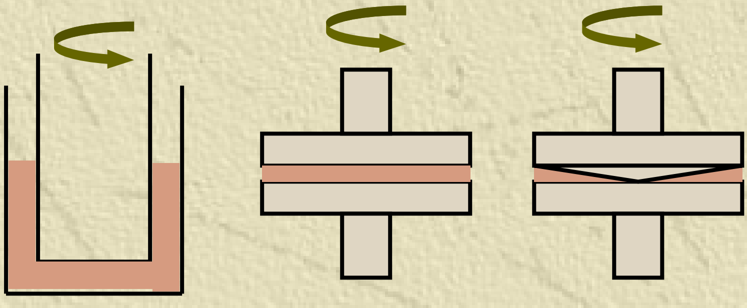
η_E ~ elongational or tensile viscosity



η_E determines melt strength [stability of melt]

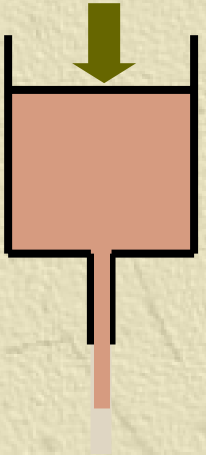
Measuring rheological behavior ~ rheometry

- rotational rheometers ~ drag
  - cylinder
  - plate
    - parallel-plate rheometer
    - cone-and-plate rheometer



📖Fig10.22 p545

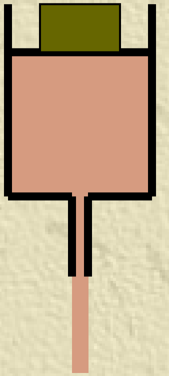
- capillary or slit rheometer ~ pressure drop



- dynamic rheometry
  - η’ = G”/ω ~ dynamic viscosity 📖eqn(10.73) p544
  - η” = G’/ω
  - η* = η’ – iη” ~ complex viscosity

Rheometry 2

- 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