2009 spring

Advanced Physical Metallurgy

"Amorphous Materials"

04. 01. 2009

Eun Soo Park

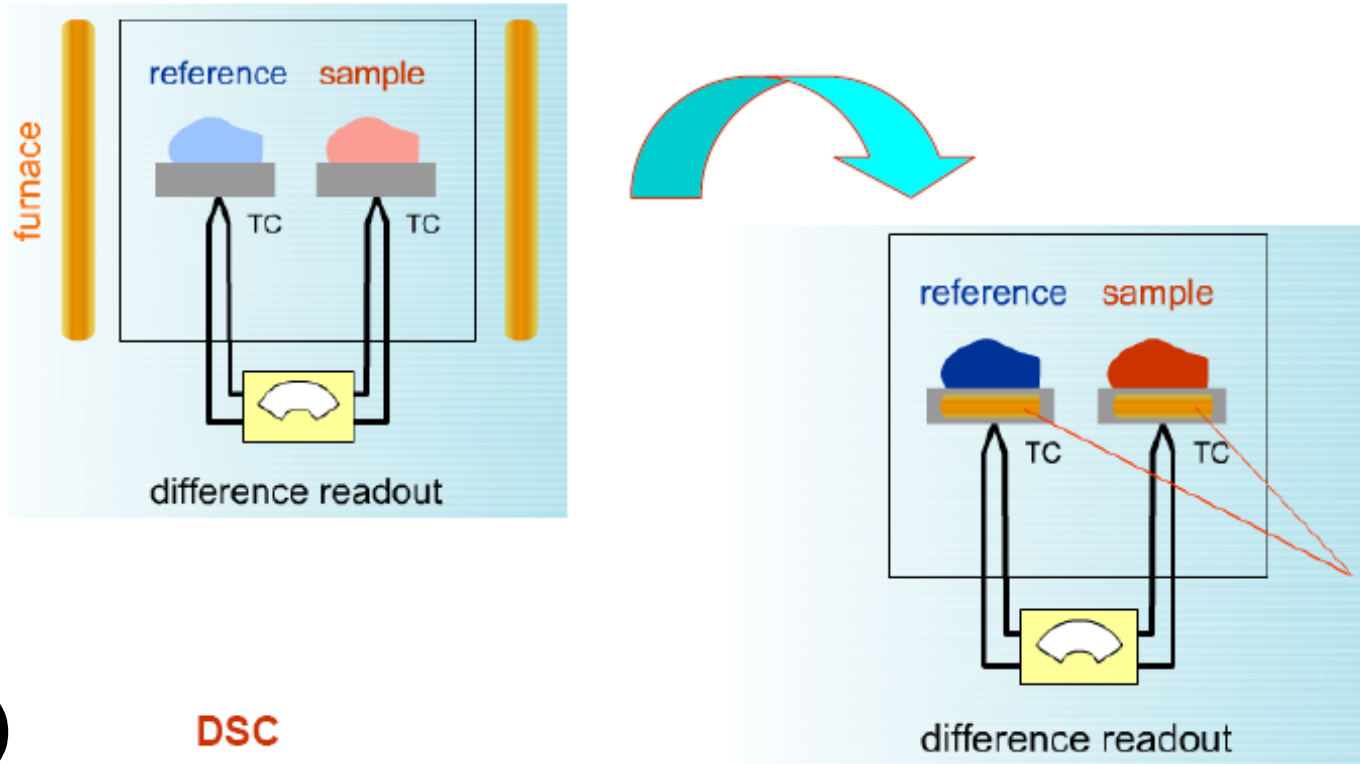
Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

- **Measuring Glass Transition Temperature**

(1) DTA

Measure sample temperature relative to a reference, for the same heat transferred



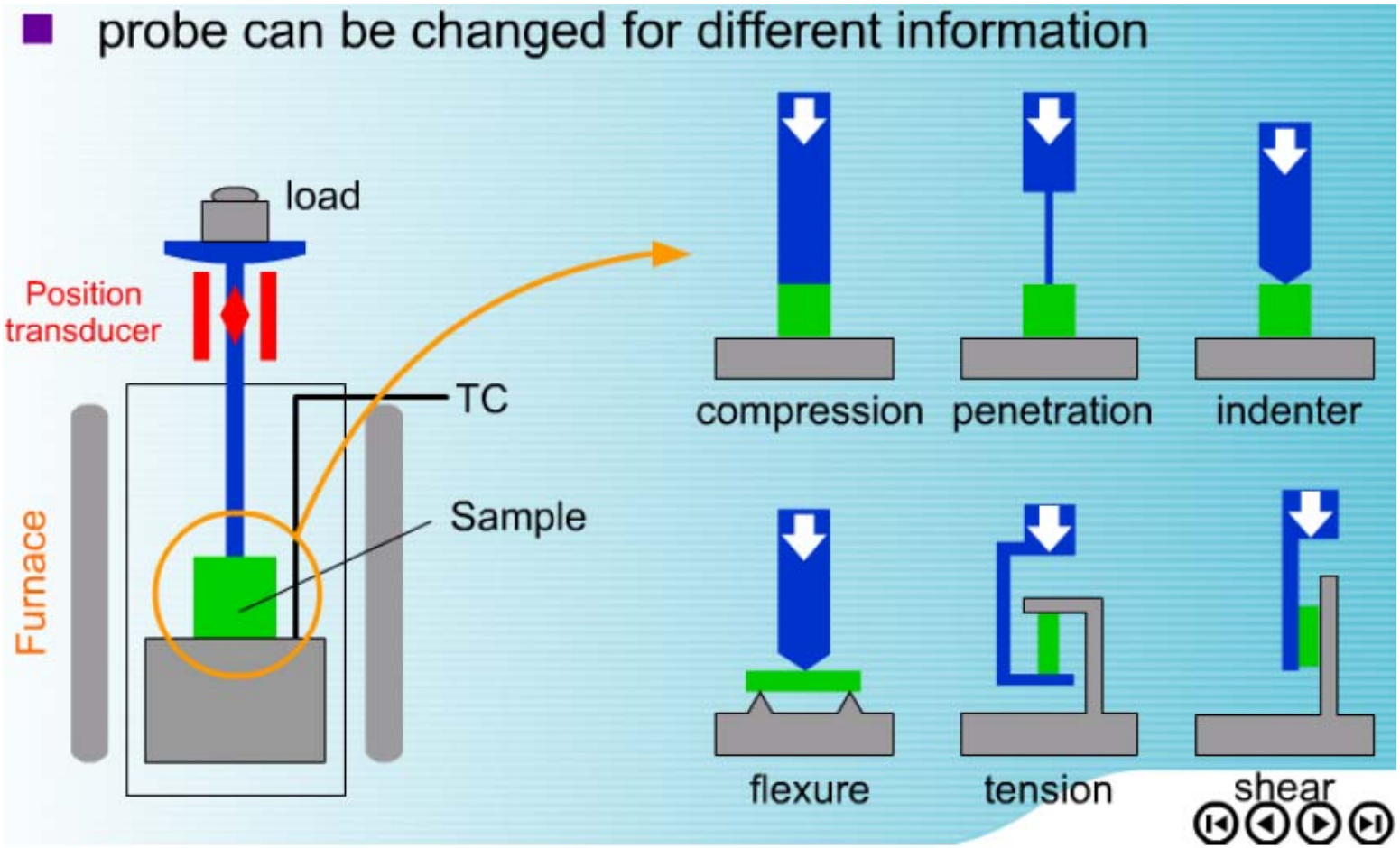
(2) DSC

- similar concept as DTA (compare sample & reference)
- measure "heat flow" required to keep both specimens same temperature

• *Measuring Glass Transition Temperature*

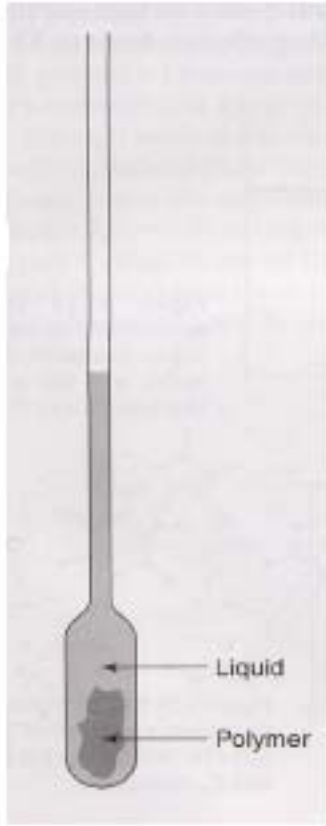
(3) Thermomechanical analysis (TMA):

Measure dimension changes under constant load, as function of temperature



• *Measuring Glass Transition Temperature*

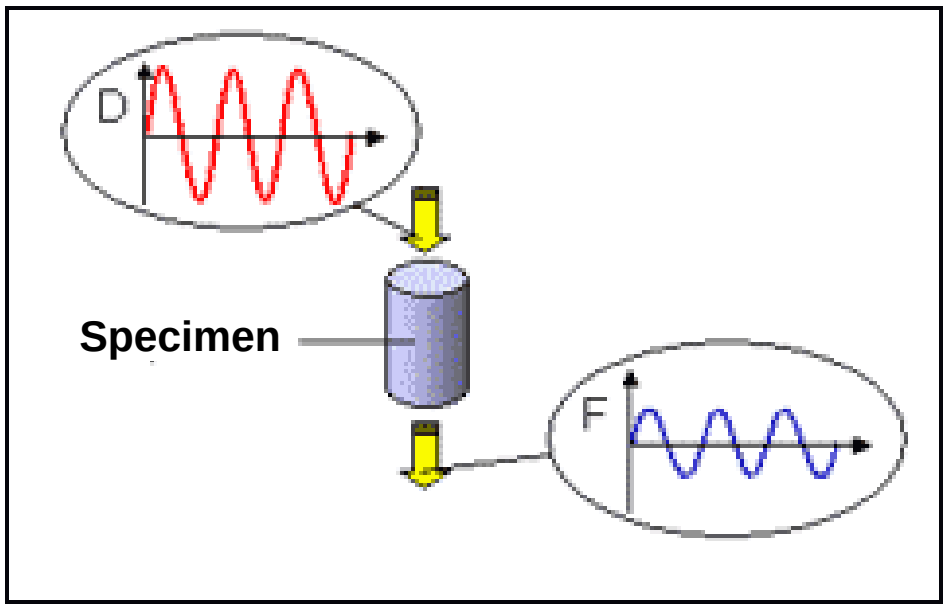
(4) Dilatometry

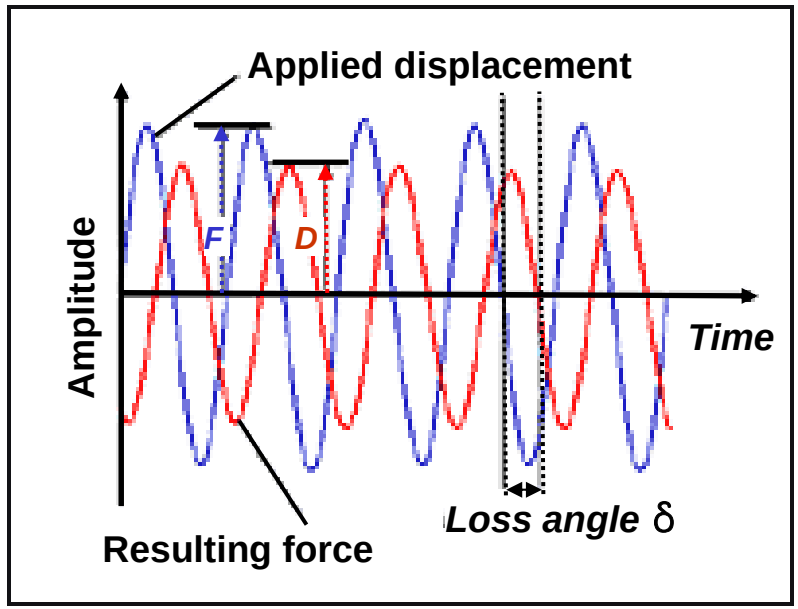


- Used to monitor change in volume of polymer plus surrounding liquid as a function of temperature by changes in height of liquid level in capillary tube.
- The liquid does not undergo sharp transitions when heated, but the polymer does.
  - Therefore, an abrupt increase in the slope of a volume versus temperature graph is attributed to a T_g transition.

• Measuring Glass Transition Temperature

(5) **The Dynamic Mechanical Analysis is a high precision technique for measuring the viscoelastic properties of materials. It consists in applying a sinusoidal deformation to a specimen of material and measuring the resulting force transmitted through the specimen.**

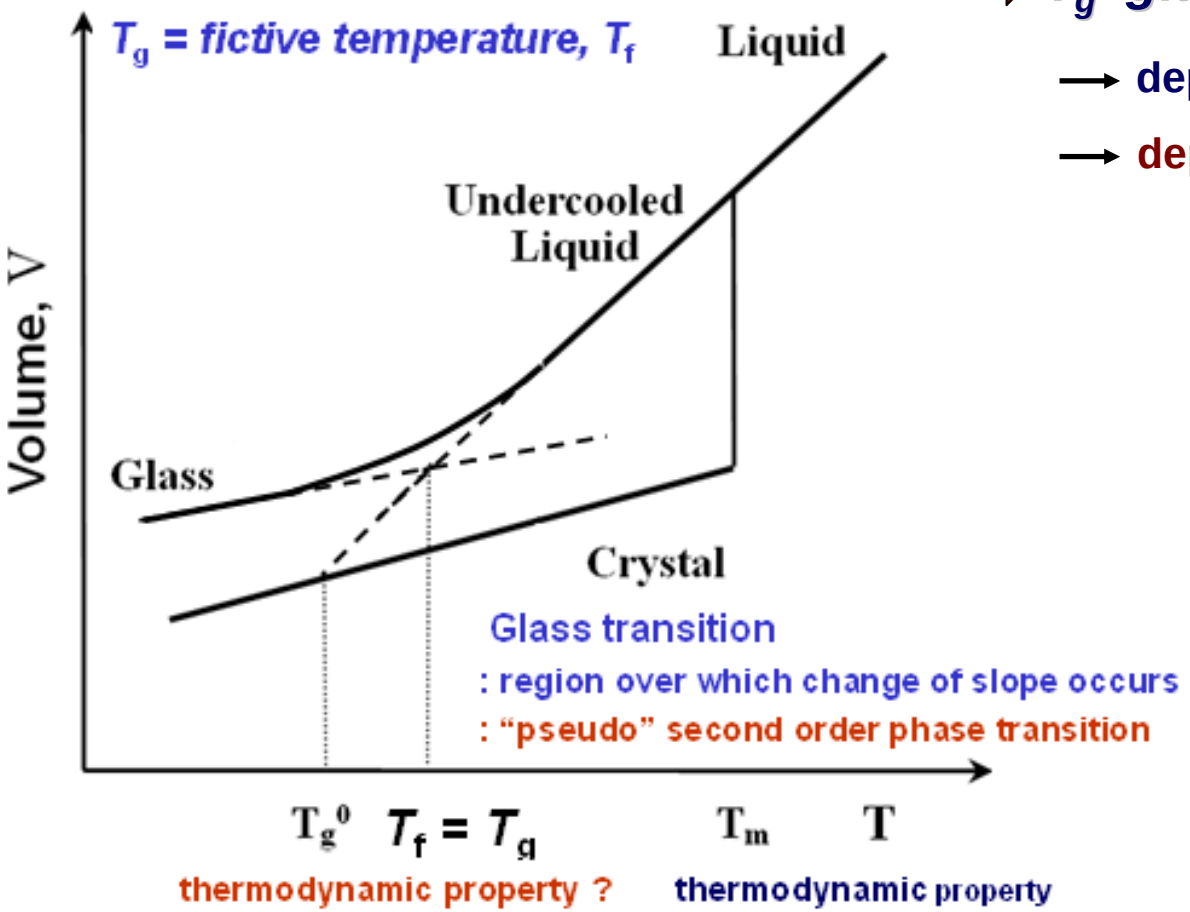




- The magnitude of the applied stress and the resultant strain are used to calculate the stiffness of the material under stress.
- The phase lag between the two (or δ) is used to determine Tanδ, the damping factor.

Contents for previous class

- **Glass:** ***all types of bonding***
- **Glass transition:** ***Volumetric measurement***



➡ T_g *glass transition temp.*

→ depends on cooling rate

→ depends on thermal history

Contents for previous class

- **Thermodynamics for glass transition**

  ~ not thermodynamic nature

  ~ close to second order phase transition

➡ ***at T_g → G changes continuously.***

→ ***V, H. S changes continuously.***

– First derivatives of G (V, S, H) are continuous at T_T

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

→ ***α_T C_P K_T changes discontinuously.***

– Second derivatives of G (α, β, C_p) are discontinuous at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Phase Transitions

Thermodynamically: what is possible!
Kinetics: speed/rate of the transition.

Thermodynamical classification: first order & second order

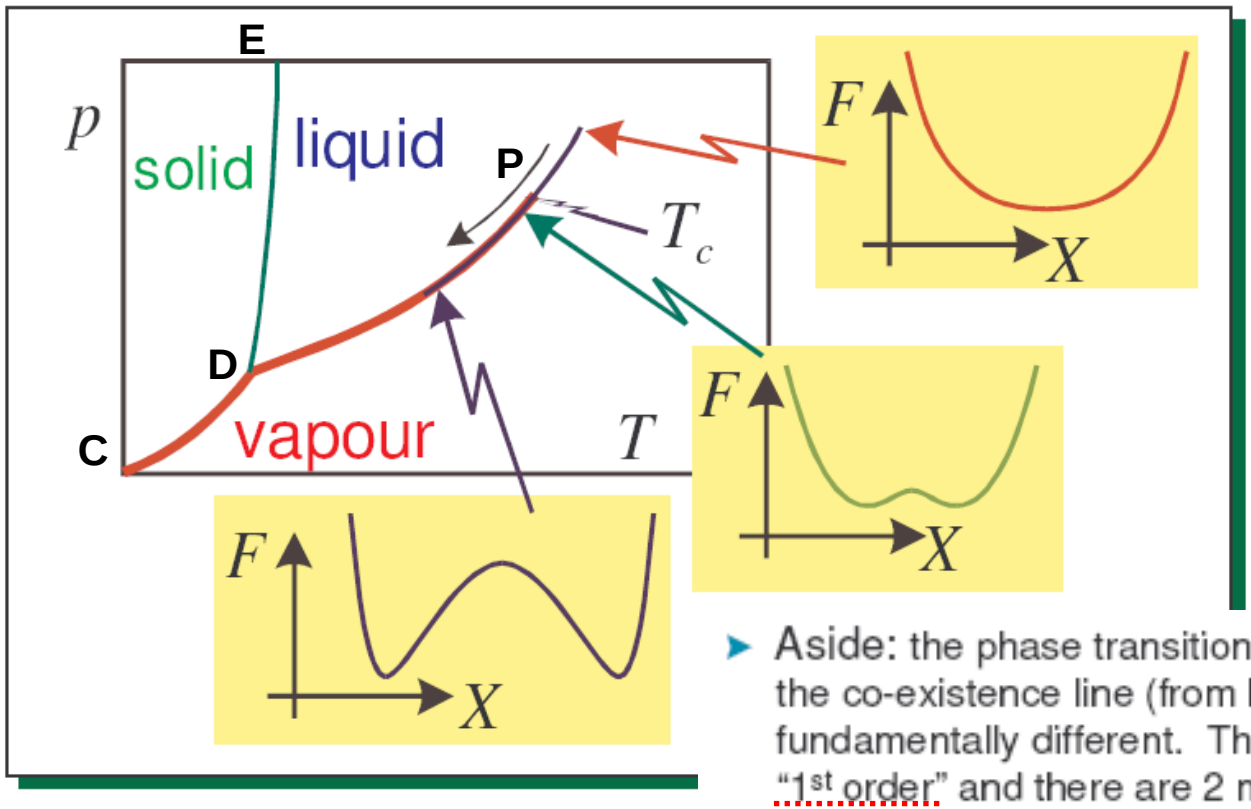
$$\Delta G = \Delta H - T\Delta S = 0$$

- **Order (degree) of transition**

***Continuous phase transitions*:**

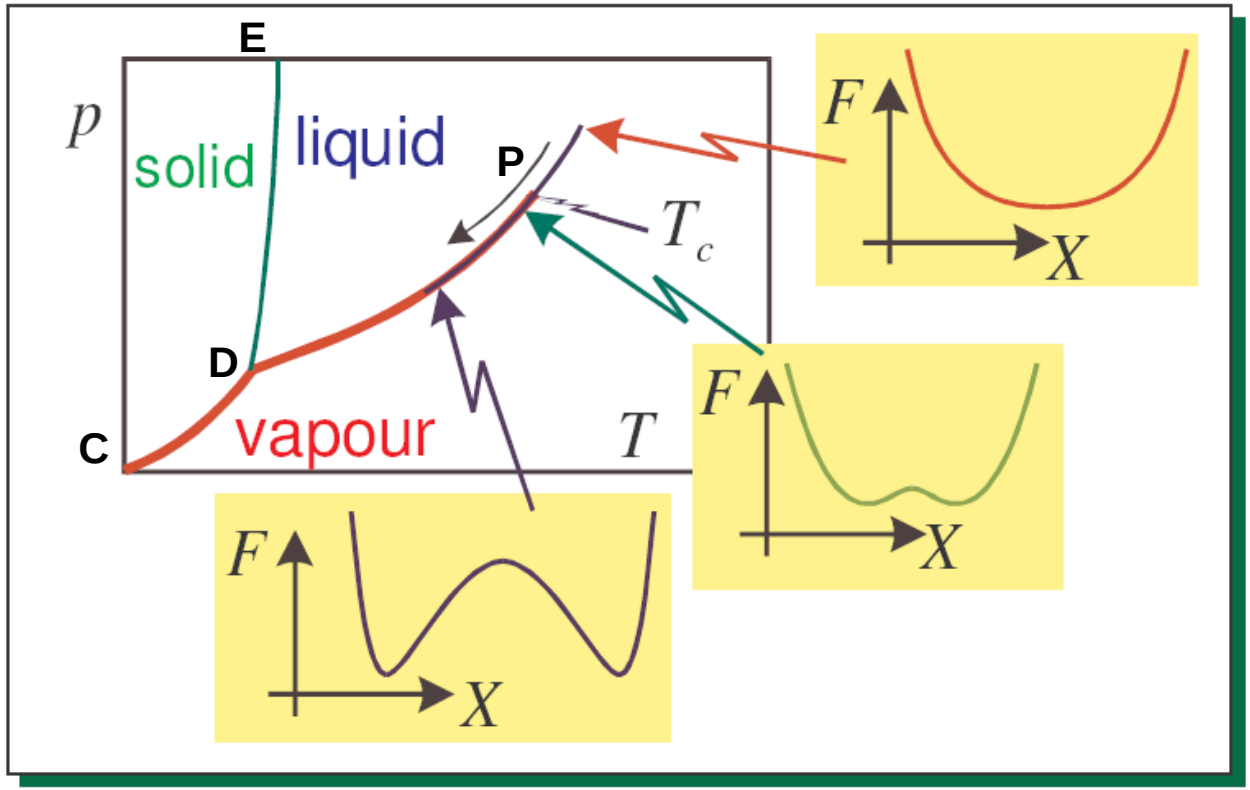
occur when the minimum in the thermodynamic potential evolves smoothly into two equal minima.

An example is seen in the model of phase separation, along the co-existence line.



- Aside: the phase transition as one moves across the co-existence line (from liquid to vapour) is fundamentally different. That transition is known as "1st order" and there are 2 minima in the potential throughout. In the transition the lowest minimum changes from liquid to vapour (and vice-versa).

- **Order (degree) of transition**



- **CD, DE, DP: Equilibrium of 2 phases**
  - → **latent heat**
  - → **Volume change**
  - → **1st order transition**

- **T and P beyond point p**
  : vapor and liquid are indistinguishable.
  - → **Single phase: only property changes.**
  - → **No boiling pt. no latent heat**
  - → **Higher order transition**

First-order transition:
a discontinuity occurs in the first derivative of the free energy with respect to T and P.

Discontinuous enthalpy, entropy and volume

$$\frac{dG}{dT} = -S$$

$$\frac{dG}{dP} = V$$

Examples: CsCl structure to NaCl structure; T =479 C.

$$\Delta V = 10.3 cm^3$$

$$\Delta H = 2.424 kJ / mol$$

Melting, freezing, vaporization, condensation…

First-order transition:
a discontinuity occurs in the first derivative of the free energy with respect to T and P.

Discontinuous enthalpy, entropy and volume

$$\frac{dG}{dT} = -S$$

$$\frac{dG}{dP} = V$$

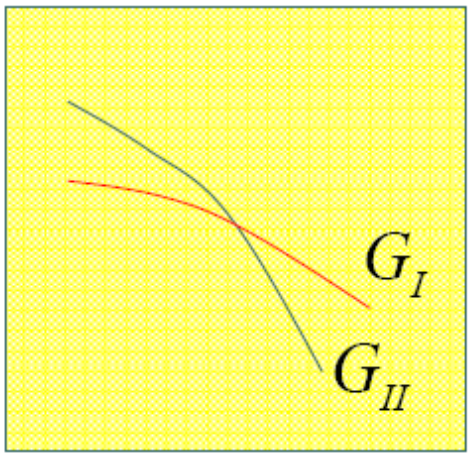
Examples: CsCl structure to NaCl structure; T =479 C.

$$\Delta V = 10.3 cm^3$$

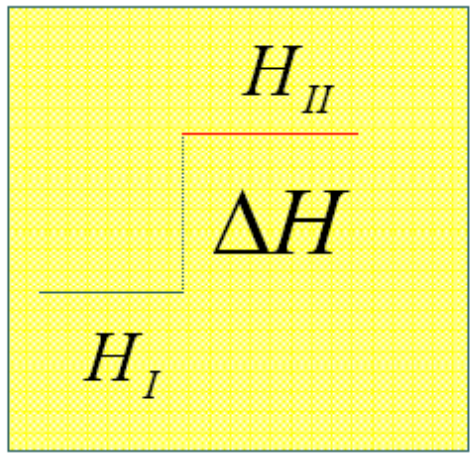
$$\Delta H = 2.424 kJ / mol$$

Melting, freezing, vaporization, condensation…

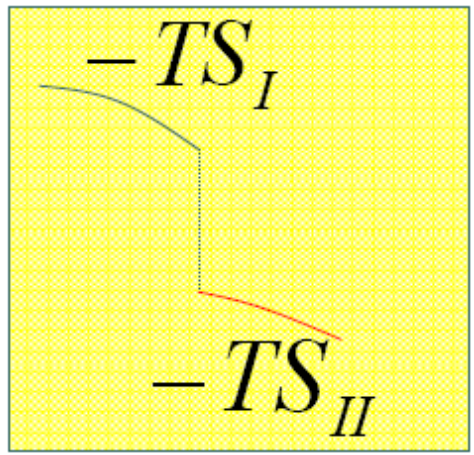
First-order transition:



T_C



T_C



T_C

Second order transition: Discontinuities in the second derivatives of the free energy, i.e. heat capacity, thermal expansion, compressibility.

Enthalpy, entropy and volume, continuous functions of T

$$\frac{\partial^2 G}{\partial P_T^2} = \frac{\partial V}{\partial P_T} = -V\beta(compressibility)$$

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial V}{\partial T_P} = V\alpha(thermal\ \exp ansion)$$

$$\frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T_P} = -\frac{C_p}{T}$$

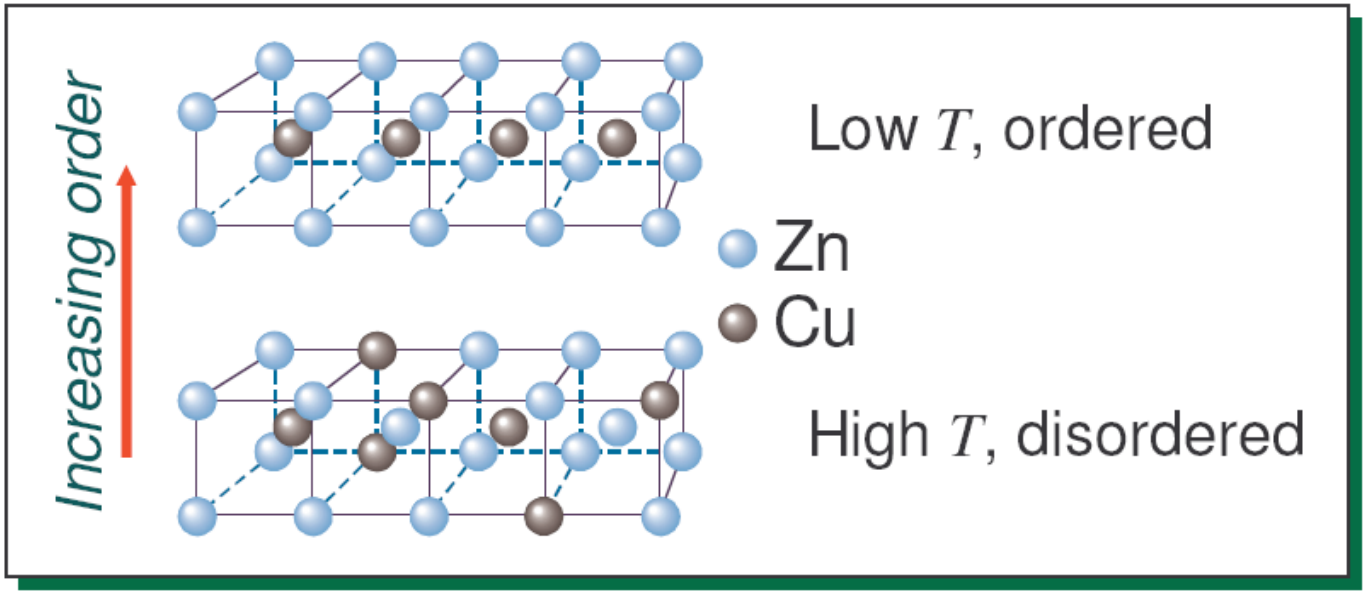
Measurement of heat capacities (calorimetry)

Order-disorder transition: 2nd order transition

- β-brass.

~ Brass is a 50:50, Cu:Zn alloy with a b.c.c structure.

~ At low temperatures, T<460K, the Zn and Cu atoms for an ordered structure (eg. Cu atoms in the body-centre sites in top diagram)

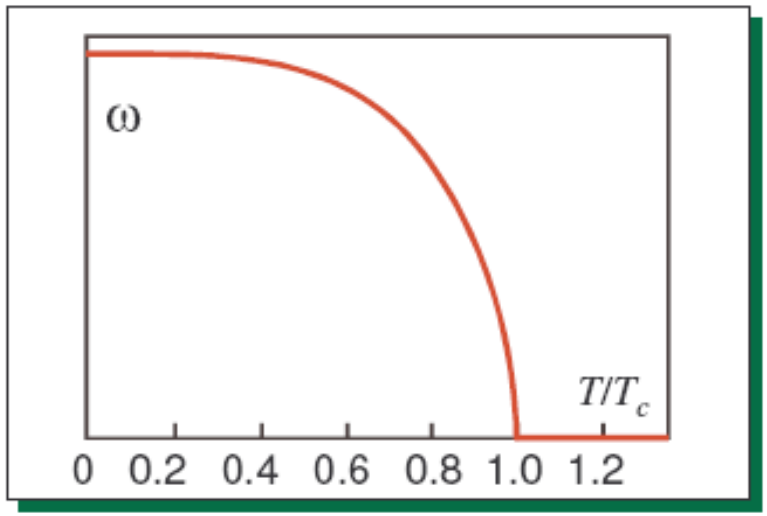


- Two types of site call them: A-sites and B-sites.
- At high T, equal probability for any site to be occupied by Cu or Zn.

Order-disorder transition: 2nd order transition

- *Transition in β-brass*

  - State of order:
    - Above T_c, the order parameter, ω, is zero
      - Cu and Zn atoms have random lattice sites.
    - Below T_c, the order parameter increases rapidly and approaches full order as $T \rightarrow 0$.



The order parameter

- **Mean-field theory**
  - The mean-field theory ignores fluctuations and spatial variation. Thus a single parameter can be used to describe the average state of the system.
  - In the present case, we look for a variable behaving like:

Order parameter

$$\omega = \begin{cases} 0 & \text{no order} \\ 1 & \text{full order} \end{cases}$$

  - with n_A as the number of Cu atoms on A sites
    n_B as the number of Cu atoms on B sites
    $n_A + n_B = N$. ($2N$ sites in all)

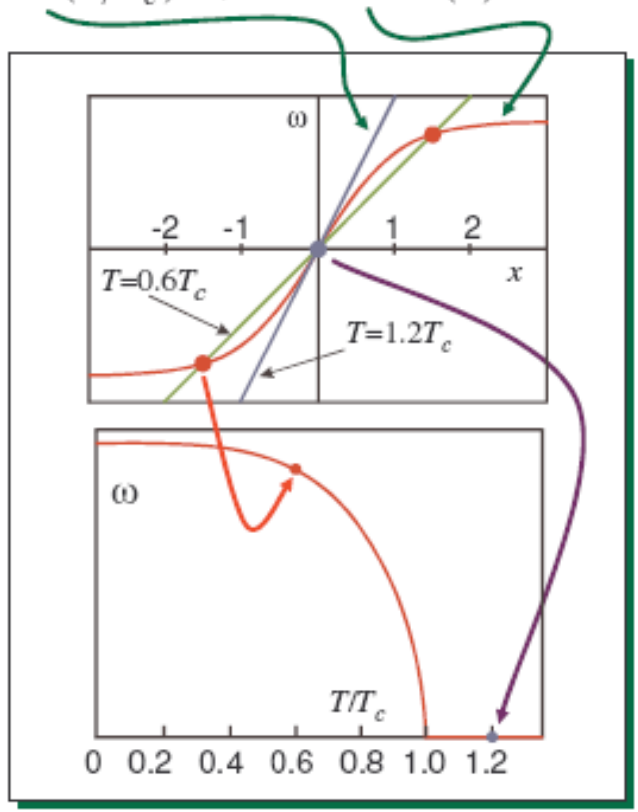
  - An order parameter with the desired property is

$$\omega = \frac{n_A - n_B}{n_A + n_B} \Rightarrow n_A = \frac{1+\omega}{2} \quad ; \quad n_B = \frac{1-\omega}{2}$$

$$\omega = \tanh(T_c\omega/T)$$

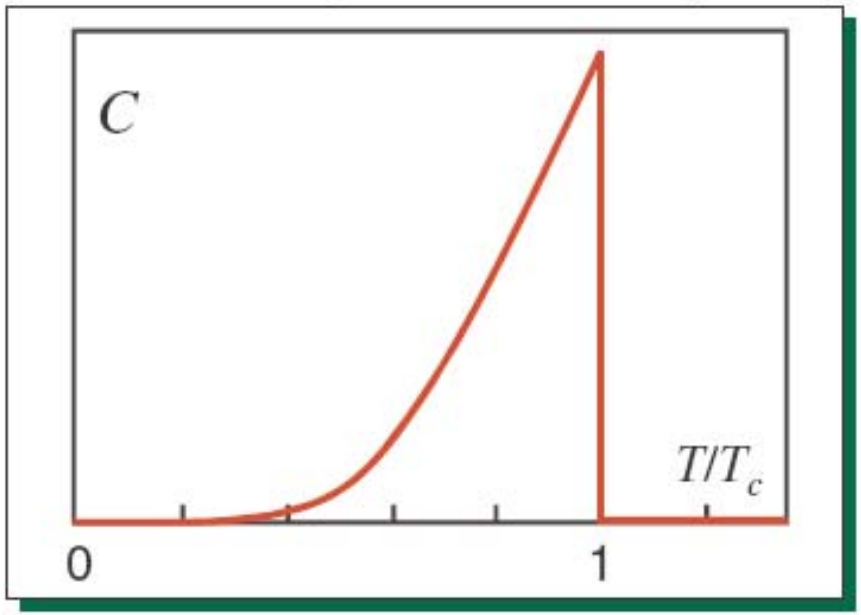
- The solution can be seen from a graphical construction:
- Plot $\omega = \alpha x$ and $\omega = \tanh(x)$, for different $\alpha = T/T_c$ is varied. Intersection gives the solutions

$$\omega = x(T/T_c) \quad ; \quad \omega = \tanh(x)$$



Order-disorder transition: 2nd order transition

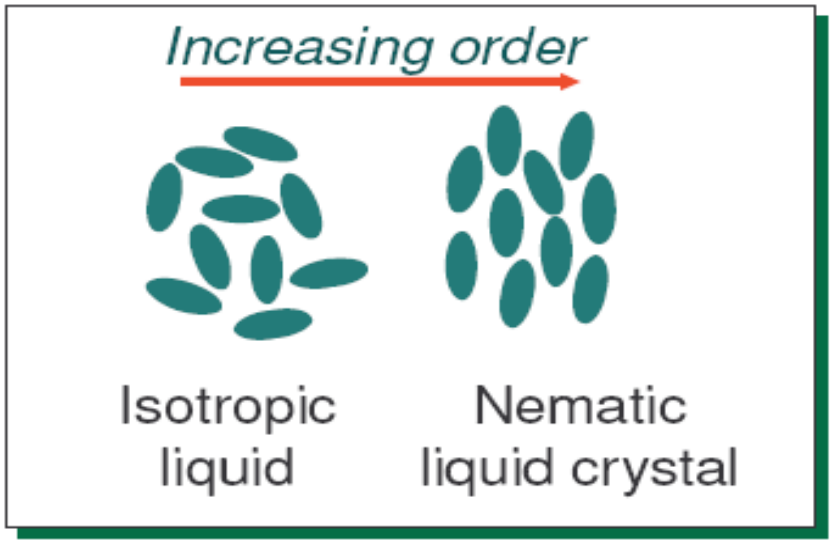
- *Transition in β-brass*
  - Heat capacity
    - Once ω is known, other thermal properties can be calculated. e.g. thermal capacity $C = \partial U / \partial T$



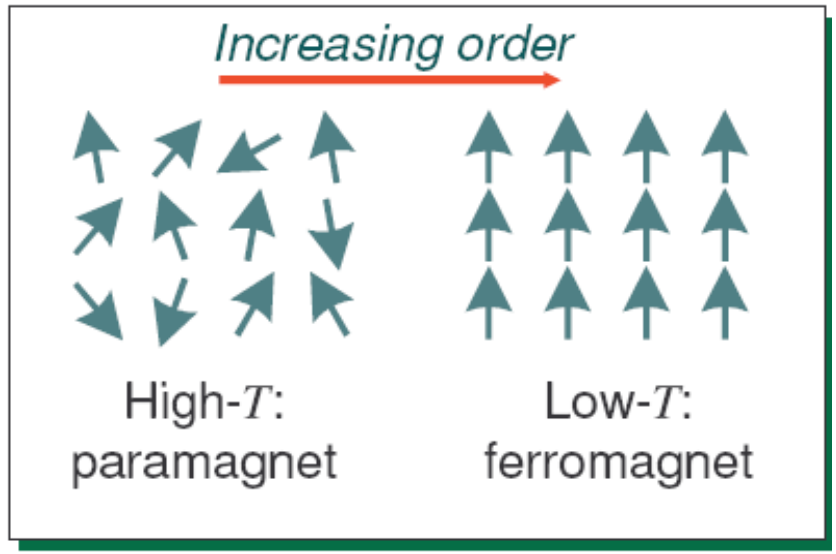
Order-disorder transition: 2nd order transition

- Other examples (there are many):

- Isotropic – nematic transition in liquid crystals: appearance of orientational order (liquid crystals have no long-range, positional order).



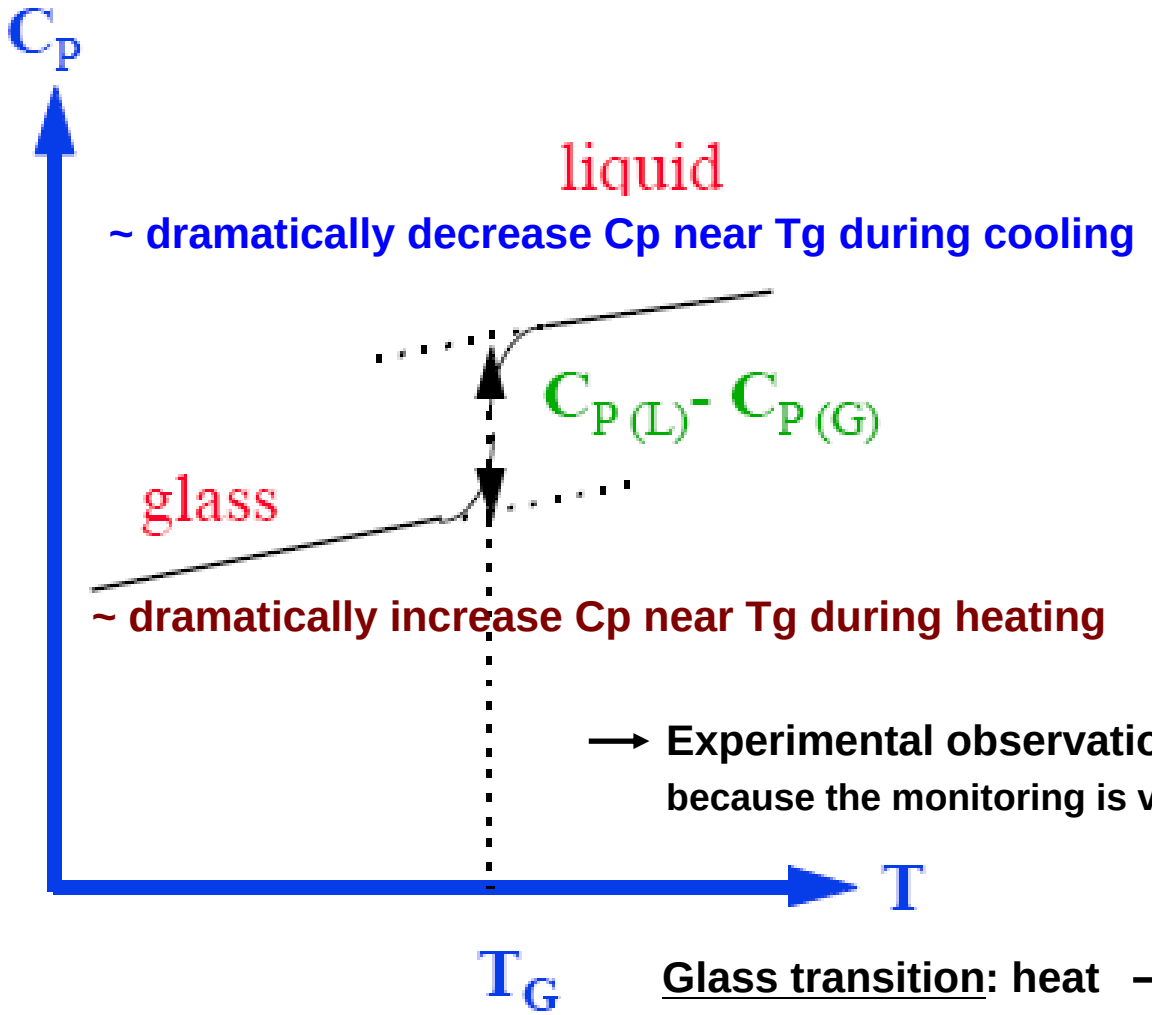
- Ferromagnetic - paramagnetic transition: manifests itself as a spontaneous polarisation, in zero external field.



Contents for previous class

- **derivative of thermodynamic properties**

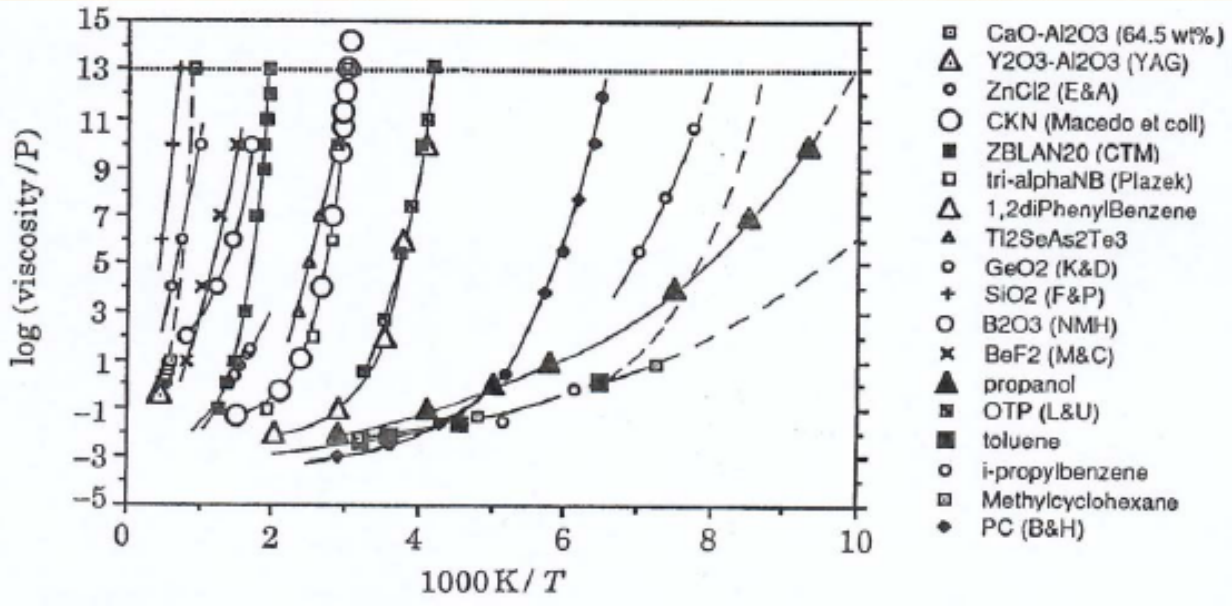
  → ***discontinuous*** **(C_p, α_T, K_T)**



→ **Experimental observation during heating**
because the monitoring is very difficult during cooling

Glass transition: heat → endothermic

Glass transition defined by typical viscosity η. Arbitrary but convenient



Arrhenius plot: log(time) or log(viscosity) versus 1/T.

Similar behaviour for relaxation times obtained using different methods (dielectric relaxation, NMR) . α relaxation time τ_α

Fragility

- **Fragility** ~ ability of the liquid to withstand changes in medium range order with temp.
  ~ extensively use to figure out liquid dynamics and glass properties corresponding to "frozen" liquid state

< Classification of glass >

Strong network glass : Arrhenius behavior

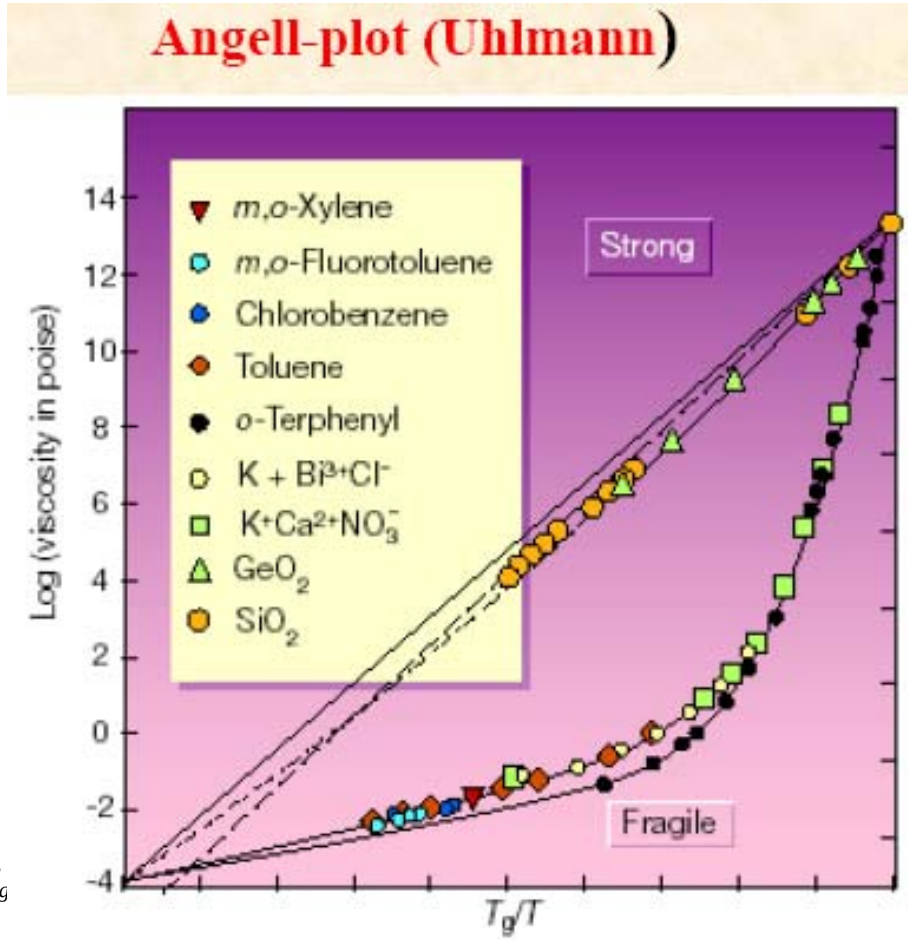
$$\eta = \eta_0 \exp[\frac{E_a}{RT}]$$

Fragile network glass : Vogel-Fulcher relation

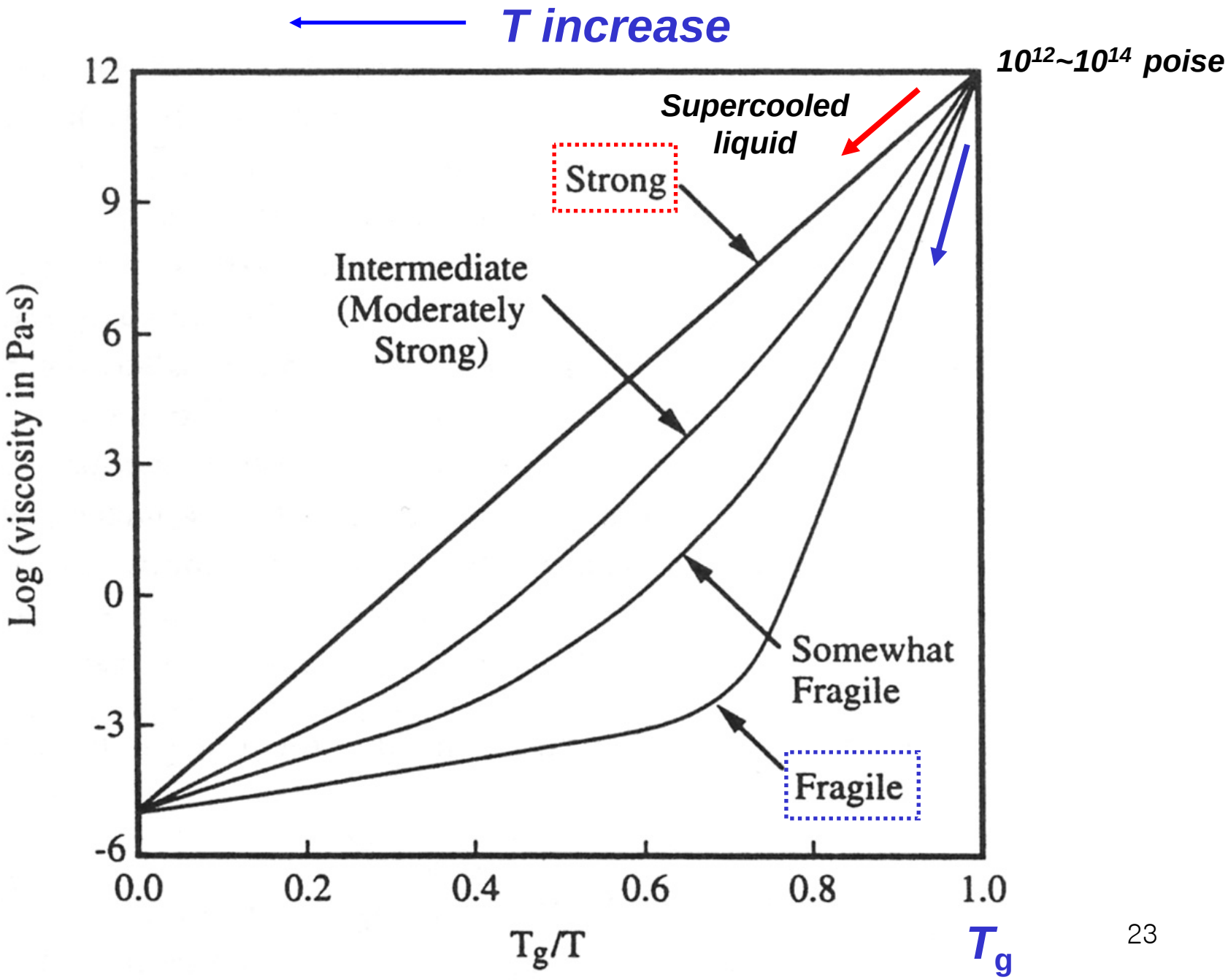
$$\eta = \eta_0 \exp[\frac{B}{T - T_0}]$$

< Quantification of Fragility >

$$m = \left.\frac{d \log \eta(T)}{d(T_{g,n}/T)}\right|_{T=T_{g,n}} = \left.\frac{d \log \tau(T)}{d(T_g/T)}\right|_{T=T_g}$$



Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at T_g


T increase
10^12~10^14 poise
Supercooled liquid
Strong
Intermediate (Moderately Strong)
Somewhat Fragile
Fragile
Log (viscosity in Pa-s)
12
9
6
3
0
-3
-6
0.0
0.2
0.4
0.6
0.8
1.0
Tg/T
Tg

Strong curvature: 'fragile' glass. Organic (OTP: Orthoterphenyl), ionic (CKN: CaK NO3)

Weak curvature : 'strong' glass .covalent bonding, SiO2, ZnCl2, BeF2

NB: Arrhenius law $\tau(T) = \exp(E_a/k_BT)$

Covalent $E_a = 1\text{eV}$ $T_1 = 300K = (1/40)\text{eV}$ $T_2 = 2000K = (1/6)\text{eV} \rightarrow \log_{10}(\tau_1/\tau_2) = 15$

Organic $E_a = 0,1\text{eV}$ $T_1 = 100K = (1/120)\text{eV}$ $T_2 = 500K = (1/24)\text{eV}$ $\rightarrow \log_{10}(\tau_1/\tau_2) = 4$

Fragility

Strong liquid vs. Fragile liquid

- ***Strong glass forming liquid***

  → **covalent bond of SiO_2**

  → **small difference of C_p between SCL and glass at T_g**
  (***small difference of structure***)

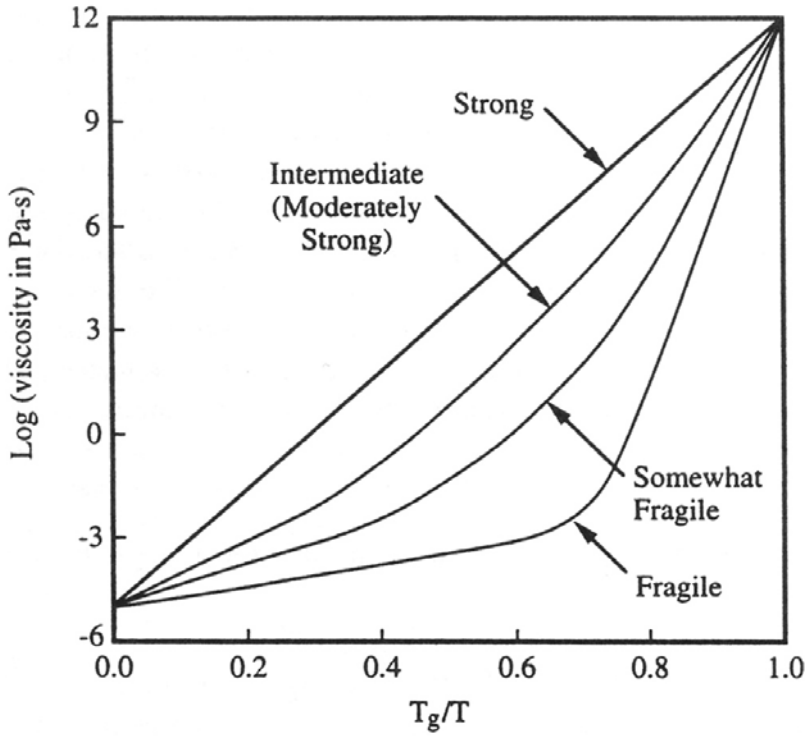
  → **SCL: relatively low entropy**

- ***fragile glass forming liquid***

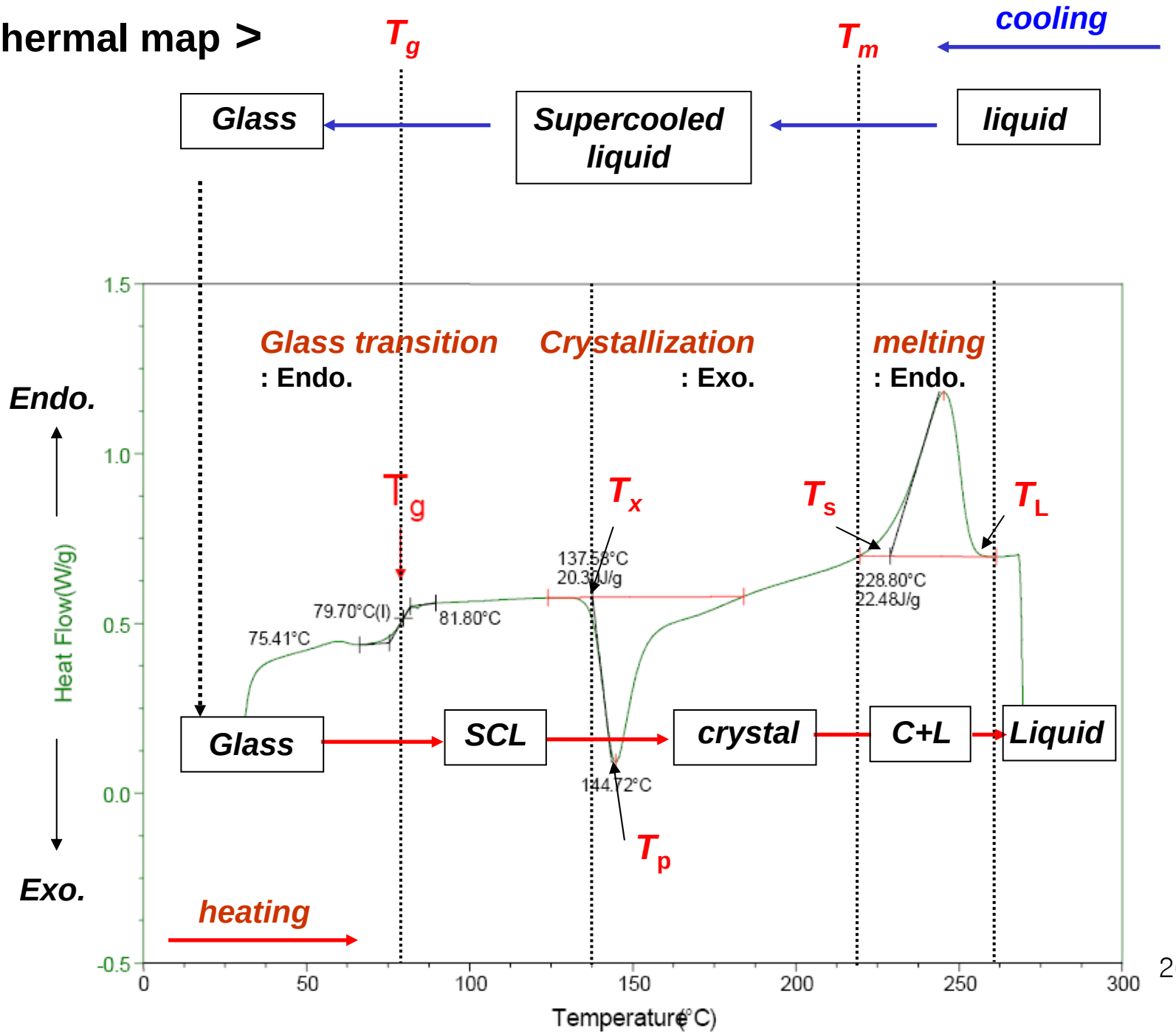
  → **non-directional bonding**
  (***Van der waals bonding***)

  → **large difference of C_p at T_g**
  (***relatively large free volume***)

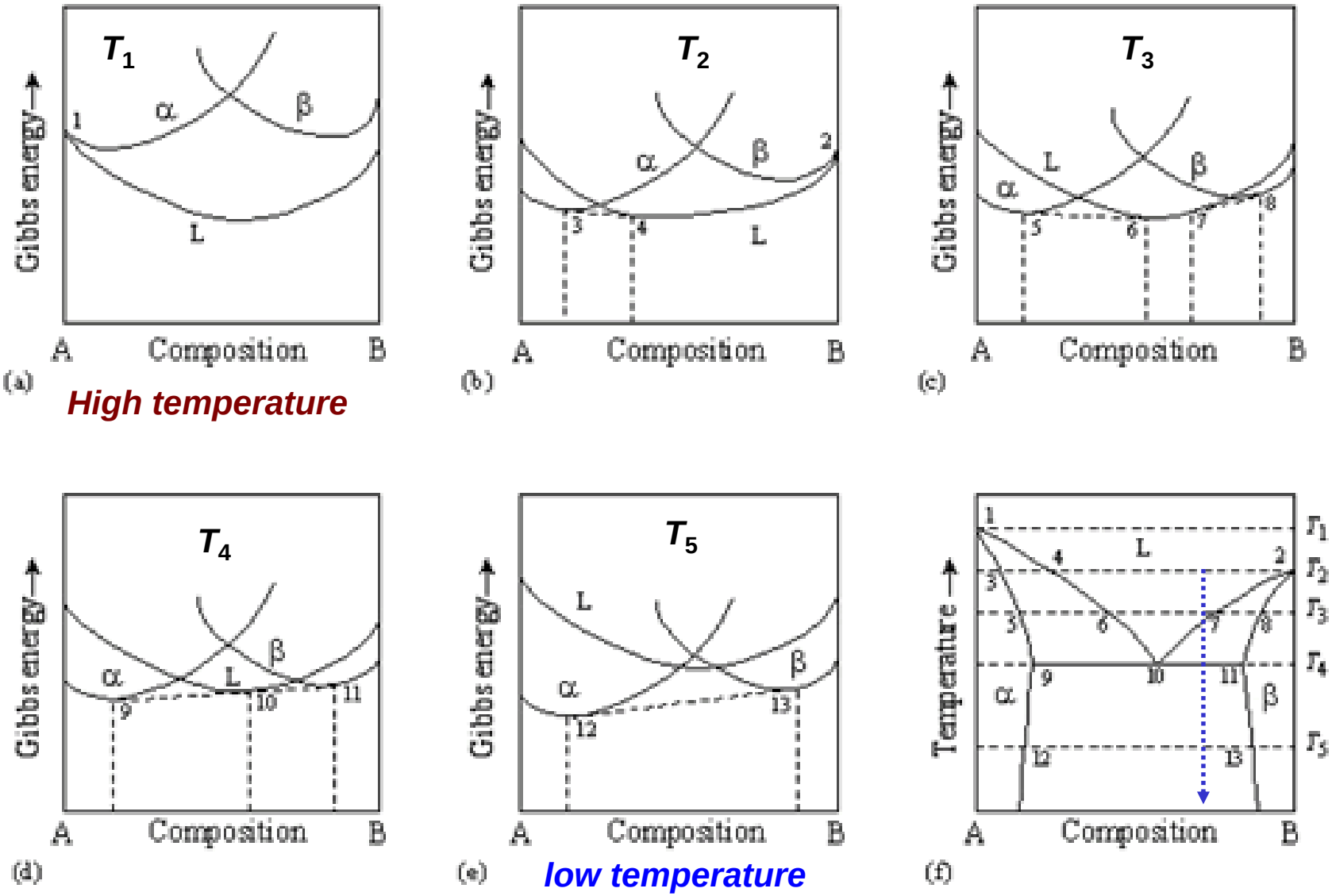
  → **SCL: relatively high entropy**



< Thermal map >


T_g
T_m
cooling
Glass
Supercooled liquid
liquid
Glass transition
: Endo.
Crystallization
: Exo.
melting
: Endo.
Endo.
Exo.
Heat Flow(W/g)
Temperature(°C)
T_g
T_x
T_s
T_L
T_p
79.70°C(I)
75.41°C
81.80°C
137.58°C
20.32J/g
144.72°C
228.80°C
22.48J/g
Glass
SCL
crystal
C+L
Liquid
heating

Use of Gibbs energy curves to construct a binary phase diagram of the eutectic type.



High temperature

low temperature

Liquid: metastable ⟶ glass