2019 Fall

“Advanced Physical Metallurgy”

- Non-equilibrium Solidification -

09.23.2019

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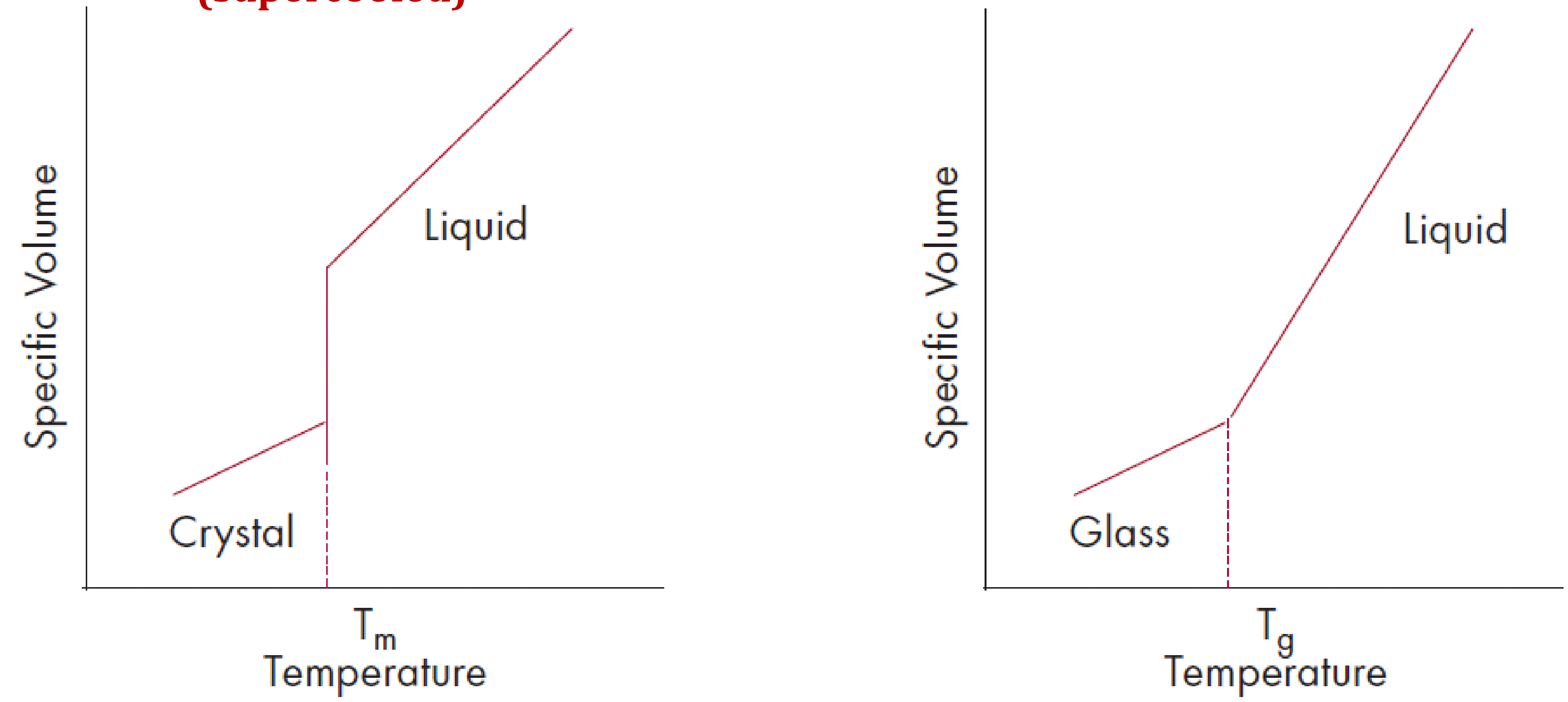
Fundamentals of the Glass Transition

If liquid is cooled, two events can occur.

1) Crystallization (solidification at $T_{m.p.}$)

2) Undercooled below $T_{m.p.}$ → More viscous → Glass
(supercooled)



Crystal Transition

Amorphous Transition

Figure 4. Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).

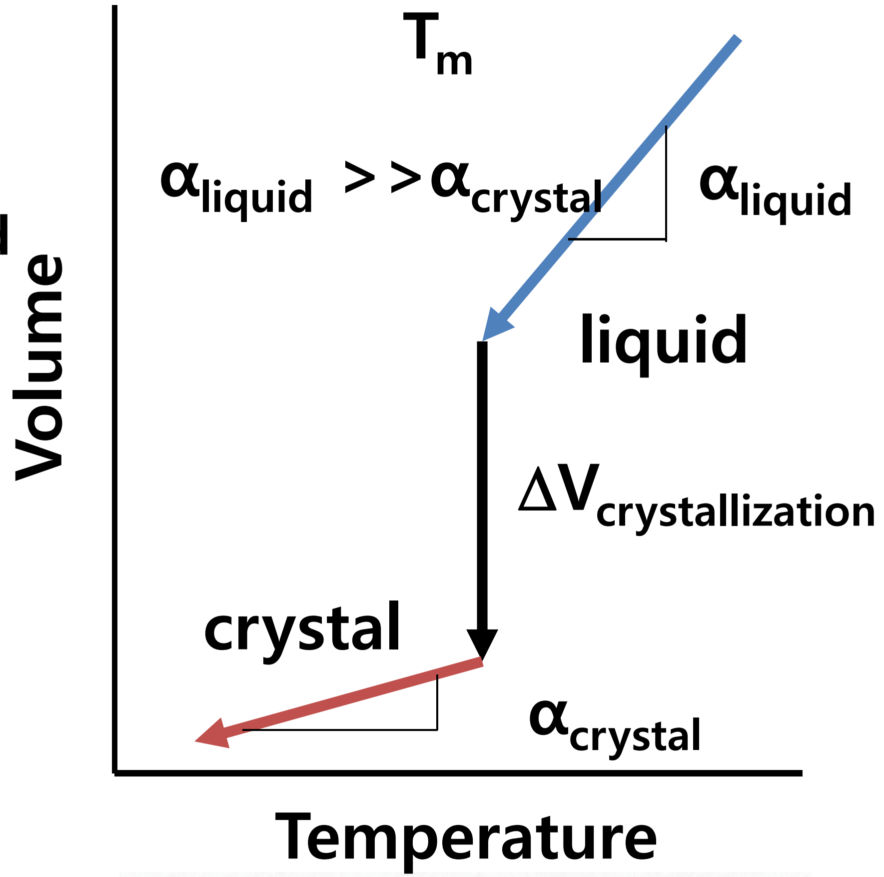
Fundamentals of the Glass Transition

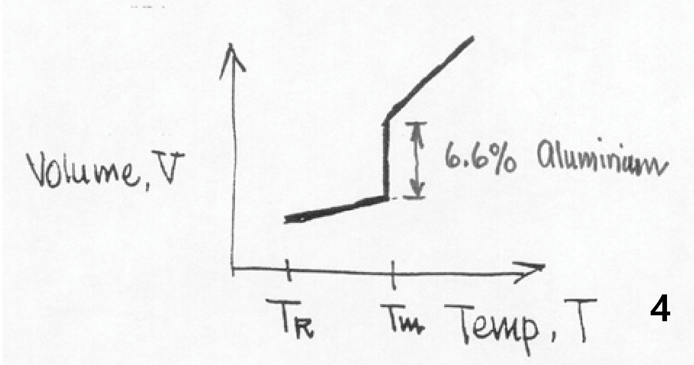
- **Melting and Crystallization are Thermodynamic Transitions**
  - Discontinuous changes in structure and properties at T_m
  - Structures are thermodynamically controlled and described by the Phase Diagram
  - $T_{melting}$ and $T_{liquidus}$ have fixed and specific values, 1710 ^oC for SiO_2, for example

- **The Glass Transition is a Kinetic Transition**
  - Continuous changes in structure and properties near T_g
  - Structure and properties are continuous with temperature
  - Structures and properties can be changed continuously by changing the kinetics of the cooled or reheated liquid

Crystallization is Controlled by Thermodynamics

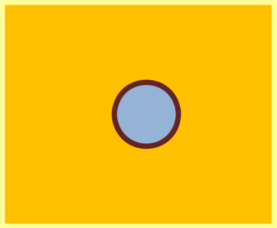
- Volume is high as a hot liquid
- Volume shrinks as liquid is cooled
- At the melting point, T_m, the liquid crystallizes to the thermodynamically stable crystalline phase
- More compact (generally) crystalline phase has a smaller volume
- The crystal then shrinks as it is further cooled to room temperature
- Slope of the cooling curve for liquid and solid is the thermal expansion coefficient, α





Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

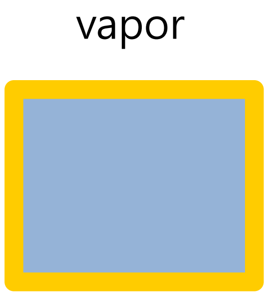
- Interfacial energy ⇨ ΔT_N

No superheating required!

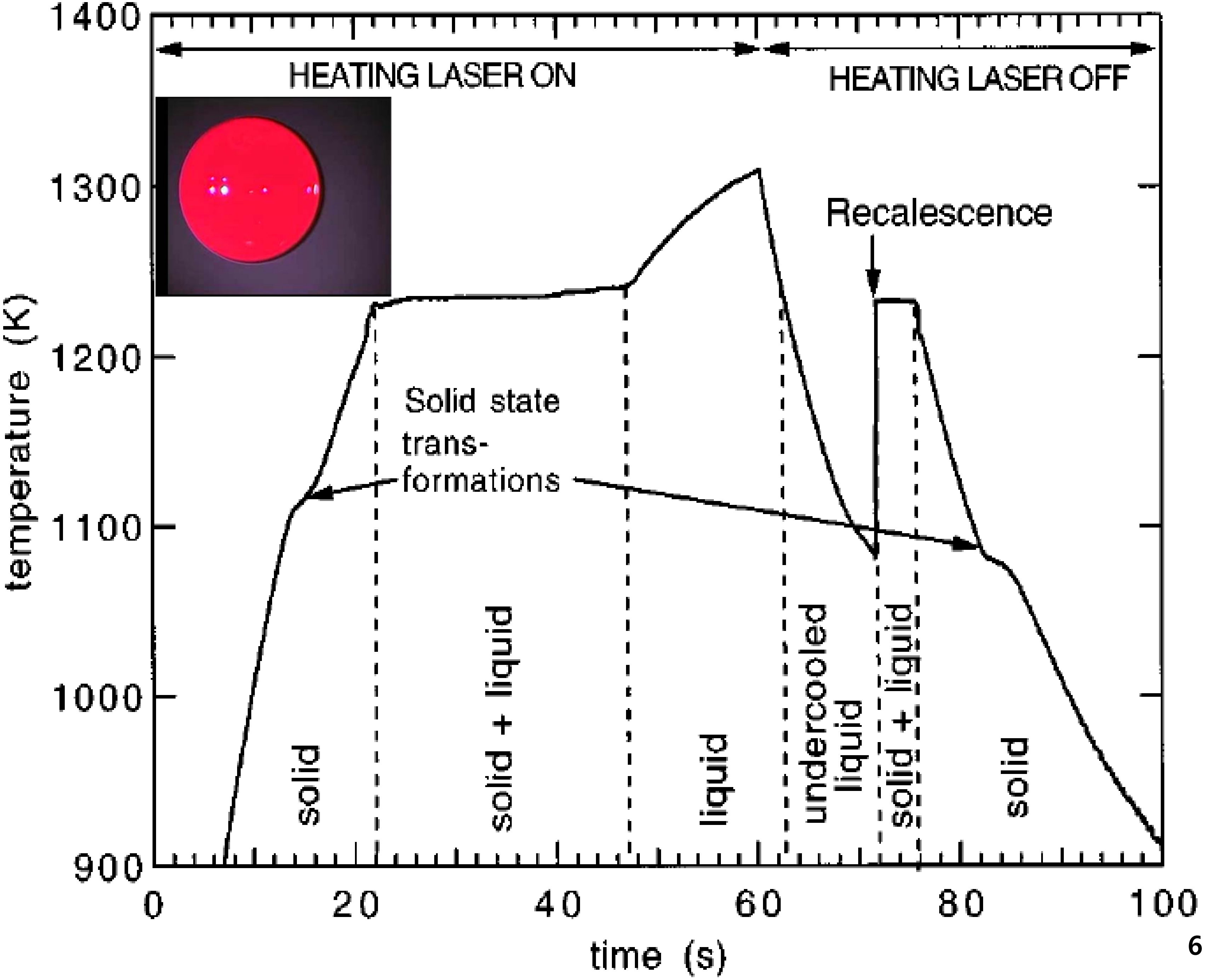
- Interfacial energy ⇨ No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

Melting: Liquid ← Solid

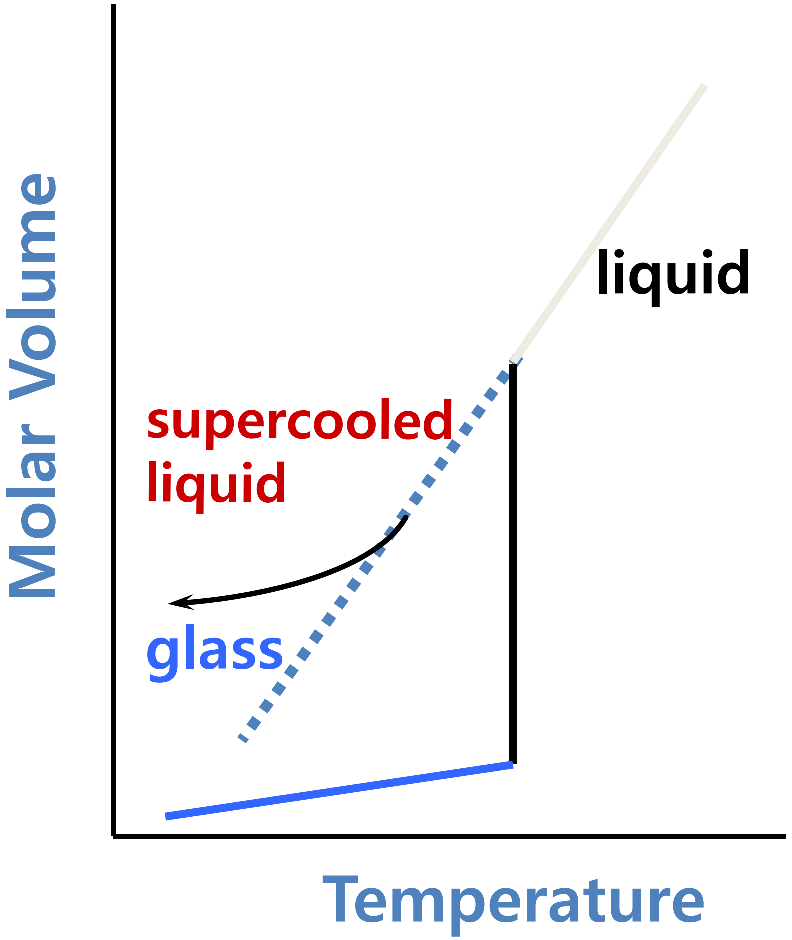


In general, wetting angle = 0 ➡ No superheating required!


1400
1300
1200
1100
1000
900
temperature (K)
0
20
40
60
80
100
time (s)
HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state trans-formations
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid

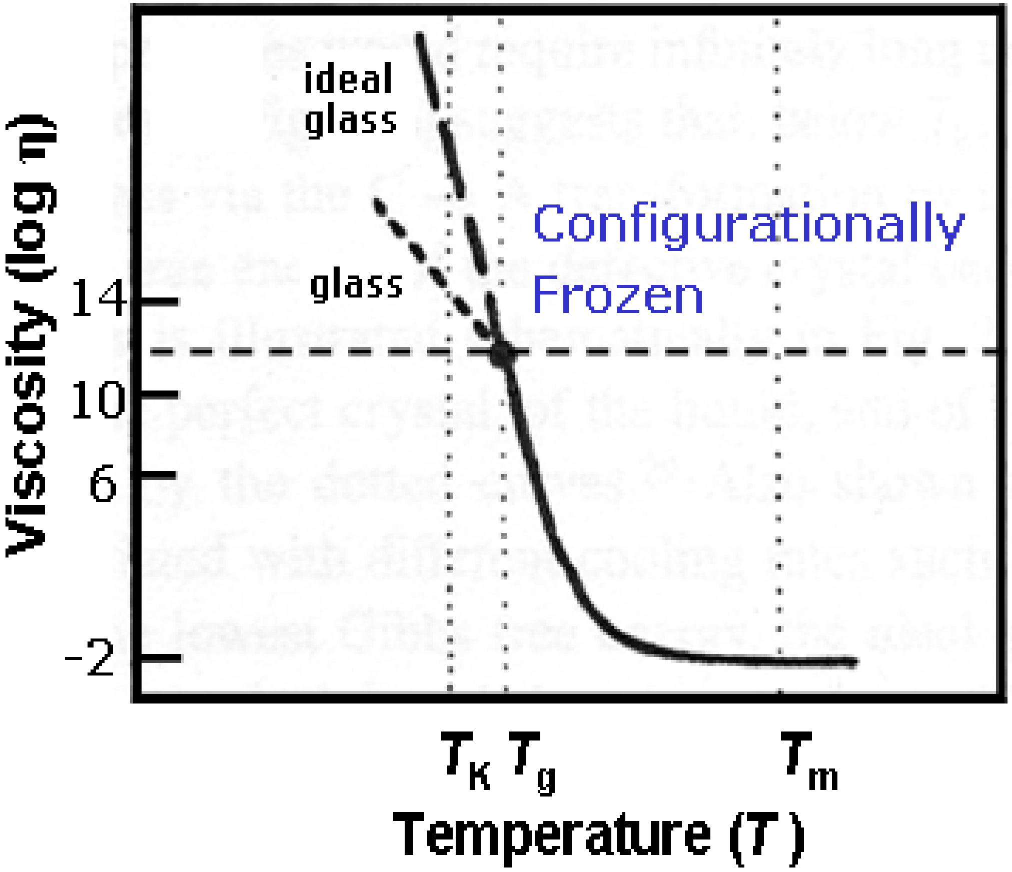
Glass Formation is Controlled by Kinetics

- Glass-forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a "high viscosity" that <u>makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure</u>
- Liquid maybe cooled so fast that it does not have enough time to crystallize
- Two time scales are present
  - "Internal" time scale controlled by the viscosity (bonding) of the liquid
  - "External" timescale controlled by the cooling rate of the liquid



Glass : undercooled liquid with high viscosity

The higher the structural relaxation, the closer it moves toward a "true" glass.

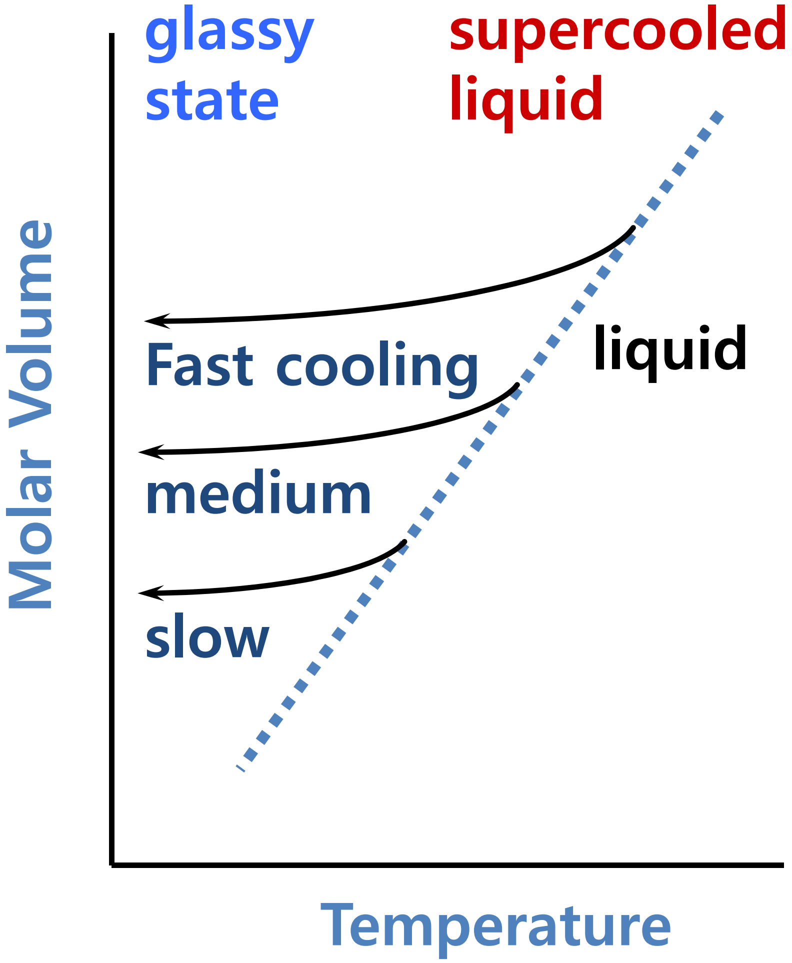


A solid is a materials whose viscosity exceeds $10^{14.6}$ centiPoise (10^{12} Pa s)

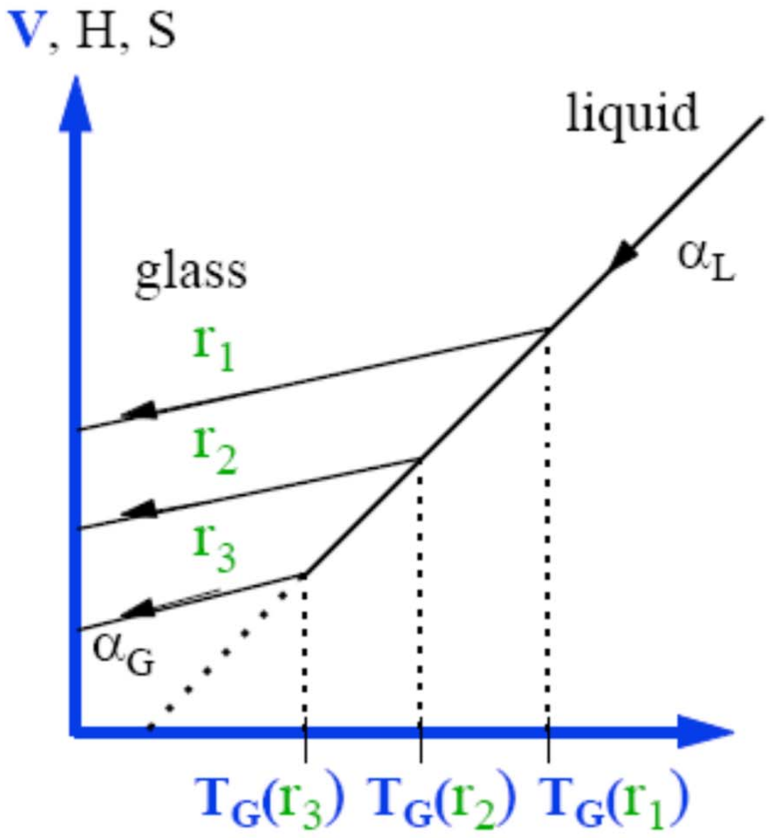
cf) liquid ~*10^{-2} poise*

The Cooling Rate Affects the Properties of Glass

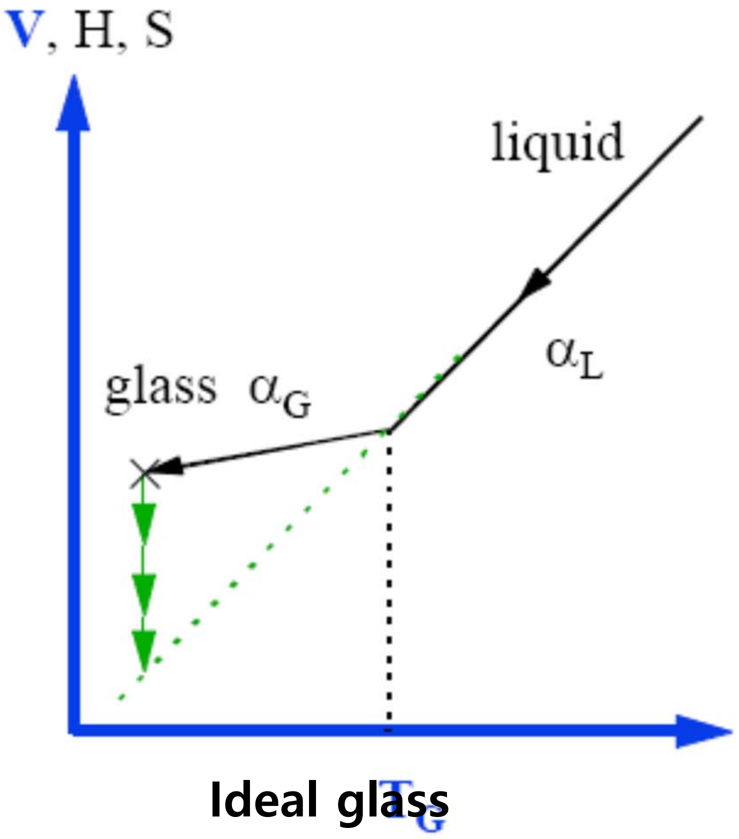
- Faster cooling freezes in the glass at a higher temperature
- The temperature is lowered so fast that the liquid does not have time to relax to the properties at the next lower temperature, glass is formed at a high temperature
- Slower cooling freezes in the glass at a lower temperature
- The temperature is lowered slowly enough that the liquids can relax to properties at lower and lower temperatures, glass is eventually formed at a lower temperature



* Kinetic Nature of the Glass Transition



Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$



Specific Volume (density) of the glass depends on the time at a given $T < T_g$

*** Glass → exited state –(sufficient time)→ relax and eventually transform to crystalline ground state**

2.5 Thermodynamics and Kinetics of Glass Formation

“Phase Transition”

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

Thermodynamical classification: first order & second order

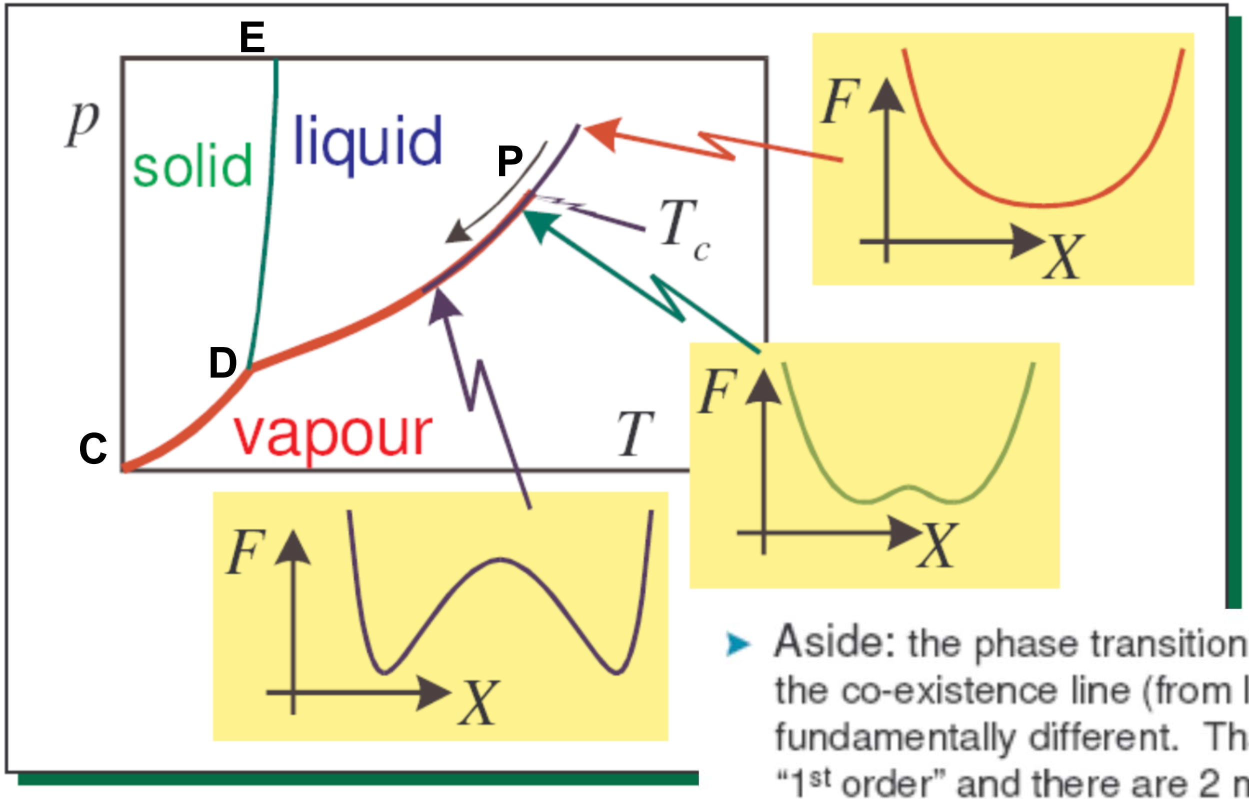
$$\Delta G = \Delta H - T\Delta S = 0$$

- **Order (degree) of transition**

***Continuous phase transitions*:**

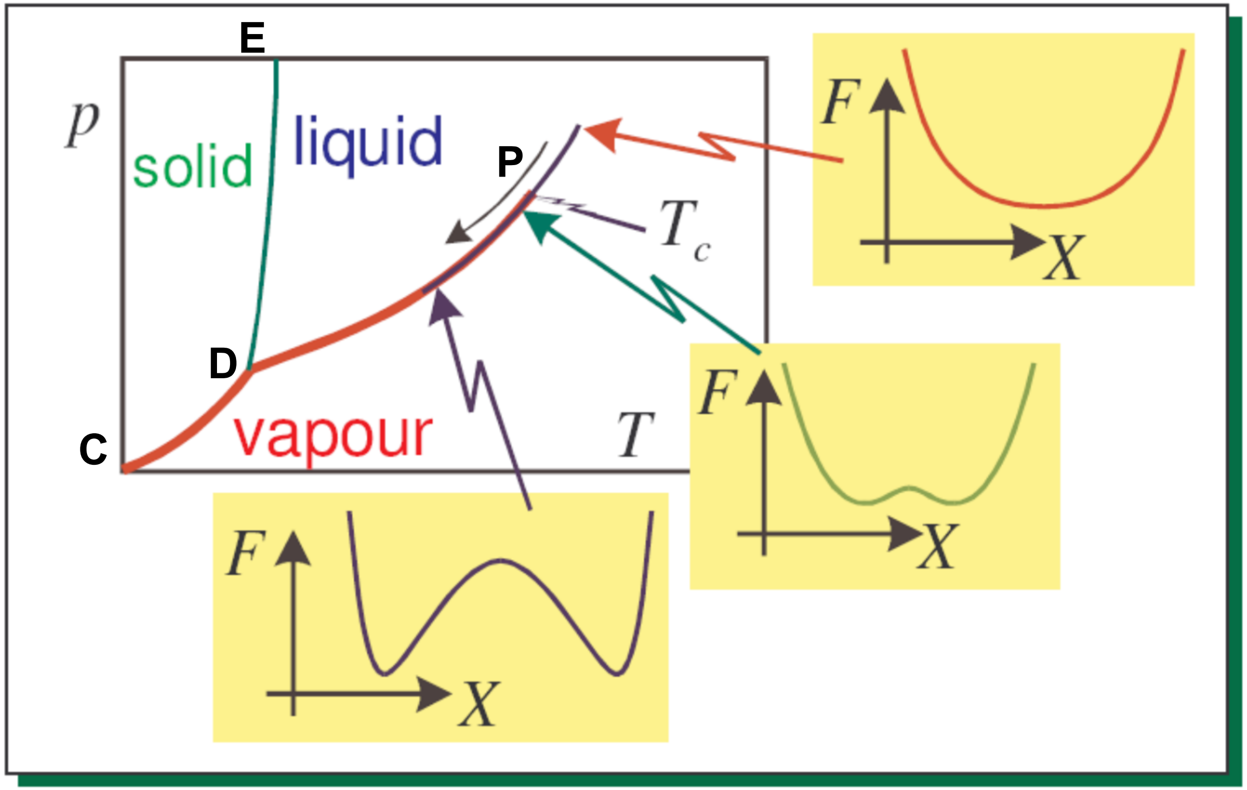
occur when the minimum in the thermodynamic potential evolves smoothly into two equal minima.

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

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

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

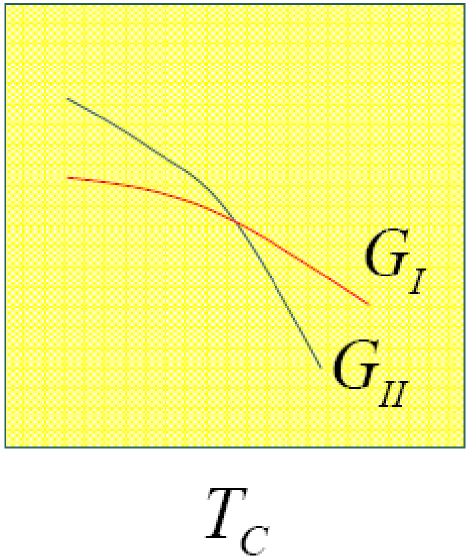
Examples: CsCl structure to NaCl structure; T =479 C.

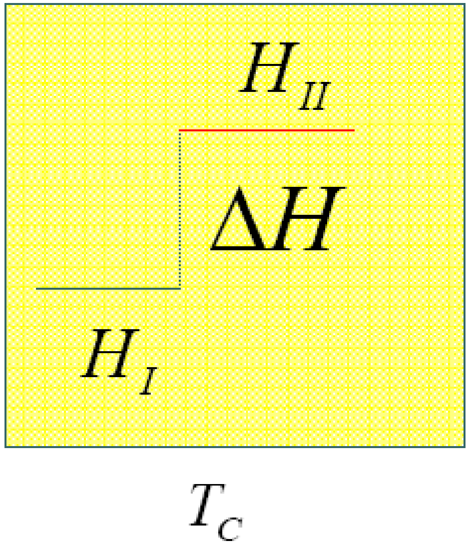
$$\Delta V = 10.3 cm^3$$

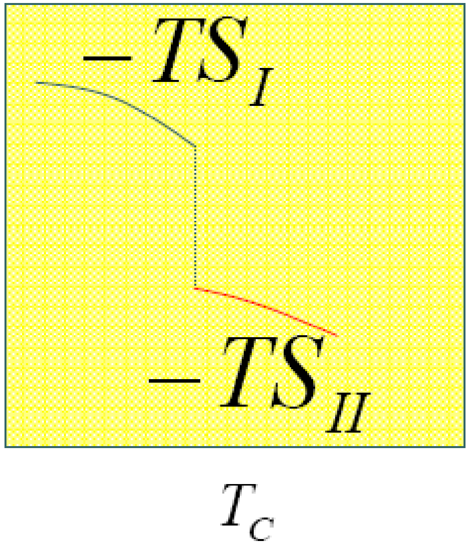
$$\Delta H = 2.424 kJ / mol$$

Melting, freezing, vaporization, condensation…

First-order transition:







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

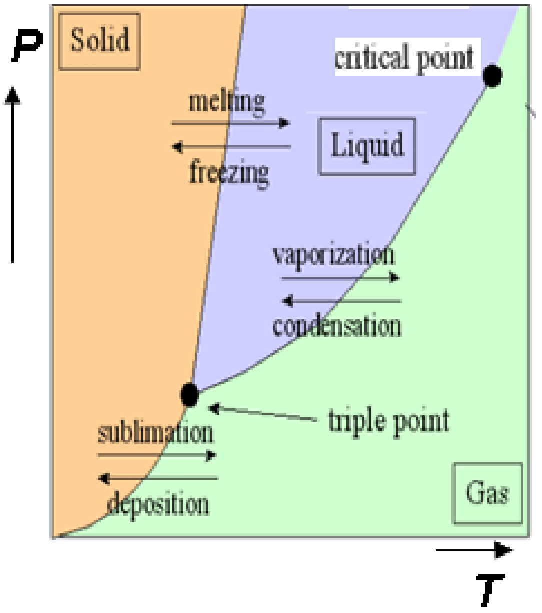
Enthalpy, entropy and volume, continuous functions of T

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

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

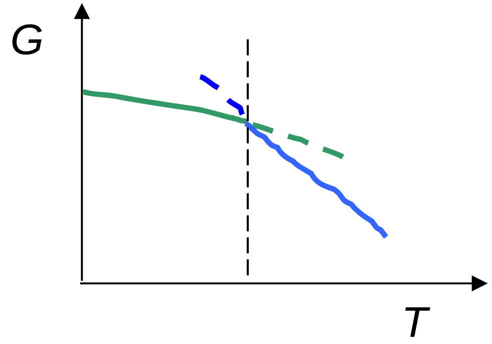
$$\frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T_P} = -\frac{C_p}{T}$$

Measurement of heat capacities (calorimetry)



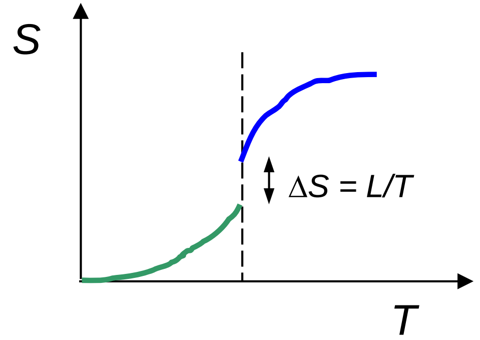
The First-Order Transitions

Latent heat
Energy barrier
Discontinuous entropy, heat capacity



- First Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are discontinuous at T_T

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

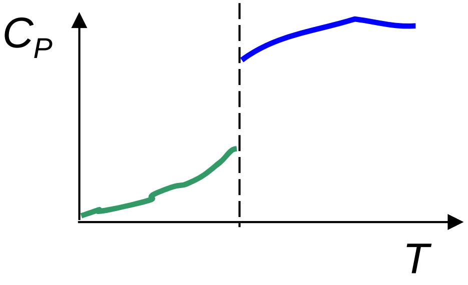


$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

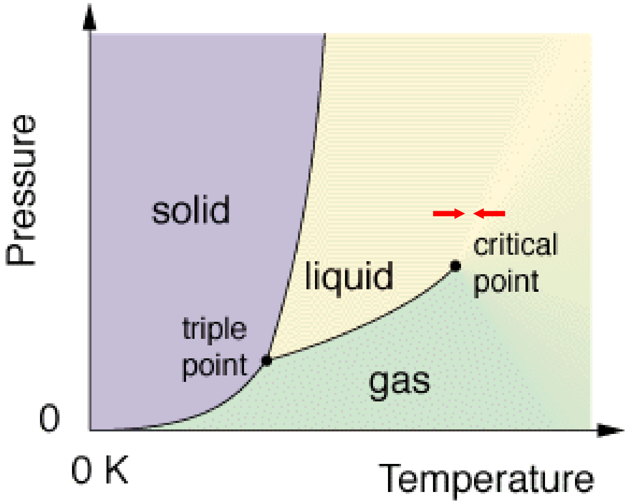
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

  - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

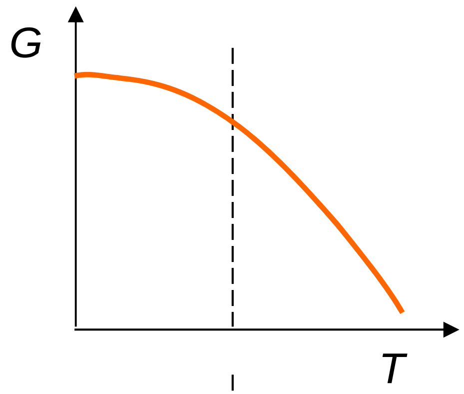


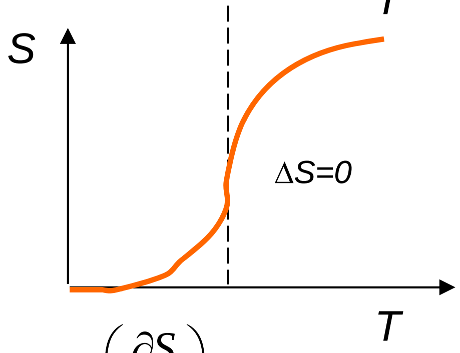
The Second Order Transition



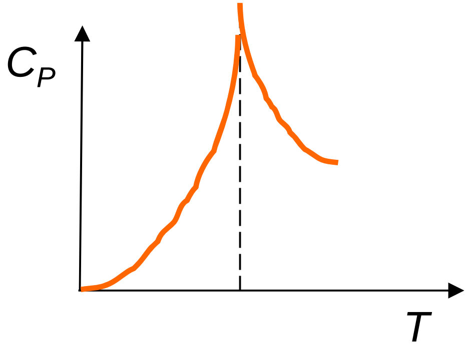
No Latent heat
Continuous entropy

Second-order transition





$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} \rightarrow \infty$$



- Second Order Phase Transition at T_T:
  - G is continuous at T_T
  - First derivatives of G (V, S, H) are continuous at T_T

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

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

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

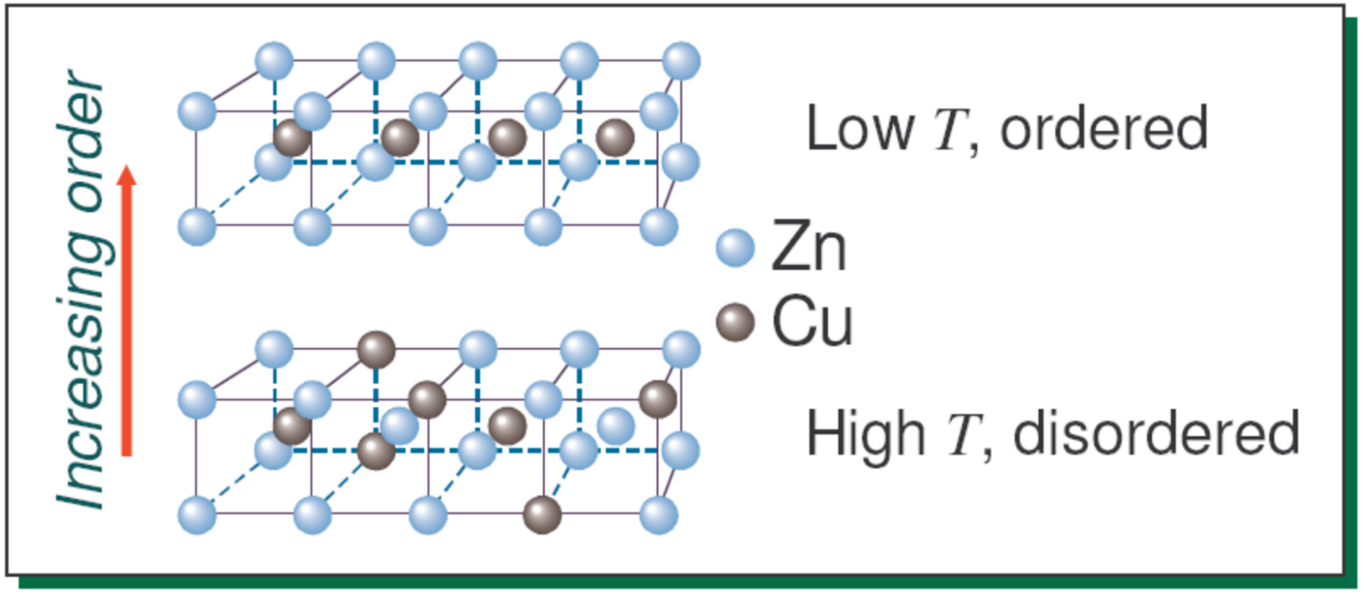
  - Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.

Order-disorder transition: 2nd order transition

- *β*-brass.

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

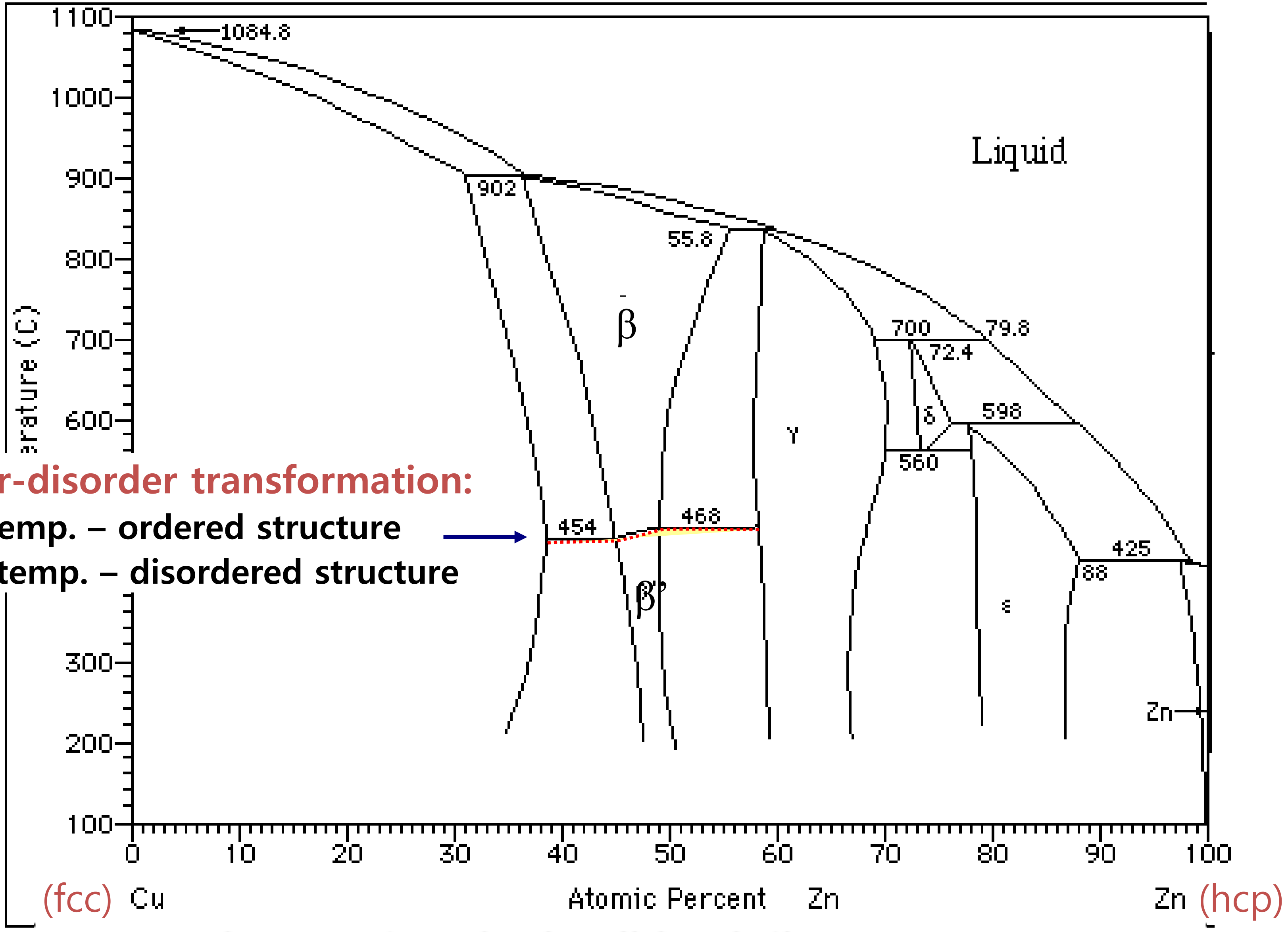
~ **At low temperatures, T<460K, the Zn and Cu atoms for an ordered structure (eg. Cu atoms in the body-centre sites in top diagram)**



- 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.

Intermediate Phase

$\varepsilon < 0$, $\Delta H_{mix} < 0$ / $\Delta H_{mix} \sim -21$ kJ/mol



Order-disorder transformation:

Low temp. – ordered structure

High temp. – disordered structure

- α and η are terminal solid solutions
- β, β', γ, δ and ε are intermediate solid solutions.

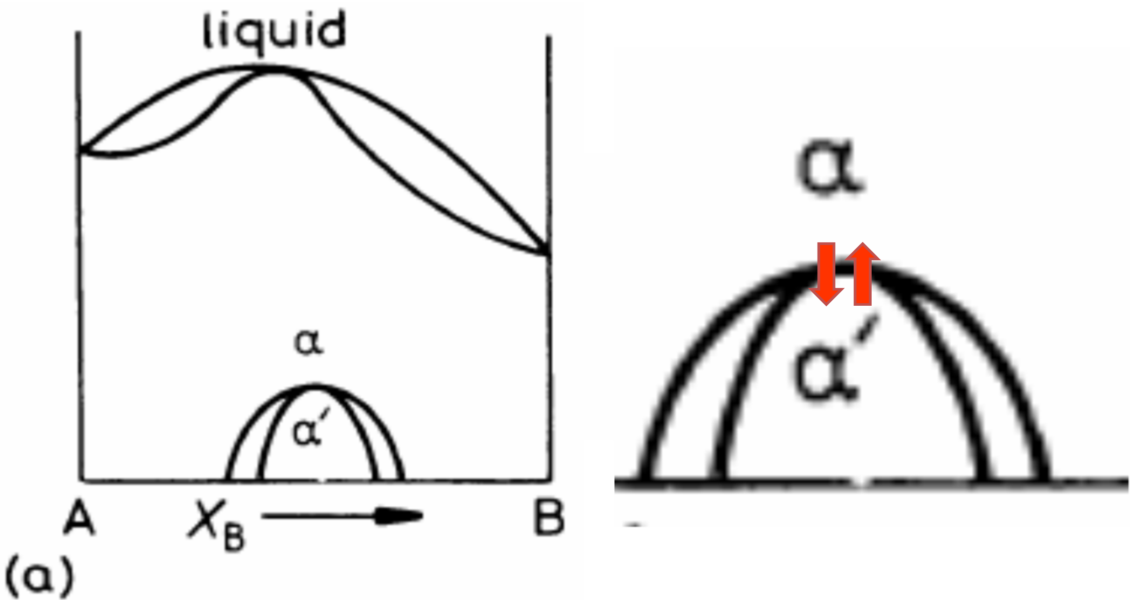
Ordered Alloys $\Delta H^{L}_{mix} = 0 \quad \Delta H^{S}_{mix} < 0$

a. $\Delta H_{mix} < 0$ → **A atoms and B atoms like each other.**

How does the phase diagram differ from the previous case?

b. **What would happen when $\Delta H_{mix} << 0$?**

→ **The ordered state can extend to the melting temperature.**

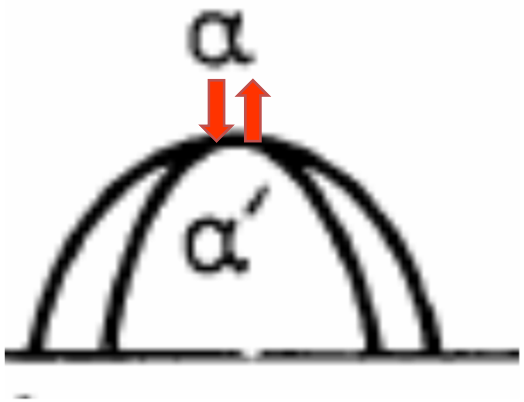


congruent maxima

Order-disorder phase transformation

- Not classical phase change=~not depend on diffusion process
- change of temperature allowed a continuous re-arrangement of atoms without changing the phase
- boundary: ordered lattice & disordered lattice/phase rule could not applied

  there are cases in which an ordered phase of one composition exists in equilibrium with a disordered phase of a different composition.
- Simple composition of the type AB or AB_3 can the transformation (i.e. at the temperature maximum) be considered diffusionless.



* Solid solution

→ random mixing

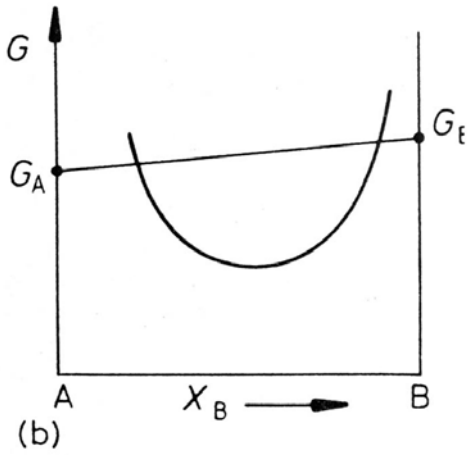
→ entropy ↑

negative enthalpy ↓

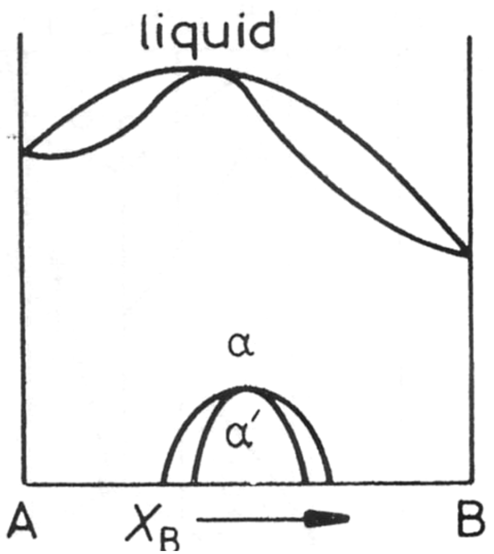
$$\boxed{\Delta H^{S}_{mix} < 0}$$

Large composition range

➔ G ↓



diate phases: (a) for an intermetallic com-
(b) for an intermediate phase with a wide



* Compound : AB, A_2B…

→ entropy↓

→ covalent, ionic contributio

→ enthalpy more negative ↓

$$\boxed{\Delta H^{S}_{mix} << 0}$$

Small composition range

➔ G ↓

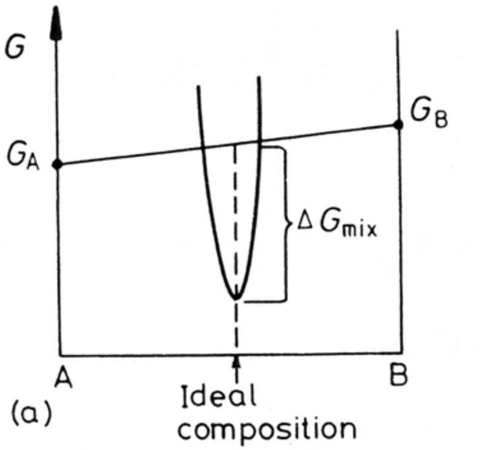
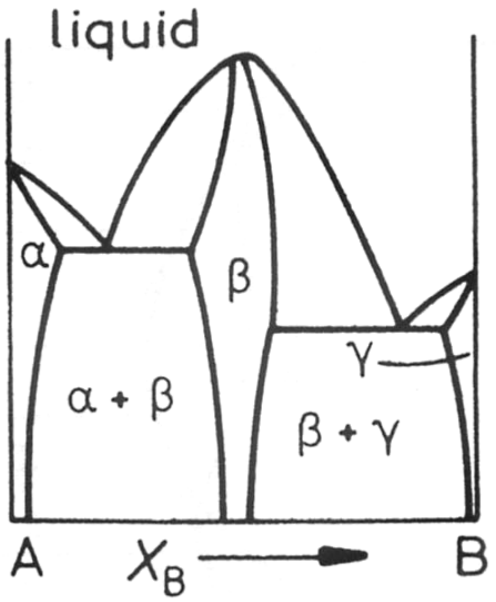


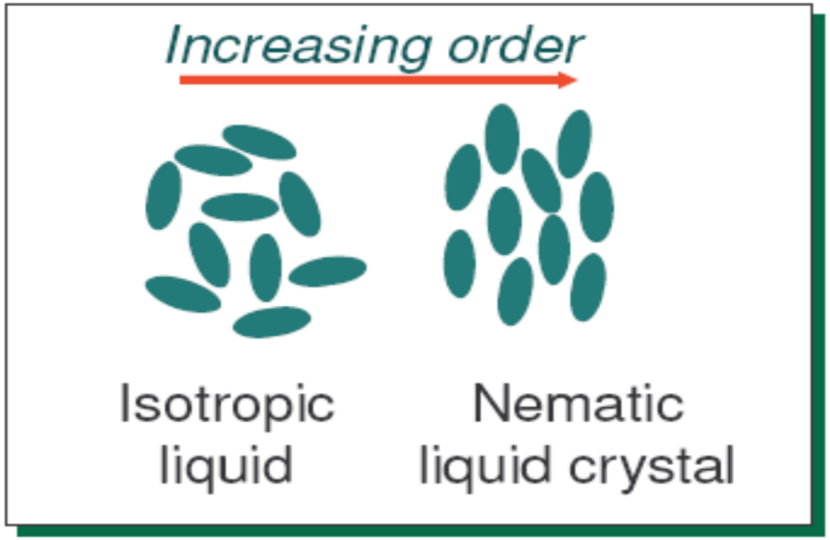
Fig. 1.23 Free energy curves for intermed
pound with a very narrow stability range, (
stability range.

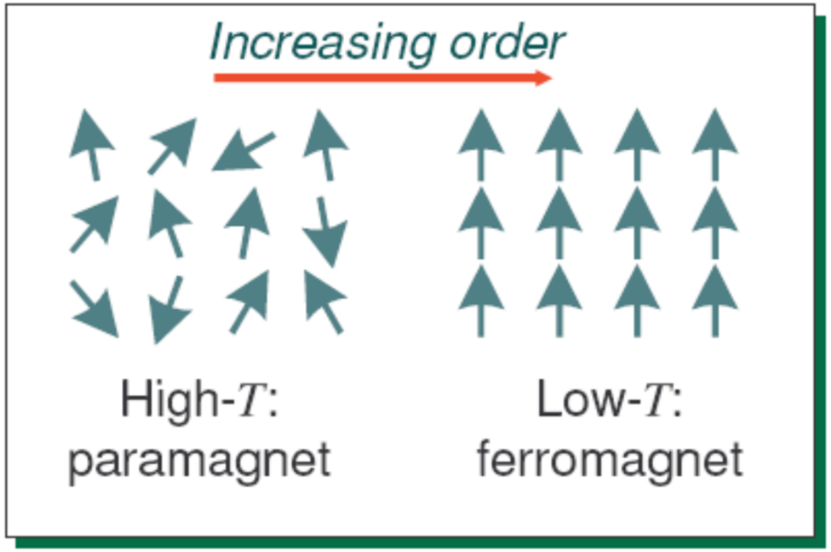


Order-disorder transition: 2nd order transition

- Other examples (there are many):

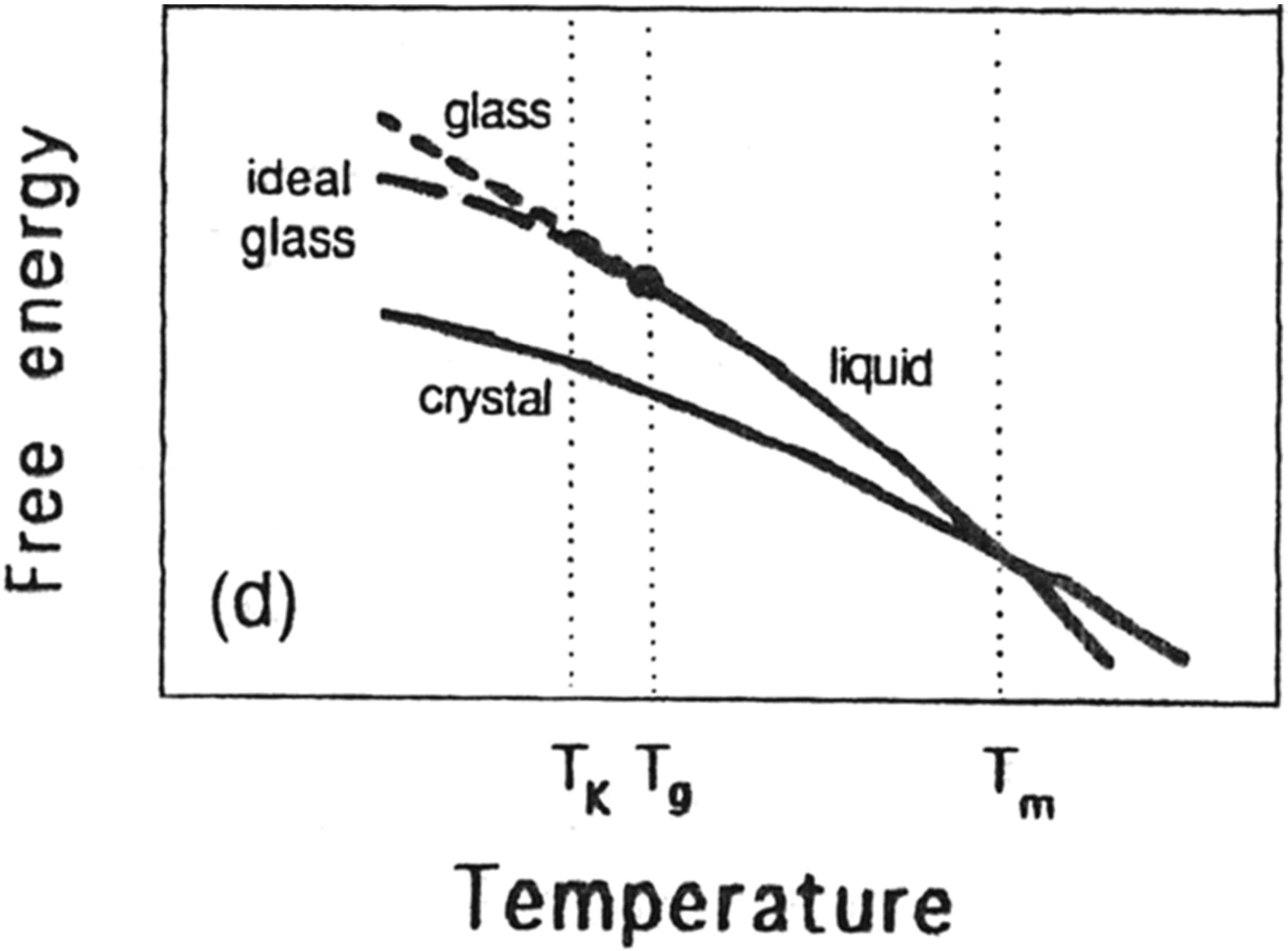
- Isotropic – nematic transition in liquid crystals: appearance of orientational order (liquid crystals have no long-range, positional order).
- Ferromagnetic - paramagnetic transition: manifests itself as a spontaneous polarisation, in zero external field.

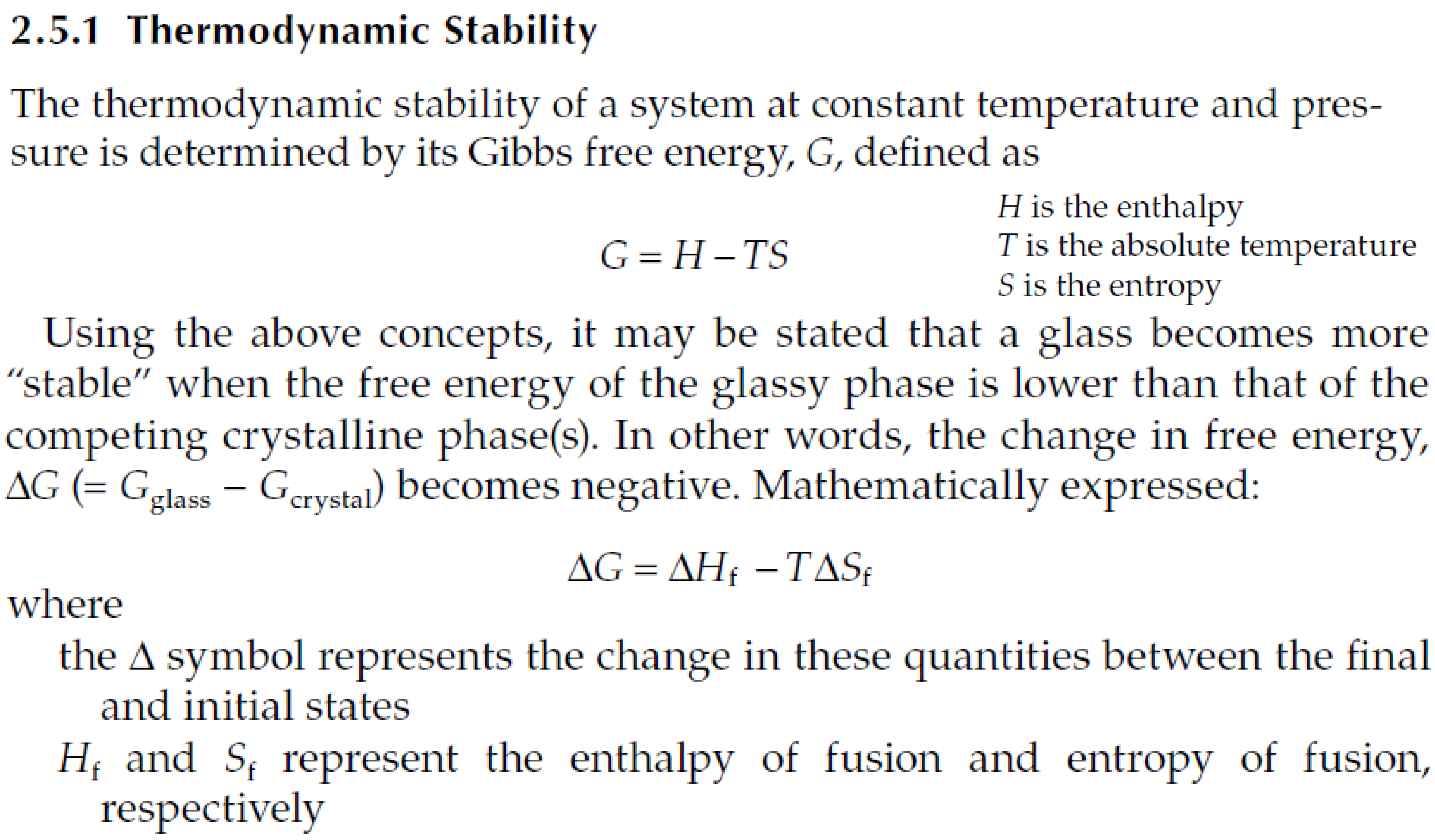




액정의 가는 분자가 서로의 위치는 불규칙하지만 모두 일정방향으로 향하고 있는 상태

Schematic of the glass transition showing the effects of temperature on free energy





2.5.1 Thermodynamic Stability

The thermodynamic stability of a system at constant temperature and pressure is determined by its Gibbs free energy, G, defined as

$$G = H - TS$$

H is the enthalpy
T is the absolute temperature
S is the entropy

Using the above concepts, it may be stated that a glass becomes more "stable" when the free energy of the glassy phase is lower than that of the competing crystalline phase(s). In other words, the change in free energy, ΔG ($= G_{glass} - G_{crystal}$) becomes negative. Mathematically expressed:

$$\Delta G = \Delta H_f - T\Delta S_f$$

where

the Δ symbol represents the change in these quantities between the final and initial states

H_f and S_f represent the enthalpy of fusion and entropy of fusion, respectively

1) multi component system: ΔS↑_high order alloy → easy

2) low chemical potential due to ① low enthalpy ② large interfacial E between liquid and solid phase :
ΔH_f↓ _constituents with large negative heat of mixing → solid/liquid interface E ↑

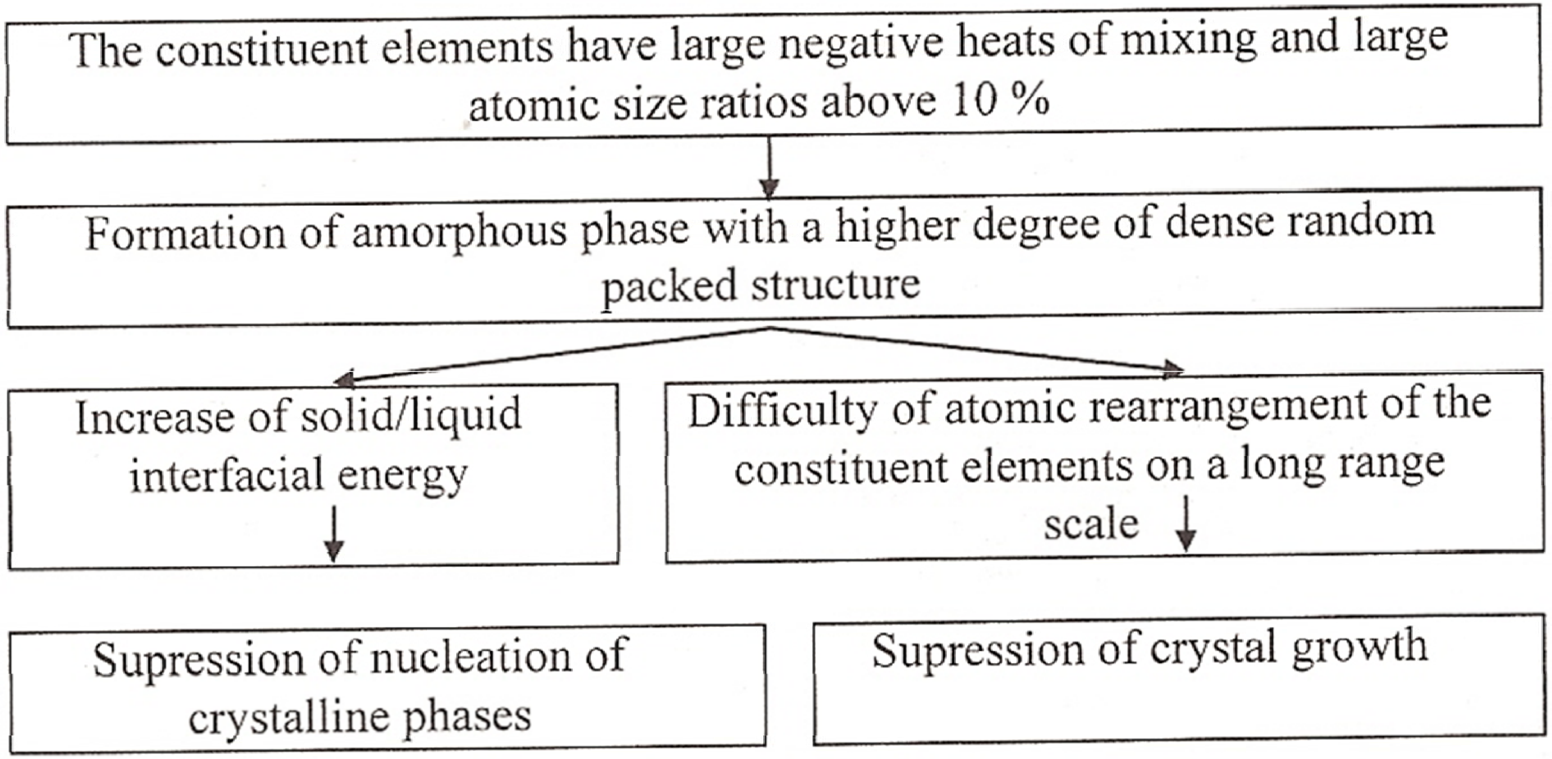


Fig. 5. *Summary of the reasons for the achievement of the high glass-forming ability for some ternary alloy systems such as Ln-Al-TM, Mg-Ln-TM and Zr-Al-TM, etc. (Ln=lanthanide metal, TM=transition metal).*

• 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 κ_T *changes discontinuously.*

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

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

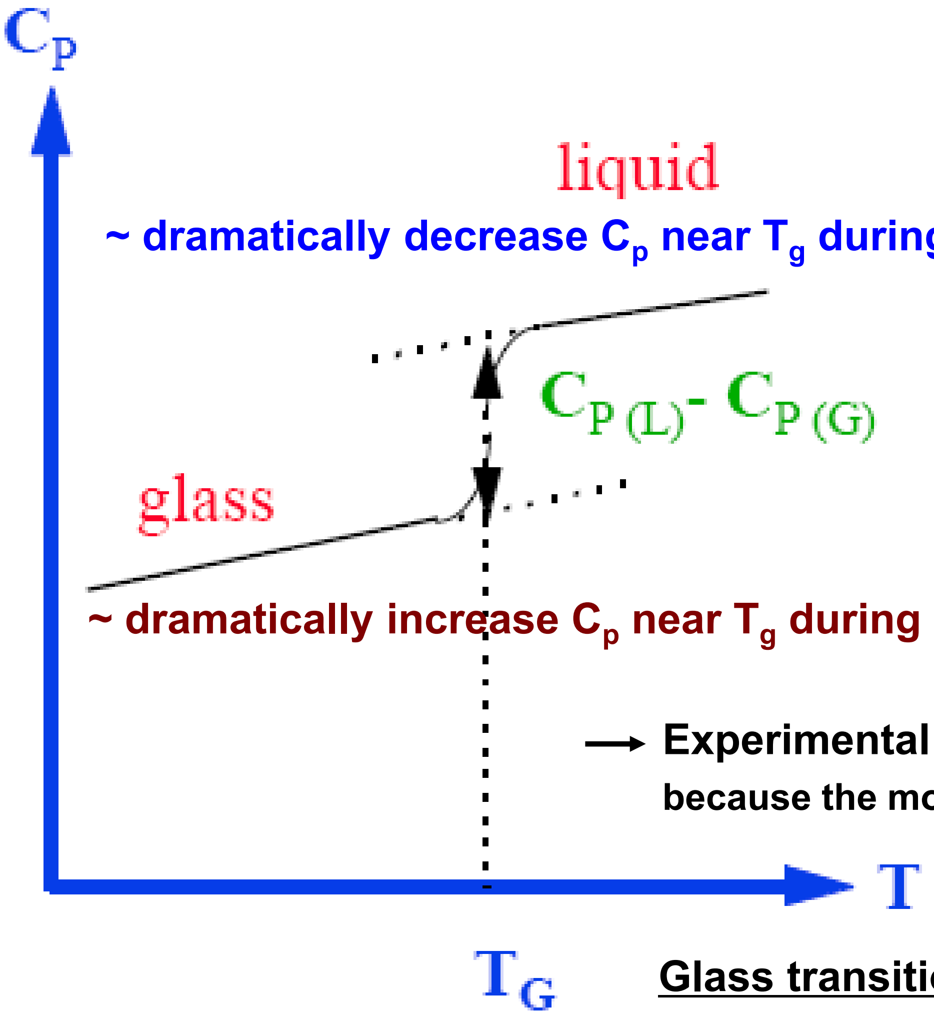
Heat capacity at constant P or V	Coefficient of thermal expansion	Compressibility at constant T or S

❖ **The glass transition is 'pseudo' second-order phase transition.**

And the transition depends on kinetic factors.

- **derivative of thermodynamic properties**

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



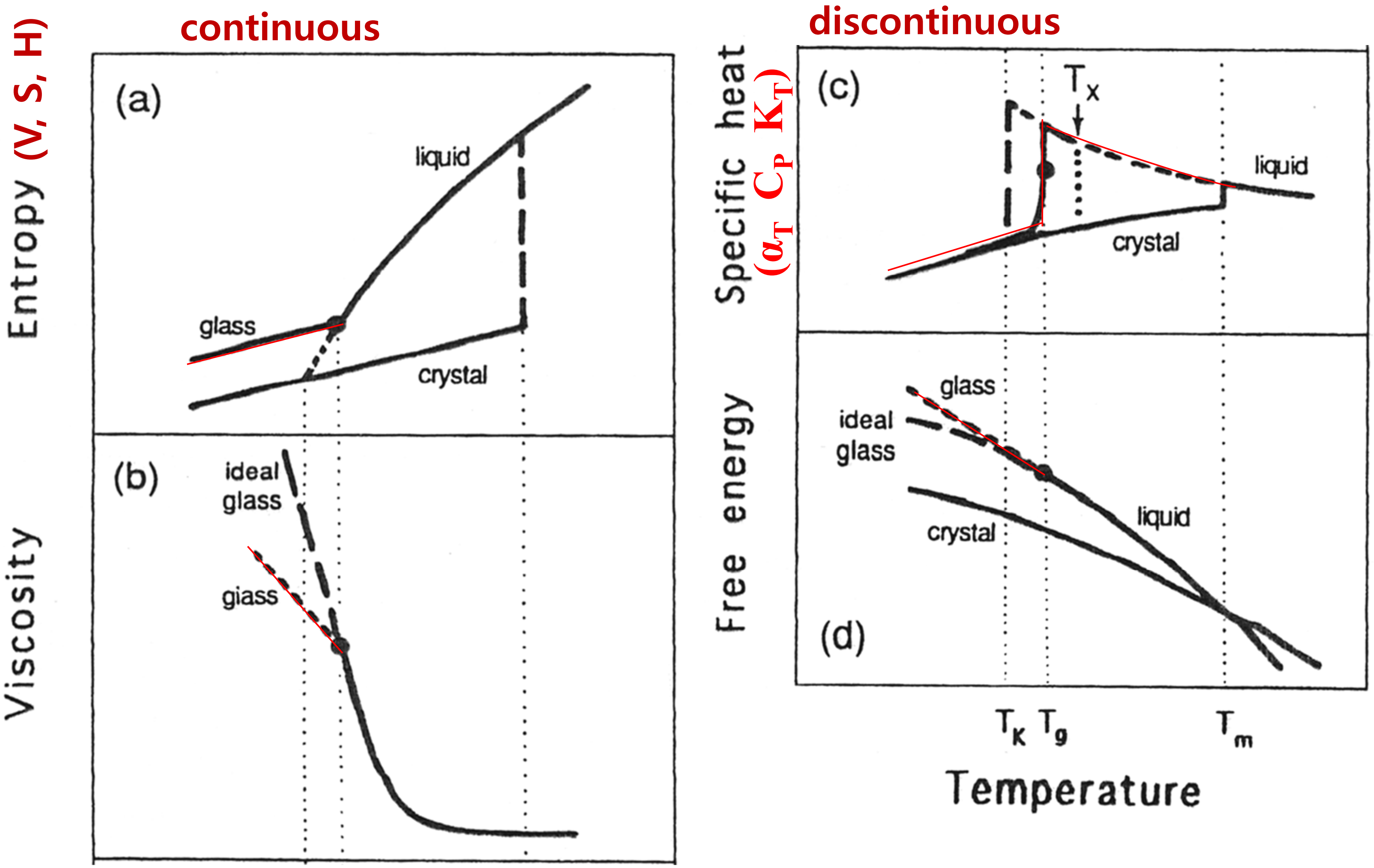
~ dramatically decrease C_p near T_g during cooling

~ dramatically increase C_p near T_g during heating

→ **Experimental observation during heating**

because the monitoring is very difficult during cooling

<u>Glass transition</u>: heat → endothermic



Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

Intermetallics 30 (2012) 19–24

Contents lists available at SciVerse ScienceDirect

Intermetallics

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The world's biggest glassy alloy ever made

Nobuyuki Nishiyama [a,*], Kana Takenaka [a], Haruko Miura [a], Noriko Saidoh [a], Yuqiao Zeng [b], Akihisa Inoue [b]

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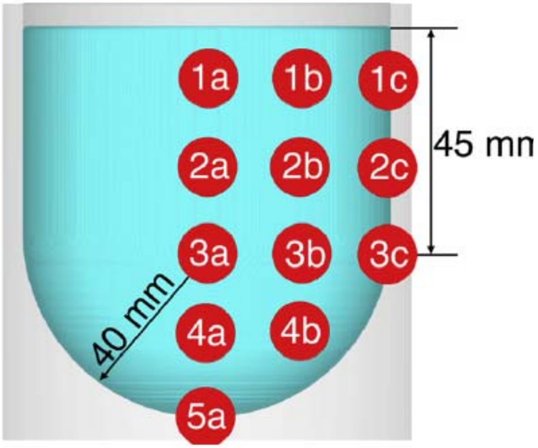
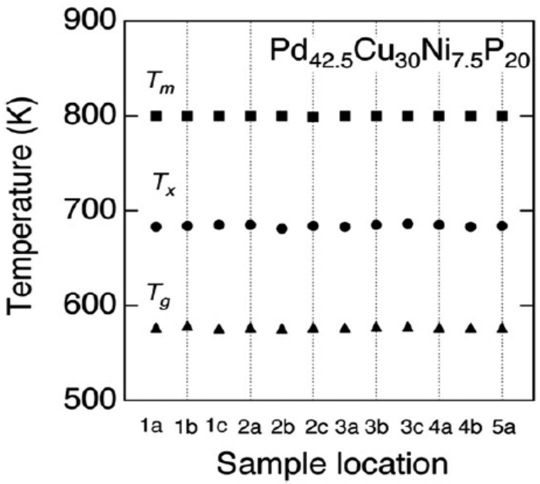
[b] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan





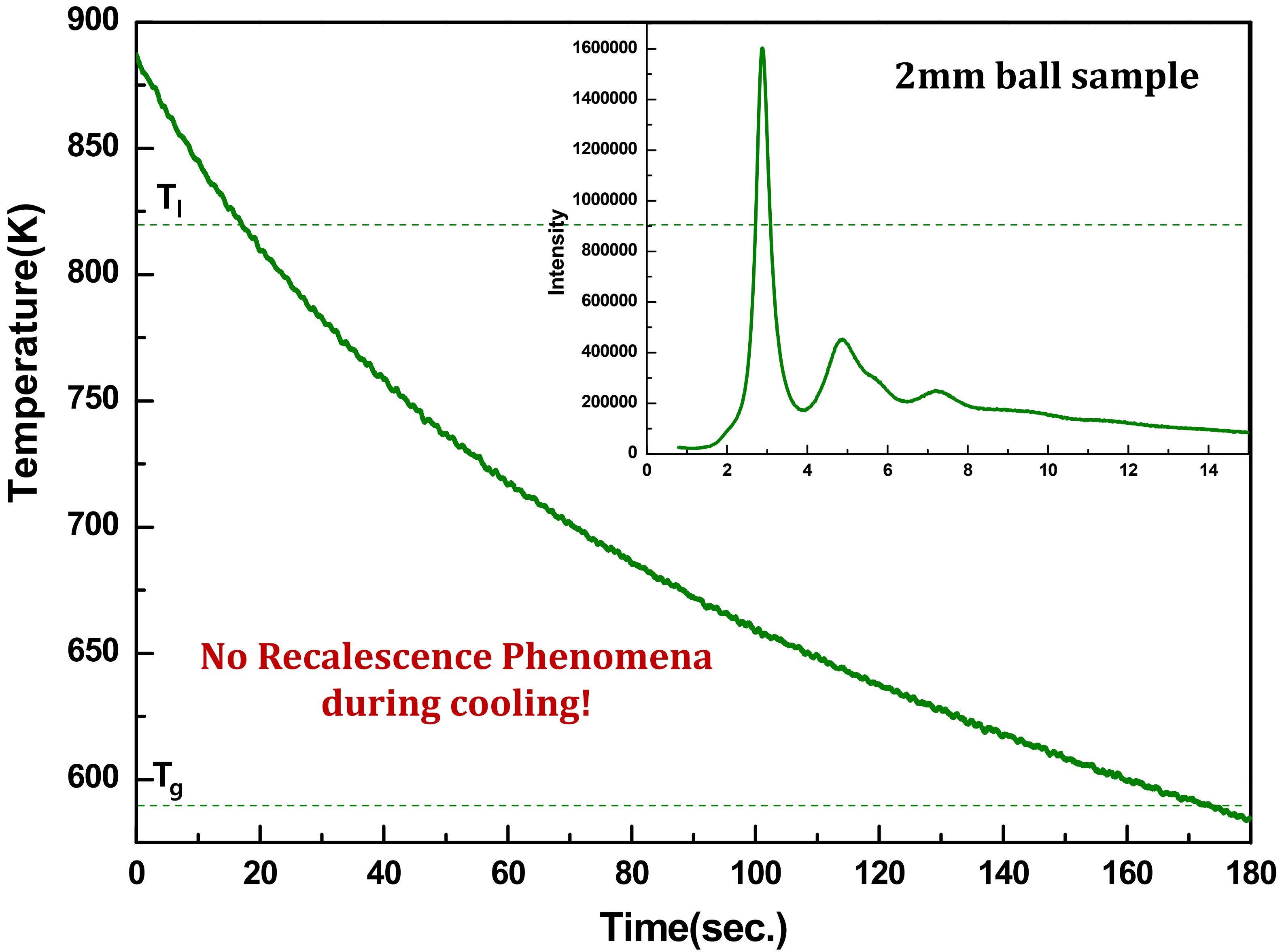
$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$

2012

D_{max} 80mm

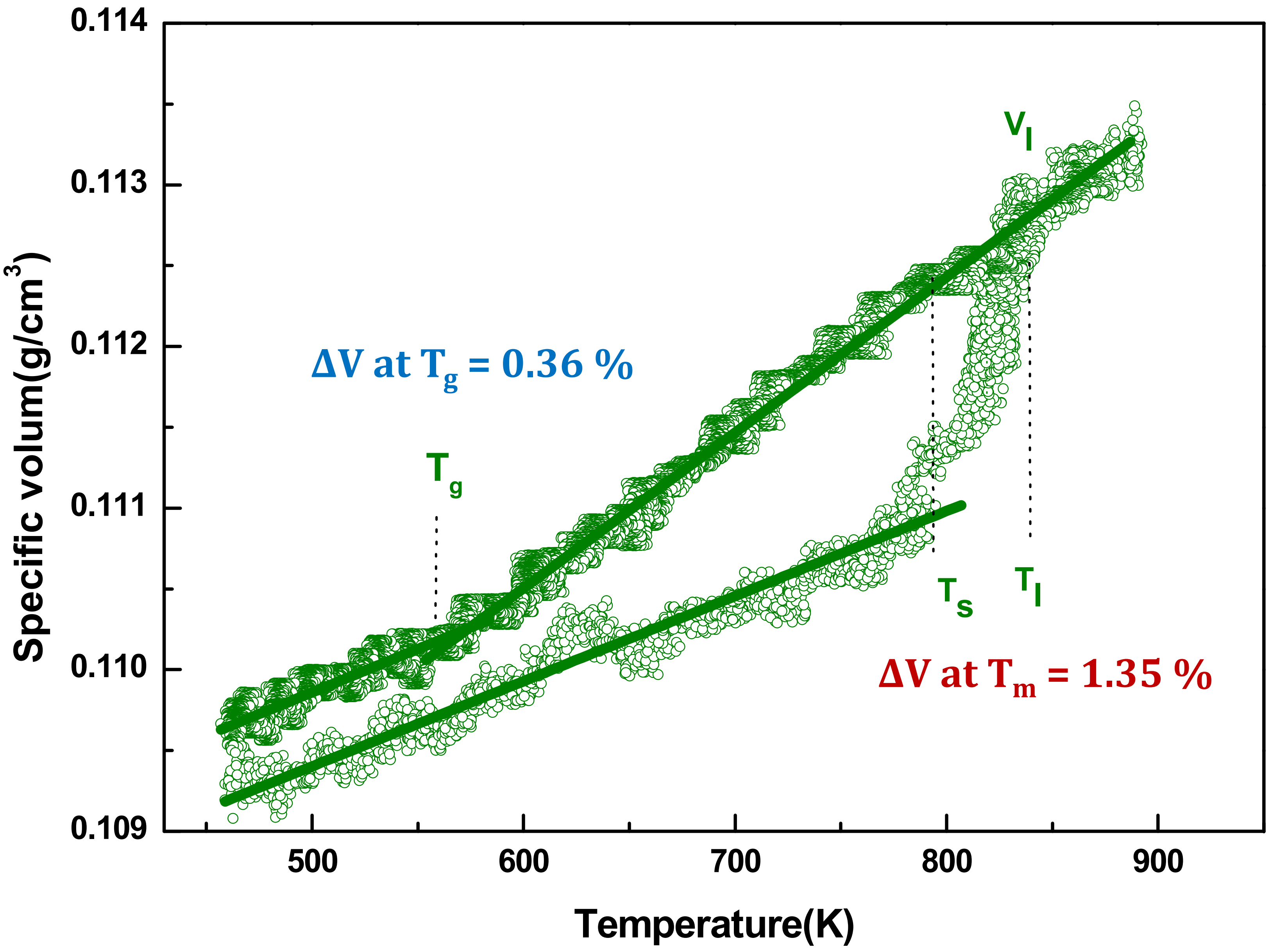
Intermetallics, Vol30, Nov2012, P 19–24

BMG-formation of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ Alloy under Radiative Cooling



No Recalescence Phenomena during cooling!

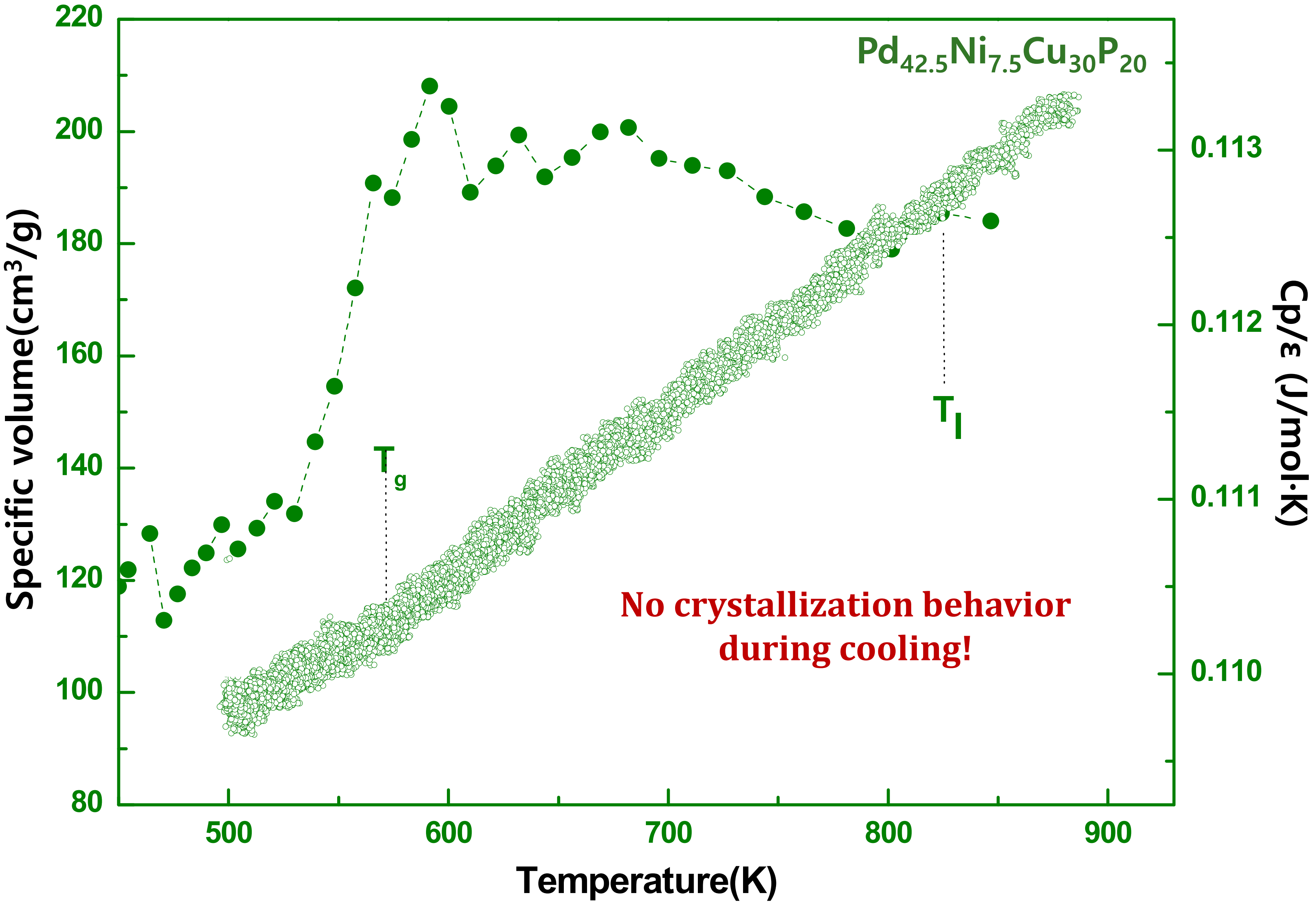
V-T Diagram of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$



ΔV at T_g = 0.36 %

ΔV at T_m = 1.35 %

V-T Diagram & C_p/ε-T Diagram of $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$



No crystallization behavior during cooling!

Q1: Theories for the glass transition

Theories for the glass transition

A. Thermodynamic phase transition

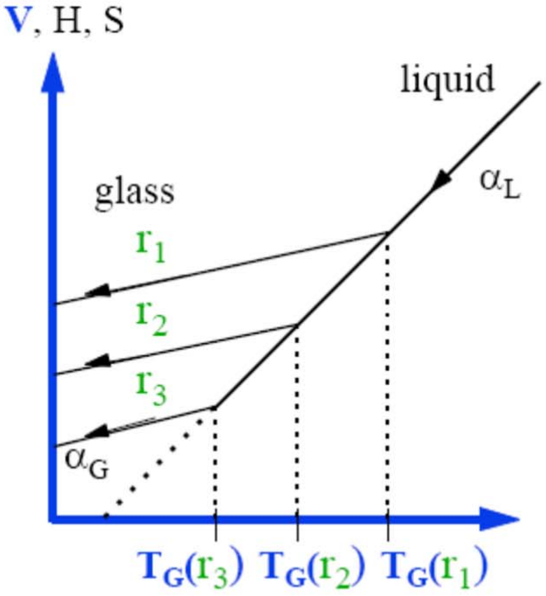
- ***Glass transition***

  H , V , S : continuous ***$C_p\ \alpha_T\ K_T$: discontinuous***

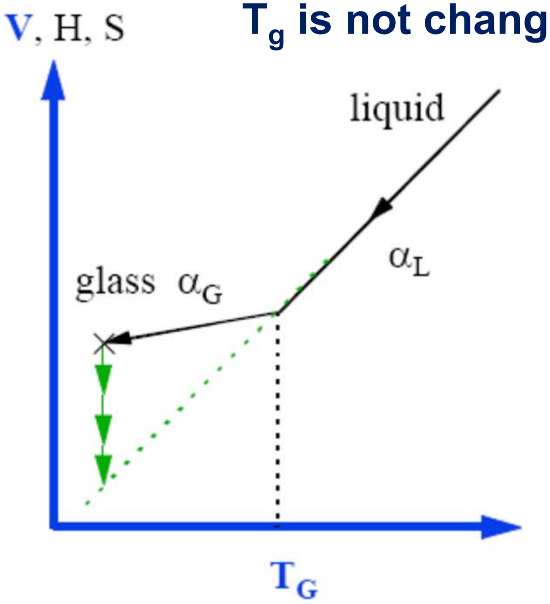
→ **by thermodynamic origin, 2^{nd} order transition**

But, ***1) Tg is dependent on thermal history of sample.***

→ **If 2^{nd} order transition,**
T_g is not changed by kinetic factor.



Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$



Specific Volume (density) of the glass depends on the time at a given $T < T_g$

• 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 κ_T *changes discontinuously.*

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

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

Heat capacity at constant P or V	Coefficient of thermal expansion	Compressibility at constant T or S

❖ **The glass transition is ‘pseudo’ second-order phase transition.**

And the transition depends on kinetic factors.

Maxwell relations $\left(\frac{\partial T}{\partial p}\right)_{V,N} = \left(\frac{\partial V}{\partial S}\right)_{T,N}$

$$\therefore \frac{dT_g}{dP} = \frac{TV(\alpha_{T_2} - \alpha_{T_1})}{(C_{P_2} - C_{P_1})} = \frac{TV\boxed{\Delta\alpha_T}}{\boxed{\Delta C_P}} \qquad \text{(1)}$$

measureable

$$\therefore \frac{dT_g}{dP} = \frac{\boxed{\Delta\kappa_T}}{\Delta\alpha_T} \qquad \text{(2)}$$

→ **Eq. (1) & (2) should be proved experimentally.**

It is found by measuring the discontinuities $\Delta\alpha_T$, ΔC_P, $\Delta\kappa_T$ at the glass transition that Eq. (1) is almost always obeyed within experimental error, but that values for $\Delta\kappa_T/\Delta\alpha_T$ are generally appreciably higher than those of dT_g/dP (Eq. (2)).

→ **Eq. (1) = satisfy** **Eq. (2) = dissatisfy :** $\frac{dT_g}{dP} < \frac{\Delta\kappa_T}{\Delta\alpha_T}$

→ **Therefore, it appears on this evidence that the glass transition is “not a simple second-order phase transition.”**

Prigogine Defay Ratio

If a single ordering parameter determines the position of equilibrium in a relaxing system,

$$R = \frac{\Delta\kappa_T \Delta C_P}{TV(\Delta\alpha_T)^2} = 1$$

If more than one ordering parameter is responsible,

$$R = \frac{\Delta\kappa_T \Delta C_P}{TV(\Delta\alpha_T)^2} > 1$$

➡ The latter case seems to describe most glasses.

Goldstein (1973) has suggested that

“ The specific volume V_g of the glass depends not only on the temperature, being continuous through the transition, but also on the pressure of formation”

Jäckle (1989) has shown that

$$\frac{dT_g}{dP} = \frac{\Delta\kappa_T}{\Delta\alpha_T} \Rightarrow \frac{dT_g}{dP} = \frac{\Delta\kappa_T + \boxed{\partial(\ln V_g)/\partial p_f}}{\Delta\alpha_T}$$

Additional consequence of the experimental verification,

“ Glasses prepared under high pressures have higher than normal densities but normal entropies or enthalpies. ”

Homework :

1) Find application of value of the Prigogine Defay Ratio : R and summary in 3 pages of ppt file.

Due date: 9 April 2018

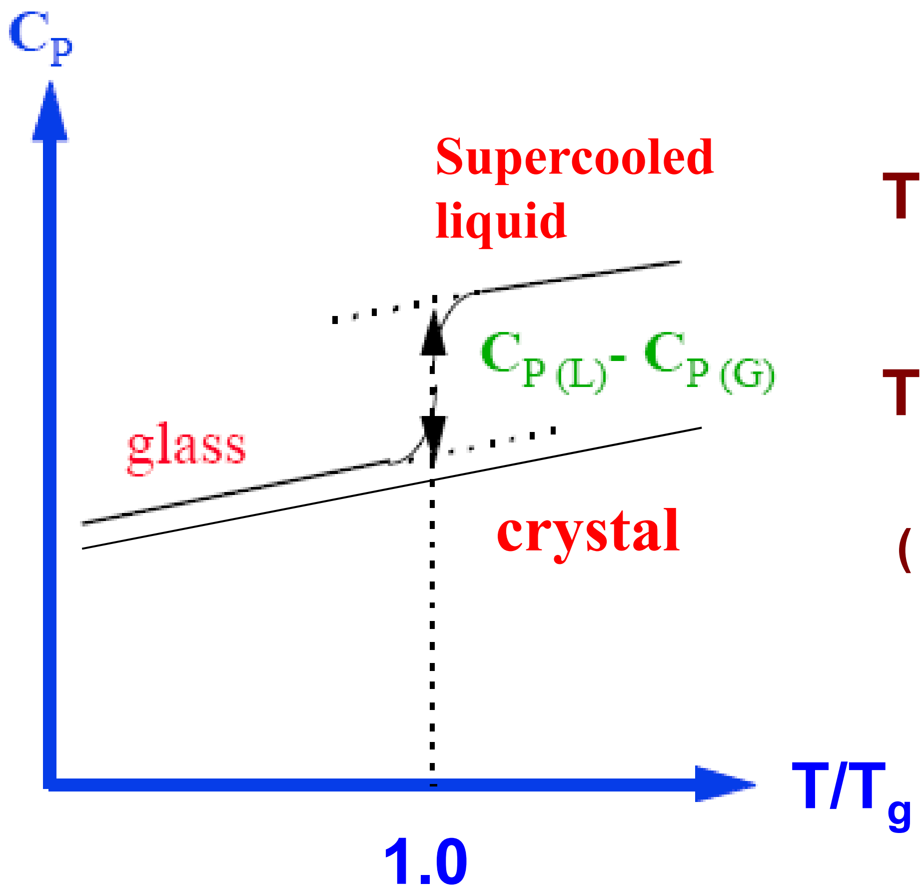
Theories for the glass transition

B. Entropy

$$\boxed{S = \int C_P \, d \ln T}$$

- ***Description of glass transition by entropy*** **(Kauzmann)**

1) Heat capacity → **dramatic change at T_g**



$T < T_g$ $\quad C_{P_{glass}} \approx C_{P_{crystal}}$

$T > T_g$ $\quad C_{P_{SCL}} > C_{P_{crystal}}$

(∵ high configurational degree of freedom in S.C.L.)

Theories for the glass transition

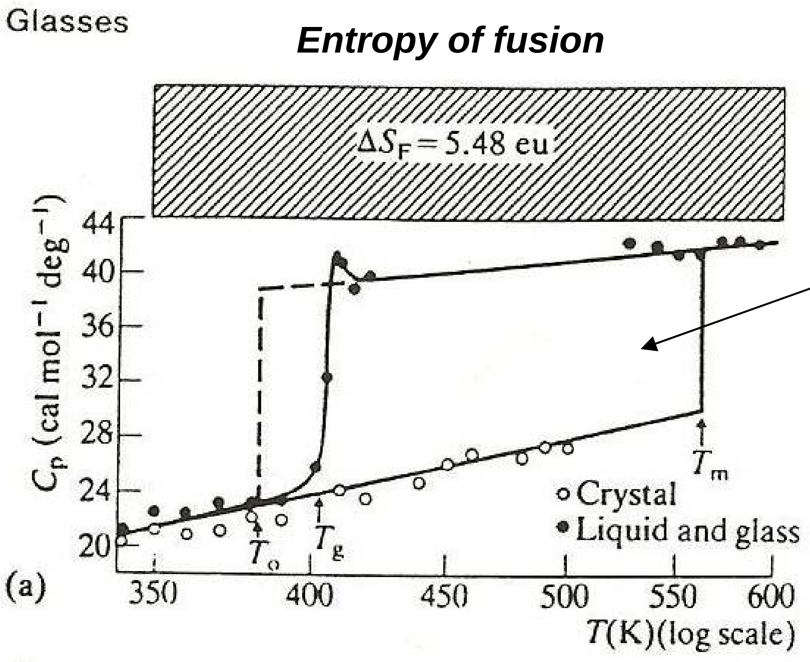
B. Entropy

- ***Description of glass transition by entropy* (Kauzmann)**

  2) The slow cooling rate, the lower T_g

  → **ideal glass transition temperature exist?**

  → **YES**



Entropy of fusion

$$\boxed{S = \int C_P \, d \ln T}$$

The data are plotted against in T so that integrated areas under the curves yield entropies directly, and the entropy of fusion is shown shaded in the upper part of the figure.

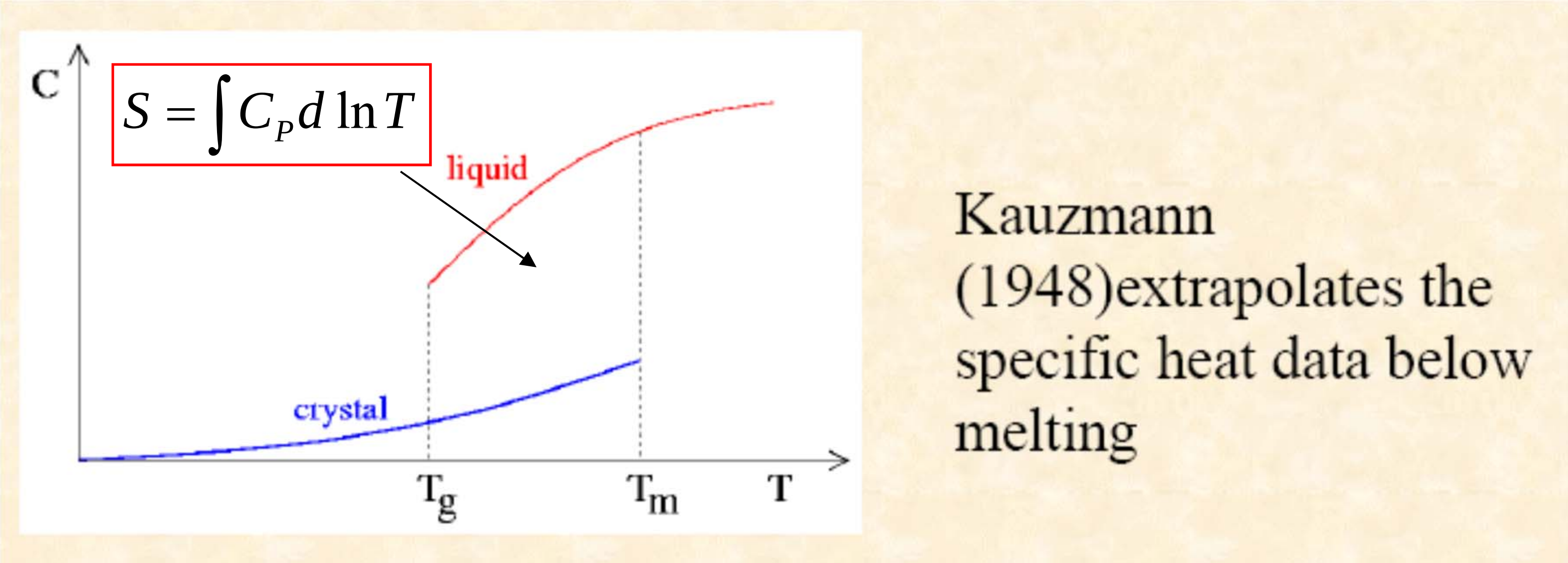
Heat capacities of glassy, liquid and crystalline phases of lithium acetate

Theories for the glass transition

B. Entropy

- ***Description of glass transition by entropy* (Kauzmann)**

Entropy of the liquid larger than in the crystal. Typically:



Kauzmann (1948)extrapolates the specific heat data below melting

$$S_\alpha(T_m) = S_\alpha(T) + \int_T^{T_m} \frac{C_\alpha}{T} \mathrm{dT} \quad \alpha \in \{liquid, crystal\}$$

$C_{liquid} > C_{crystal}$: ***entropy in the liquid decreases faster with T than in the crystal.***

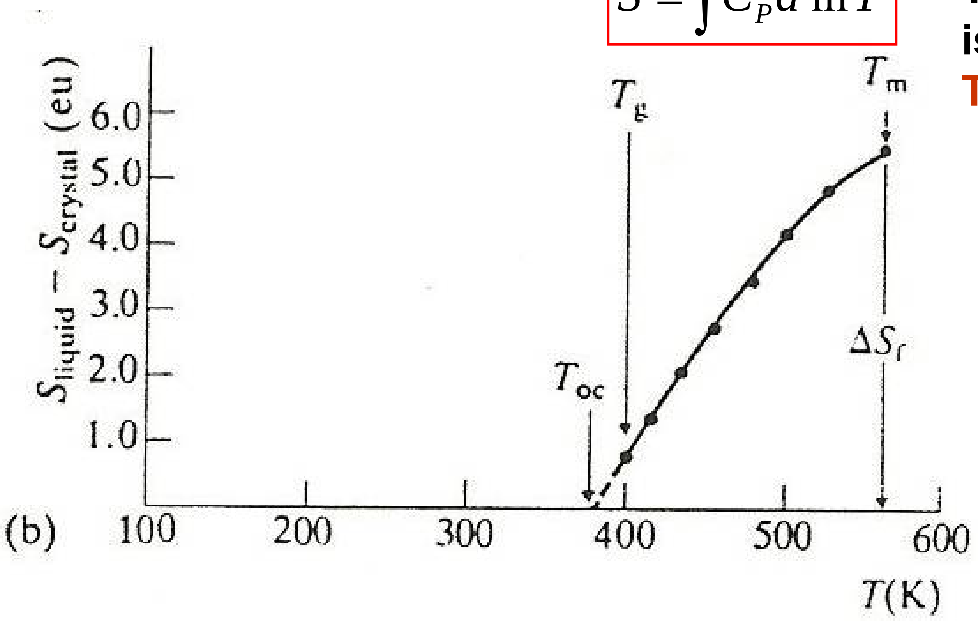
Theories for the glass transition

B. Entropy

- ***Description of glass transition by entropy* (Kauzmann)**

2) The slow cooling rate, the lower T_g

$$\boxed{S = \int C_P \, d \ln T}$$



The difference in entropy between liquid and crystalline phases as a function of temperature

The temperature vanishing excess entropy is termed the "ideal' glass transition temp. T_{oc} (Wong and Angell 1976)

$$T_g \rightarrow T_{0C} \quad as \quad \frac{dS}{dT} \rightarrow 0$$

If $T_g < T_{0C}$, $S_{liquid} < S_{crystal}$

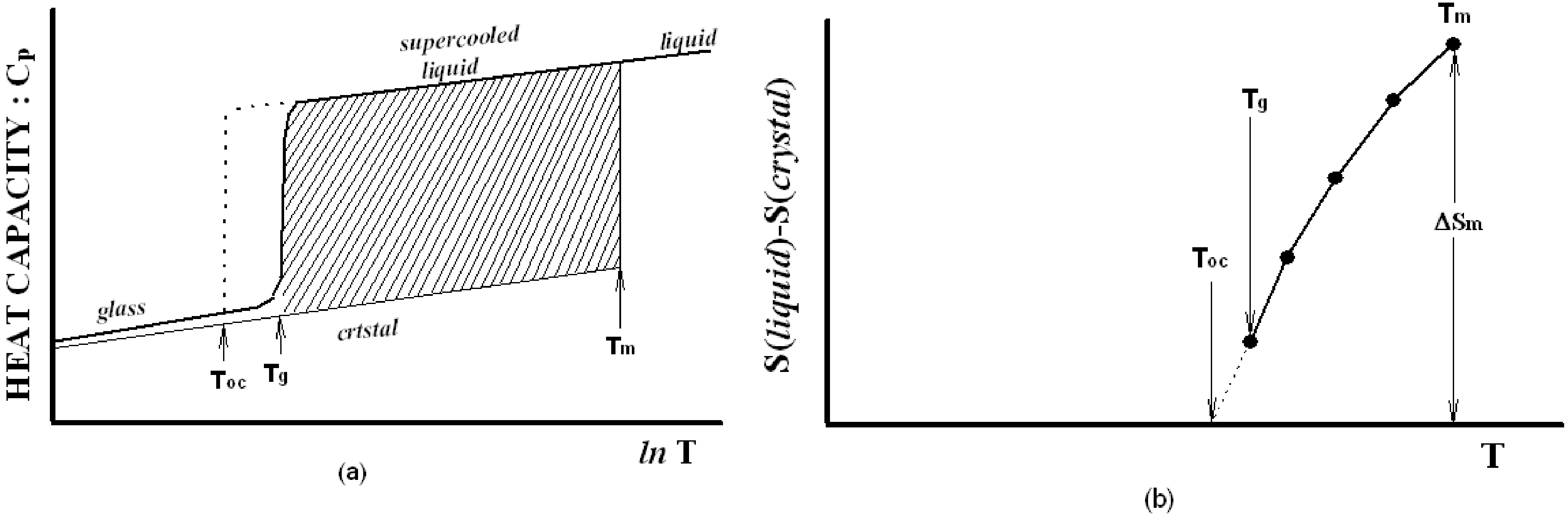
violating third law of thermodynamics

엔트로피의 기본적인 개념: 절대 영도에서 계는 반드시 최소의 에너지를 가지는 상태에만 존재

T_{OC}: lower temperature limit to occur glass transition thermodynamically

- **Ideal glass transition temperature ($T_{oc} = T_g^0$)**

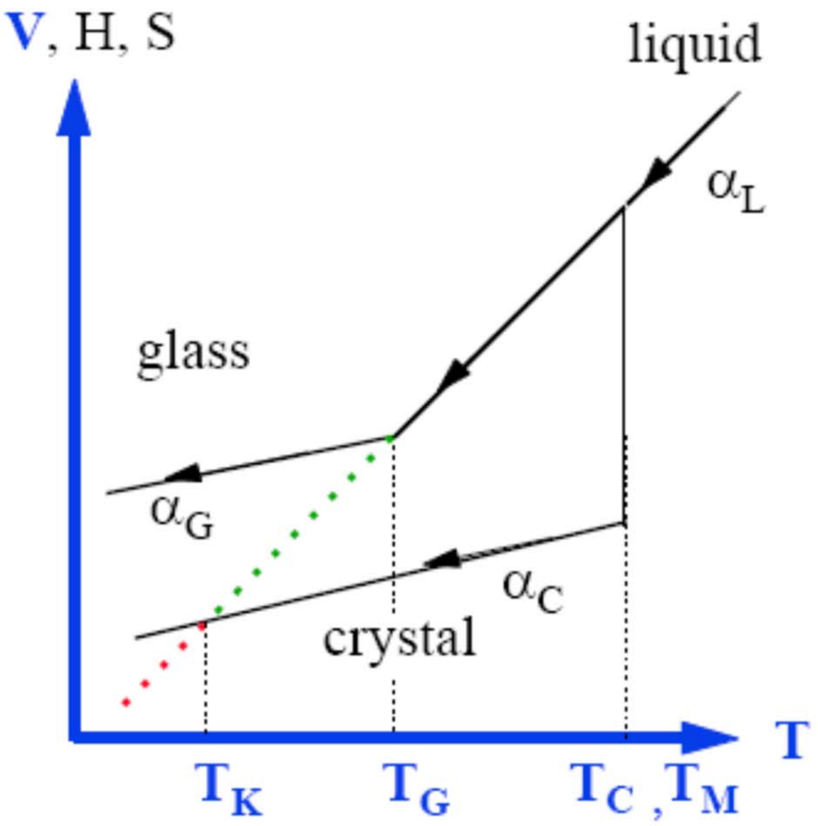
: lower temperature limit to occur glass transition thermodynamically



Variation of (a) C_p and (b) excess entropy, S depending on temp. for glass, crystal and liquid. Ideal glass transition temp, T_{oc}. is the temperature when excess entropy is disappeared.

Controversies in Amorphous Solids: The Kauzmann Paradox

If we extrapolate the specific volume of the liquid from above T_M to temperatures much below T_G, one must accept that at some temperature T_K well above 0 K, the specific volume, the enthalpy and the entropy of the equilibrium liquid would become lower than that of the crystal... Since the above statement is not possible (Kauzmann paradox) , two solutions are possible:

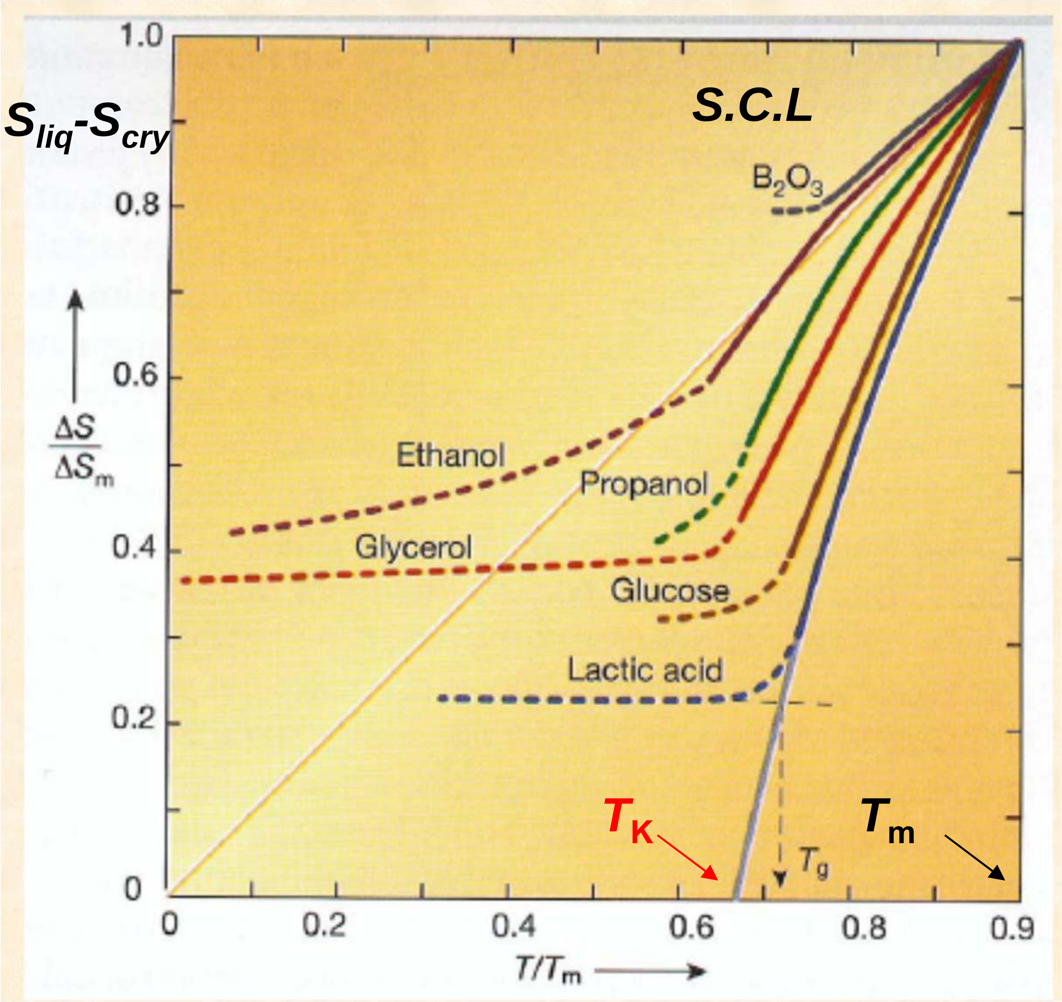


1) at some temperature (T_K), there is a true 2nd order phase tansition between the liquid and the glass or 2) the extrapolation to temperatures far below T_G is not valid. So far no one has found the answer !!

* Kauzmann's paradox

The configurational entropy apparently extrapolates to zero at low temperatures.

$$\boxed{S = S_{th} + \cancel{S_{config}}}$$



T_K defined by an extrapolation of equilibrium properties. Not really justified. If point defect with finite formation energy are present in a reference configuration, the extrapolation is incorrect (Stillinger).

→ Measurement of Kauzmann temp. is almost impossible.

(∵ very slow cooling rate → longer relaxation time → crystallization)

Homework :

2) Which glass has been reported as closest one to T_k?

3) How to make ideal glass?

Due date: 8 October 2019