2016 Spring

“Advanced Physical Metallurgy”

- Bulk Metallic Glasses -

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Q1: Theories for the glass transition

Theories for the glass transition

A. Thermodynamic phase transition

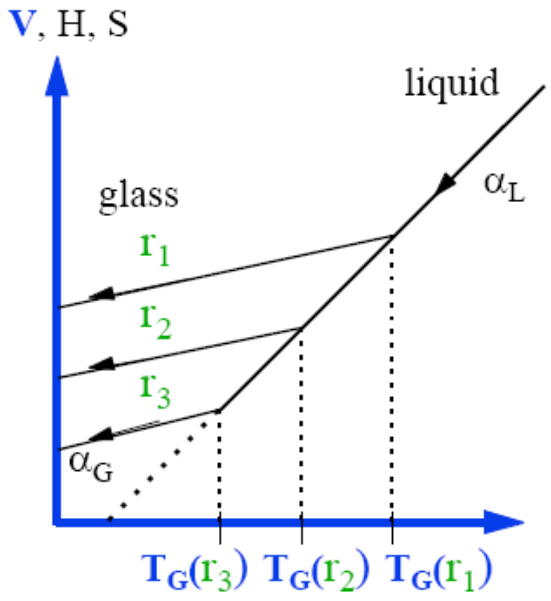
- ***Glass transition***

  H , V , S* : *continuous ***C_p α_T K_T* : *discontinuous***

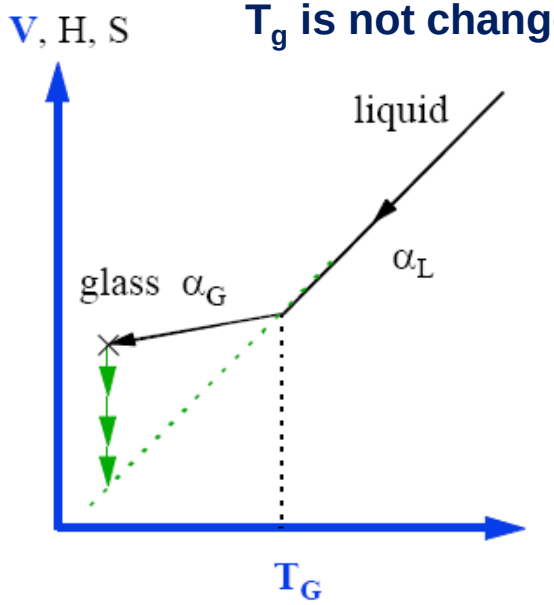
→ **by thermodynamic origin, 2nd order transition**

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

→ **If 2nd 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 $\left(\frac{\partial T}{\partial p}\right)_{V,N} = \left(\frac{\partial V}{\partial S}\right)_{T,N}$

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

$$\therefore \frac{dT_g}{dP} = \frac{\Delta\kappa_T}{\Delta\alpha_T} \quad \textbf{(2)}$$

measureable

→ **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

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

Additional consequence of the experimental verification,

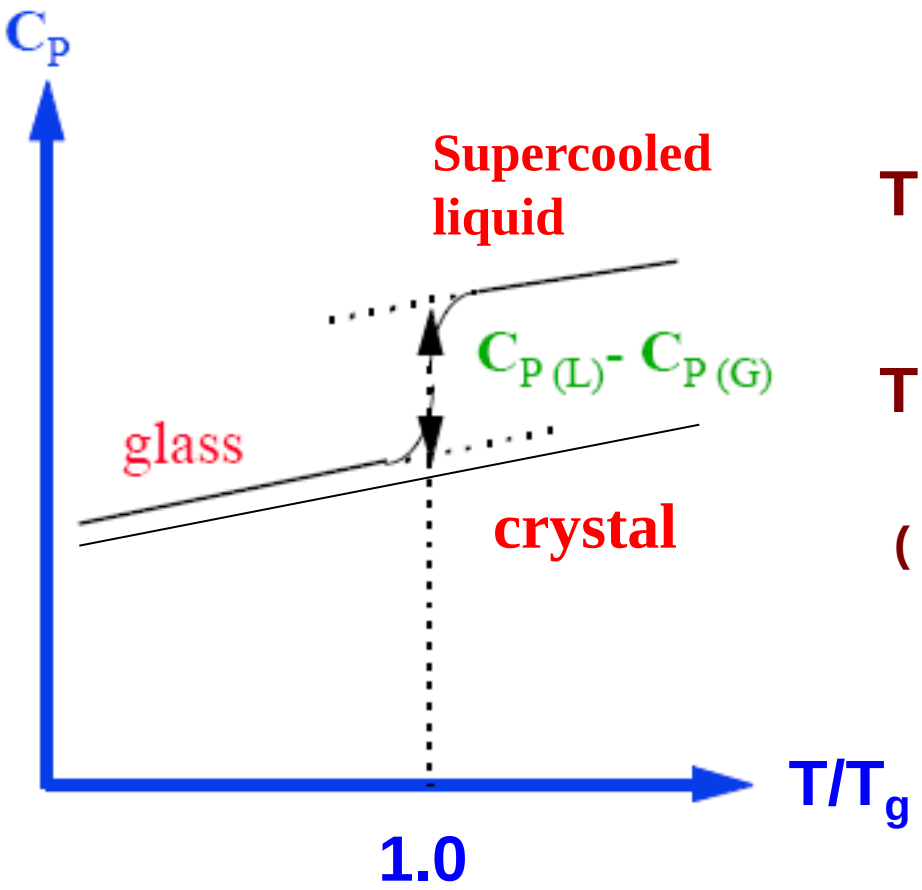
" Glasses prepared under high pressures have higher than normal densities but normal entropies or enthalpies. "

Theories for the glass transition

B. Entropy $S = \int C_P d \ln T$

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

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



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

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

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

Theories for the glass transition

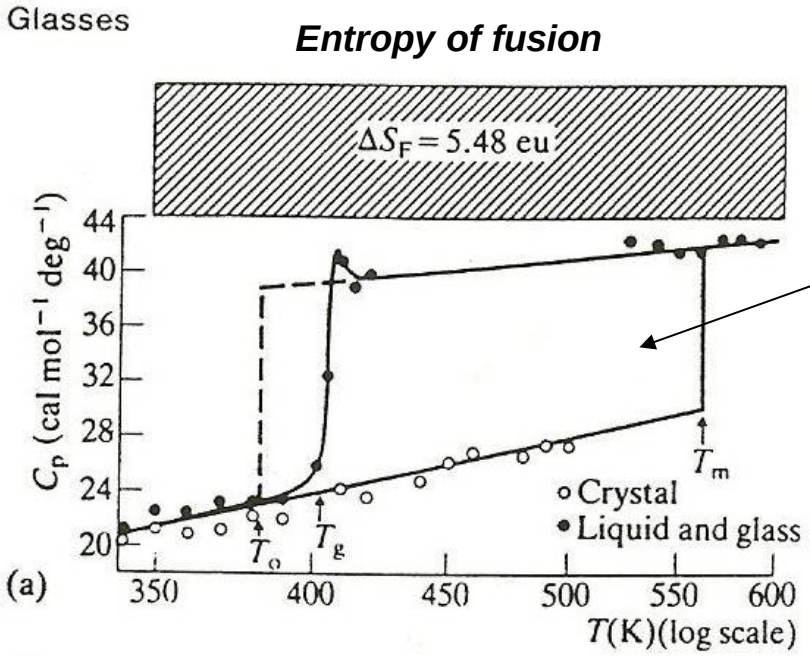
B. Entropy

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

2) The slow cooling rate, the lower T_g

→ **ideal glass transition temperature exist?**

→ **YES**



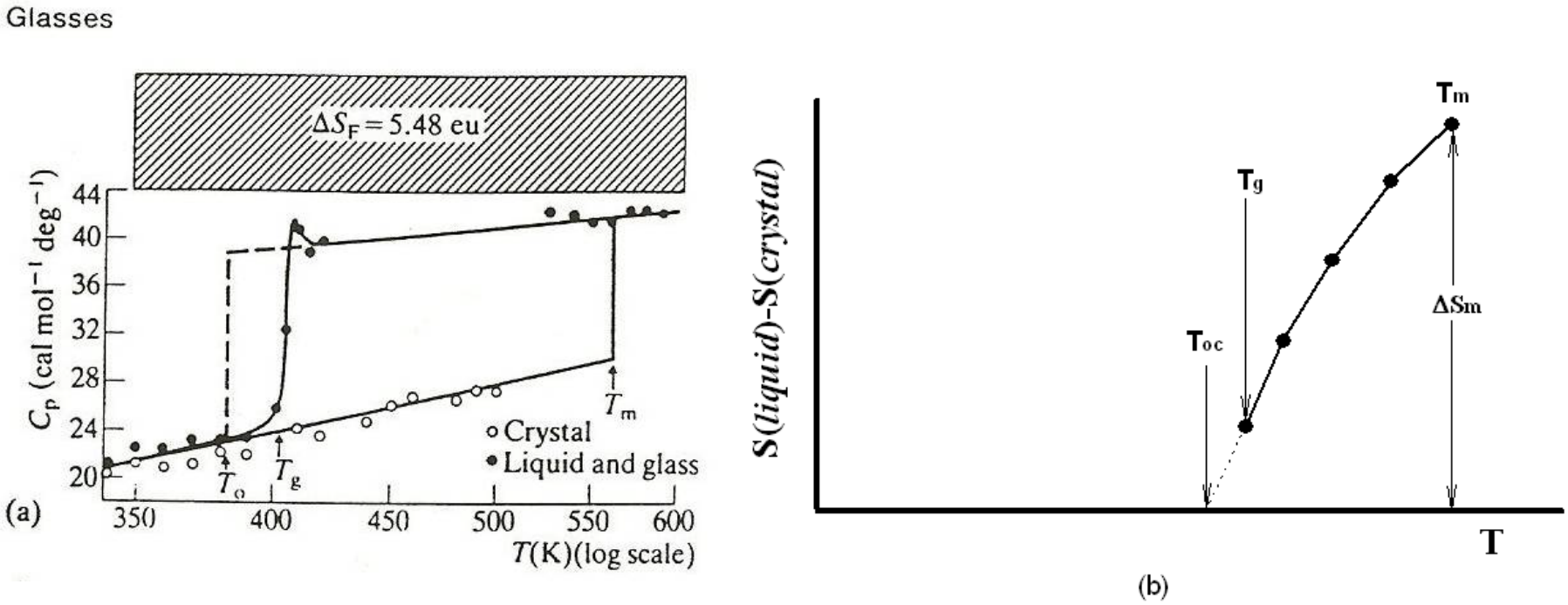
Heat capacities of glassy, liquid and crystalline phases of lithium acetate

$$S = \int C_P d \ln T$$

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.

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

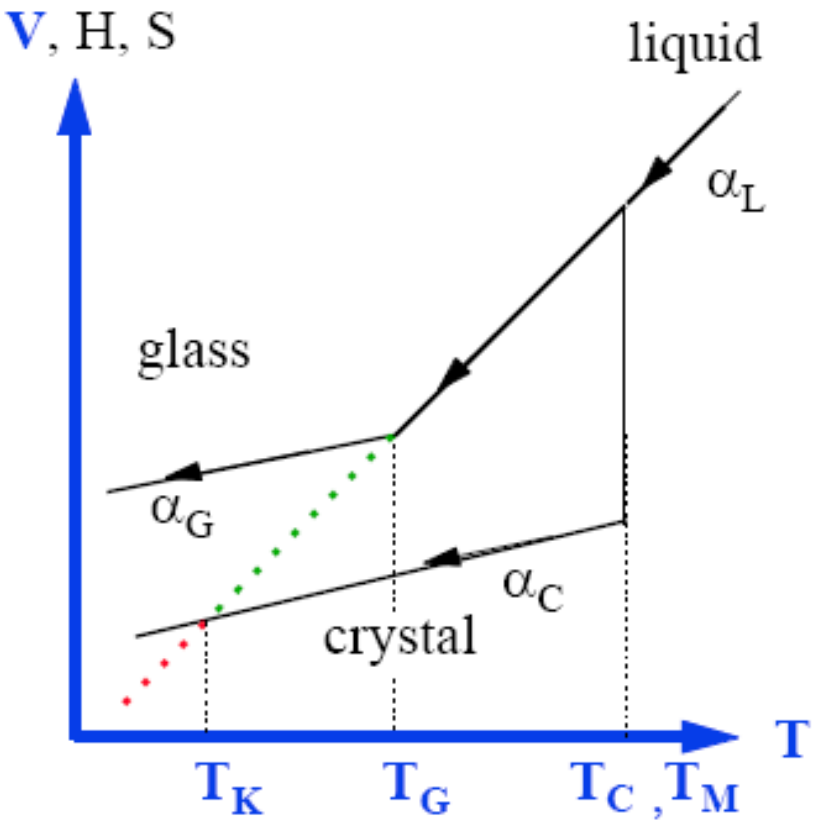
: lower temperature limit to occur glass transition thermodynamically



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

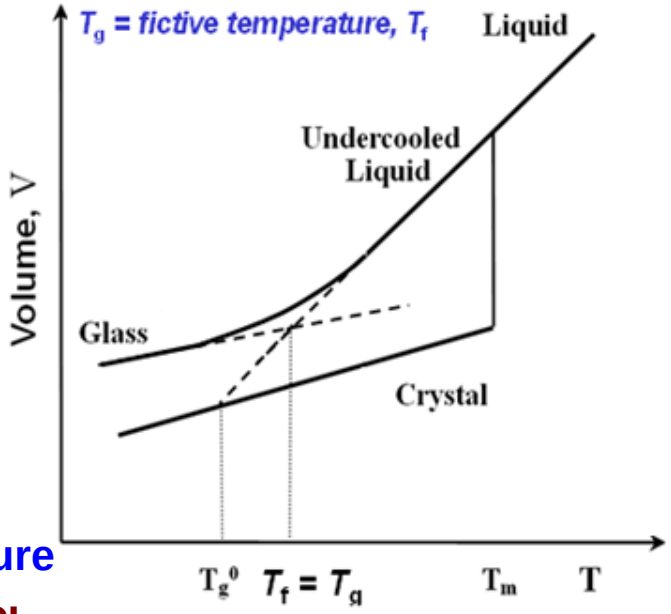
If we extrapolate the specific volume of the liquid from above T_M to temperatures much below T_G, one must accept that at some temperature T_K well above 0 K, the specific volume, the enthalpy and the entropy of the equilibrium liquid would become lower than that of the crystal... Since the above statement 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 !!

Theories for the glass transition

C. Relaxation behavior



At high temp. (SCL + Liquid)

Liquid is characterized by equilibrium amorphous structure metastable to crystalline in SCL.

Below glass transition: frozen-in liquid

→ **glass transition is observed when the experimental time scale (1) becomes comparable with the time scale for atom/molecule arrangement (2)**

→ **If (1) > (2) ➡ liquid // (1)~(2) ➡ glass transition// (1) < (2) ➡ glass**

(A concept of glass transition based on kinetic view point)

(property of liquid-like structure suddenly changes to that of solid-like structure)

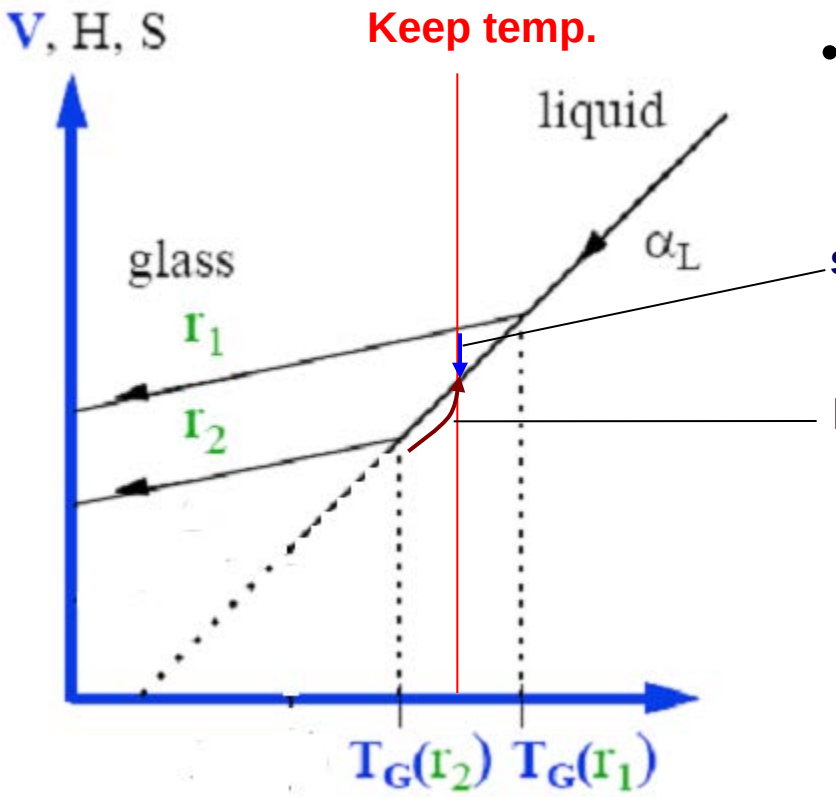
➡ **understanding of glass transition from viewpoints of relaxation**

C. Relaxation behavior

- **In glass transition region, properties change with time.**

* **Process of relaxation behavior: stabilization**

(equilibrium amorphous structure) ⟶ **closely related to glass property**

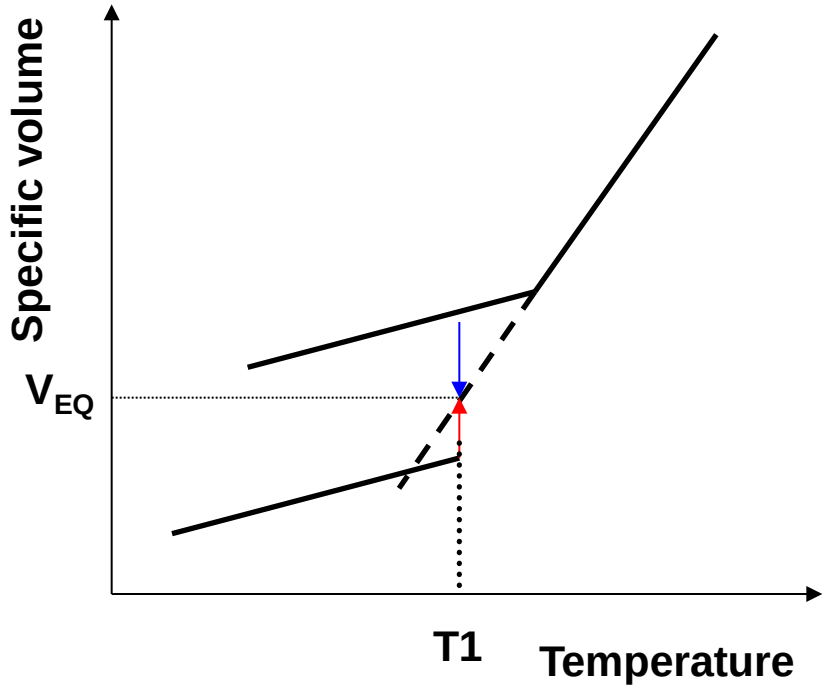


- **depending on cooling rate,**
  specific volume ⬆ **or** ⬇

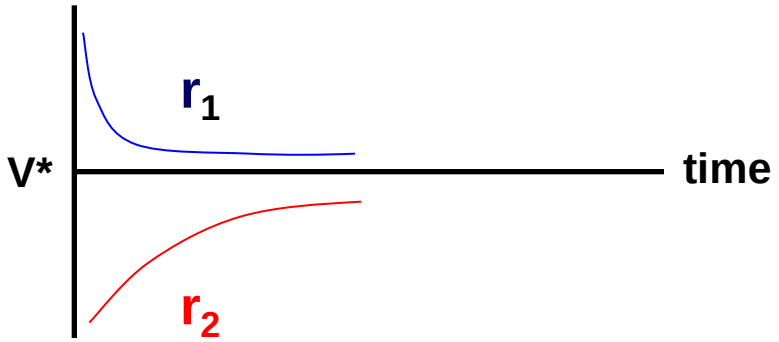
smaller volume

larger volume

Relaxation from initial volumes above and below the equilibrium volume



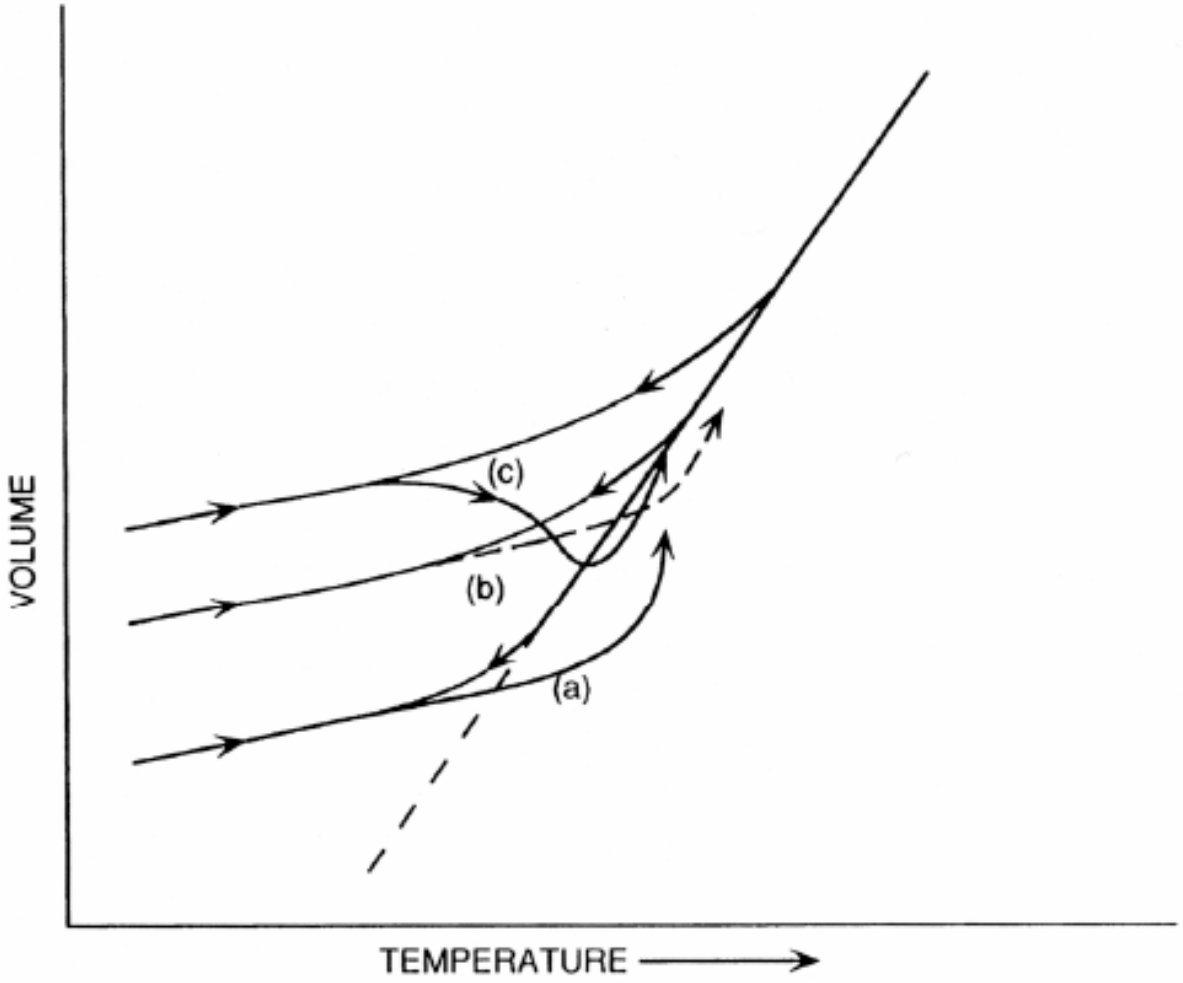
Variation of volume with time form initial volumes above and below the equil. volume



- **relaxation kinetics**

$r_1 > r_2$

Volume structural relaxation



(a) slow cool; fast reheat
(b) medium cool; medium reheat
(c) fast cool; slow reheat

Volume changes in glass upon varying cooling and reheating rates.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

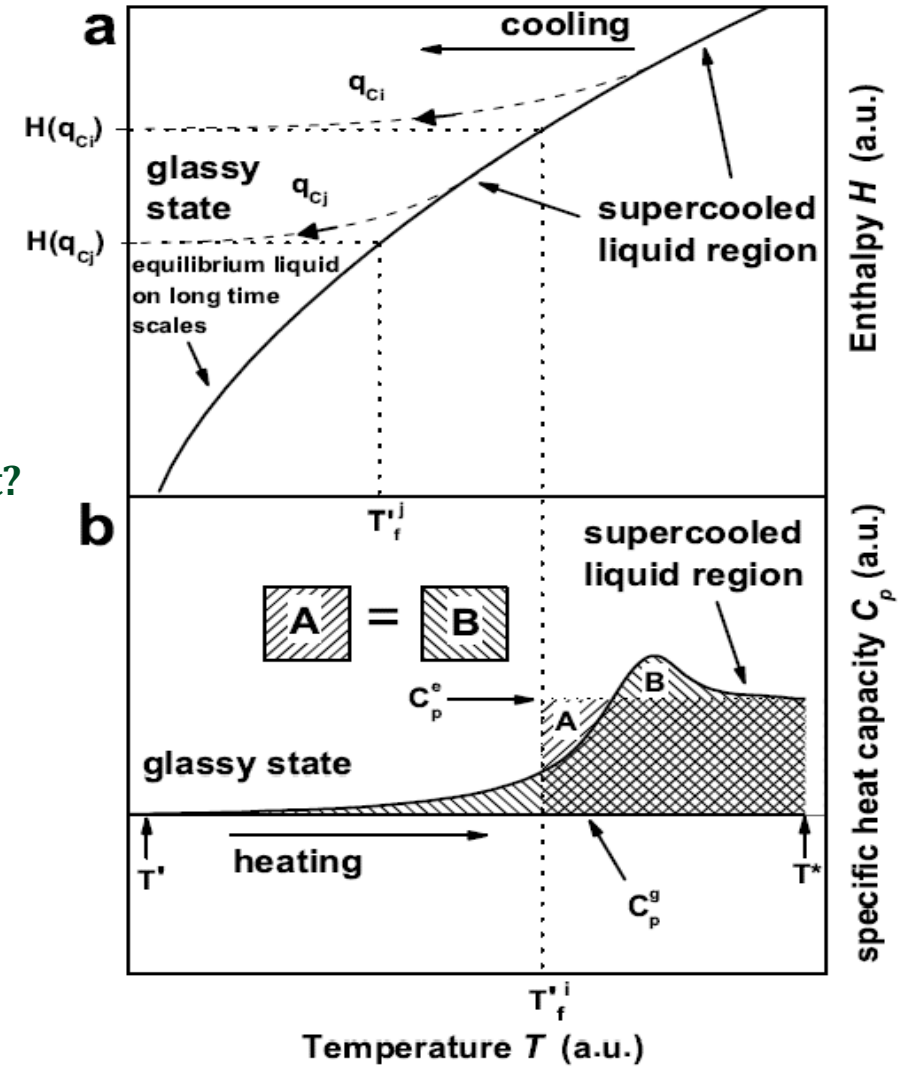
overshoot in heating process

When the kinetics become fast enough to allow the sample to regain metastable equilibrium

Heating rate dominant or cooling rate dominant?

Determined from DSC up-scan

$$\int_{T^*}^{T_f'} (C_p^e - C_p^g) dT_f = \int_{T^*}^{T'} (C_p - C_p^g) dT$$



J. Appl. Phys. 107, 123529 (2010)

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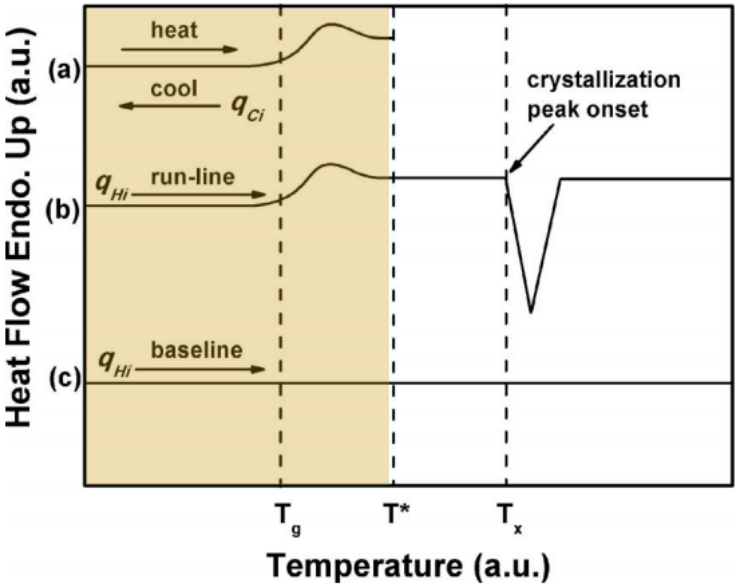
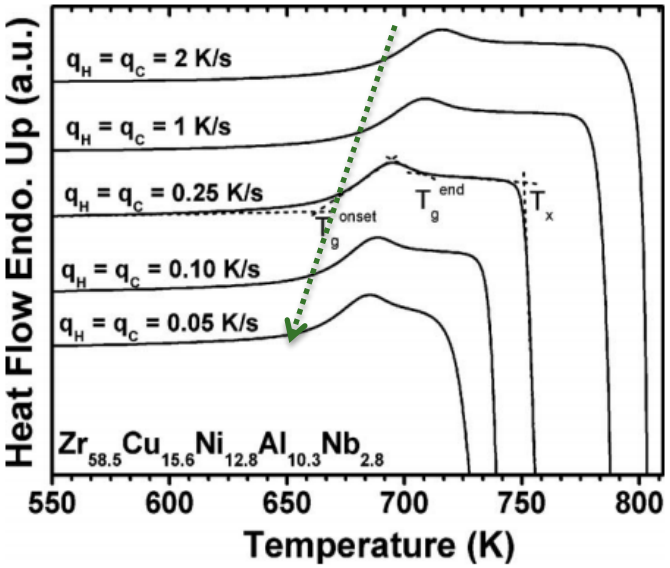
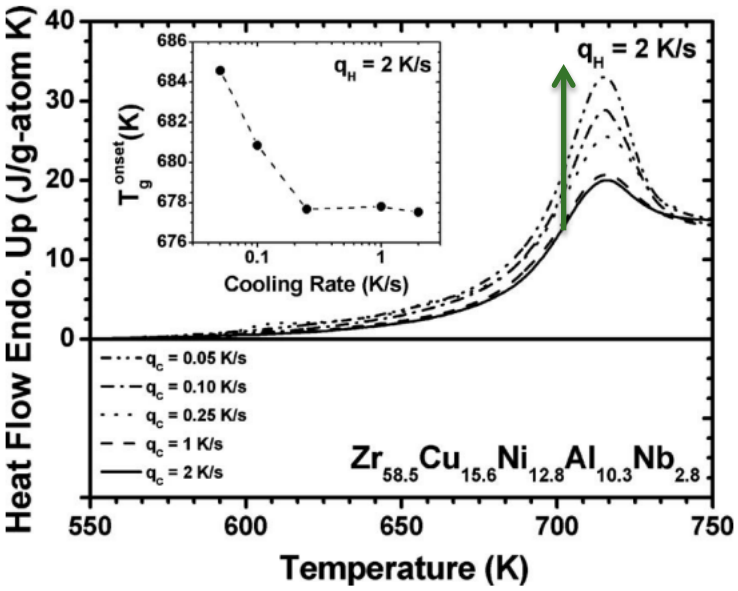
Heating and cooling rate controlled by DSC

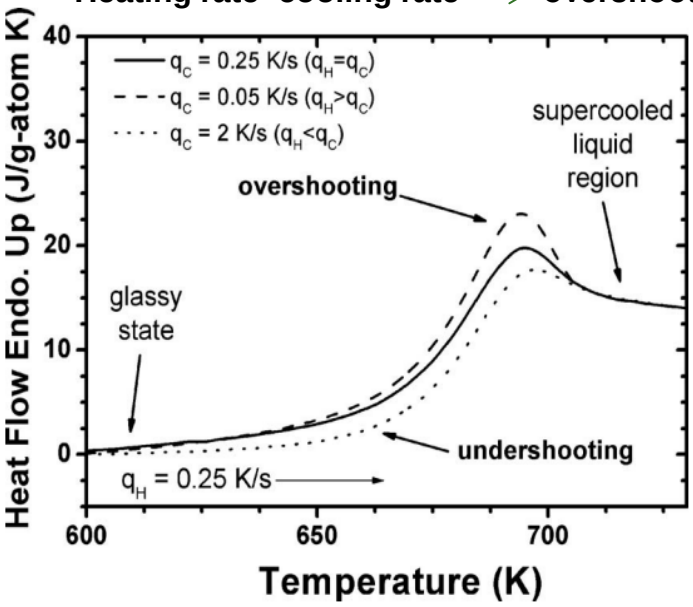




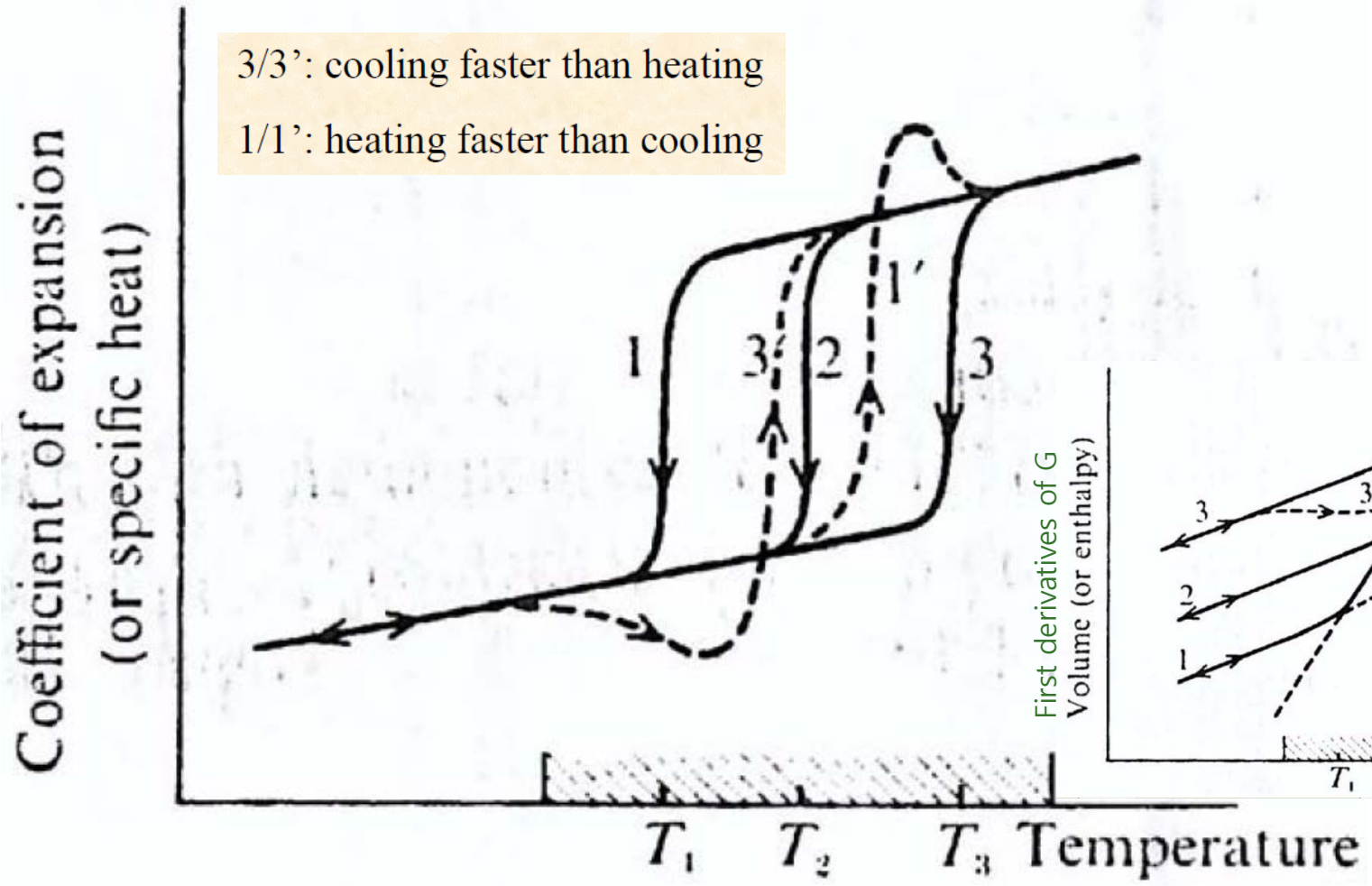
Heating rate>cooling rate → overshoot↑



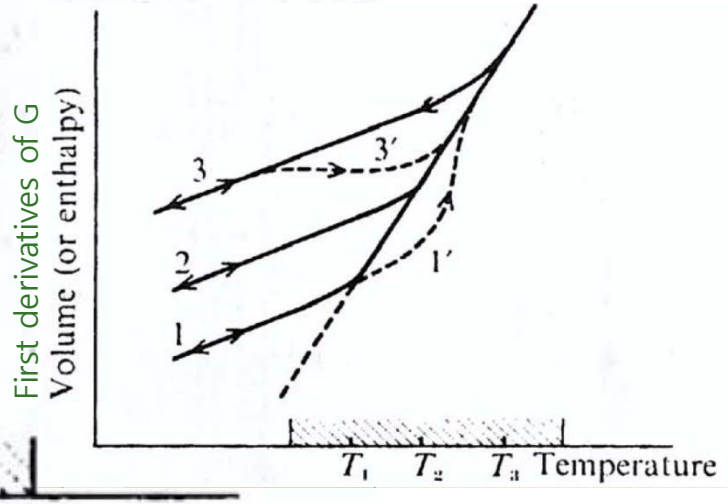
Heating rate constant



Complex relaxation effect in the transition region



Second derivatives of G

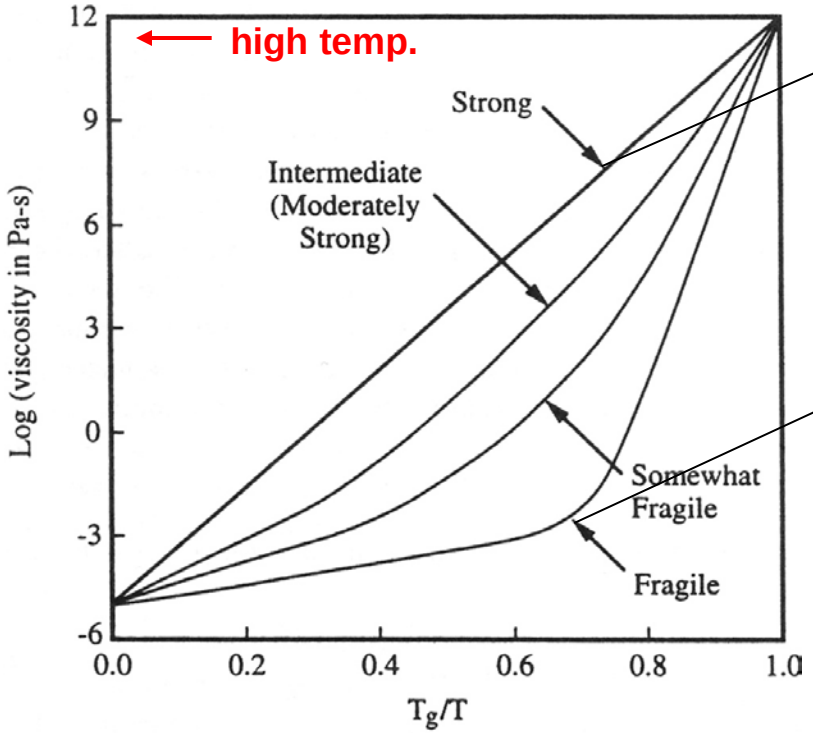


d. viscosity

*** Another definition of glass transition;**

- **Viscosity (10^{15} centiPoise= $10^{12\text{-}13}$ Pa s)**
- **most glass-forming liquid exhibit high viscosity.**
- **In glass transition region, viscosity suddenly changes.**

→ **Fragility concept: Strong vs Fragile**



Strong glass : Arrhenius behavior

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

→ **Oxide glass ex) SiO_2, GeO_2**

fragile glass : Vogel-Fulcher relation

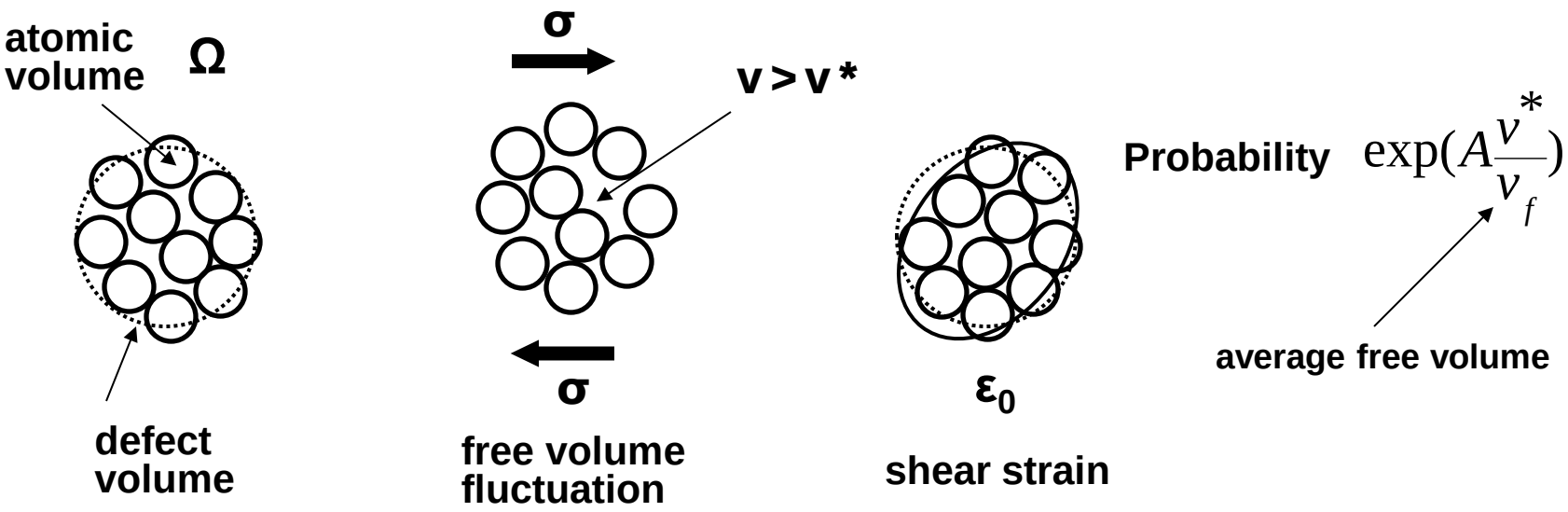
- deviation from simple Arrhenius behavior

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

→ **Ionic system, organic materials**

* Free volume model

Free volume → **excess volume originated from thermal expansion without phase change in liquid**



- **V*: activated volume for molecular movement → crucial role for flow**

➡ **Critical step in flow = opening of void of some critical volume for atoms to move by an applied stress or thermal activation**

➡ **redistribution of free volume = viscous flow** (Kinetic viewpoints)

Free volume - explanation of glass transition through free volume

- hard sphere model (thermal oscillation)

- Total volume: occupied by spheres (V_{occ})

  parts where atoms can move freely

  → permitting diffusion motion

  → free volume

- Transport of atom: voids over critical volume (by free vol. redistribution)

- As temp. decrease, V_f will decrease in liquid.

On the other hand,

- Free vol. in glass is relatively independent of temp. than that of liquid.

  → free volume → frozen-in (not happen to redistribution of free vol.)

Theories for the glass transition

A. Thermodynamic phase transition

- **Glass transition**

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

→ **by thermodynamic origin, 2nd order transition**

→ **In fact, it appears on some evidences that the glass transition is not a simple second-order phase transition.**

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

B. Entropy

- **Heat capacity** → **dramatic change at T_g**
- **Description of glass transition by entropy (Kauzmann)**

$$S = \int C_P d\ln T$$

→ **The slow cooling rate, the lower T_g** → **T_K or T_g^0**

→ **Measurement of Kauzmann temp. is almost impossible.**

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

Theories for the glass transition

C. Relaxation behavior

Below glass transition: frozen-in liquid

→ glass transition is observed when the experimental time scale (1)

becomes comparable with the time scale for atom/molecule arrangement (2)

→ If (1) > (2) ➡ liquid // (1)~(2) ➡ glass transition// (1) < (2) ➡ glass

(A concept of glass transition based on kinetic view point)

: property of liquid-like structure suddenly changes to that of solid-like structure

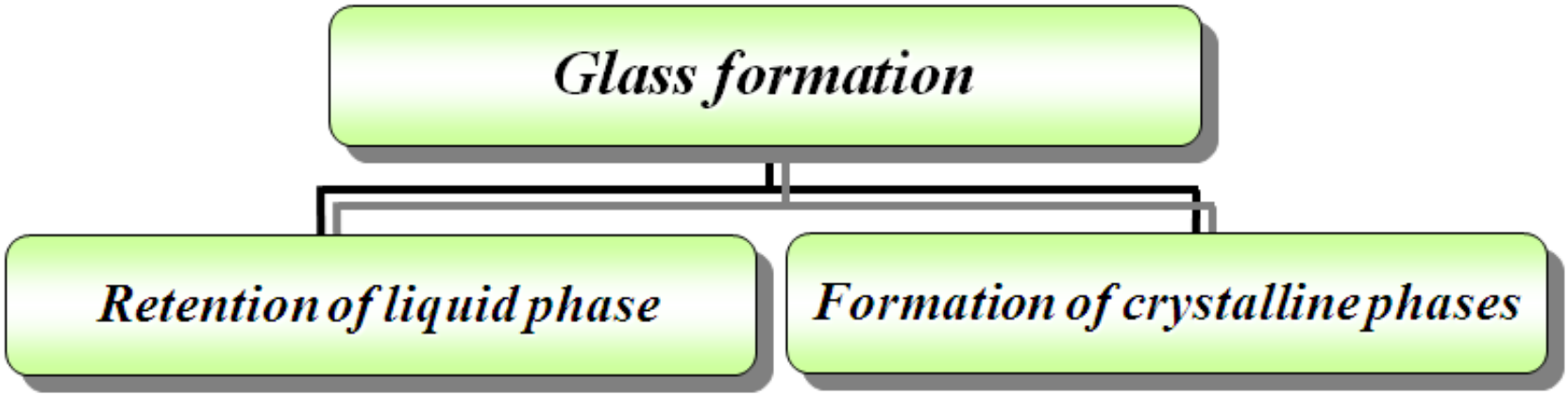
d. viscosity

- Viscosity (10^{15} centiPoise= $10^{12\text{-}13}$ Pa s) at T_g
- most glass forming liquid exhibit high viscosity.
- In glass transition region, viscosity suddenly changes. (fragile glass)

  → Fragility concept: Strong vs Fragile

- Viscous flow → Several atomistic model
  - absolute rate model
  - free volume model
  - excess entropy model

Q2: Glass formation



Glass Formation results when

Liquids are cooled to below T_m (T_L) sufficiently fast to avoid crystallization.

- **Nucleation** of crystalline seeds are avoided
- **Growth** of Nuclei into crystallites (crystals) is avoided

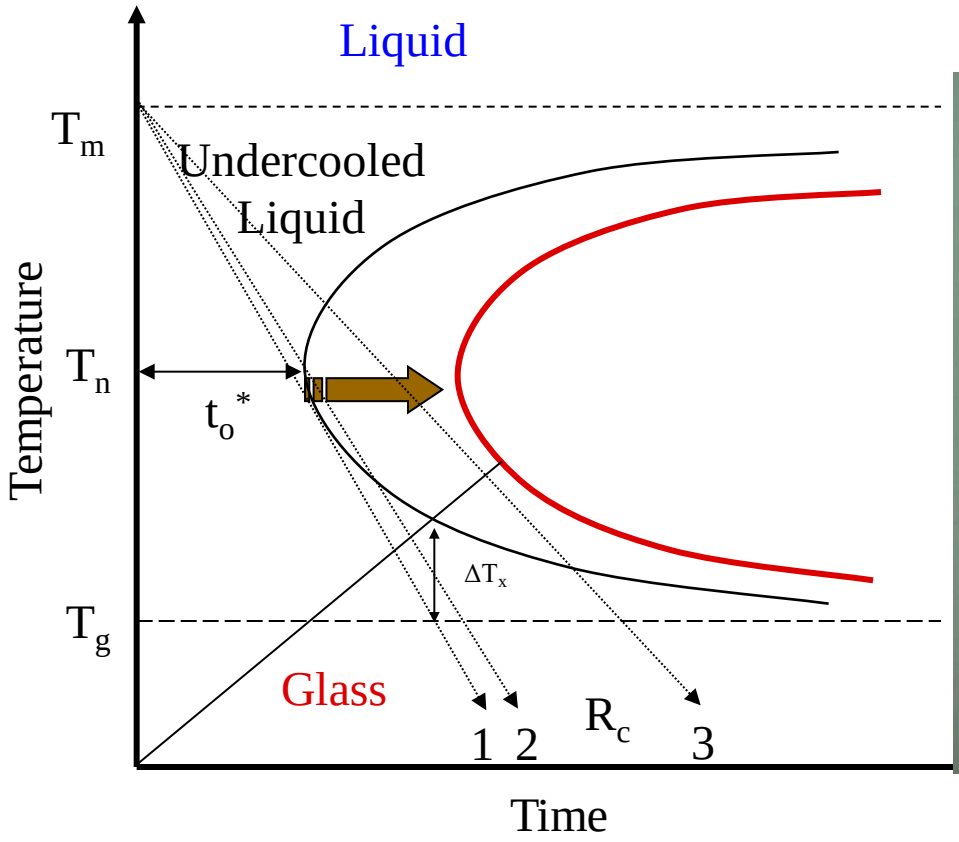
Liquid is "**frustrated**" by internal structure that hinders both events

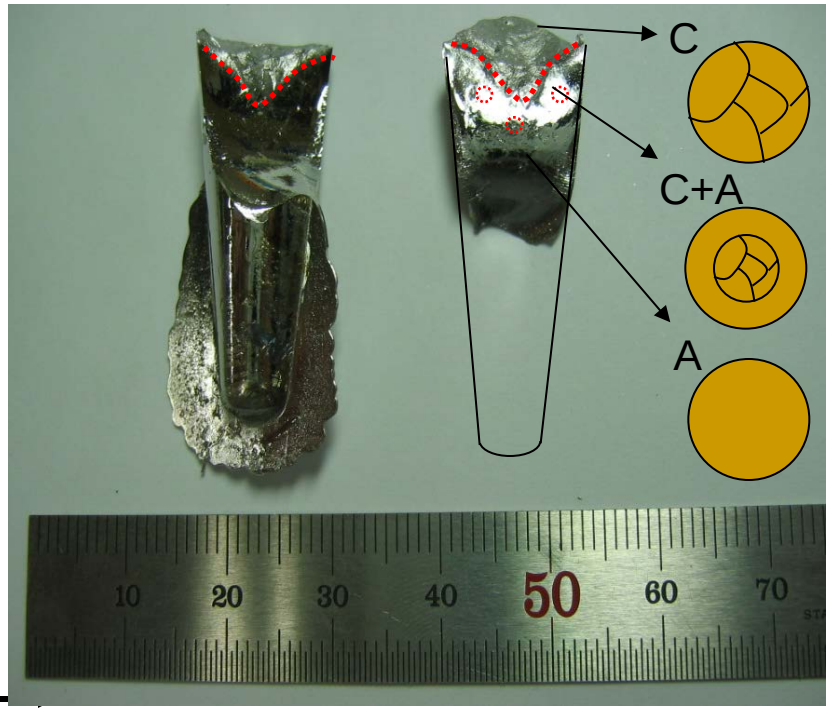
⇨ **Glass Formation**

Time Temperature Transformation diagram

Critical cooling rate

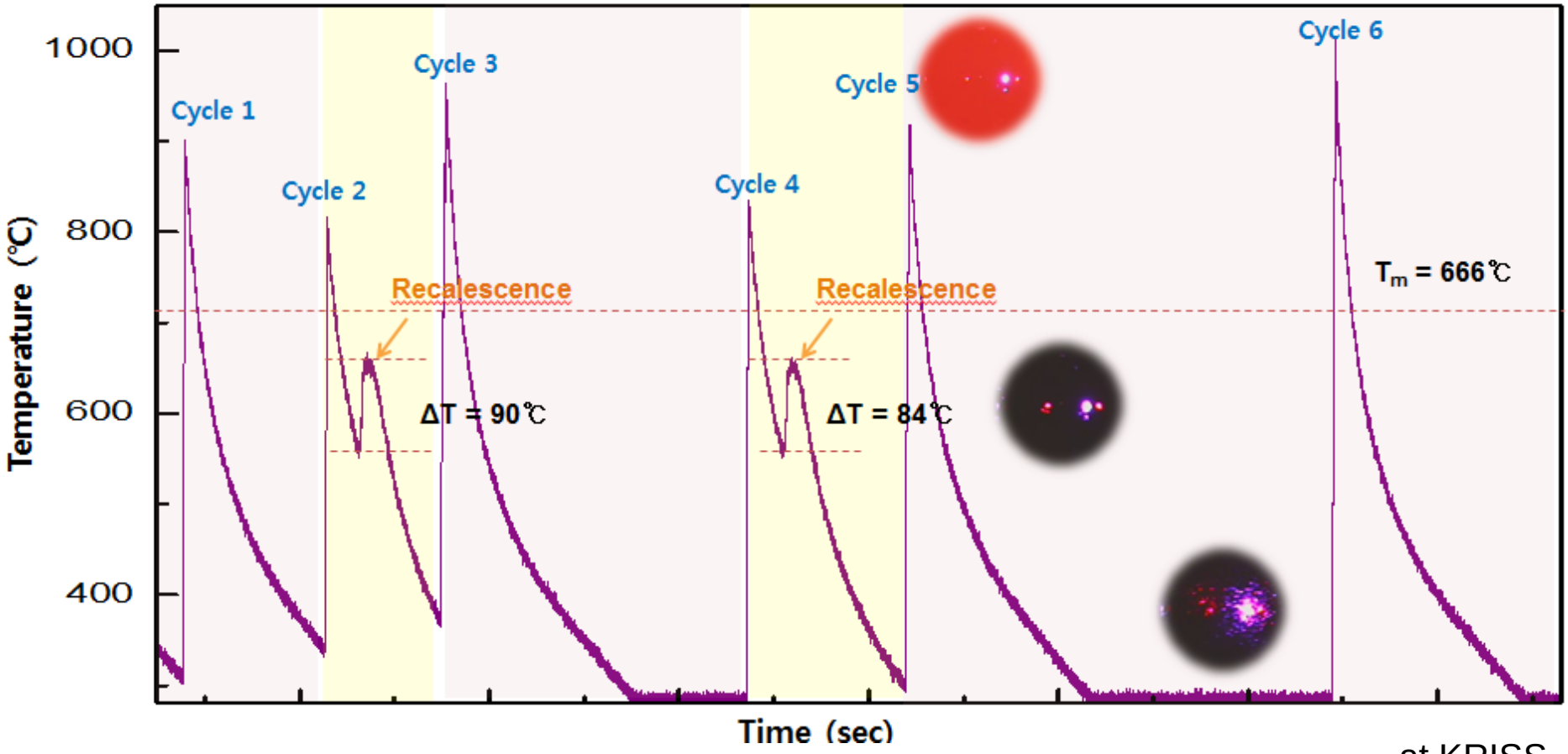
$$R_c = \frac{T_m - T_n}{t_o^*}$$



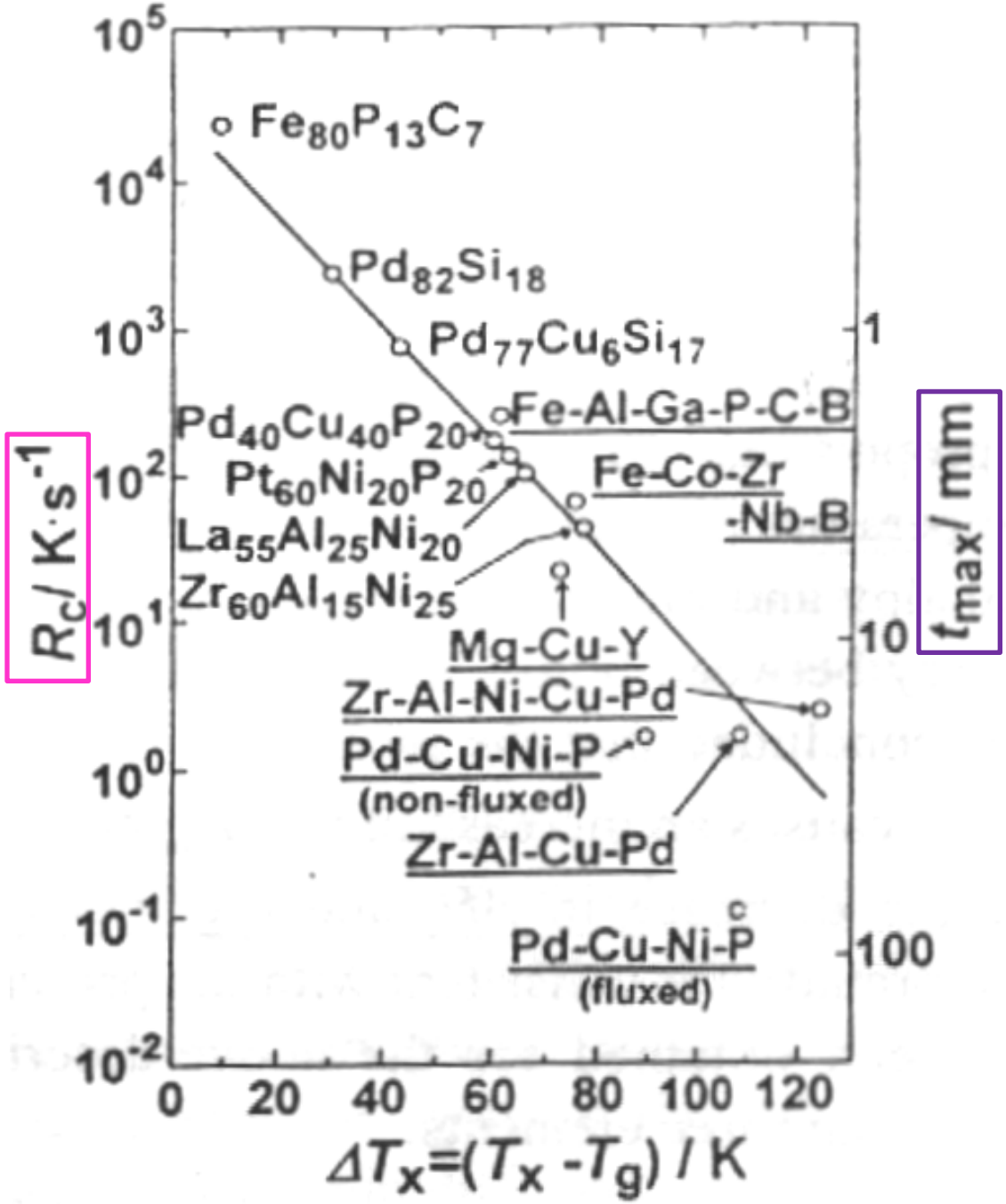


Critical cooling rate is inversely proportional to the diameter of ingot.

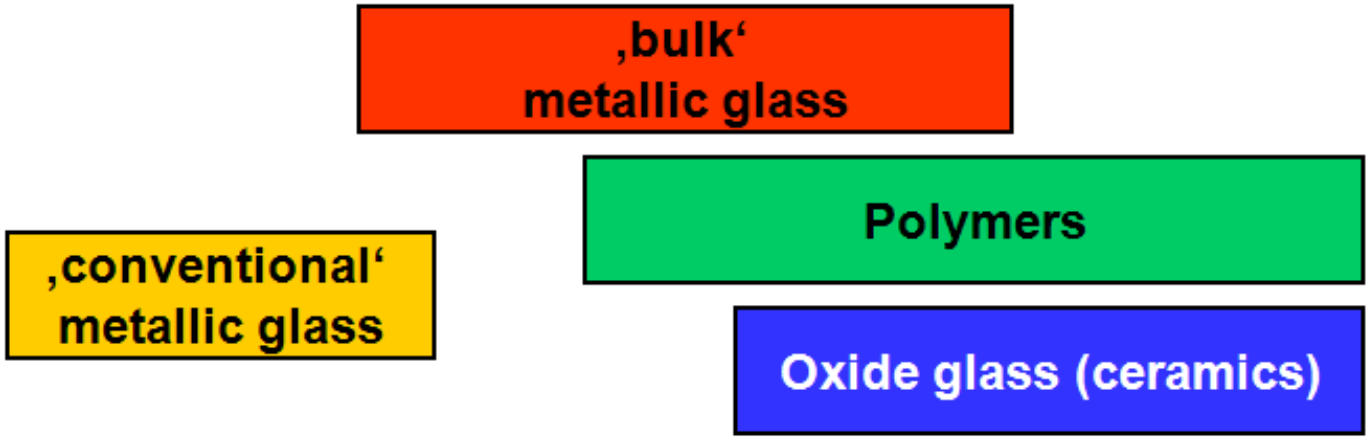
Electrostatic Levitation: cooling curve of Vitreloy 1 system

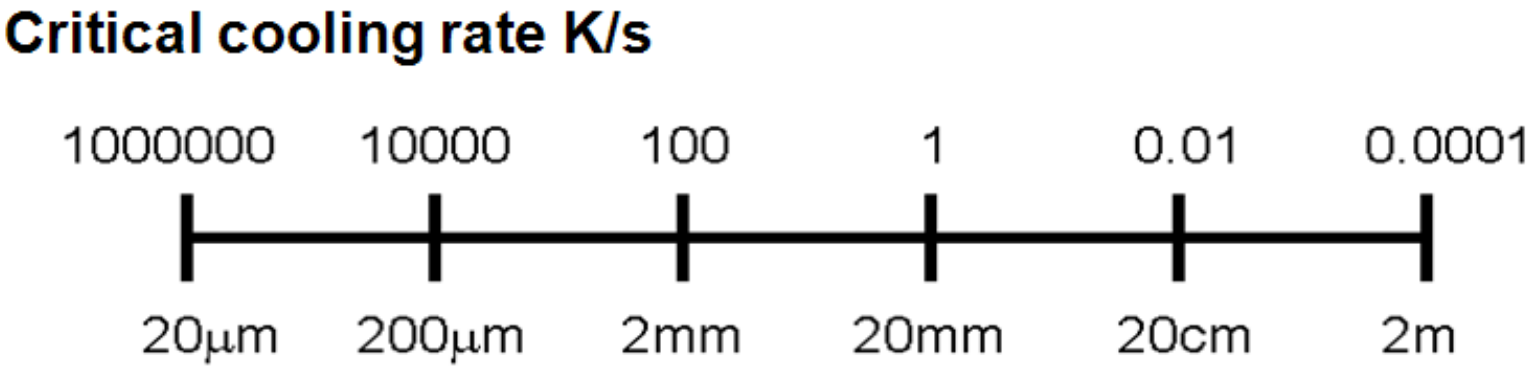


at KRISS


10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
R_c / K·s^{-1}
$Fe_{80}P_{13}C_7$
$Pd_{82}Si_{18}$
$Pd_{77}Cu_6Si_{17}$
$Pd_{40}Cu_{40}P_{20}$
$Pt_{60}Ni_{20}P_{20}$
$La_{55}Al_{25}Ni_{20}$
$Zr_{60}Al_{15}Ni_{25}$
Fe-Al-Ga-P-C-B
Fe-Co-Zr
-Nb-B
Mg-Cu-Y
Zr-Al-Ni-Cu-Pd
Pd-Cu-Ni-P
(non-fluxed)
Zr-Al-Cu-Pd
Pd-Cu-Ni-P
(fluxed)
1
10
100
t_{max} / mm
0
20
40
60
80
100
120
$\Delta T_x=(T_x - T_g)$ / K

Critical cooling rates and thicknesses for different materials





Critical Cooling Rates for Various Liquids

Table 3-5. Examples of Critical Cooling Rates (°C/s) for Glass Formation

Material	Homogeneous nucleation	Heterogeneous nucleation contact angle (deg)		
		100	60	40
SiO_2 glass[a]	9×10^{-6}	10^{-5}	8×10^{-3}	2×10^{-1}
GeO_2 glass[a]	3×10^{-3}	3×10^{3}	1	20
$Na_2O \cdot 2SiO_2$ glass[a]	6×10^{-3}	8×10^{-3}	10	$3 \times 10^{+2}$
Salol	10			
Water	10^{7}			
Ag	10^{10}			
Typical metal[a]	9×10^{8}	9×10^{9}	10^{10}	5×10^{10}

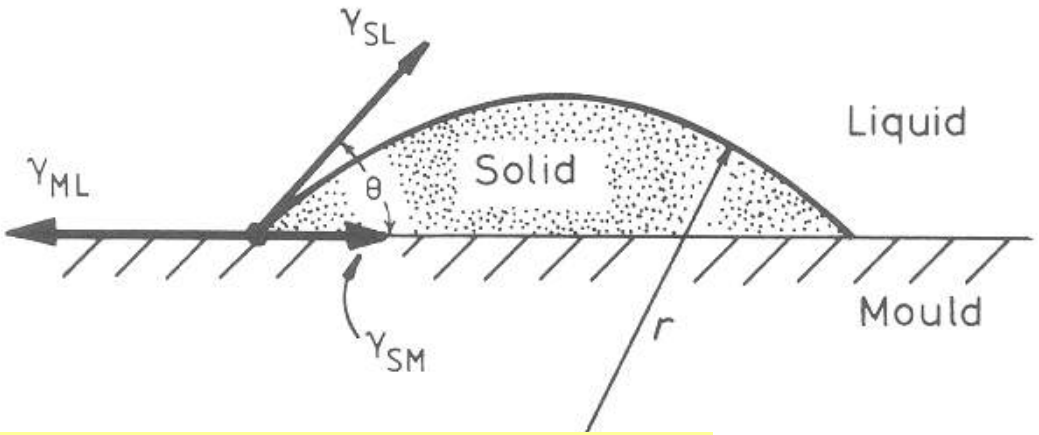
[a] After P. I. K. Onorato and D. R. Uhlmann, J. Non-Cryst. Sol., 22(2), 367–378 (1976).

4.1.3. Heterogeneous nucleation

From $$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

Nucleation becomes easy if $\gamma_{SL}\downarrow$ by forming nucleus from mould wall.

Fig. 4.7 Heterogeneous nucleation of spherical cap on a flat mould wall.



$$\gamma_{ML} = \gamma_{SL}\cos\theta + \gamma_{SM}$$

$$\cos\theta = (\gamma_{ML} - \gamma_{SM})/\gamma_{SL}$$

$$\Delta G_{het} = -V_S\Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML}$$

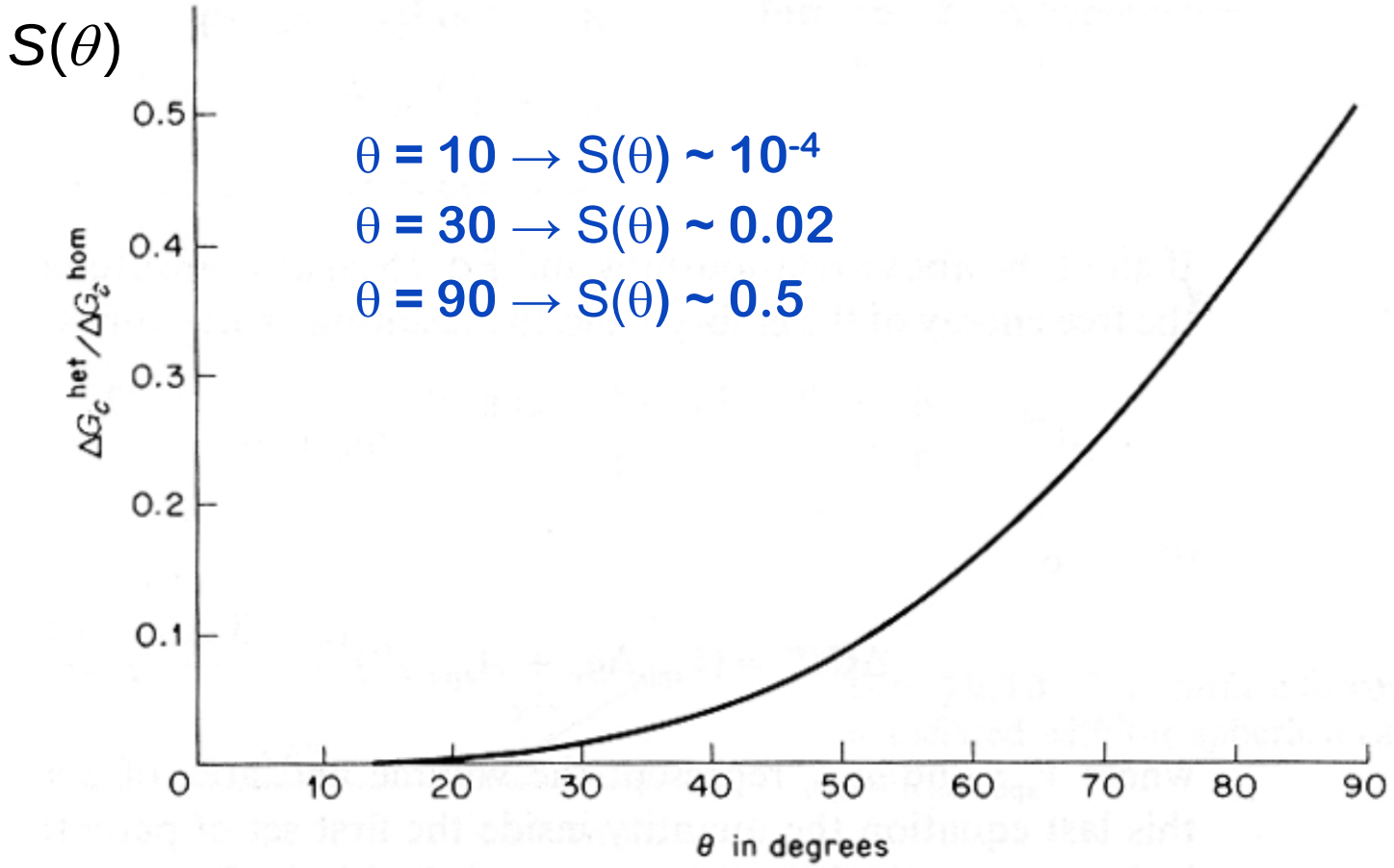
In terms of the wetting angle (θ) and the cap radius (r) (Exercies 4.6)

$$\Delta G_{het} = \left\{-\frac{4}{3}\pi r^3\Delta G_V + 4\pi r^2\gamma_{SL}\right\}S(\theta)$$

where $S(\theta) = (2+\cos\theta)(1-\cos\theta)^2/4$

S(θ) has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$\Delta G^*_{het} = S(\theta)\Delta G^*_{\text{hom}} \quad \Rightarrow \quad r^* = \frac{2\gamma_{SL}}{\Delta G_V} \quad and \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta)$$



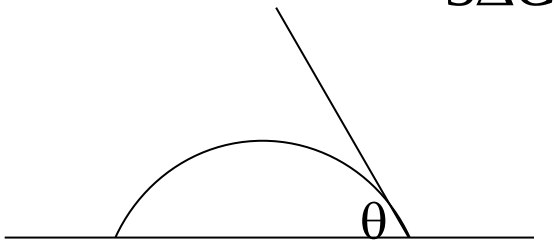
θ = 10 → S(θ) ~ 10^{-4}

θ = 30 → S(θ) ~ 0.02

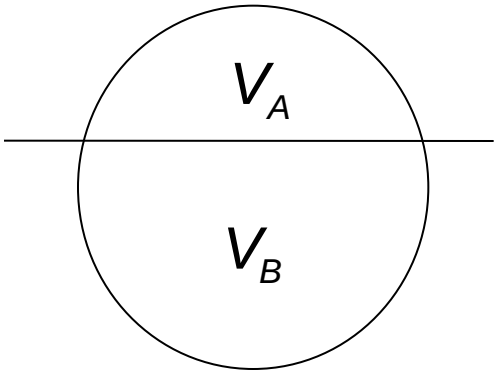
θ = 90 → S(θ) ~ 0.5

Barrier of Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot \frac{(2-3\cos\theta+\cos^3\theta)}{4}$$



$$\Delta G_{het}^* = S(\theta)\Delta G_{\text{hom}}^*$$



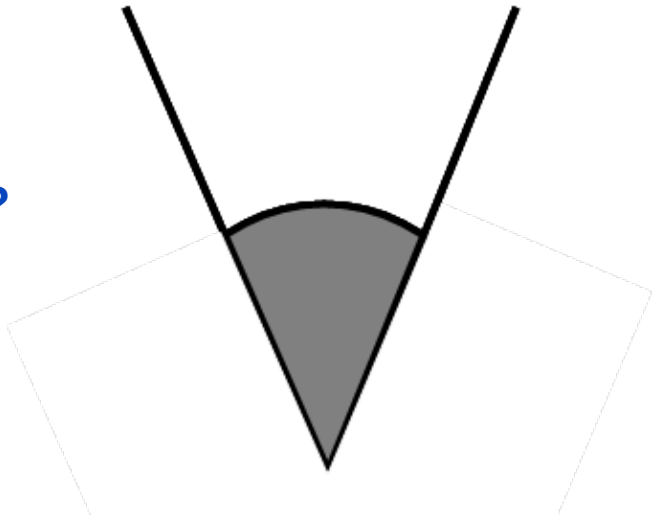
$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2-3\cos\theta+\cos^3\theta}{4} \right)$$

$$\frac{V_A}{V_A+V_B} = \frac{2-3\cos\theta+\cos^3\theta}{4} = S(\theta)$$

How about the nucleation at the crevice or at the edge?

Nucleation Barrier at the crevice

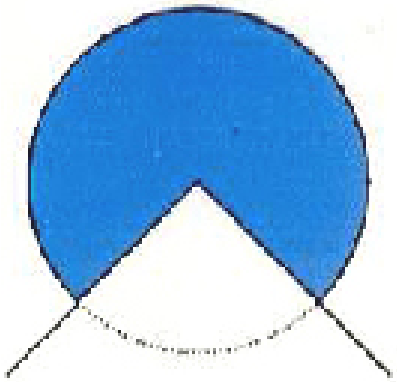
What would be the shape of nucleus and the nucleation barrier for the following conditions?



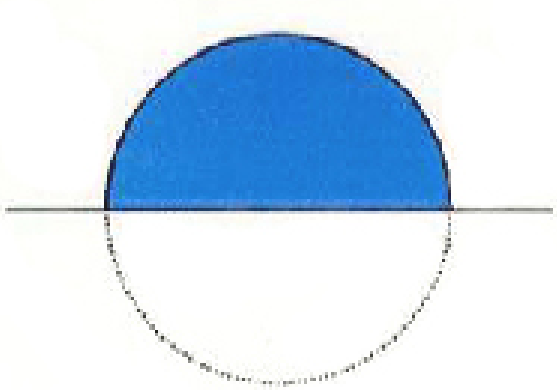
contact angle = 90

groove angle = 60

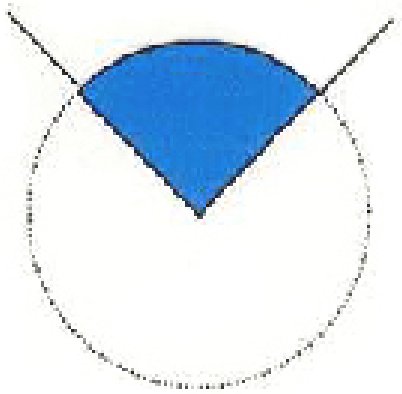
$$\frac{1}{6}\Delta G^{*}_{\text{homo}}$$



$$\frac{3}{4}\Delta G^{*}_{\text{homo}}$$

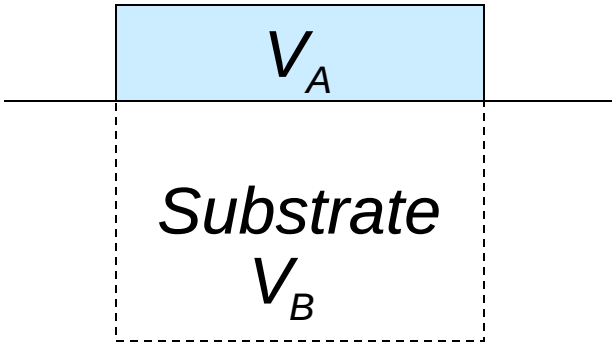


$$\frac{1}{2}\Delta G^{*}_{\text{homo}}$$

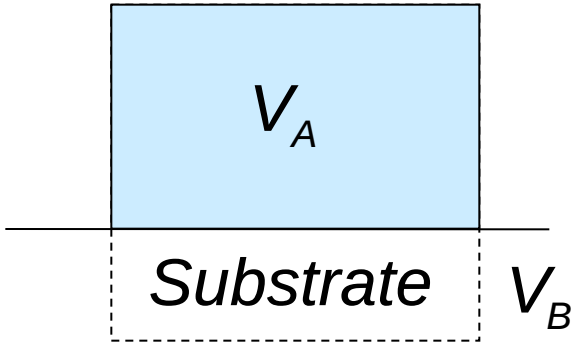


$$\frac{1}{4}\Delta G^{*}_{\text{homo}}$$

How do we treat the non-spherical shape?



Good Wetting



Bad Wetting

$$\Delta G^*_{sub} = \Delta G^*_{homo}\left(\frac{V_A}{V_A + V_B}\right)$$

Effect of good and bad wetting on substrate