Chapter 8

Glass(-Rubber) Transition

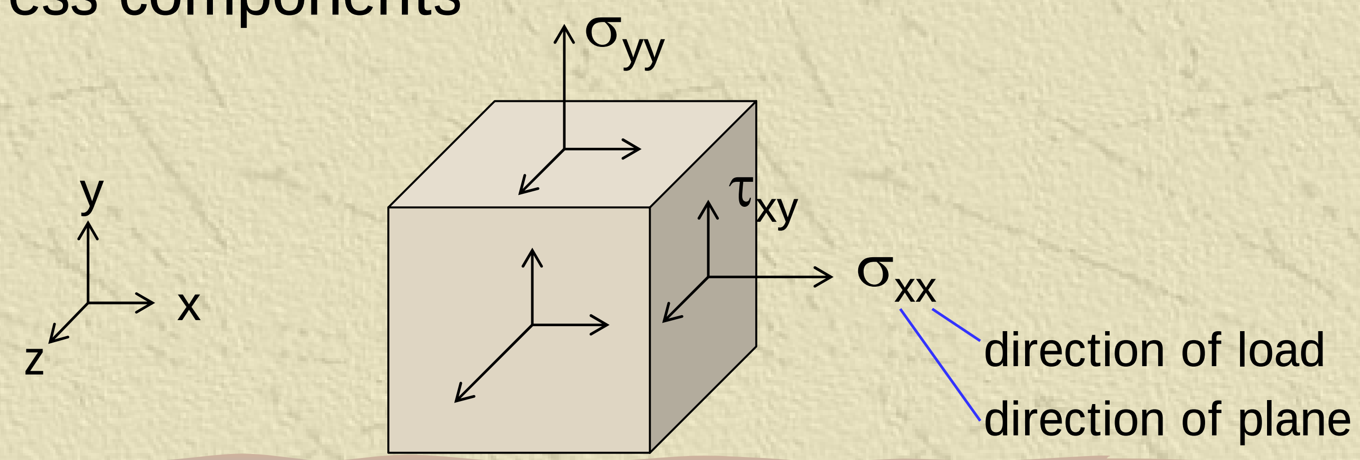
Mechanical relations

Transitions and relaxations

Glass transition theories

1. Mechanical relations

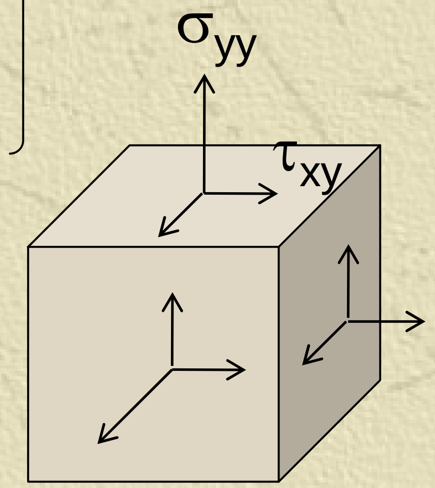
- stress and strain
  - stress (응력), $\sigma = F / A$
    - F ~ force, vector, 2nd-rank tensor, 3 components (x,y,z)
    - A ~ area, vector, 2nd-rank tensor, 3 components (x,y,z)
    - then, σ ~ 4th-rank tensor, 9 components (xx, xy, xz ---)
  - strain (변형), $\varepsilon = \Delta L / L$
    - deformation by load
    - also a 4th-rank tensor, 9 components
  - 9 stress components



Stress and strain 2

- stress components
  - 3 normal stresses (σ, 수직응력)
  - 6 shear stresses (τ, 전단응력)
    - by symmetry → 3 τ's

$$\begin{pmatrix} \sigma_x & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_y & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_z \end{pmatrix}$$



  - 9 components → 6 independent components

$\underset{\sim}{\sigma}$

$\varepsilon_{xy} = \gamma_{xy}/2$

$$\begin{pmatrix} \sigma_x & \tau_{xy} & \tau_{zx} \\ \tau_{xy} & \sigma_y & \tau_{yz} \\ \tau_{zx} & \tau_{yz} & \sigma_z \end{pmatrix} = \begin{pmatrix} & & \\ & 81 & \\ & & \end{pmatrix} \begin{pmatrix} \varepsilon_x & \varepsilon_{xy} & \varepsilon_{zx} \\ \varepsilon_{xy} & \varepsilon_y & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{yz} & \varepsilon_z \end{pmatrix}$$

xy, yz, zx
12, 23, 31

- stiffness tensor components
  - 81 → 36 → 21 → → → 2 (isotropic, 2 of E, ν, G, B)

Three types of mechanical behavior

- Elastic (탄성)
  - instantaneous
  - solid-like
- Viscous (점성)
  - rate-dependent
  - liquid-like
- Viscoelastic (점탄성)
  - time-dependent
  - polymer-like?

Elastic

- tensile deformation

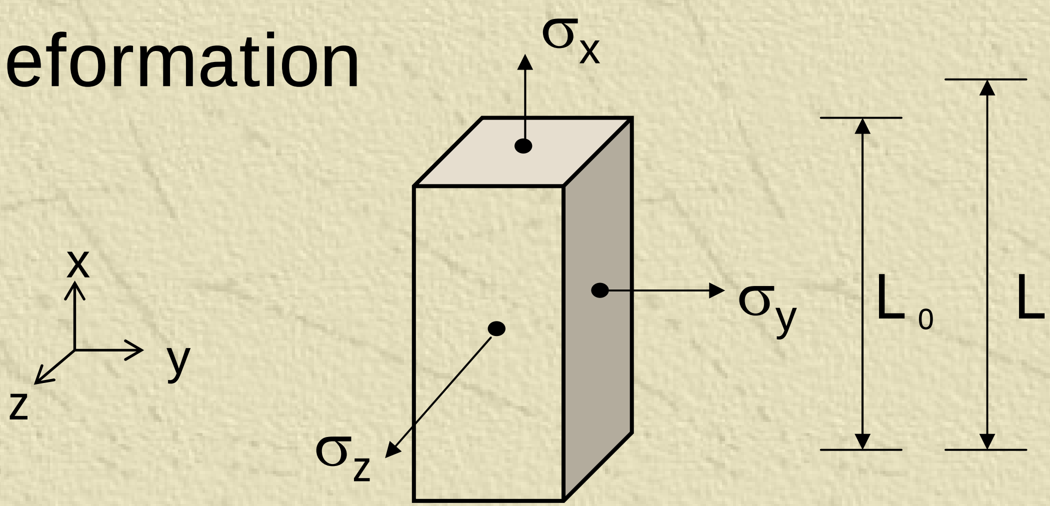


Fig 8.1(a)

$\varepsilon_{(x)} = (L-L_0)/L$

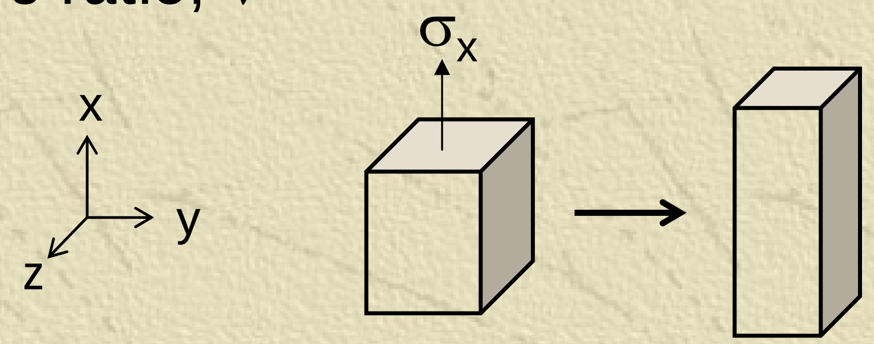
- When $\sigma_y = \sigma_z = 0$, τ's = 0 → uniaxial tension test (UTT)
- $\sigma_{(x)} = E\,\varepsilon_{(x)}$
  - Hooke's law (for UTT)
  - E ~ Young's modulus [영탄성률, 인장탄성률]
    - modulus ~ resistance to deformation p355

$$\begin{bmatrix} \sigma_x & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

- $\varepsilon = D\,\sigma$
  - D ~ (tensile) compliance [순응도]

Elastic 2

- Poisson's ratio, ν

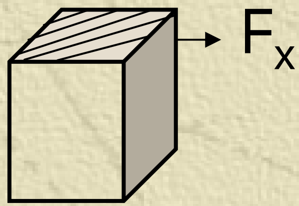


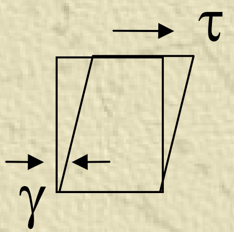
  - definition, $\nu = -\varepsilon_y / \varepsilon_x > 0$
  - rubbers, $\nu = 0.5$ ~ no volume change
  - plastics, $\nu \sim 0.4$
  - metals, $\nu < 0.4$ (~ 0.33)

📖Table 8.2

Elastic 3

shear deformation





📖Fig 8.1(b)

$$\begin{bmatrix} 0 & \tau_{xy} & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

- When $\tau_{yz} = \tau_{zx} = 0$, σ's = 0 → simple shear
- $\tau_{(xy)} = G\,\gamma_{(xy)}$
  - another Hooke's law (for simple shear)
  - G ~ shear modulus [전단탄성률]
- $\gamma = J\,\tau$
  - J ~ shear compliance

Elastic 4

- $\sigma_{(x)} = E\,\varepsilon_{(x)}$ UTT ($\sigma_y = \sigma_z = 0$, τ's $= 0$)

  $\tau_{(xy)} = G\,\gamma_{(xy)}$ simple shear ($\tau_{yz} = \tau_{zx} = 0$, σ's $= 0$)

  $\varepsilon_y = -\nu\,\varepsilon_x$ UTT

- When all stresses are present

$$\varepsilon_x = \sigma_x/E - \nu\,\varepsilon_y - \nu\,\varepsilon_z$$

$$= \sigma_x/E - \nu\,\sigma_y/E - \nu\,\sigma_z/E$$

$$= (1/E)\,[\sigma_x - \nu\,(\sigma_y + \sigma_z)]$$

$$\varepsilon_y =$$

$$\varepsilon_z =$$

$$\tau_{xy} = G\,\gamma_{xy}$$

$$\tau_{yz} =$$

$$\tau_{zx} =$$

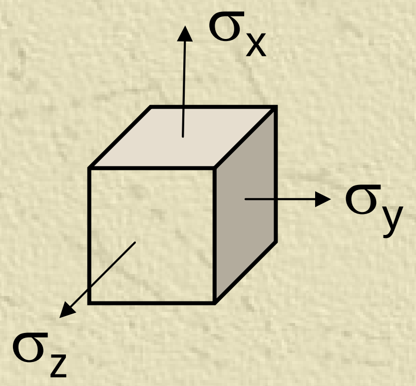
$\boxed{\varepsilon_y = \sigma_y/E}$

Generalized Hooke's law

(for isotropic materials)

Elastic 5

- dilatation



$$\frac{(\sigma_X + \sigma_y + \sigma_z)}{3} = \sigma_m$$ ~ mean normal stress

volume, $V_0 \rightarrow V$

$$\varepsilon_m = \frac{V - V_0}{V_0}$$ ~ volume strain

  - $\sigma_m = B\ \varepsilon_m$ B (K) ~ bulk modulus
  - $\varepsilon_m = \beta\ \sigma_m$ β ~ compressibility

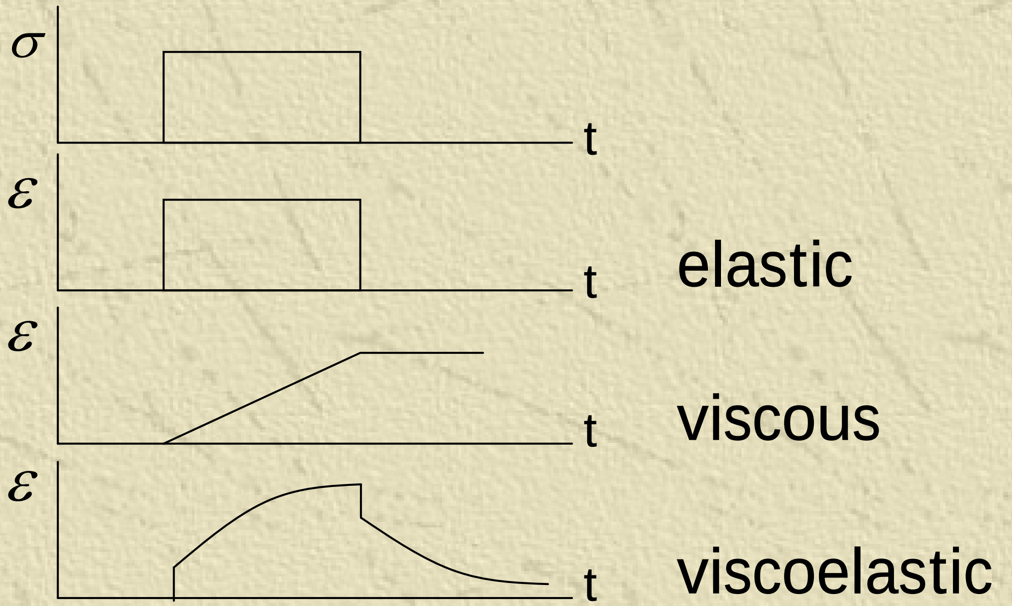
- relations betw elastic constants
  - $E = 3B(1-2\nu) = 2(1+\nu)G$
    - Only 2 of 4 (E, G, B, ν) are independent.
    - e.g., $E = 3G$, $B = \infty$ for elastomers

Viscous and Viscoelastic

- Viscous ~ liquid-like, rate-dependent
  - $\tau = \eta \dot{\gamma} = \eta_{(s)} (d\gamma/dt)$ ~ Newton's law
    - $\eta_{(s)}$ ~ (shear) viscosity ~ resistance to flow
  - $\sigma = \eta_E \dot{\varepsilon} = \eta_E (d\varepsilon/dt)$
    - η_E ~ elongational [tensile] viscosity ~ resistance to flow

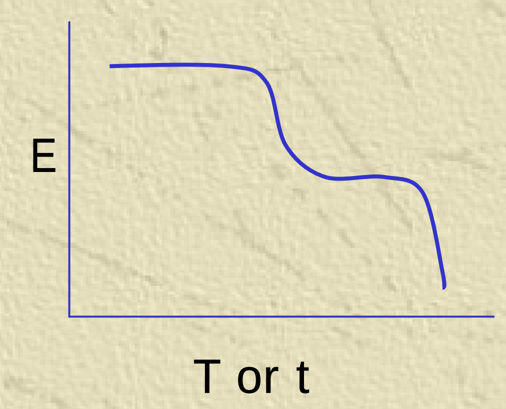
📖*Chapter 10*

- Viscoelastic ~ time-dependent



$\sigma = E(t)\varepsilon(t)$

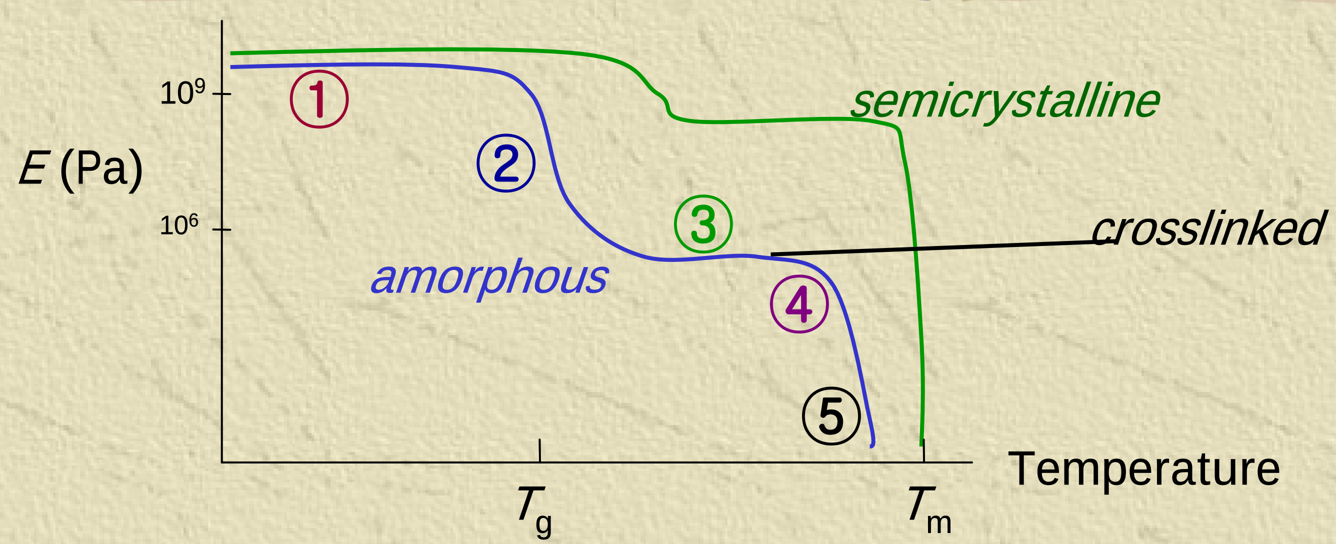
- stress (σ, τ), strain (ε, γ)
- modulus (stiffness), $\sigma = E\,\varepsilon \quad \tau = G\,\gamma$
- compliance, $\varepsilon = D\,\sigma \quad \gamma = J\,\tau$
- Poisson's ratio (ν)
- bulk modulus, B



- elastic, solid-like, Hooke's law, $\sigma = E\,\varepsilon$
- viscous, liquid-like, Newton's law, $\tau = \eta\,(d\gamma/dt)$
- viscoelastic, polymer-like (?), $\sigma = E(t)\,\varepsilon(t)$

- Every material is viscoelastic.
- Deborah number, De $= \tau/t$ [material time/expt time] 🕮p521
- t-T-ε [time-temperature-strain] equivalence

2. Five Regions of Viscoelastic Behavior



① Glassy region

- E ~ 2 – 3 GPa ~ only local motions
- 🕮p357 $E \propto B \propto \delta^2 \propto$ intermolecular interaction
  - possible, but missing chain stiffness

② Glass transition region

- E drops by 10^3 in 10 – 30 ºC
- onset of segmental motion
- 🕮Table 8.4 T_g motion involves 10 – 50 chain atoms

③ Rubbery plateau region

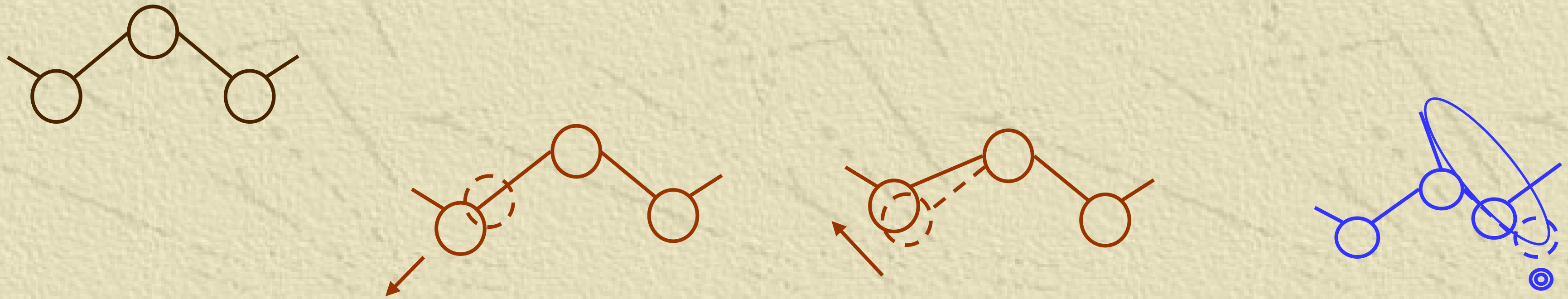
- E ~ 1 – 3 MPa
- width ∝ mol wt   📖Fig 8.3 p359
- $\nu = 0.5 \rightarrow G = E/3 = \rho RT/M = G_N^0$
  - G_N^0 ~ plateau modulus
  - M ~ M_e for linear; M_c for crosslinked polymers

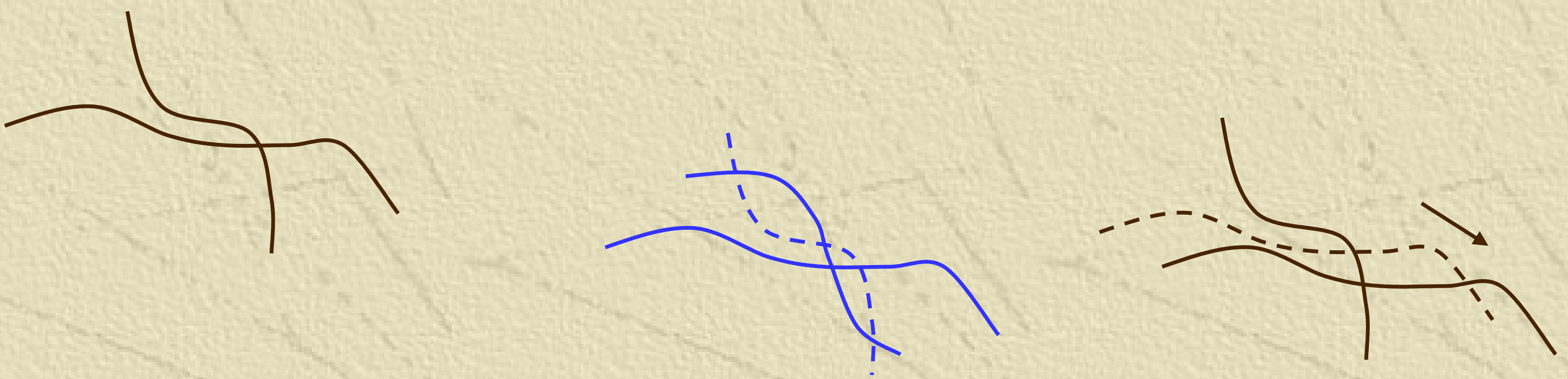
④ Rubbery flow region

- time-dependent flow (Silly-Putty)

⑤ Liquid [viscous] flow region

- slip & translation of individual molecules

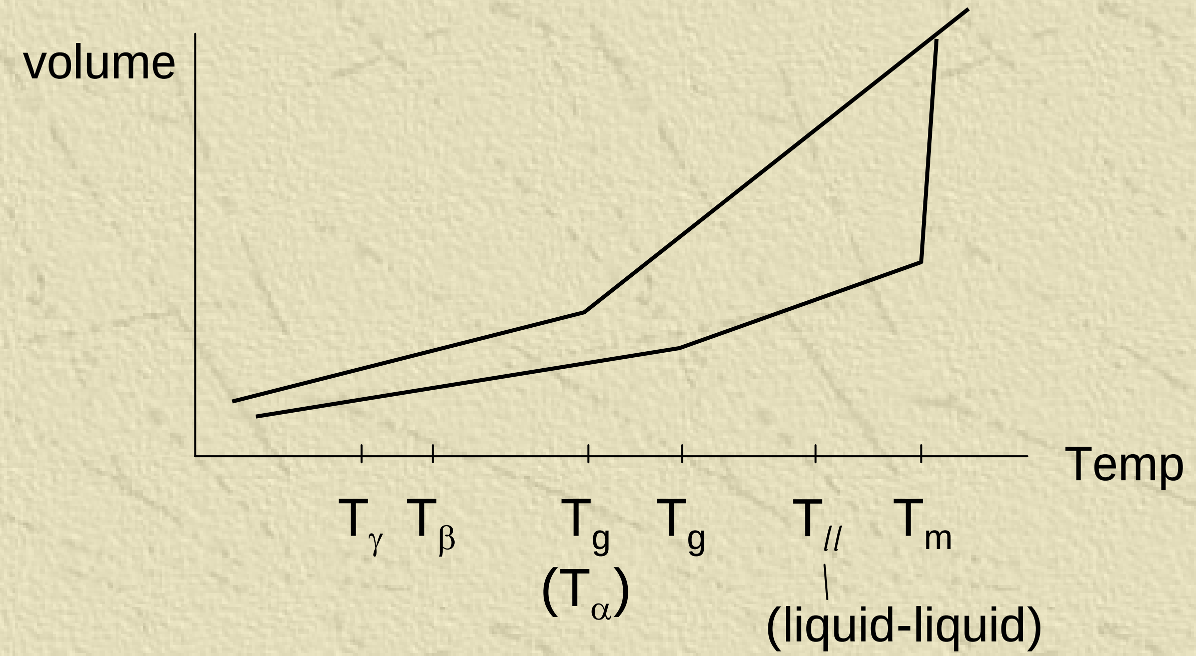




3. Measuring Transitions (Relaxations)

- transition ~ change of state ~ T_m, T_g 🕮 ¶8.2.7 p361
  relaxation ~ molecular motion ~ dielectric, mechanical
  cf. dispersion, damping, loss (of energy)

(1) Dilatometry ~ change in volume [expansion coeff]

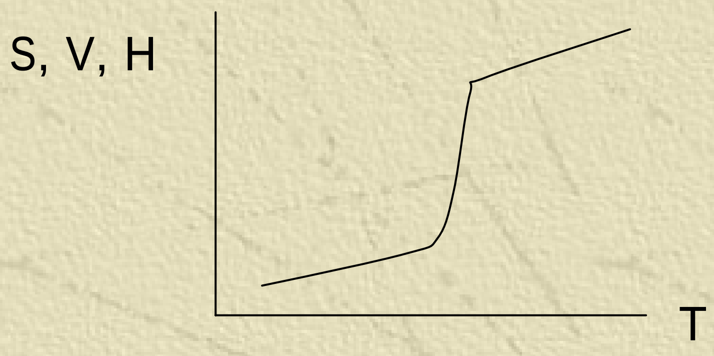


Dilatometry 2

- Thermodynamics of phase transition (Ernfest)
  - 1^{st}-order phase transition
    - Discontinuous 1^{st} derivatives of free energy
    - dG = VdP –SdT

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial (G/T)}{\partial (1/T)}\right)_P = H$$

    - At T_m, T_b



Dilatometry 3

- 2^{nd}-order phase transition
  - discontinuous 2^{nd} derivatives of G

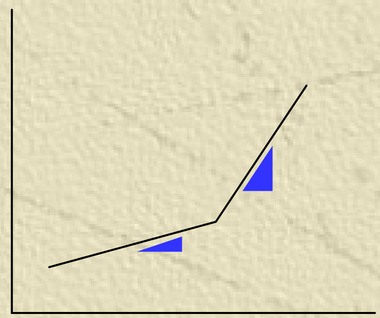
superconducting
para-ferro magnetic

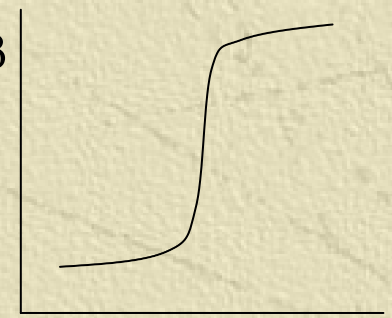
$$\left(\frac{\partial^2 G}{\partial T^2}\right)_p = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_P}{T} \qquad \left(\frac{\partial H}{\partial T}\right)_P = C_P$$

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = -\left(\frac{\partial V}{\partial P}\right)_T = -\beta V \qquad \left(\frac{\partial V}{\partial T}\right)_P = \alpha V$$

  - At T_g

Fig8.5 p363





Dilatometry 4

- Rate-dependent T_g

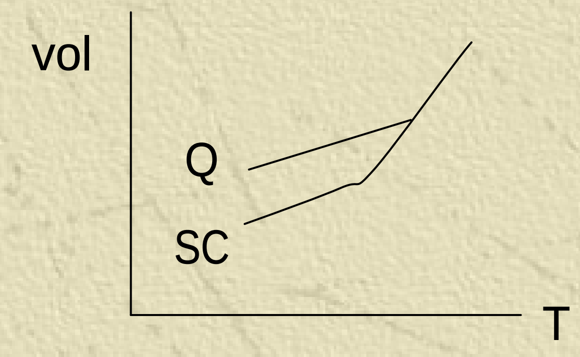
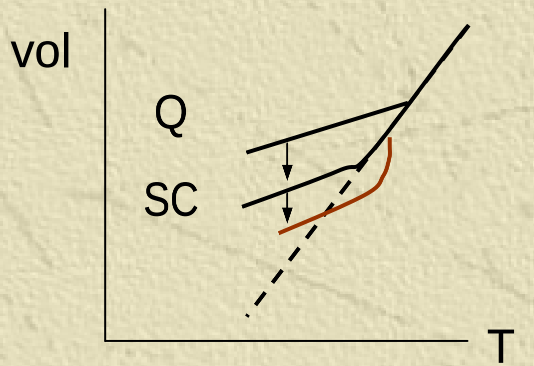


Fig8.18 p378

  - kinetic T_g
  - Glassy state is not in equilibrium.
  - Glass transition is a pseudo-2nd-order phase transition.

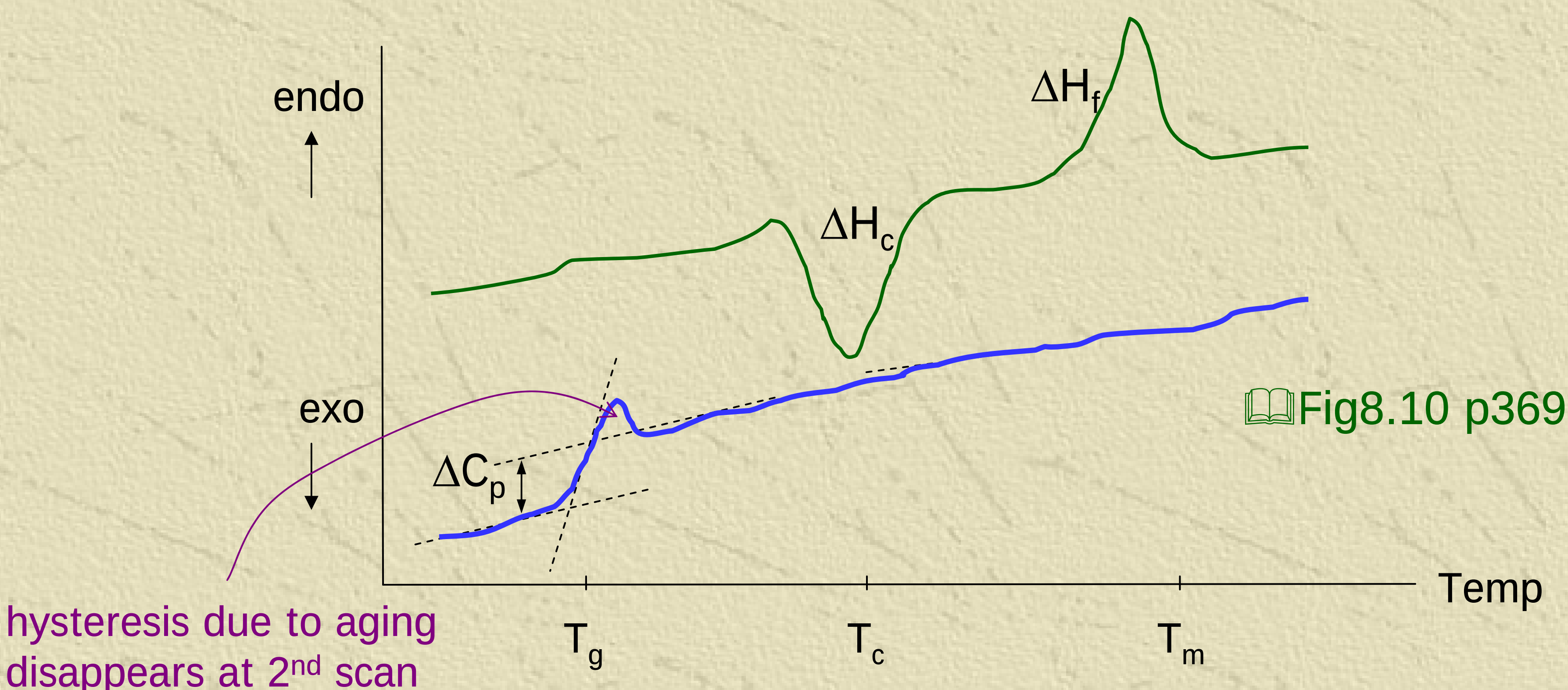
- Physical aging
  - Holding glassy polymer at a $T < T_g$
  - moves to equilibrium
  - $T_g \uparrow$, $E \uparrow$, brittleness $\uparrow$



Thermal Analysis

(2) Thermal Analysis

- DSC
  - Heating (scan) at a constant rate (usually 10-20 K/min)
  - measures difference in heat flow cf. DTA



📖Fig8.10 p369

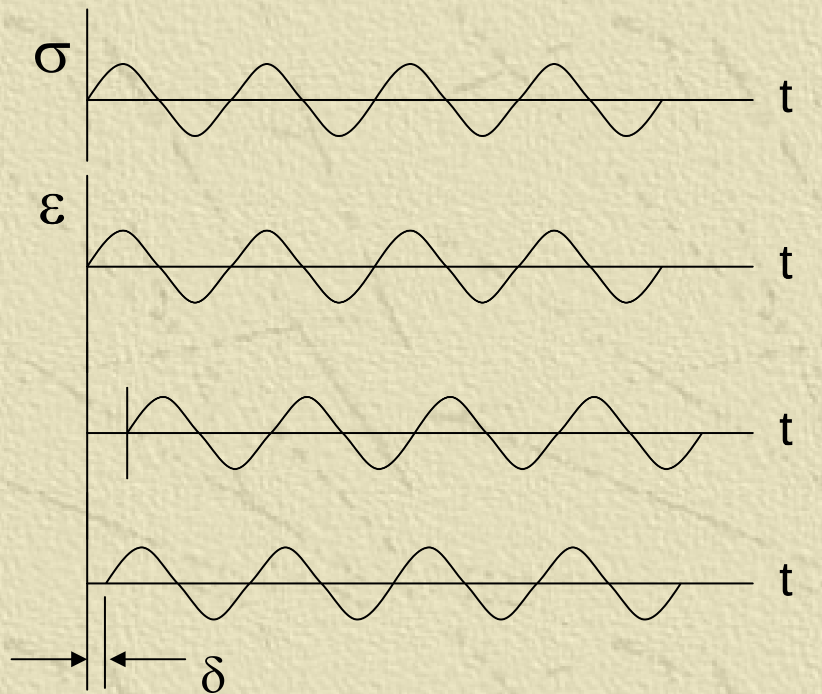
Mechanical Measurement

(3) Mechanical Measurement

- Static test
  - Measuring initial modulus at various T ?
- Dynamic mechanical test

Dynamic Mechanical Analyzer (DMA) [TA]
Dynamic Mechanical Thermal Analyzer (DMTA) [Rheometrix]

cf. Rheovibron® p370



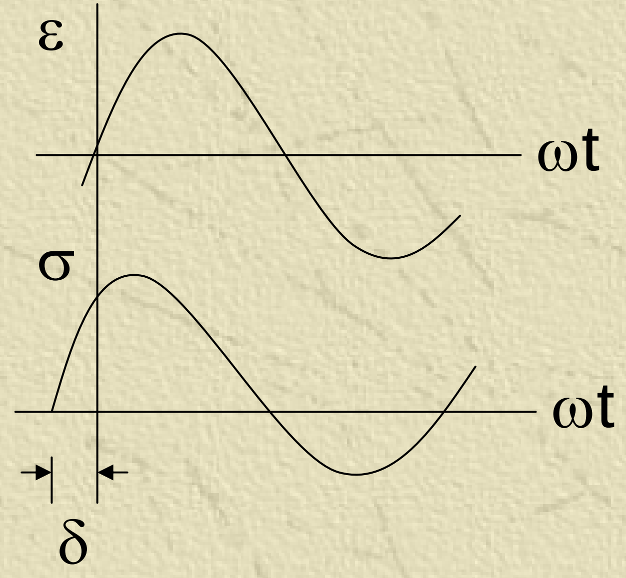
elastic ~ in-phase with σ

viscous ~ $\pi/2$ out of phase with σ

VE ~ $0 < \delta < \pi/2$

δ ~ loss angle

DMA 2



$$\varepsilon = \varepsilon_0 \sin\omega t$$

📖 ¶8.12 p412

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$

$$= \sigma_0 \sin\omega t \cos\delta + \sigma_0 \cos\omega t \sin\delta$$

$$= \varepsilon_0 \underbrace{(\sigma_0/\varepsilon_0)\cos\delta}_{E'} \sin\omega t + \varepsilon_0 \underbrace{(\sigma_0/\varepsilon_0)\sin\delta}_{E''} \cos\omega t$$

E' storage modulus

E" loss modulus

$$= \underbrace{\varepsilon_0 E' \sin\omega t}_{\text{in-phase with } \varepsilon} + \underbrace{\varepsilon_0 E'' \cos\omega t}_{\pi/2 \text{ out-of-phase with } \varepsilon}$$

in-phase with ε
elastic
energy stored

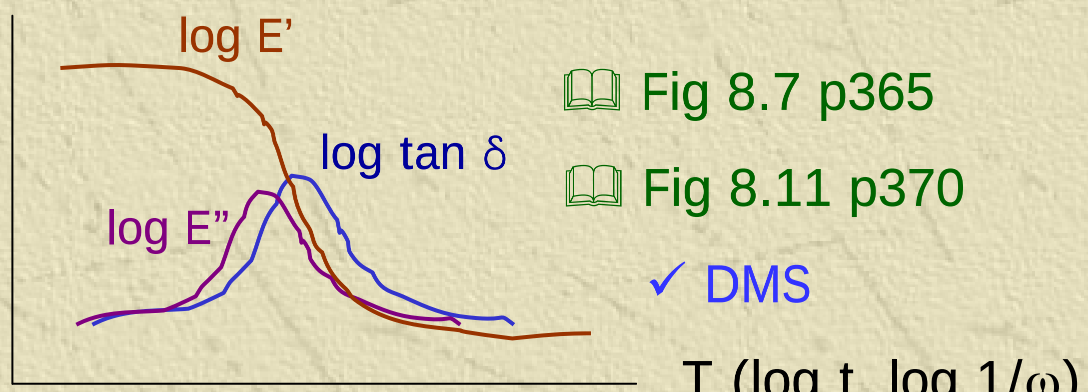
π/2 out-of-phase with ε
viscous
energy dissipated

📖 Fig 8.6 p364

DMA 3

- $\varepsilon = \varepsilon_0 \, e^{i\omega t}$
- $\sigma = \sigma_0 \, e^{i(\omega t + \delta)}$
- $E = \sigma/\varepsilon = E^* = (\sigma_0/\varepsilon_0)\, e^{i\delta} = (\sigma_0/\varepsilon_0) \cos\delta + (\sigma_0/\varepsilon_0)\, i \sin\delta$

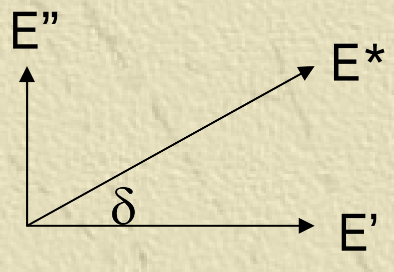
  $= E' + i E''$ 🕮 eqn (8.14) p355
- $\tan\delta = E''/E'$
- Actually, $\tan\delta$ is small (0.1 at T_g) → $E \approx E^* \approx E'$ (in magnitude)



🕮 Fig 8.7 p365

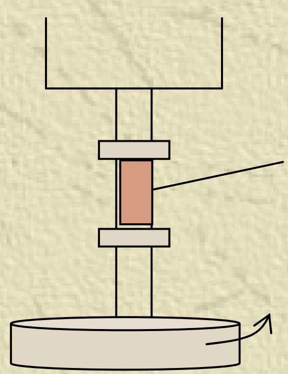
🕮 Fig 8.11 p370

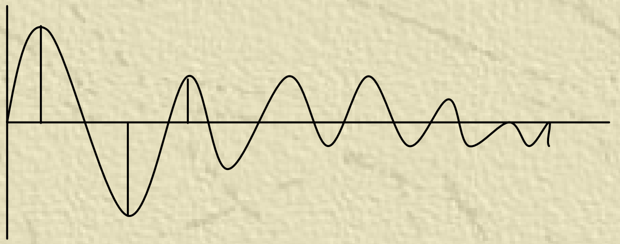
✓ DMS



- T_g depends on frequency (ω)
  - T_g (1 Hz) ~ T_g (10 °C/min, DSC)

- Torsional pendulum test
  Torsional braid analysis (TBA)



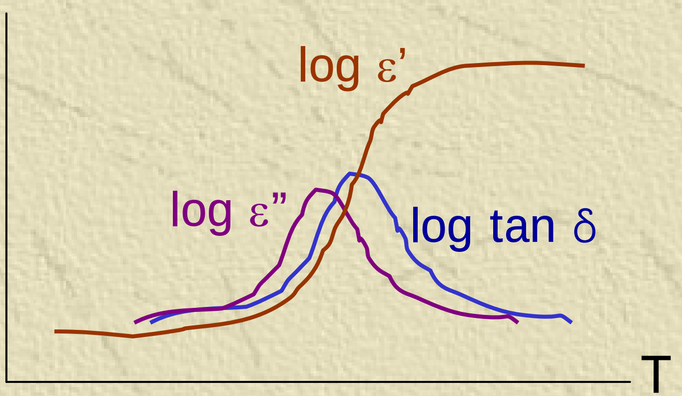


- log decrement, $\Delta = \ln (A_1/A_2)$
- $\Delta = \pi (G''/G') = \pi \tan \delta$

📖 Fig 8.12 p371

(4) Dielectric Measurement

Dielectric Analyzer (DEA) [TA]
Dielectric Thermal Analyzer (DETA) [Rheometrix]



📖 Fig 8.13 p372

✓ T_g depends on frequency

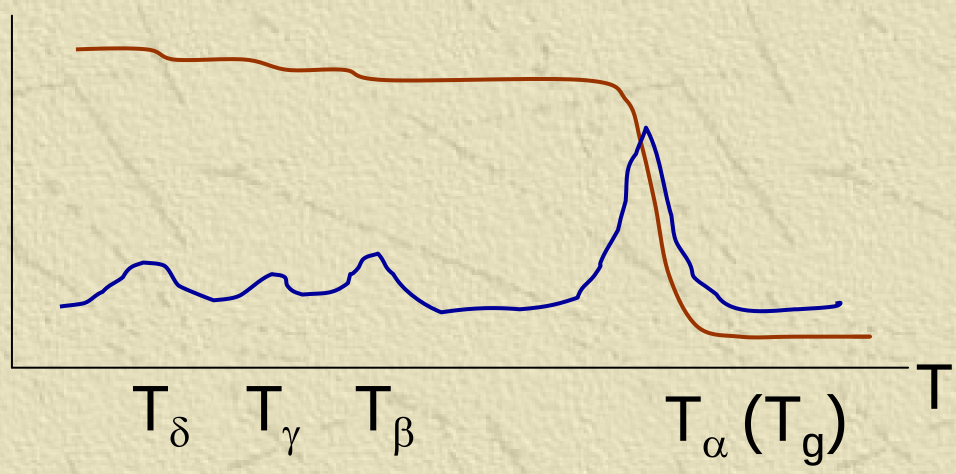
(5) NMR

- chain mobility ↑ → faster relaxation → signal sharpens

📖 Fig 8.14 p372

4. Other Transitions than Tg

- Secondary relaxations (at $T < T_g$)



  - at lower temperatures than T_g
  - with smaller E_a (~10 kcal/mol; ~100 kcal/mol for T_g)
  - with smaller motion
    - local main-chain motion (crankshaft (?))
    - side-chain motion
  - Affect property at room temp for glassy polymers
    - like toughness, especially for main-chain motion

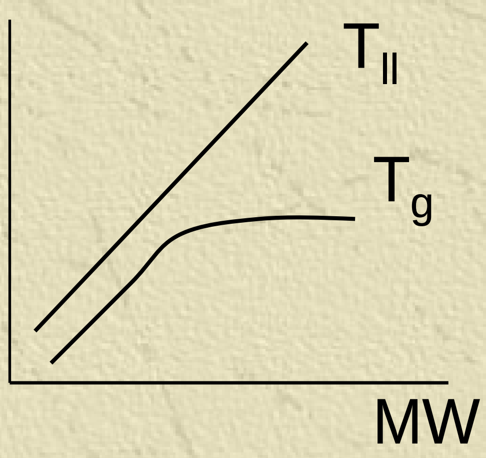
Fig 8.20 p380
Fig 8.16 p375
Table 8.6 p377

Liquid-liquid transition (T_{ll})

- ‘fixed’ liquid to ‘true’ liquid
- moition of entire chain
- At $T > T_g$

- Artifact of TBA?

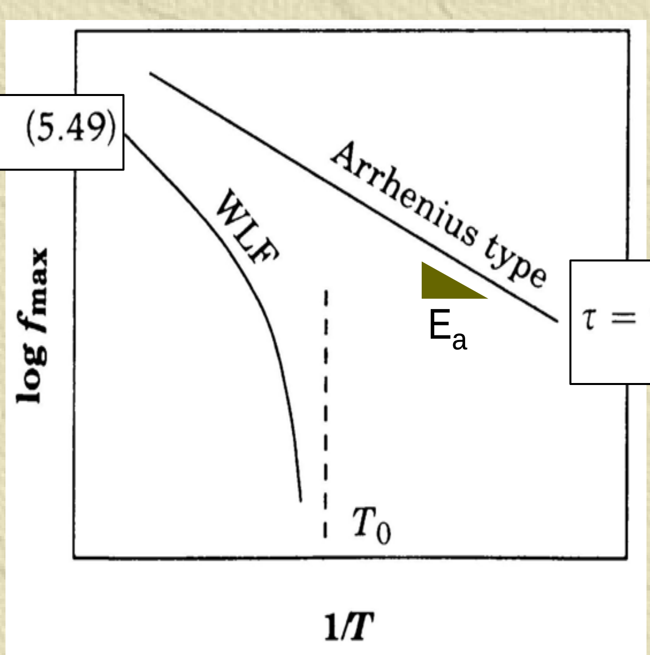
Fig 8.17 p376



5. Time and frequency effects in measurements

- Figs 8.18, 19, 20
- Why dependent?
  - De

$$\tau = \tau_0 \exp[+C/(T - T_0)] \quad (5.49)$$



$$\tau = \tau_0 \exp\left(+\frac{\Delta E}{RT}\right) \quad (5.45)$$

6. Theories of glass transition

- Three groups
  - free volume theories
  - kinetic theories
  - thermodynamic theories

- Free volume theory
  - free volume ~ unoccupied volume ($v_f = v - v_o$)

    v_f/v at T_g of 2 – 25% suggested 🕮Fig 8.22 p383

    ~ <u>not</u> a physical volume (hole)

    ~ for explanation only cf. PALS 🕮 p391-392

    ~ volume for molecular motion 🕮Fig 8.21 p382

Free volume theory

- By Doolittle (1950's)

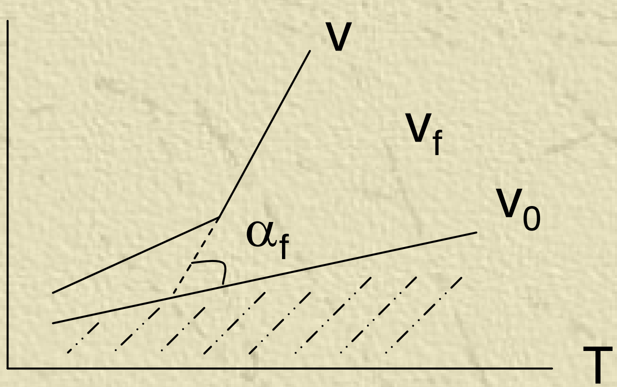
¶8.6.1.2 p384-390

  - $\ln \eta = \ln A + B/f$

    η ~ viscosity ~ modulus

    $f = v_f / v$ ~ fractional free volume (FFV)

- By W, L, and F (1970's)
  - free vol, $f = f_0 + \alpha_f (T - T_0)$
  - $\ln [\eta(T)/\eta(T_0)] = B\,(1/f - 1/f_0)$
  - When $T_0 = T_g$, $f_0 = f_g$
  - shift factor, a_T



$$a_T = \frac{\eta(T)}{\eta(T_g)} = \exp\left[\frac{(-B/f_g)\,(T - T_g)}{(f_g/\alpha_f) + (T - T_g)}\right]$$

Free volume theory 2

- WLF equation   📖 eqn (8.42) p329

$$\log a_T = \frac{-(B/2.303f_g)\,(T - T_g)}{(f_g/\alpha_f) + (T - T_g)} = \frac{-C_1\,(T - T_g)}{C_2 + T - T_g}$$

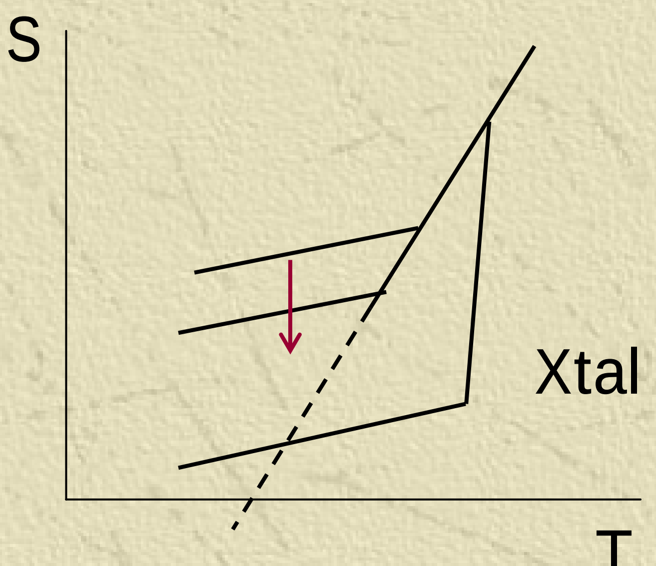
  - Empirically, $C_1 = 17.44$, $C_2 = 51.6$ ~ universal constants
  - When $B = 1$ (arbitrarily), $f_g = 1/(2.303)(17.44) = 0.025$
    - f_g of 0.025 is arbitrary!
  - At T_g, FFV is constant.
    - may be 2.5% (or 8, 11.3, even 25%)
  - **T_g is an iso-free-volume state.**

Kinetic theory

- Kinetic theory
  - T_g is rate-dependent
    - cooling rate (dilatometry)
    - heating rate (DSC)
    - frequency (DMA, DEA)
  - Glass transition when $t = \tau$ [$De = \tau/t = 1$]
  - rate ↑ (freq ↑) → t ↓ → De ↑ → T_g ↑
  - According to WLF eqn, T_g ↑ by 3 K by log t ↓ by 1
    - $C_2/C_1 \sim 3$ 🕮 p390
    - not always

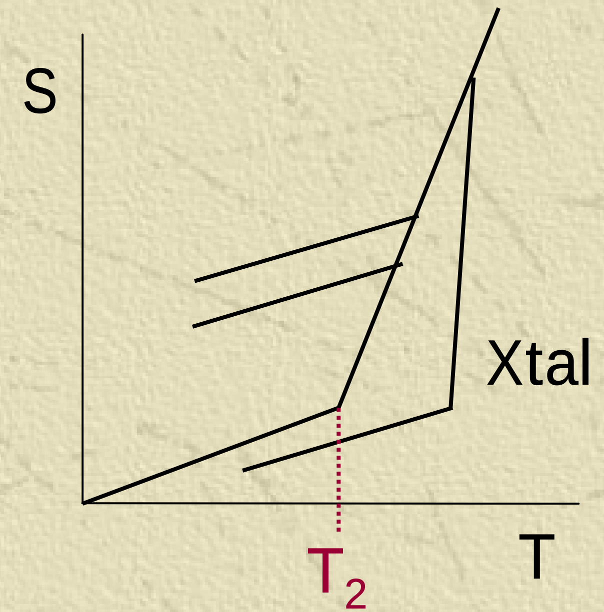
Thermodynamic theory

- Thermodynamic theory
  - Ernfest ~ pseudo-2nd-order phase transition
  - Kauzmann Paradox
    - S(glass) < S(crystal)
    - S < 0 at T > 0 K

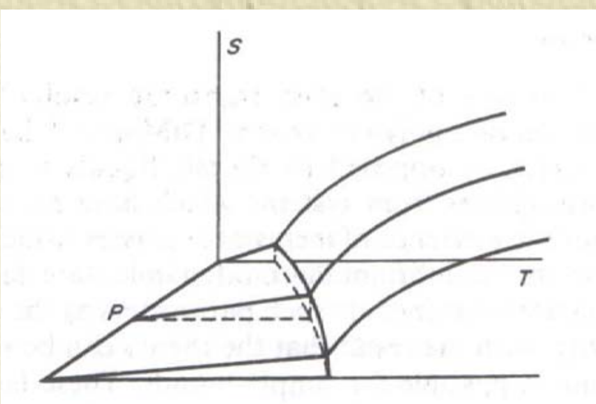


Thermodynamic theory 2

- Gibbs-DiMarzio theory
  - metastable glassy state above crystal state
  - At T_2, $S_{conf} = k \ln \Omega = 0$
  - T_2 obtained by infinitely slow cooling.
  - T_2 is the true 2^{nd}-order phase transition temperature.
    - not rate-dependent
  - How low is T_2?
    - From WLF eqn, $a_T \rightarrow \infty$ (shift to t_∞)
    - $T - T_g = C_2 = -51.6$
    - $T_2 \sim T_g - 50$ K



📖 Fig 8.25 p393

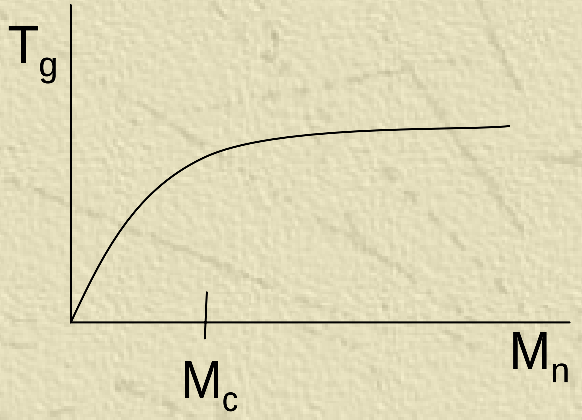


7. Factors affecting T_g

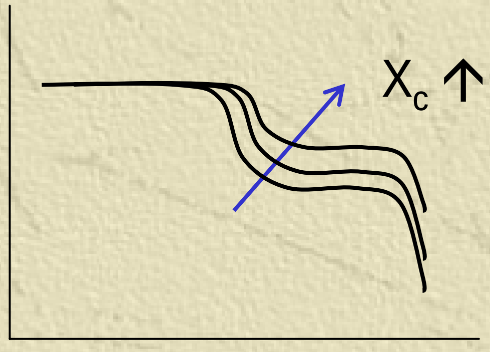
- Repeat unit structure (chemical structure)
  - chain stiffness (intramolecular steric hindrance)
    - aromatic > aliphatic
    - substitutents, branching > linear
    - single bond > double bond
    - syndiotactic > isotactic   Table 8.12 p409
  - intermolecular interactions (2ndary bonding, CED)
    - London dispersion forces (VdW forces)
      - substitutents → distance ↑ → forces ↓ → T_g ↓
        - compete with stiffening effect   PE < PP > PB > C3 -- < C8 < C9   Fig 8.32 p409
    - dipole interactions   PE < PVC > PVDC
    - H-bonding   polyamides, polyurethanes

Factors affecting T_g 2

- Molecular weight 📖 p397-398
  - $T_g = T_g^{\infty} - K/M_n$
  - $T_g \uparrow$ up to M_c
  - mol wt $\uparrow \rightarrow$ # of chain ends $\downarrow$ $\rightarrow$ FFV $\downarrow \rightarrow T_g \uparrow$

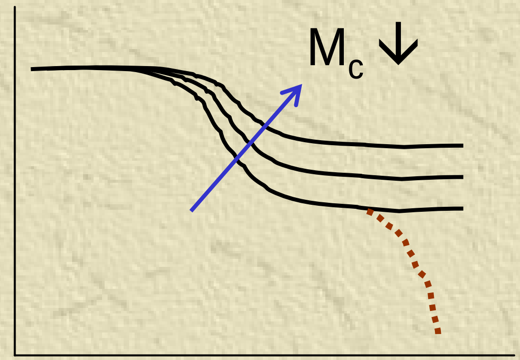


- Crystallinity 📖 p404-406
  - fringed-micelle explanation



Factors affecting T_g 3

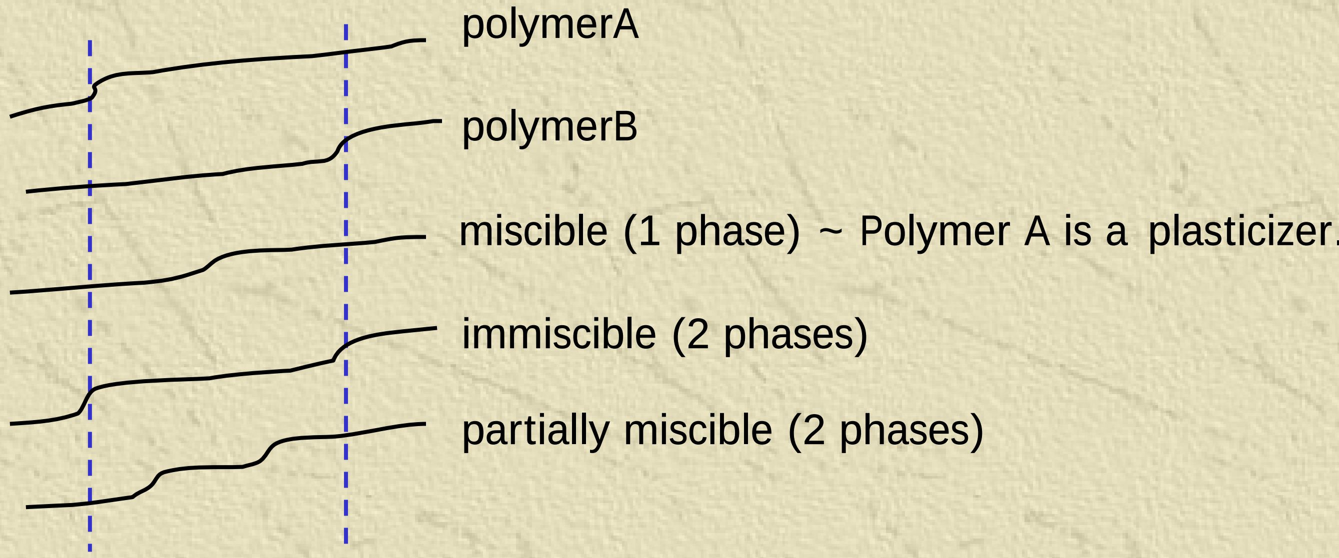
- Crosslinking Density
  - $M_c \downarrow \rightarrow XD \uparrow \rightarrow FFV \downarrow \rightarrow T_g \uparrow$
  - $G = \rho RT/M_c$



- Plasticization (가소화)
  - plasticizer (가소제) ~ low mol wt agent that reduces T_g
  - plasticization ~ increasing FFV

T_g of copolymers and blends

- Copolymers 📖 p399-404
  - alternating and random ~ 1 phase
  - block and graft ~ 2 phases when long (phase-separated)
- Blends 📖 Fig 8.29 p403
  - compatible (miscible) ~ 1 phase
  - incompatible (immiscible) ~ 2 phases



Relation between T_g and T_m [T_f]

- $T_m^0 = \Delta H_f^0 / \Delta S_f^0$
  - ΔH_f ~ interchain interaction
  - ΔS_f ~ chain flexibility
- Two-thirds rule 📖 Fig 8.31 p407
  - T_g ~ 0.5 T_m for linear polymers (symmetrical)
    - PE , POM , PVDF, ---
  - T_g ~ 2/3 T_m for vinyl polymers (asymmetrical)
    - PS, PVC, PMMA, Pester, nylon, ---
  - T_g ~ 0.8 T_m for unusual polymers
    - branched polymers, PC, PPO

Miscellaneous

¶8.9.4 p406

- Glass transition temperature (T_g)
- Heat distortion temperature (HDT)
- Vicat softening temperature

¶8.13 p415

- plastics (합성수지) ~ below T_g
- rubbers (합성고무) ~ above T_g ,crosslinked
- fibers (합성섬유) ~ drawn
- adhesives
- coatings and paints