2018 Spring

“Advanced Physical Metallurgy”

- Bulk Metallic Glasses -

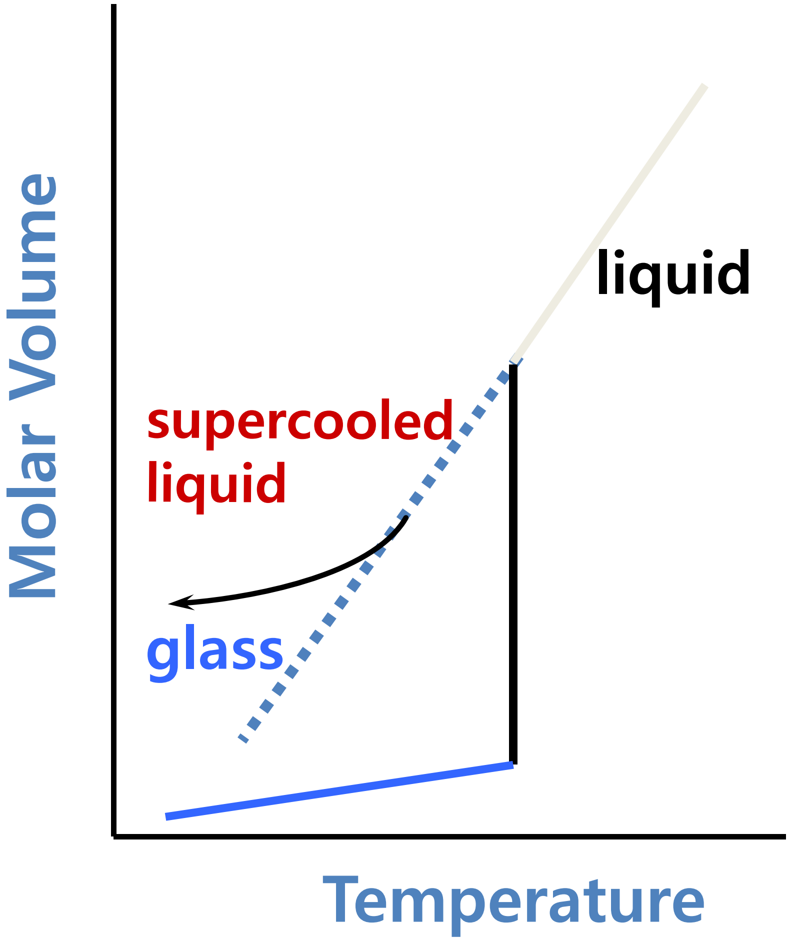
04.02.2018

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

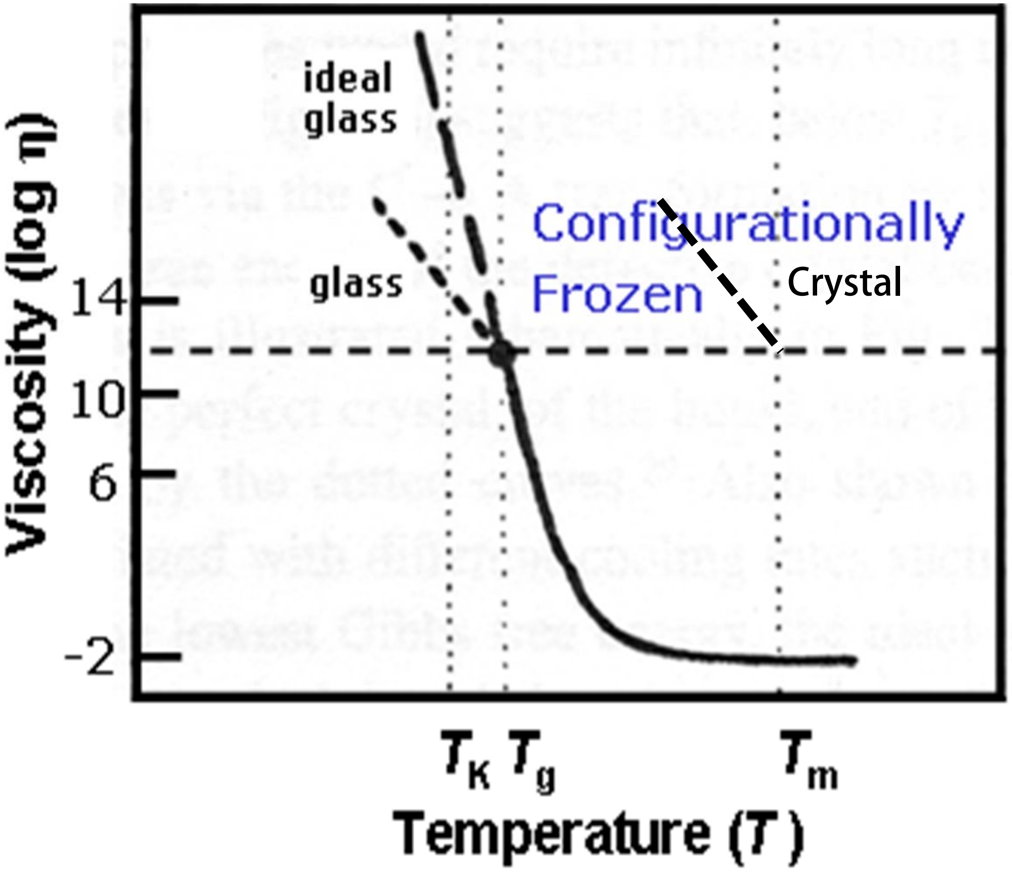
Glass Formation is Controlled by Kinetics

- Glass-forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a "high viscosity" that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- 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



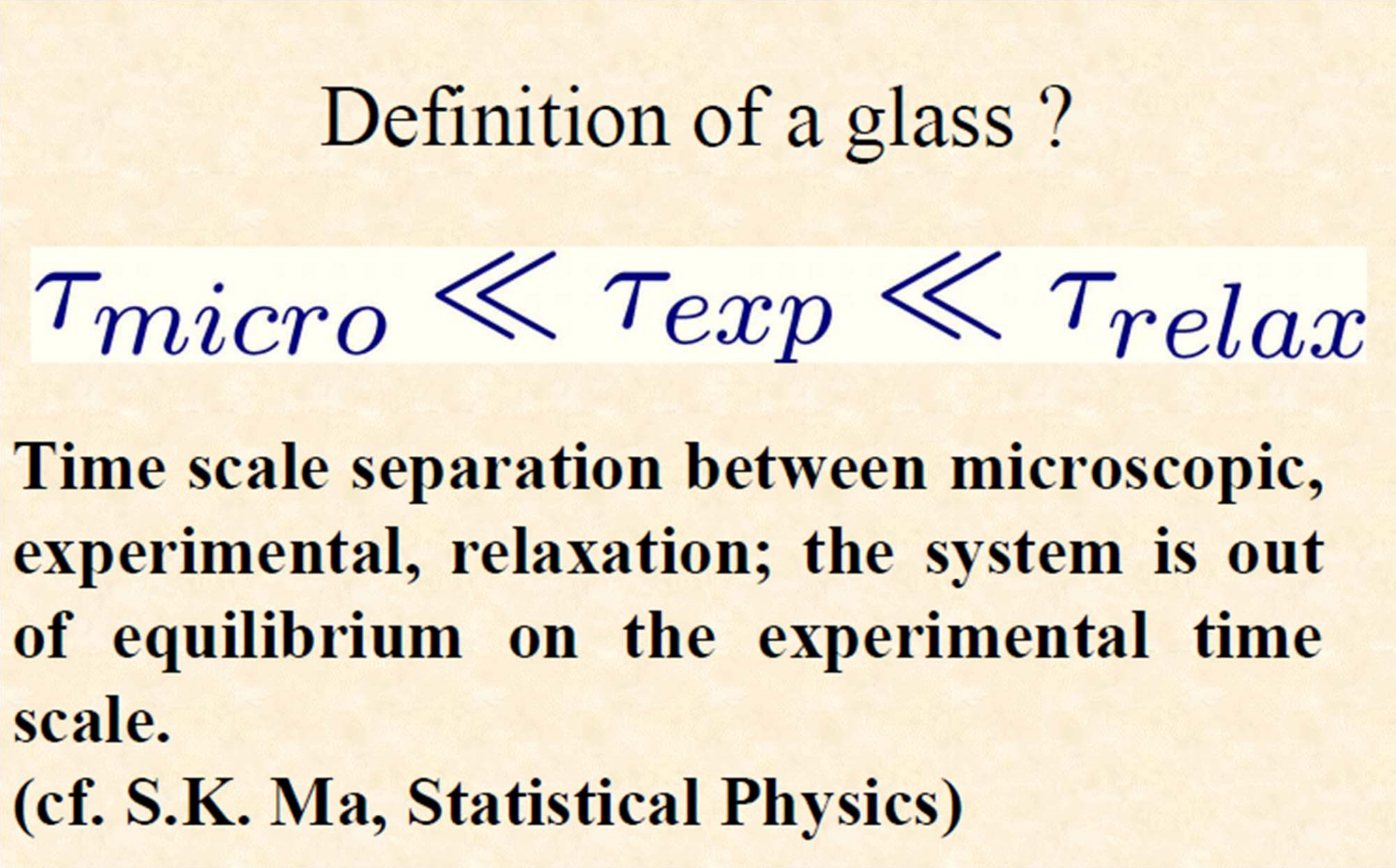
Glass : undercooled liquid with high viscosity

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*



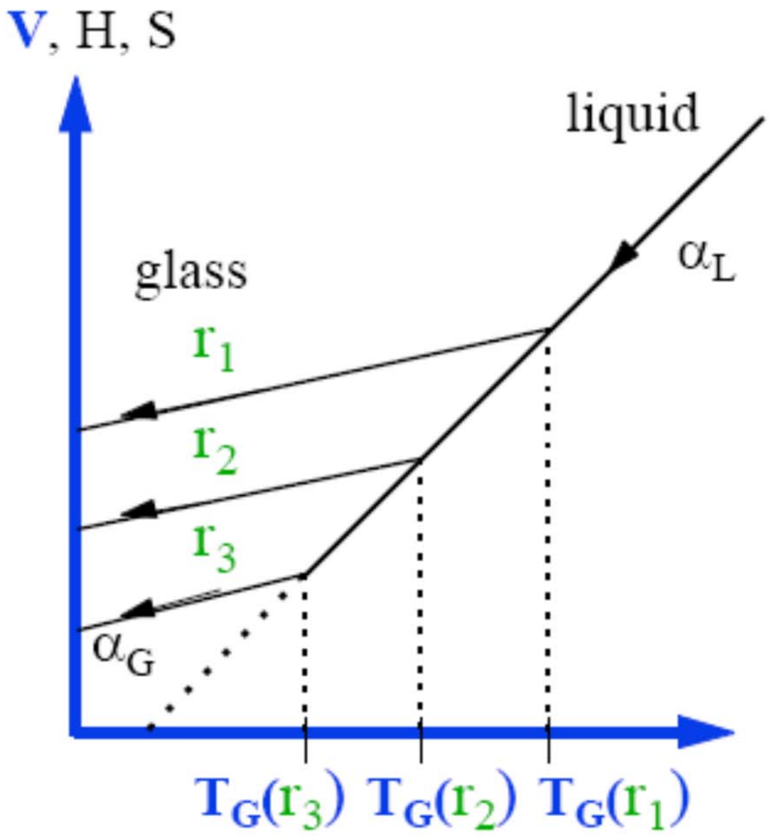
Definition of a glass ?

$$\tau_{micro} \ll \tau_{exp} \ll \tau_{relax}$$

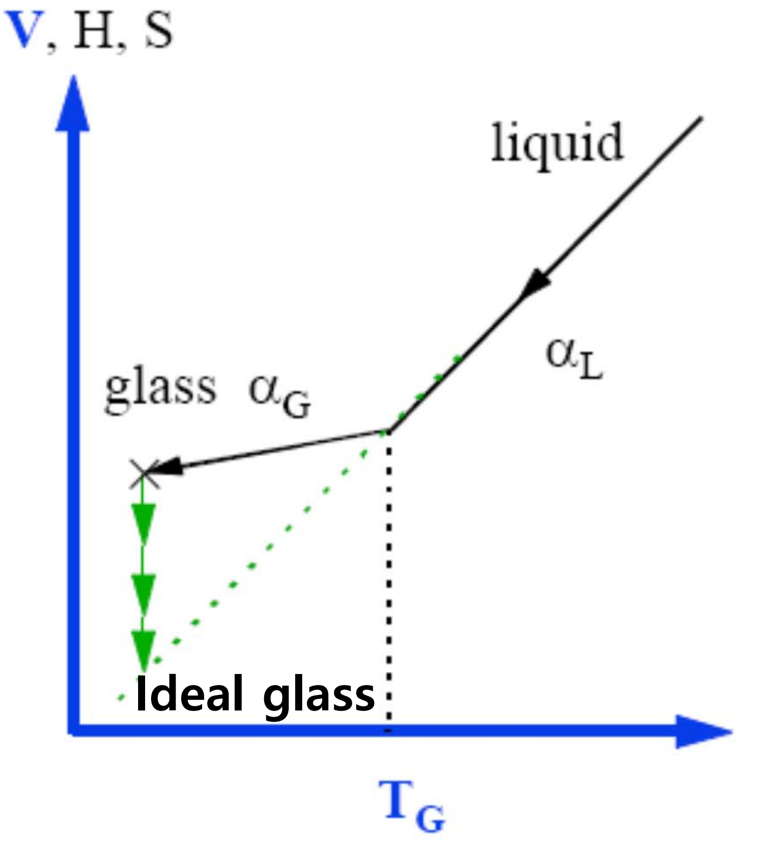
Time scale separation between microscopic, experimental, relaxation; the system is out of equilibrium on the experimental time scale.
(cf. S.K. Ma, Statistical Physics)

Microscopic time: time for events at sub-atomic distance and duration

* 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**

• 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

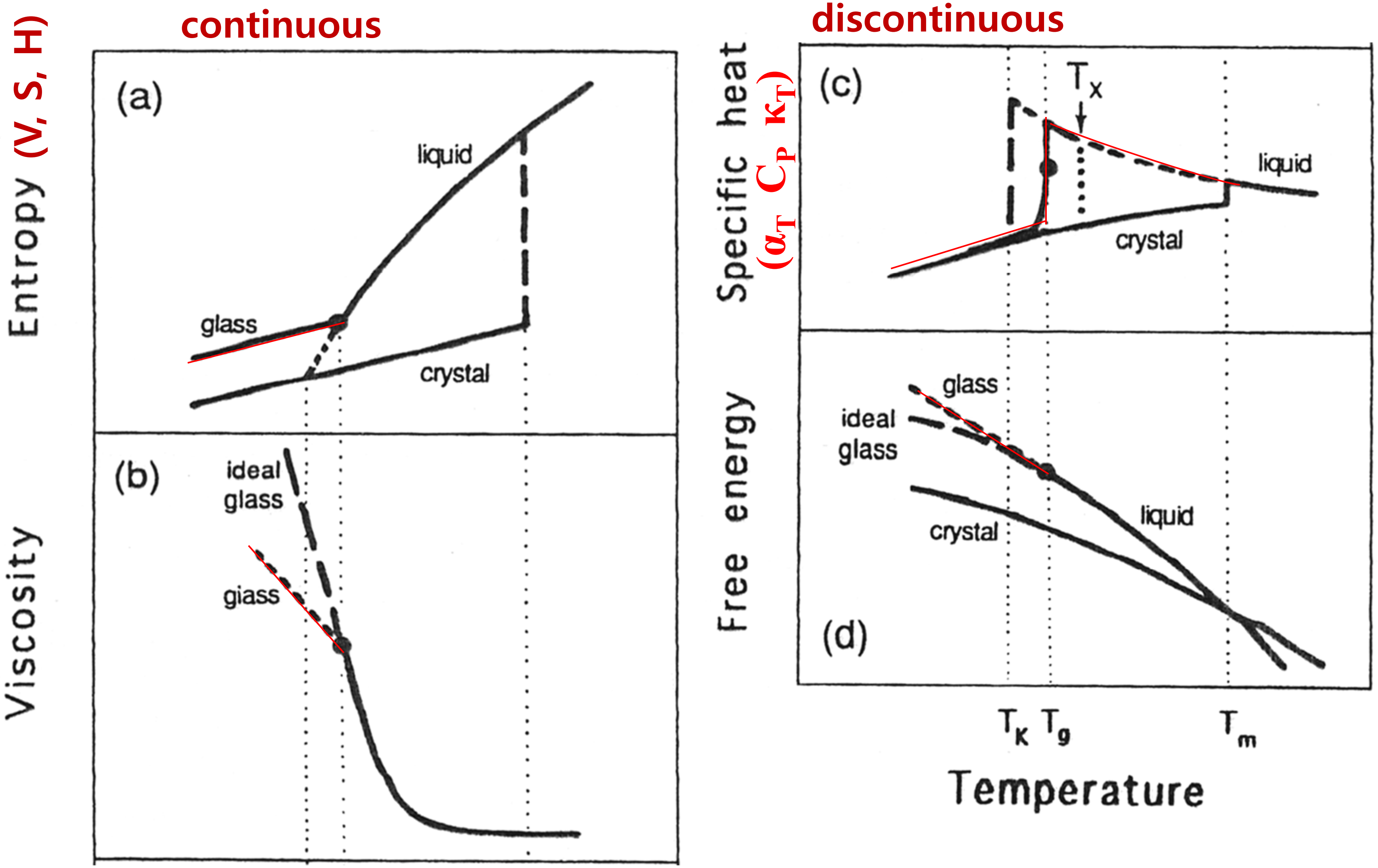
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Heading capacity: 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.**



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.

Q1: Theories for the glass transition

Theories for the glass transition

A. Thermodynamic phase transition

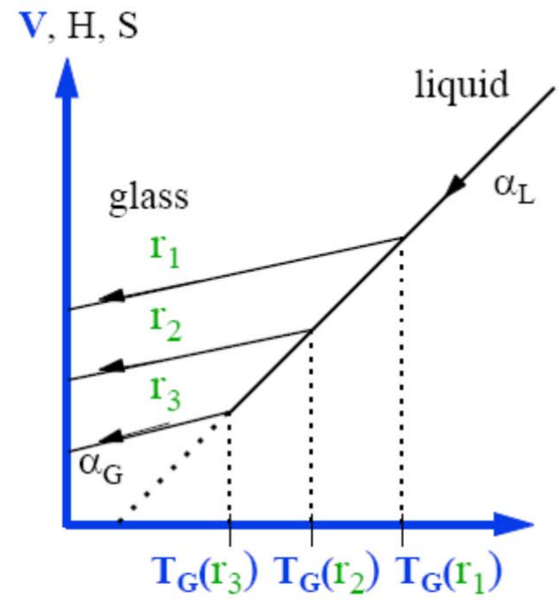
- ***Glass transition***

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

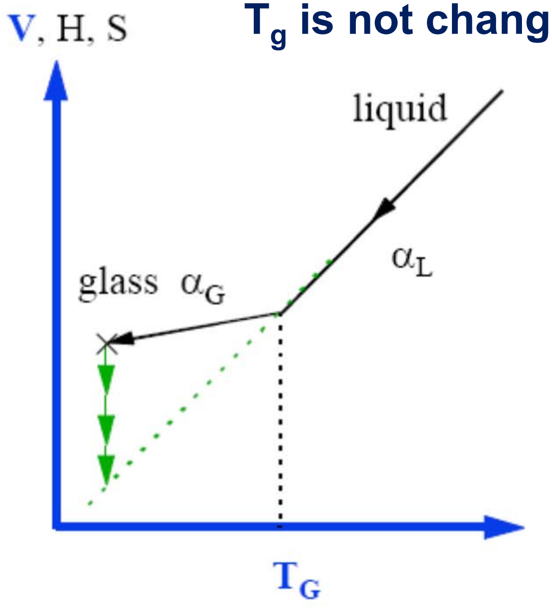
→ **by thermodynamic origin, 2nd order transition**

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

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

measureable

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

→ **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 :

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

Due date: 9 April 2018

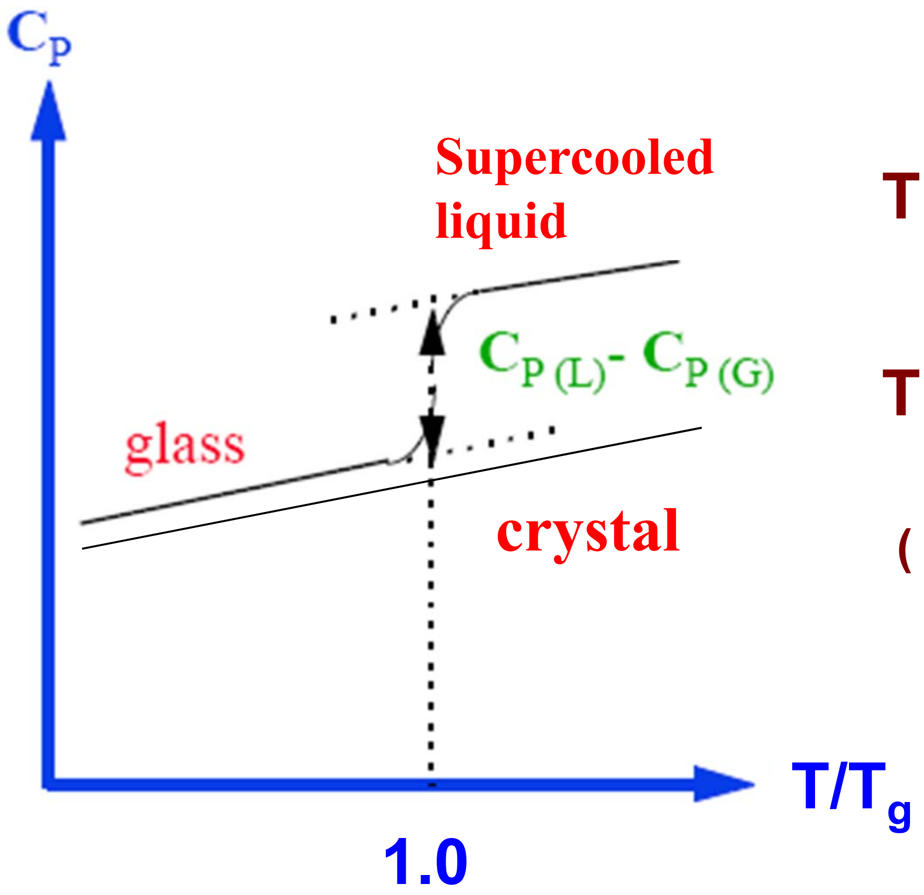
Theories for the glass transition

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**



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

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

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

Theories for the glass transition

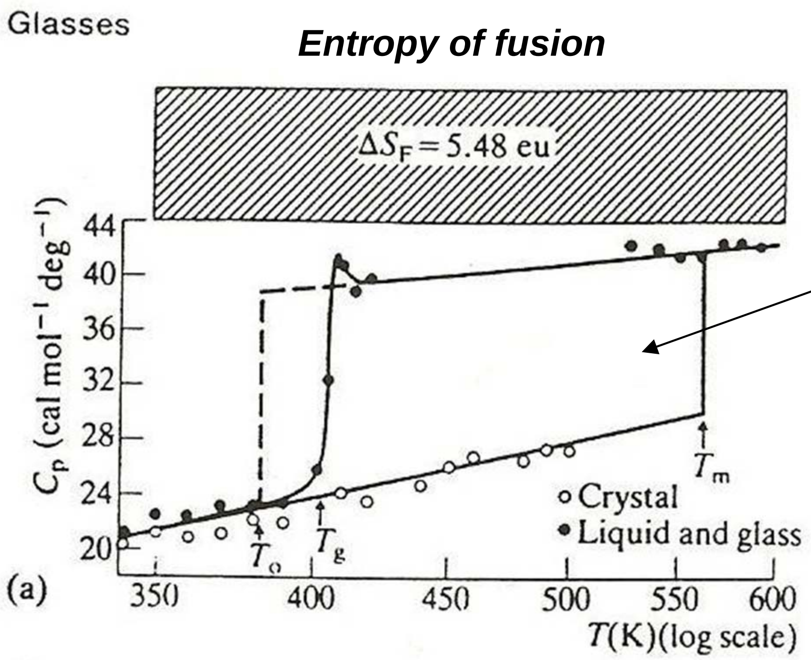
B. Entropy

- ***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.

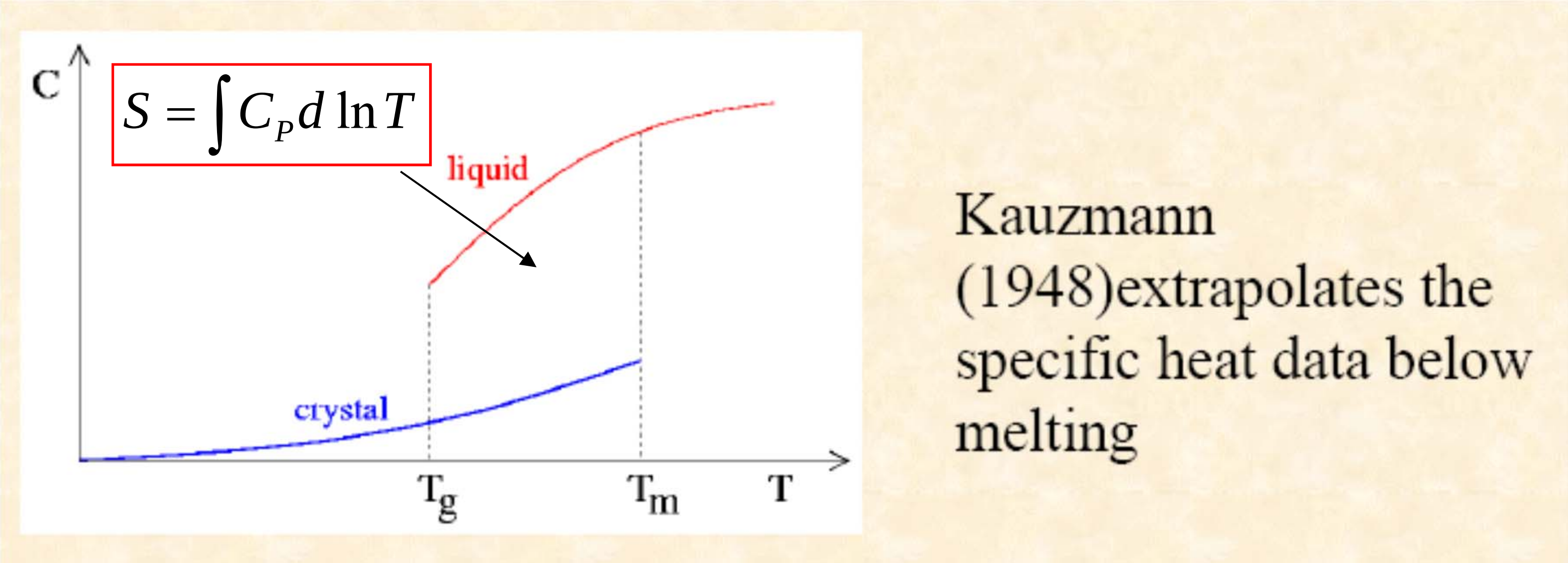
Heat capacities of glassy, liquid and crystalline phases of lithium acetate

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.***

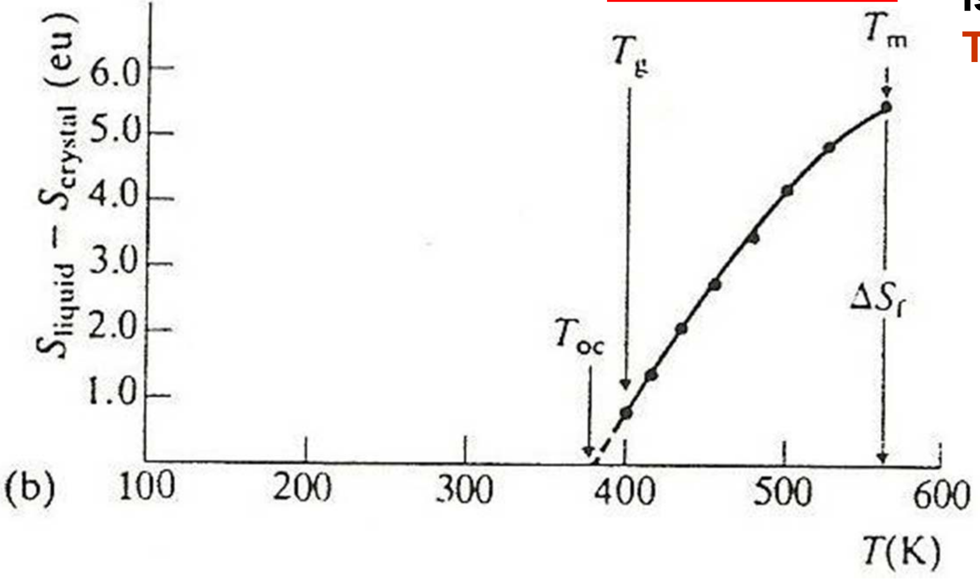
Theories for the glass transition

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

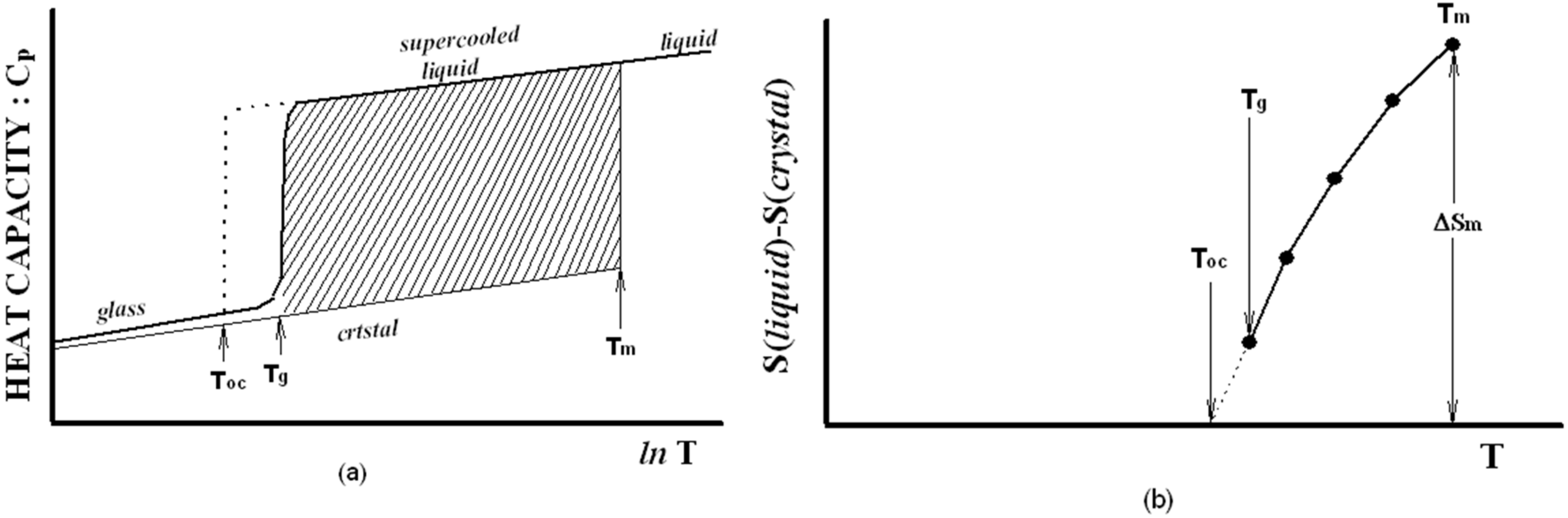
violating third law of thermodynamics

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



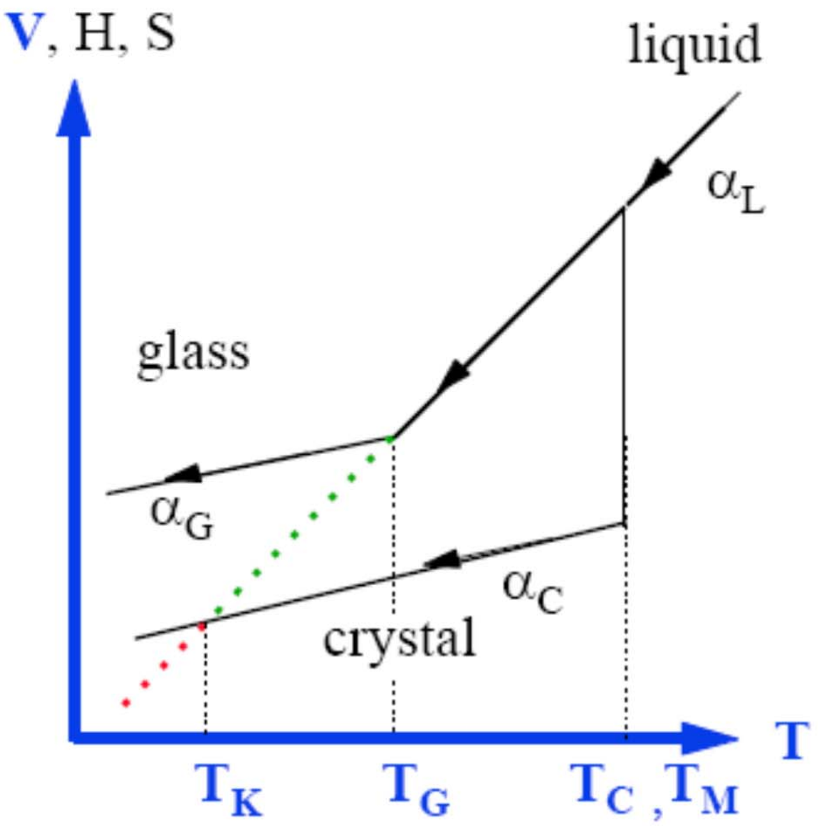
(a)

(b)

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:

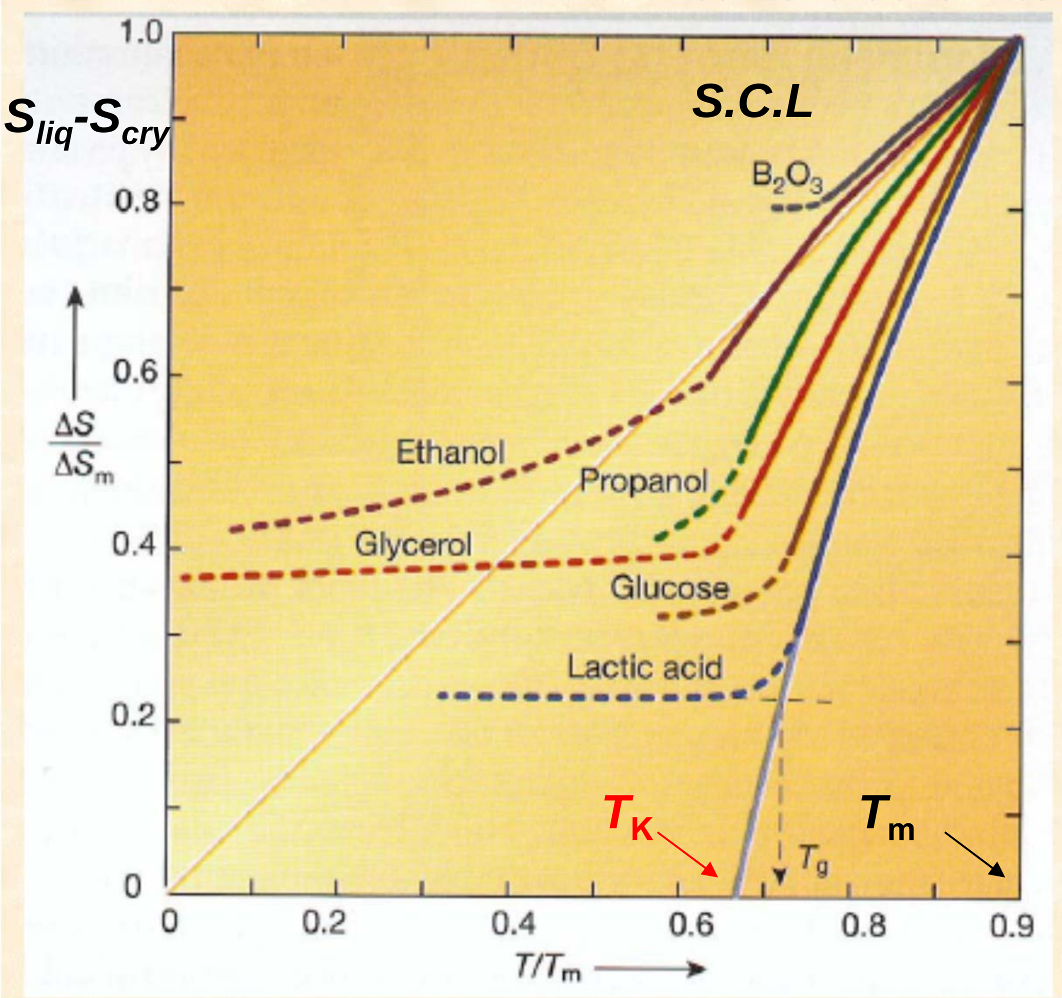


1) at some temperature (T_K), there is a true 2nd order phase tansition between the liquid and the glass or 2) the extrapolation to temperatures far below T_G is not valid. So far no one has found the answer !!

* Kauzmann's paradox

The configurational entropy apparently extrapolates to zero at low temperatures.

$$S = S_{th} + S_{config}$$



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.**

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

Homewor _Which glass has been reported as closest one to T_k?

How does thermodynamics different from kinetics?

Thermodynamics → There is **no time variable.**

says which process is possible or not and never says how long it will take.

The existence of a thermodynamic driving force does not mean that the reaction will necessarily occur!!!

There is a driving force for diamond to convert to graphite

but there is (huge) nucleation barrier.

How long it will take is the problem of kinetics.

The **time variable** is a **key parameter.** → **Relaxation & Viscosity**

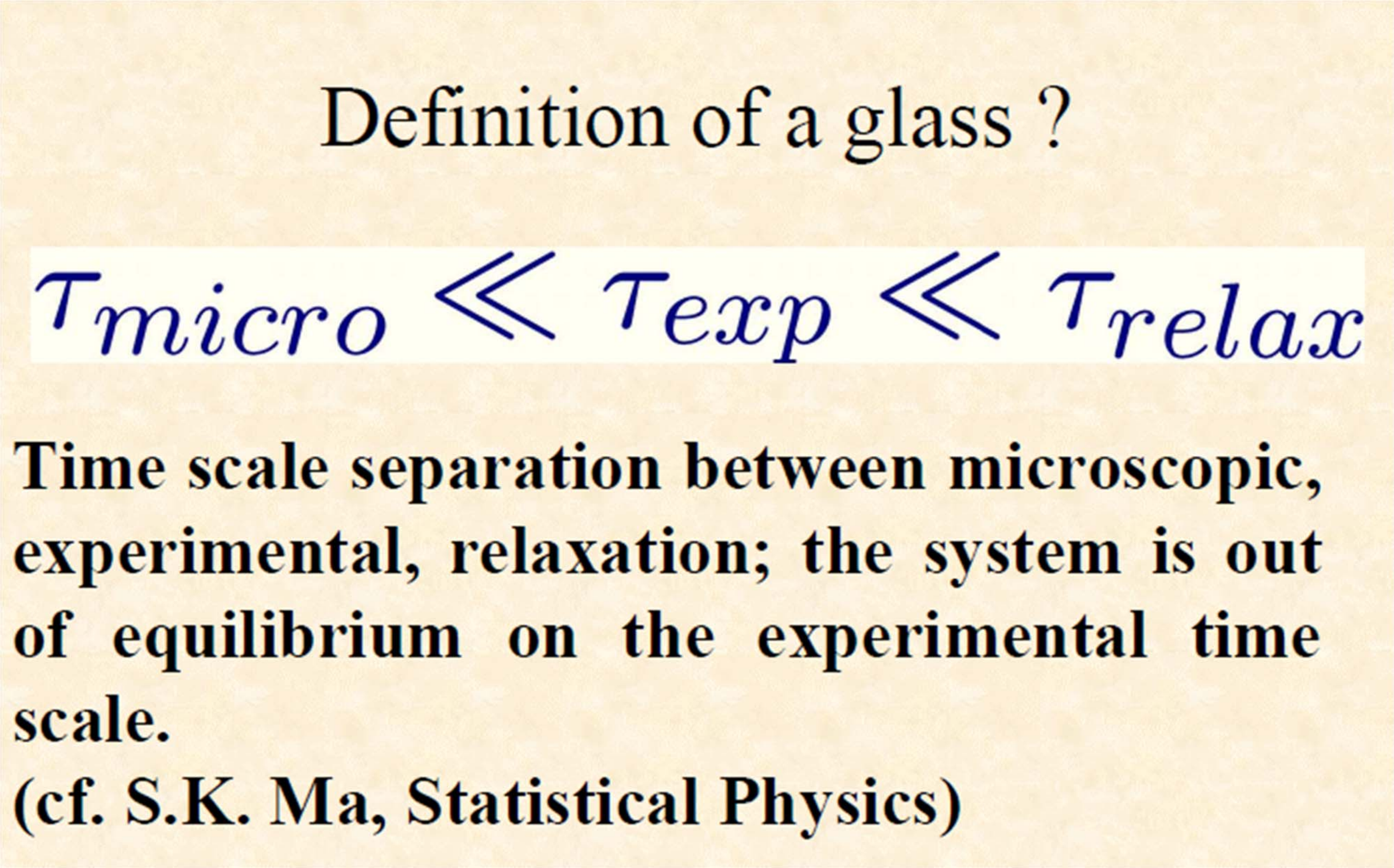
Kinetic Nature of the Glass Transition (cont.)

- The glass transition is not a true second order transition but only a "pseudo" second order phase transition
  - 1) the glass is not an equilibrium phase (i.e. its properties depend on time)
  - 2) the glass transition temperature depends on the rate at which it is measured. The glass transition will therefore be defined over a range of temperatures and pressures.
- An approximate but useful relationship is $\boxed{T_G = (2/3)\ T_M}$
- What is the origin of the kinetic nature of T_G ?

  The answer to this question is associated with the time scale for "relaxation of the structure" (return to equilibrium after a perturbation is communicated to the material: change in T or P). It is therefore related to whether or not the material properties (e.g density) can preserve their equilibrium value during the perturbation.

* *Formation of glass during cooling*

- At high T, molecular motion in the liquid is very fast and a change in T can lead to rapid ("instantaneous") molecular rerrangements. During cooling at high temperatures, the system's average free energy is always minimum (i.e. the liquid is at equilibrium at all times during cooling).
- At lower T, the rate of molecular motion becomes lower. The material preserves equilibrium properties during cooling as long as the rate of molecular rearrangement (required by the change in T) is larger than the rate at which the perturbation is exerted on the material (i.e. cooling rate).
- At some temperature (which we will denote as T_g), molecular motions become slower than the rate at which the temperature is changed. The material has no longer sufficient time during cooling to remain in equilibrium (i.e. to exhibit the equilibrium properties, e.g. specific volume) : the relaxation time scale is larger than the experimental time scale, the material does not respond instantaneously to the perturbation.



Definition of a glass ?

$$\tau_{micro} \ll \tau_{exp} \ll \tau_{relax}$$

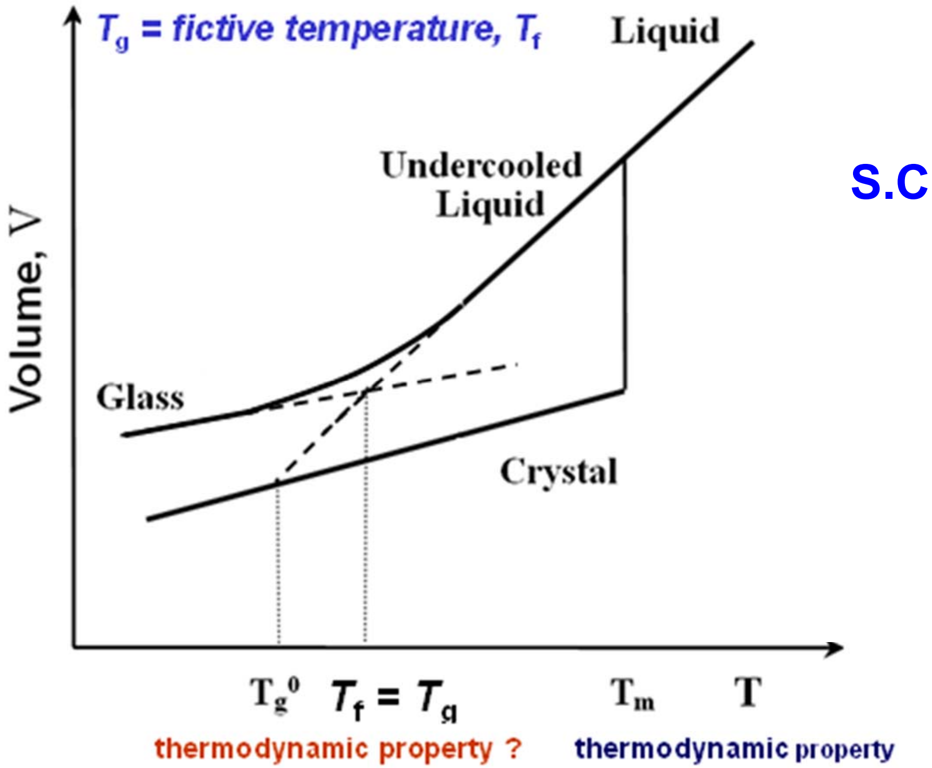
Time scale separation between microscopic, experimental, relaxation; the system is out of equilibrium on the experimental time scale.
(cf. S.K. Ma, Statistical Physics)

Microscopic time: time for events at sub-atomic distance and duration

- The above statements explain the dependence of the measured glass transition temperature on the rate of cooling.
- A similar discussion can be applied to the effect of pressure.
- The fact that the rate of molecular motion decreases with temperature can be qualitatively explained on the basis of free volume concepts* (molecular motion is afforded by the existence of empty spaces between molecules). The higher the temperature, the higher the specific volume of the material (for a given number of molecules), the higher the free volume in the material, the higher the rate of molecular motion.
- The fact that the material is not in equilibrium below Tg because it did not have sufficient time to reach the equilibrium configuration (S) and density, therefore energy or enthalpy (H) during cooling explains why the specific volume decreases with time at a given $T < T_G$ (phenomenon of physical aging of glasses)

Theories for the glass transition

C. Relaxation behavior



Liquid: enough time scale for atomic redistribution with respect to temp. change
⟶ equilibrium state

S.C.L: thermodynamically metastable with respect to crystalline
⟶ considering atomic configuration, enough time scale for atomic redistribution
⟶ equilibrium state

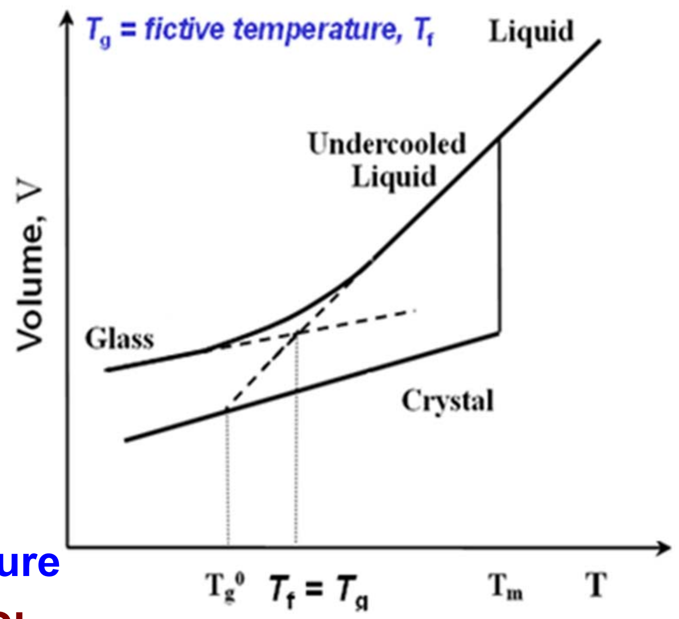
If time scale is not enough,

SCL transform to glass.

Atomic configuration of glass
: try to move to equilibrium state
⟶ **relaxation behavior**

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)

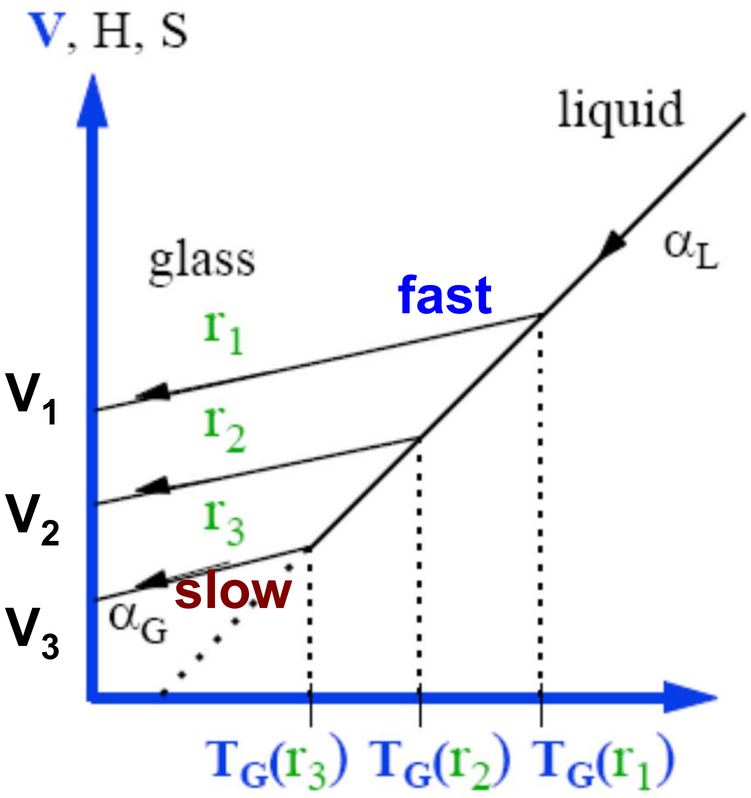
→ If (1) > (2) ➡ liquid // (1)~(2) ➡ glass transition// (1) < (2) ➡ glass

(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



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

If cooling rate become fast, glass transition can be observed in liquid region in case of slow cooling rate.

*** Specific volume $V_3 < V_2 < V_1$**

- max. difference: ~ a few %

- **Fast cooling → lower density structure**
  → higher transport properties

- **If sample is held at glass transition range (during heating), its configuration will change toward equil. amorphous structure.**

➡ "Relaxation behavior"

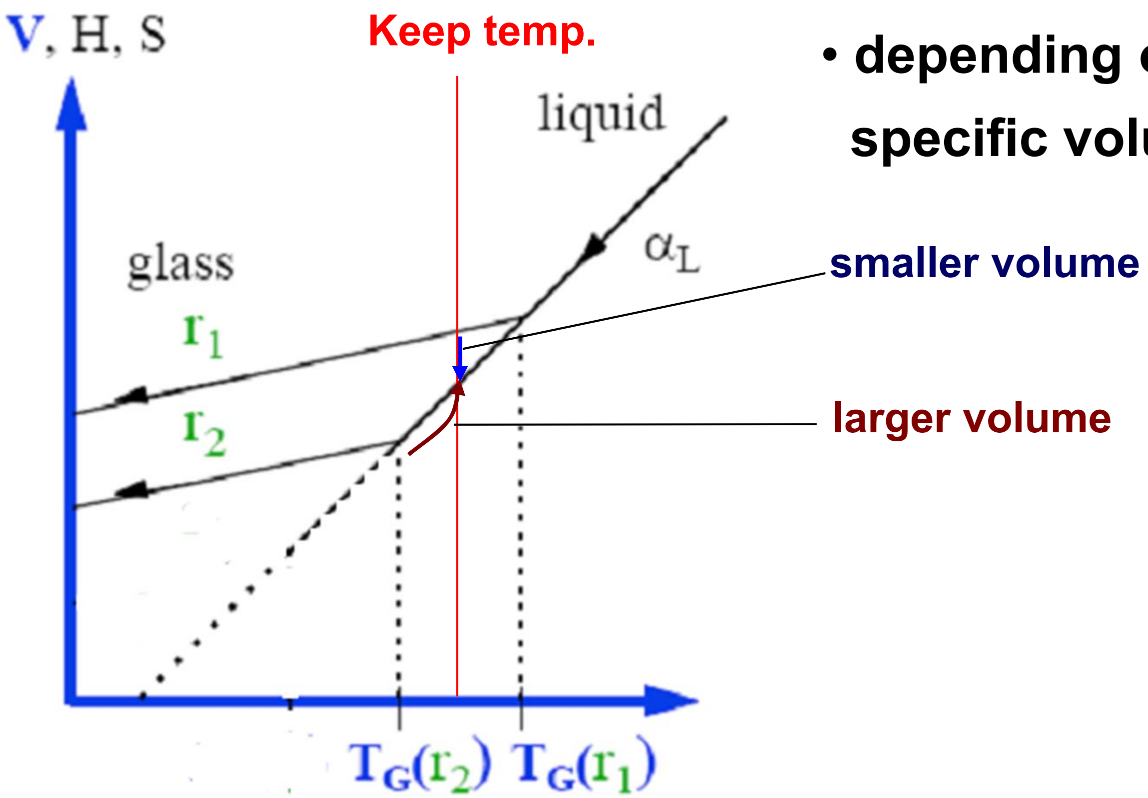
In fact, many properties of glass changes depending on relaxation behavior.

C. Relaxation behavior

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

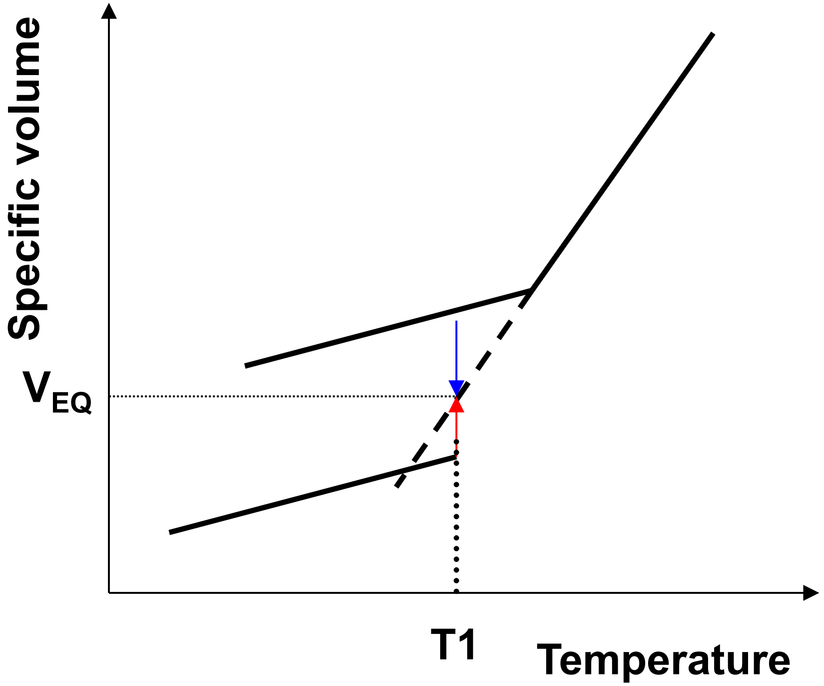
* **Process of relaxation behavior: stabilization**

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

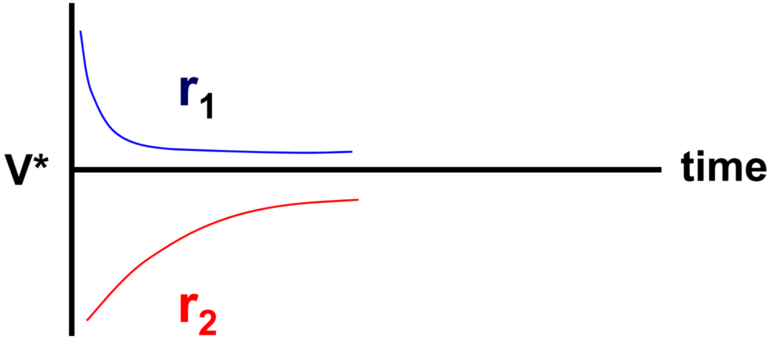


- **depending on cooling rate,**
  specific volume ⬆ or ⬇

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**

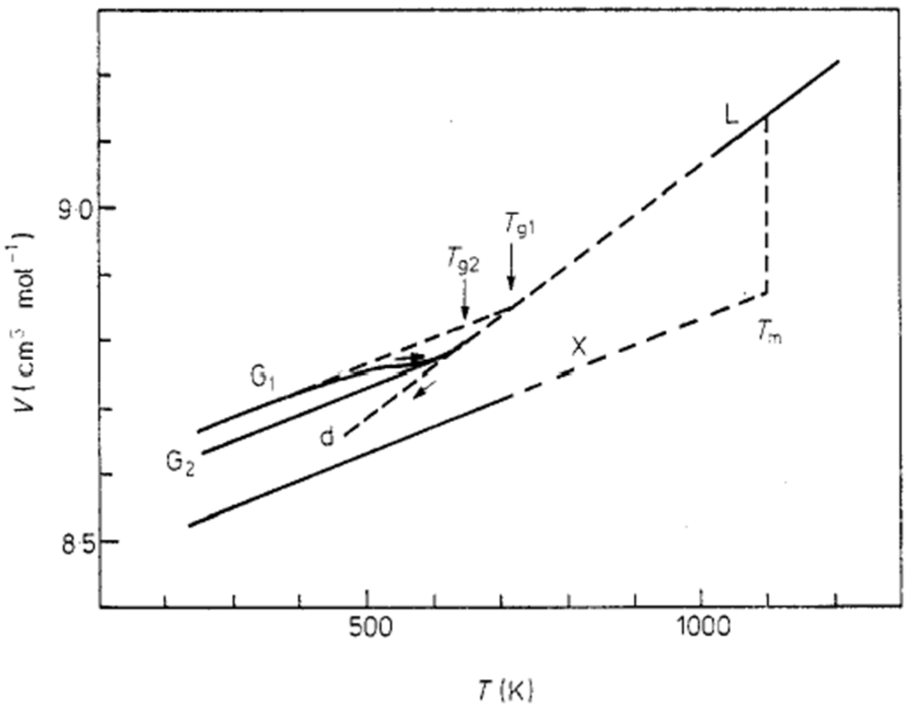
$r_1 > r_2$

C. Relaxation behavior

- **Correlation between structural relaxation time and cooling rate**

At T_g, $$\tau_g \approx \left(\frac{kT_g^{\,2}/Q}{q}\right)$$

q=-dT/dt : cooling rate
Q : activation energy of viscous flow



<Specific volume of PdCuSi>

- **different glass state G_1, G_2 according to different cooling rate**

- **relaxation ($G_1 \rightarrow G_2$)**

- **high cooling rate**
  (greater frozen-in structural disorder)
  → short relaxation time
  → high T_g
  → low viscosity, high diffusivity
  great specific volume & internal energy

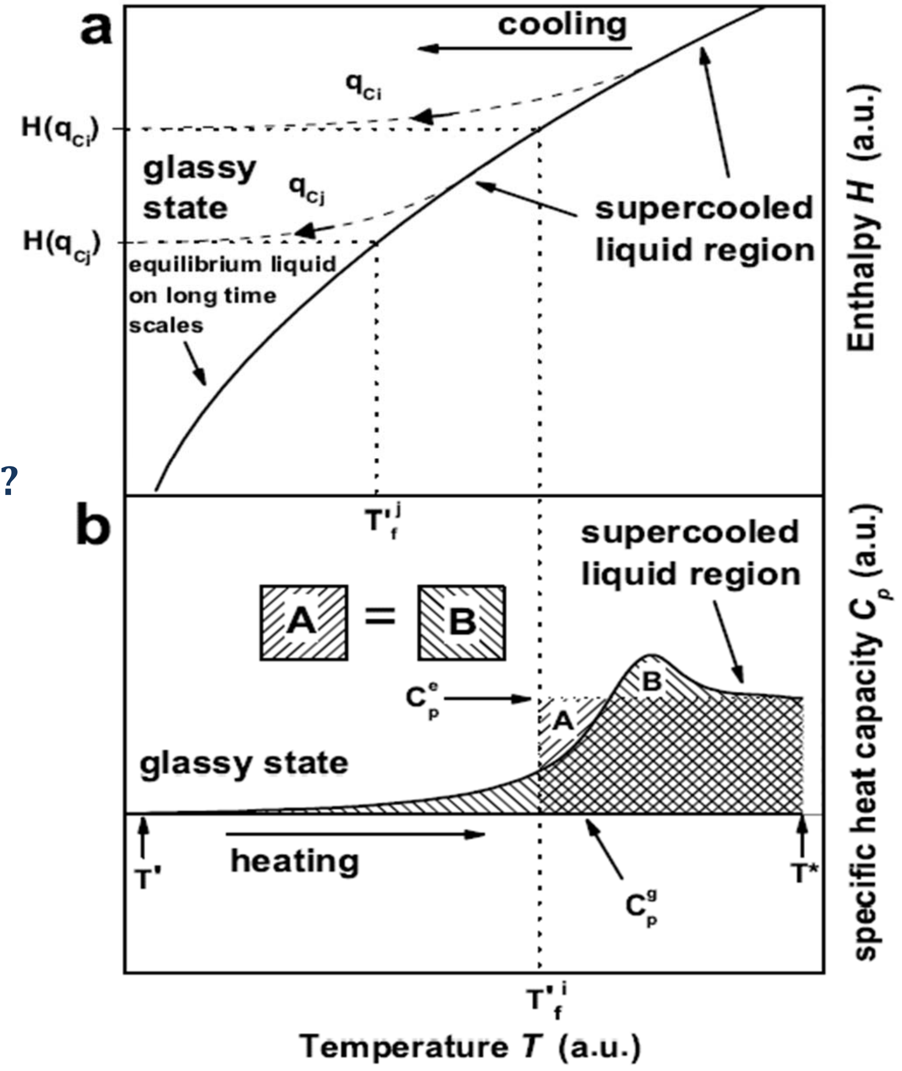
overshoot in heating process

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

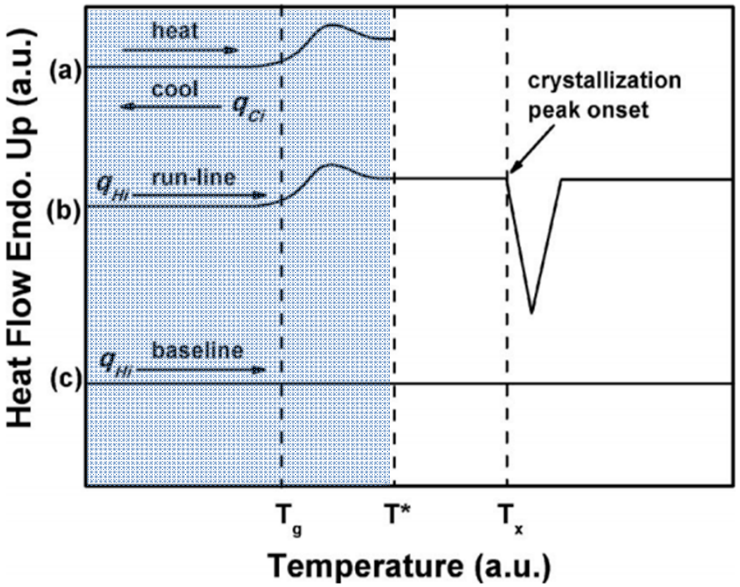
$$\int_{T^*}^{T'_f} (C_p^e - C_p^g)\,dT_f = \int_{T^*}^{T'} (C_p - C_p^g)\,dT$$

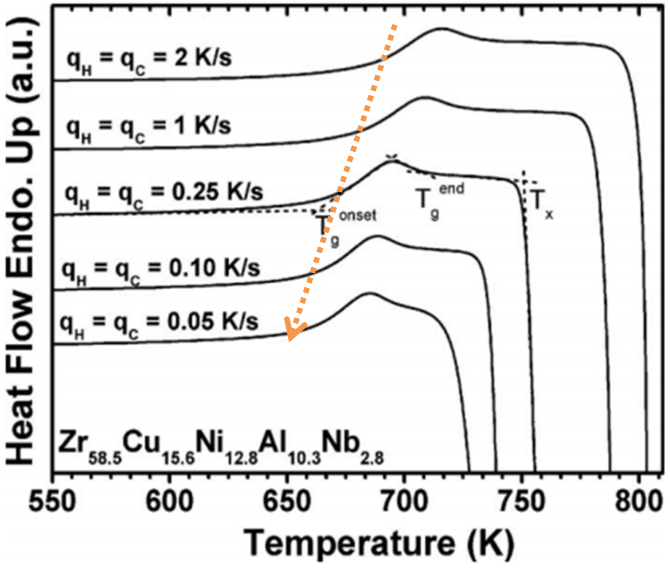


J. Appl. Phys. 107, 123529 (2010)

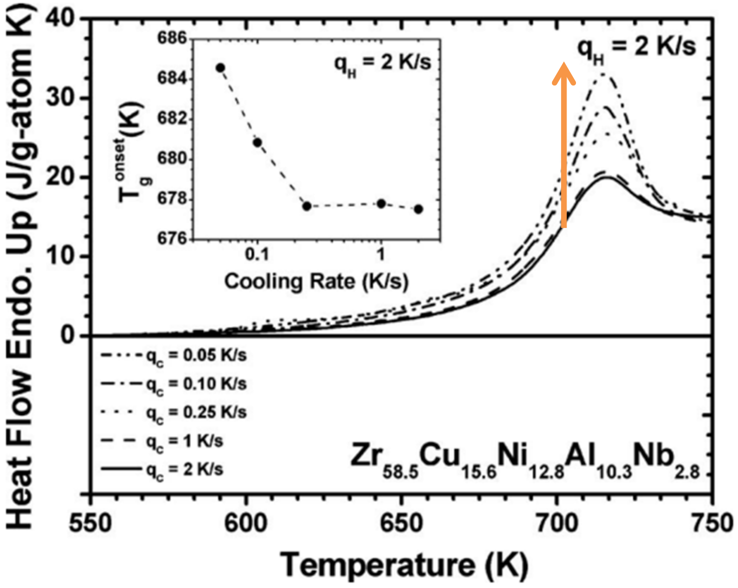
J. Appl. Phys. 107, 123529 (2010)

Heating and cooling rate controlled by DSC

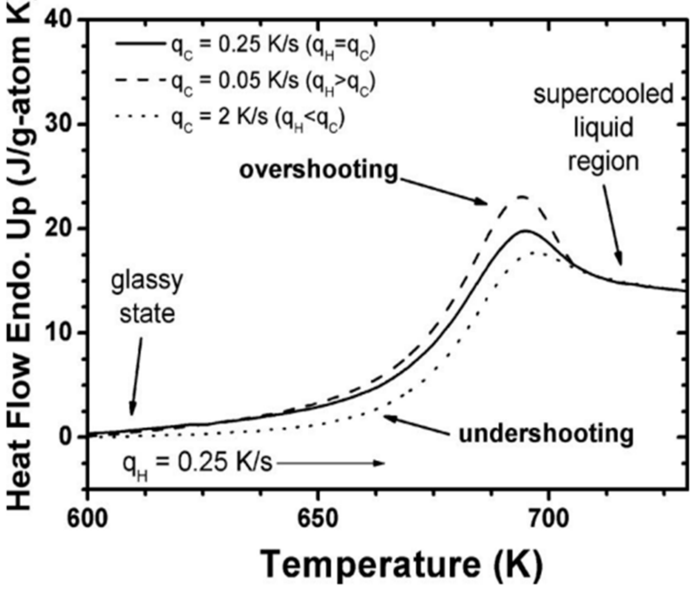




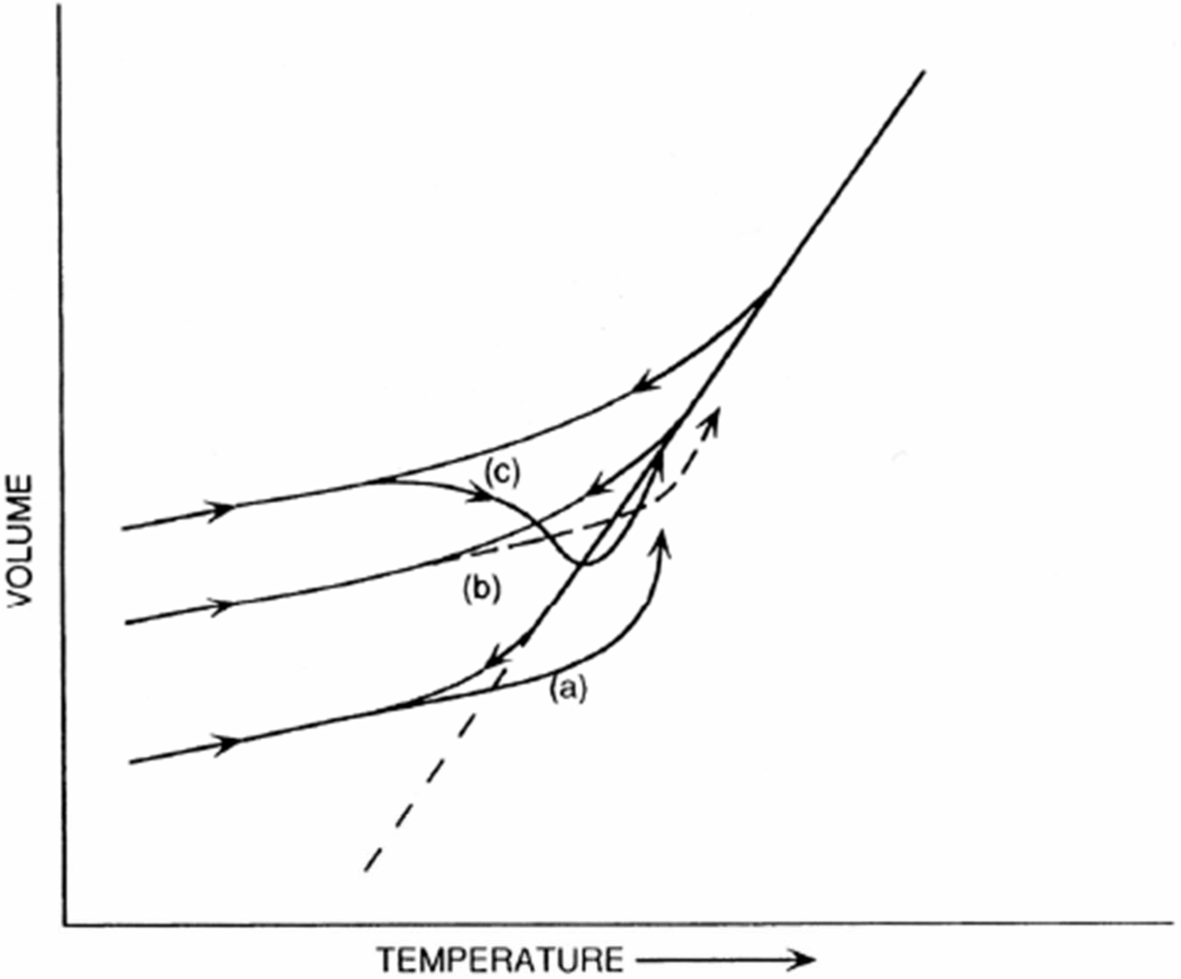
Heating rate>cooling rate → overshoot↑



Heating rate constant



Volume structural relaxation

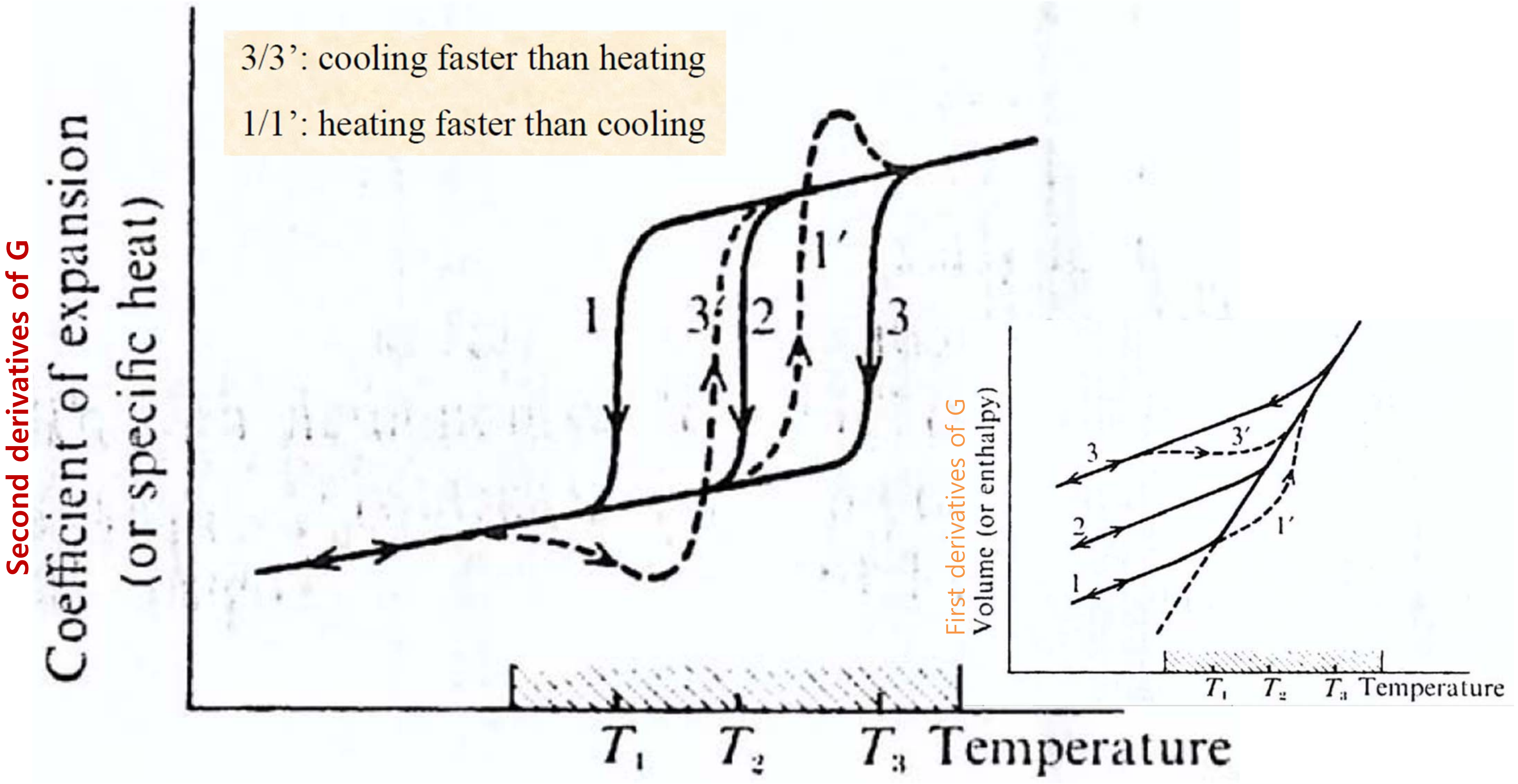


(a) slow cool; fast reheat
(b) medium cool; medium reheat
(c) fast cool; slow reheat

Volume changes in glass upon varying cooling and reheating rates.

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

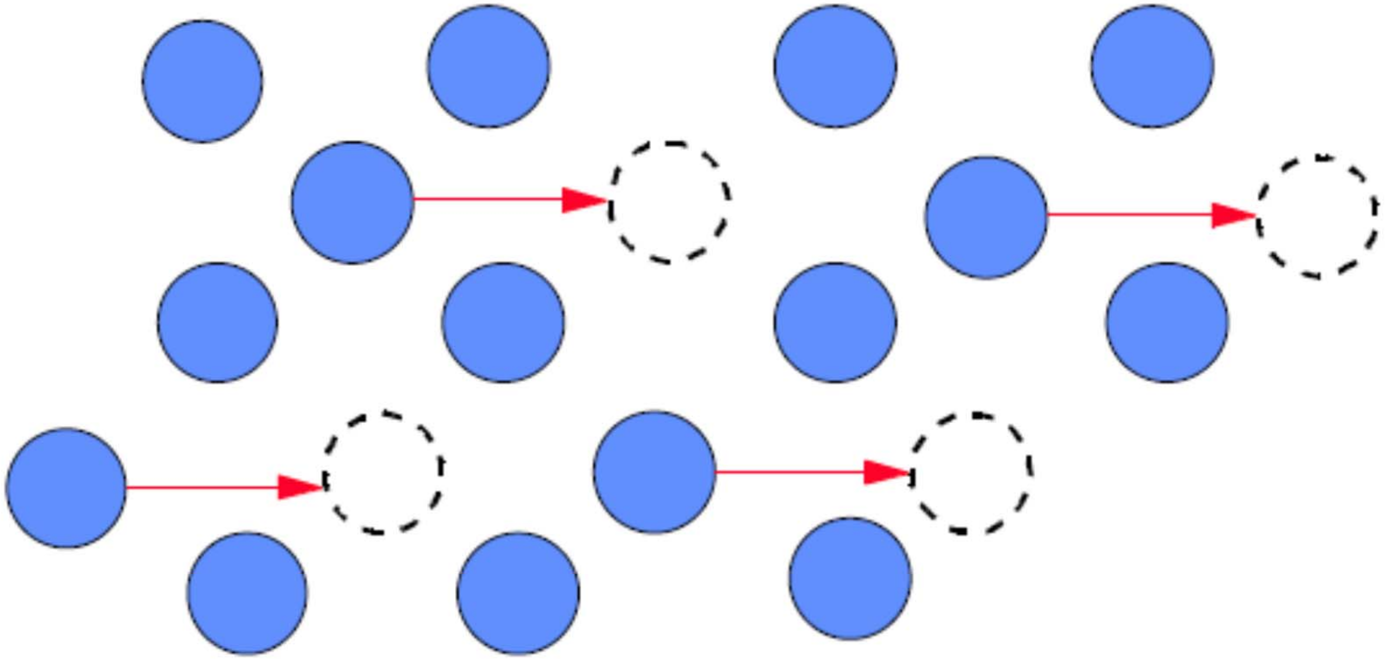
Complex relaxation effect in the transition region



3/3’: cooling faster than heating

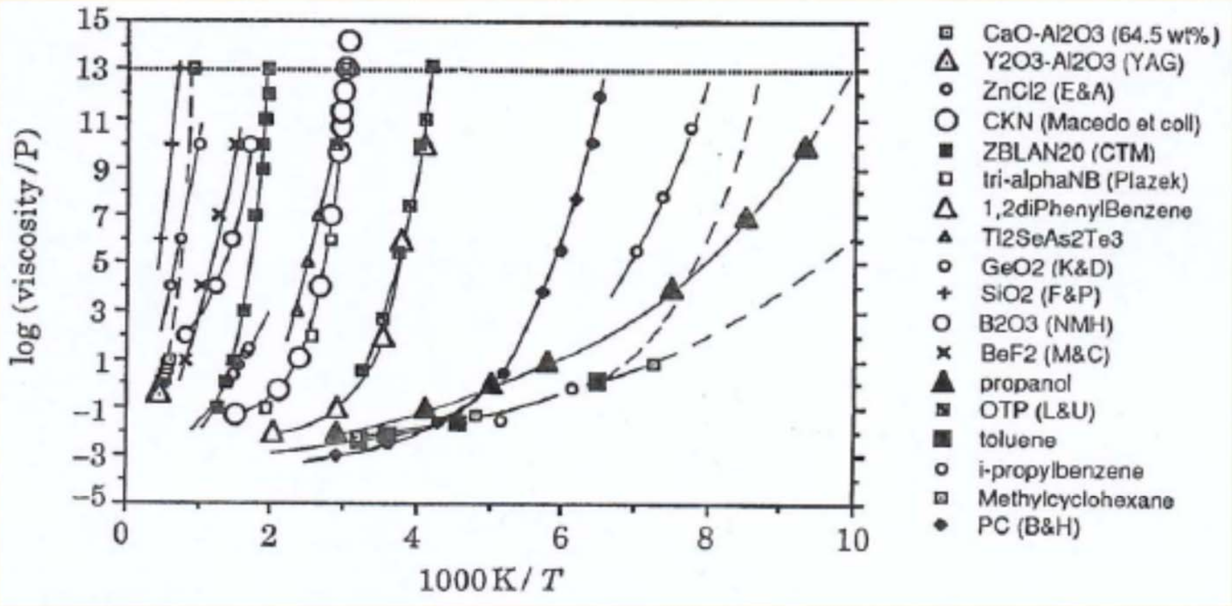
1/1’: heating faster than cooling

Temperature Dependence of Liquid Viscosity



Viscosity is a measure of the resistance to flow. The higher T, the larger the average size of the holes and the larger the energy of the molecules, the easier the molecule move past oneanother, the lower the resistance to flow.

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

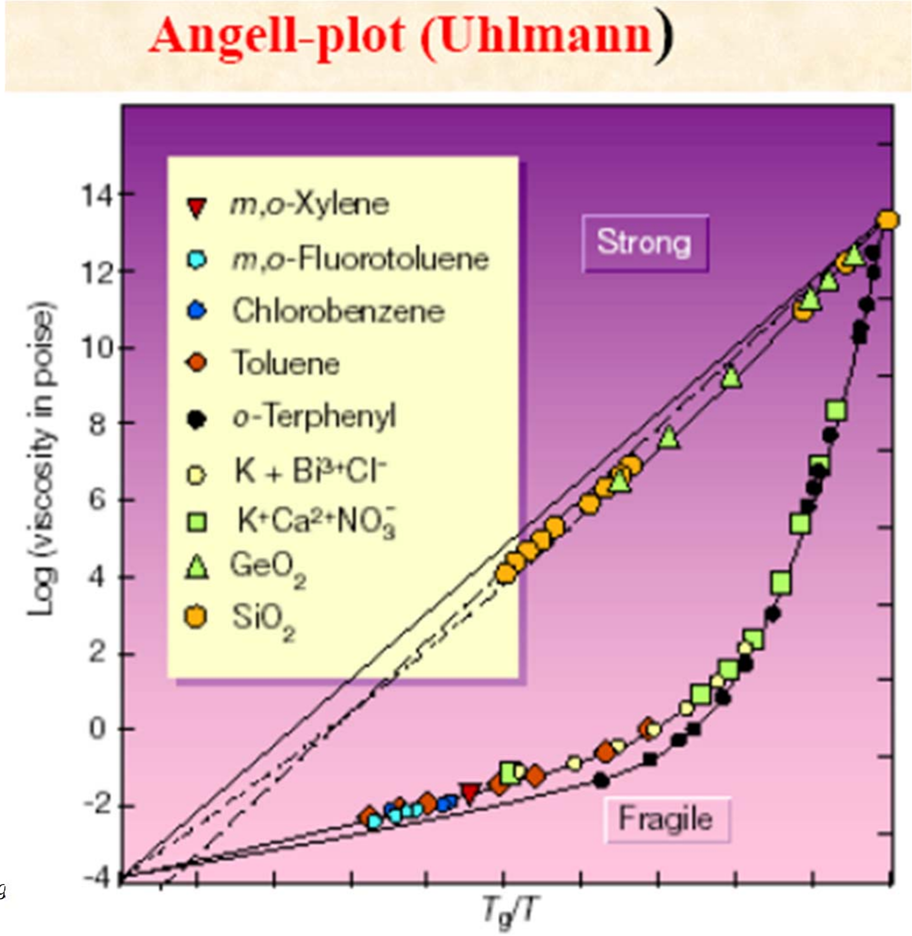
< Classification of glass >

Strong network glass : Arrhenius behavior

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

Fragile network glass : Vogel-Fulcher relation

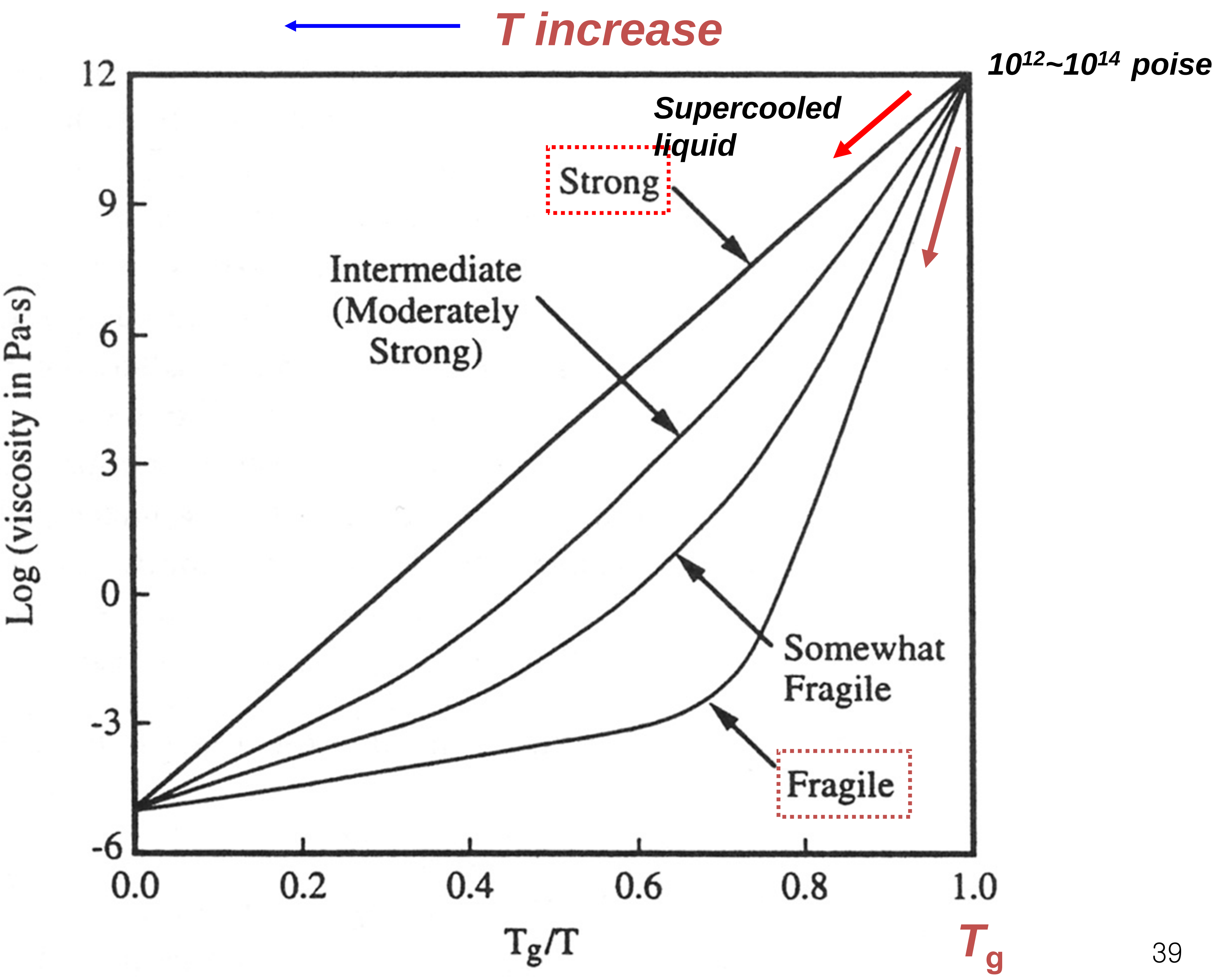
$$\eta = \eta_0 \exp[\frac{B}{T - T_0}]$$



< 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
12
9
6
3
0
-3
-6
Log (viscosity in Pa-s)
0.0
0.2
0.4
0.6
0.8
1.0
Tg/T
T_g

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**

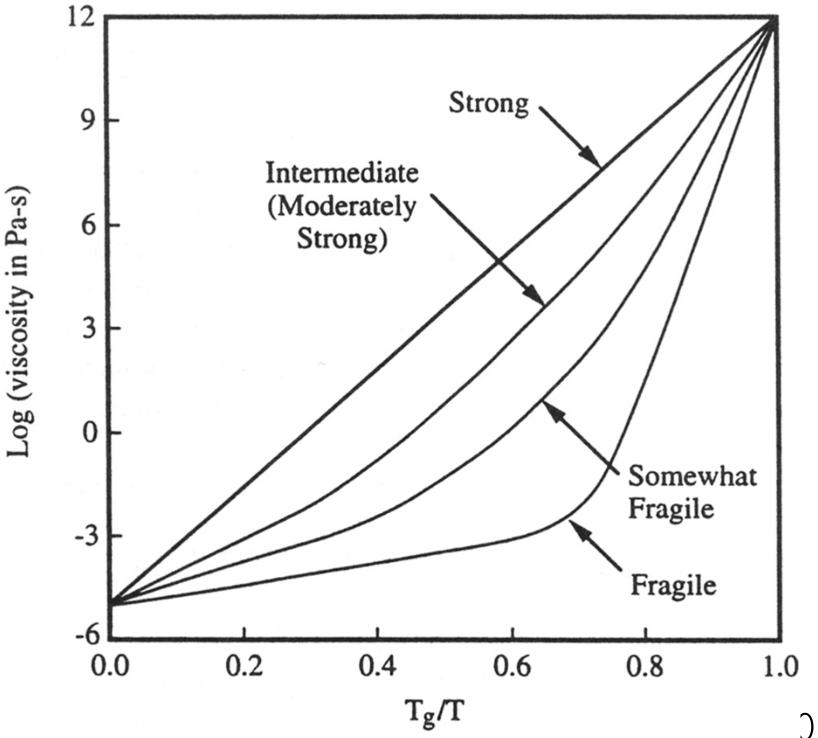
- ***fragile glass-forming liquid***

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

→ **large difference of C_p at T_g**

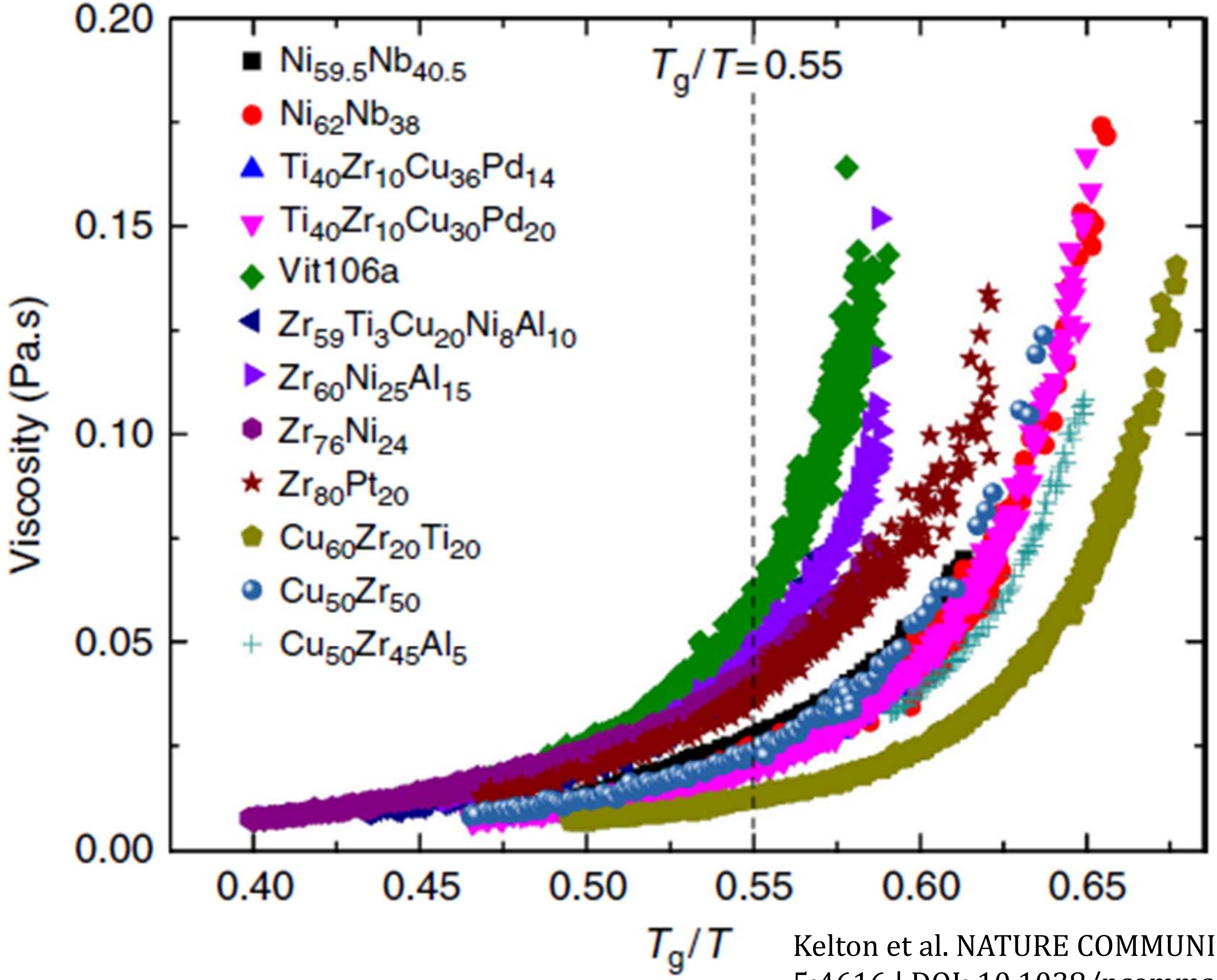
(relatively large free volume)

→ **SCL: relatively high entropy**



Viscosity variation of liquid during cooling

No clear relationship btw viscosity variation of liquid vs GFA!



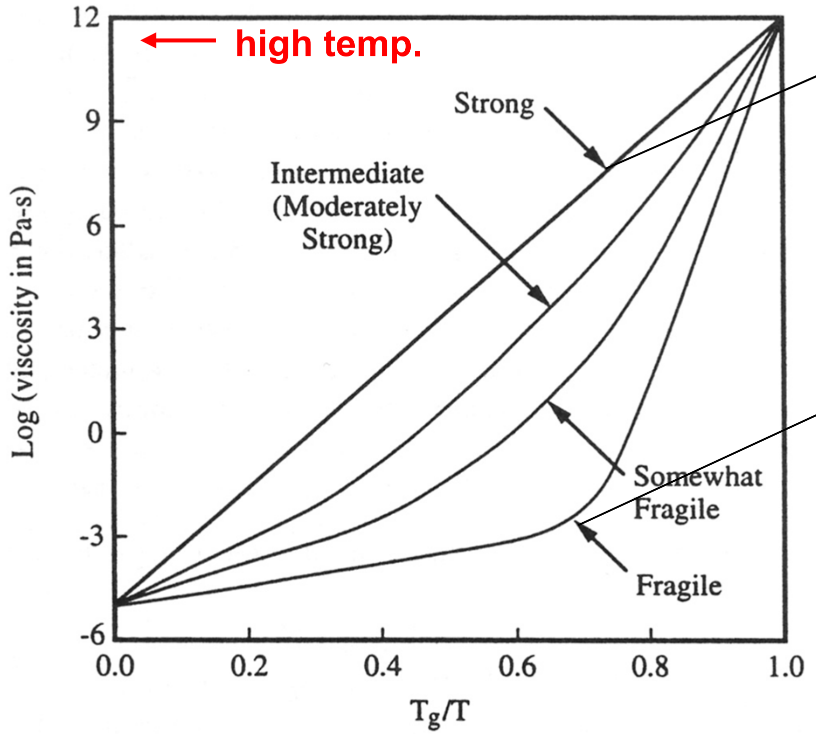
Kelton et al. NATURE COMMUNICATIONS | 5:4616 | DOI: 10.1038/ncomms5616

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

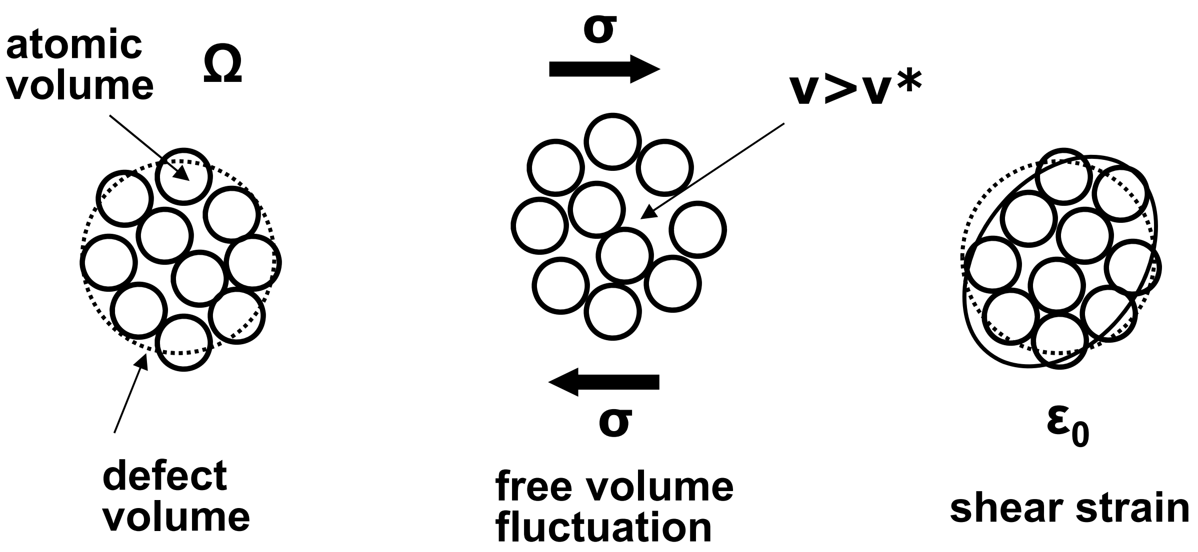
\- deviation from simple Arrhenius behavior

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

→ Ionic system, organic materials

* Free volume model

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



Probability $\exp(A\frac{v^*}{v_f})$

average free volume

- **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**

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

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

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

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

(Θ 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

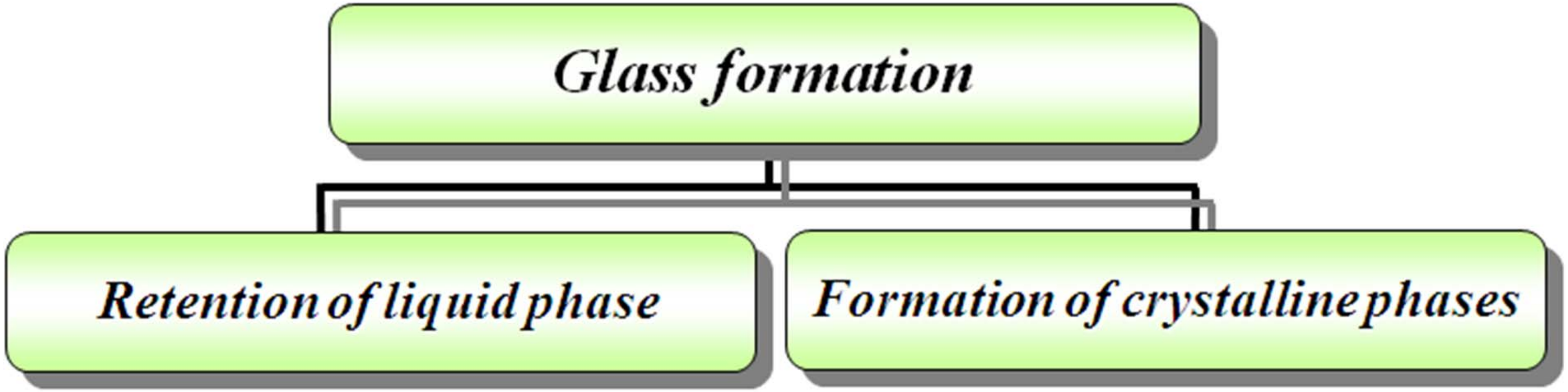
d. viscosity

- 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

Retention of liquid phase

Formation of crystalline phases

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

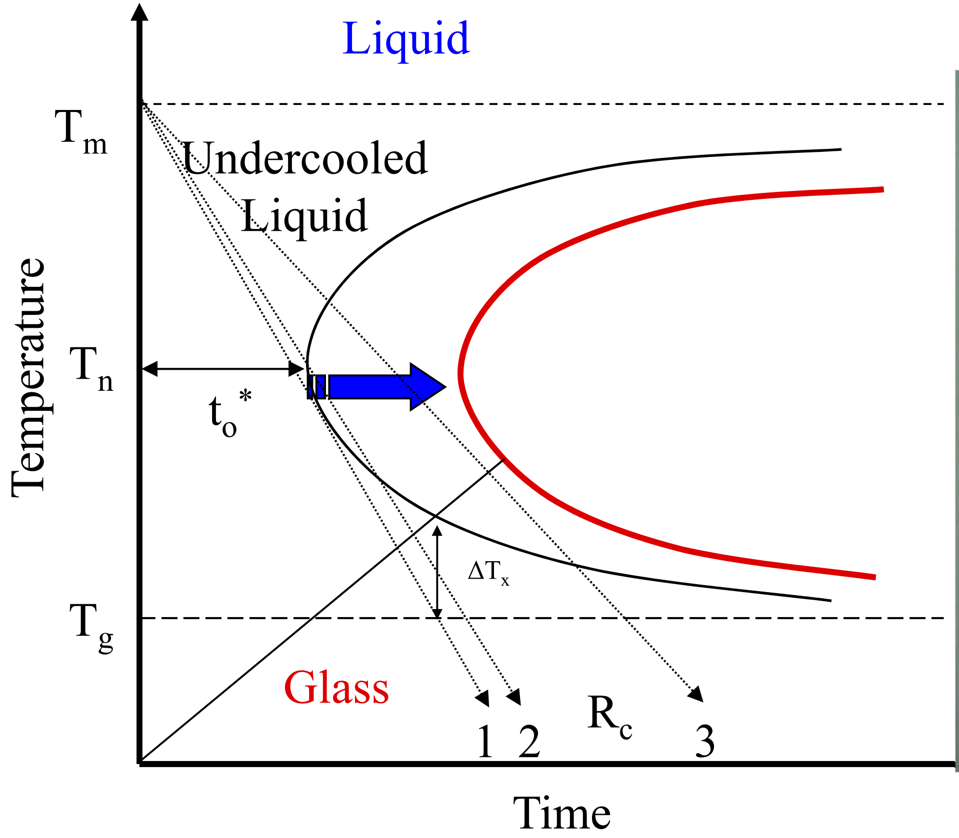
Liquid is “**frustrated**” by internal structure that hinders both events

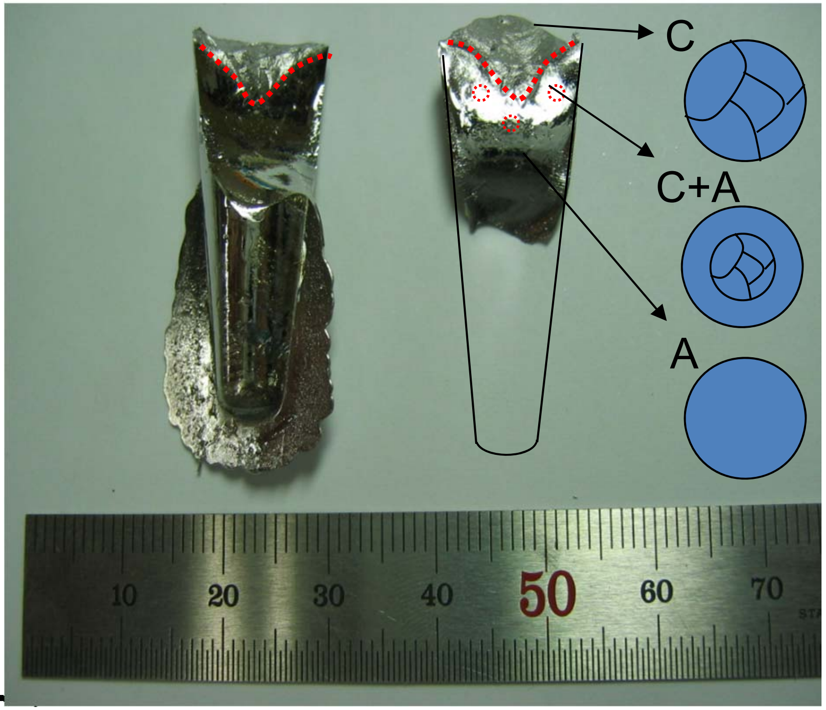
→ **Glass Formation**

Time Temperature Transformation diagram

Critical cooling rate

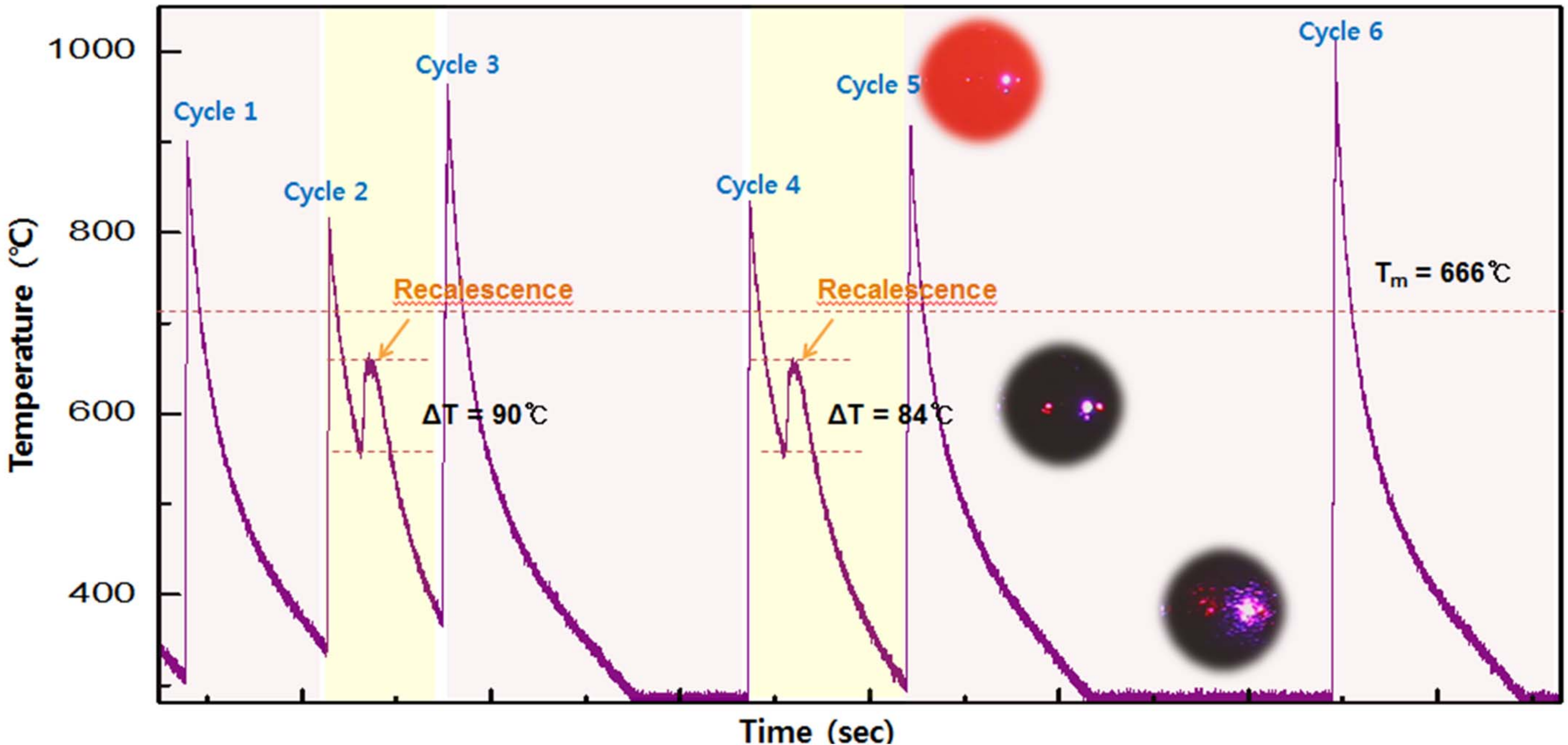
$$R_c = \frac{T_m - T_n}{t_o^*}$$



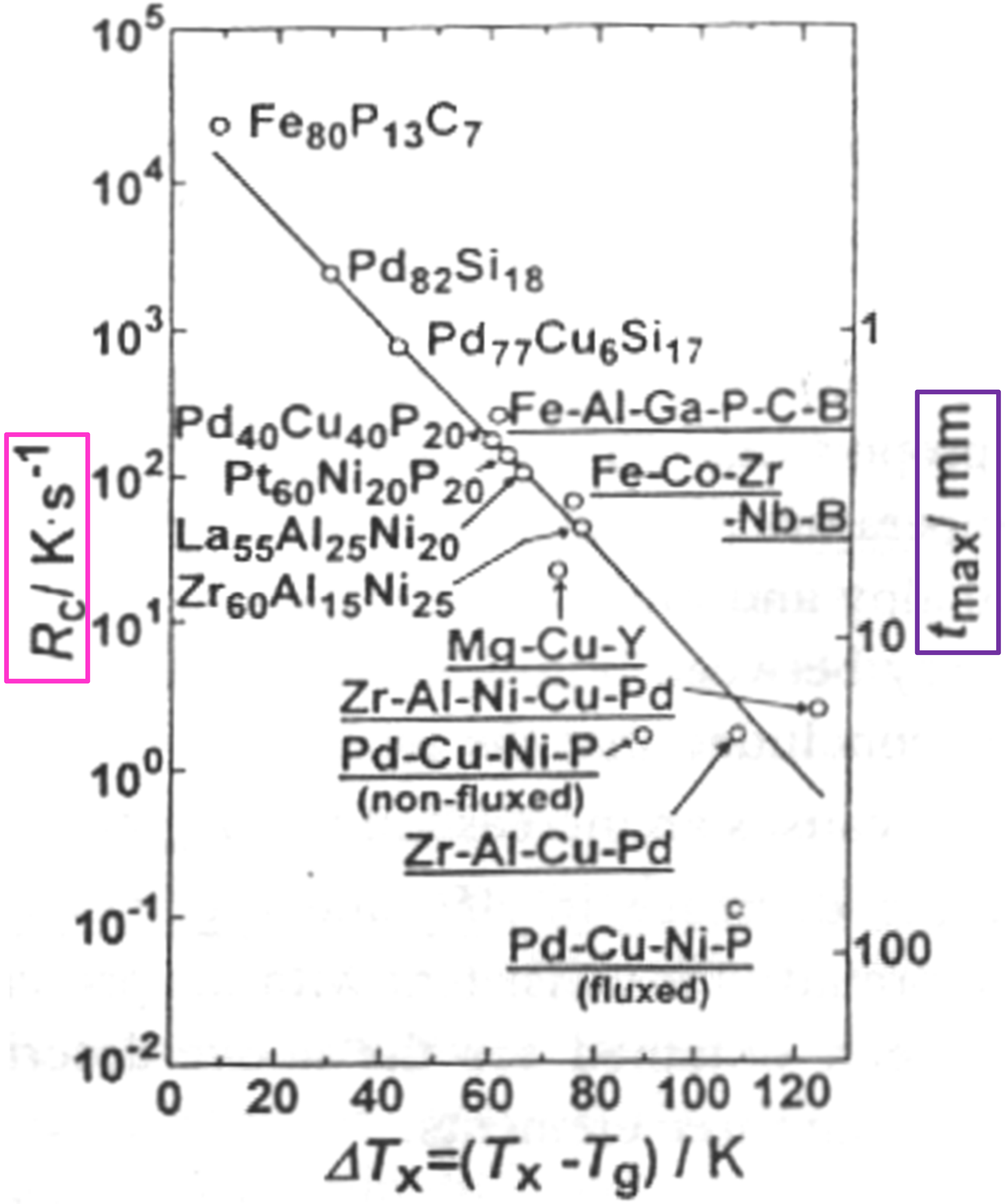


Critical cooling rate is inversely proportional to the diameter of ingot.

Electrostatic Levitation: cooling curve of Vitreloy 1 system

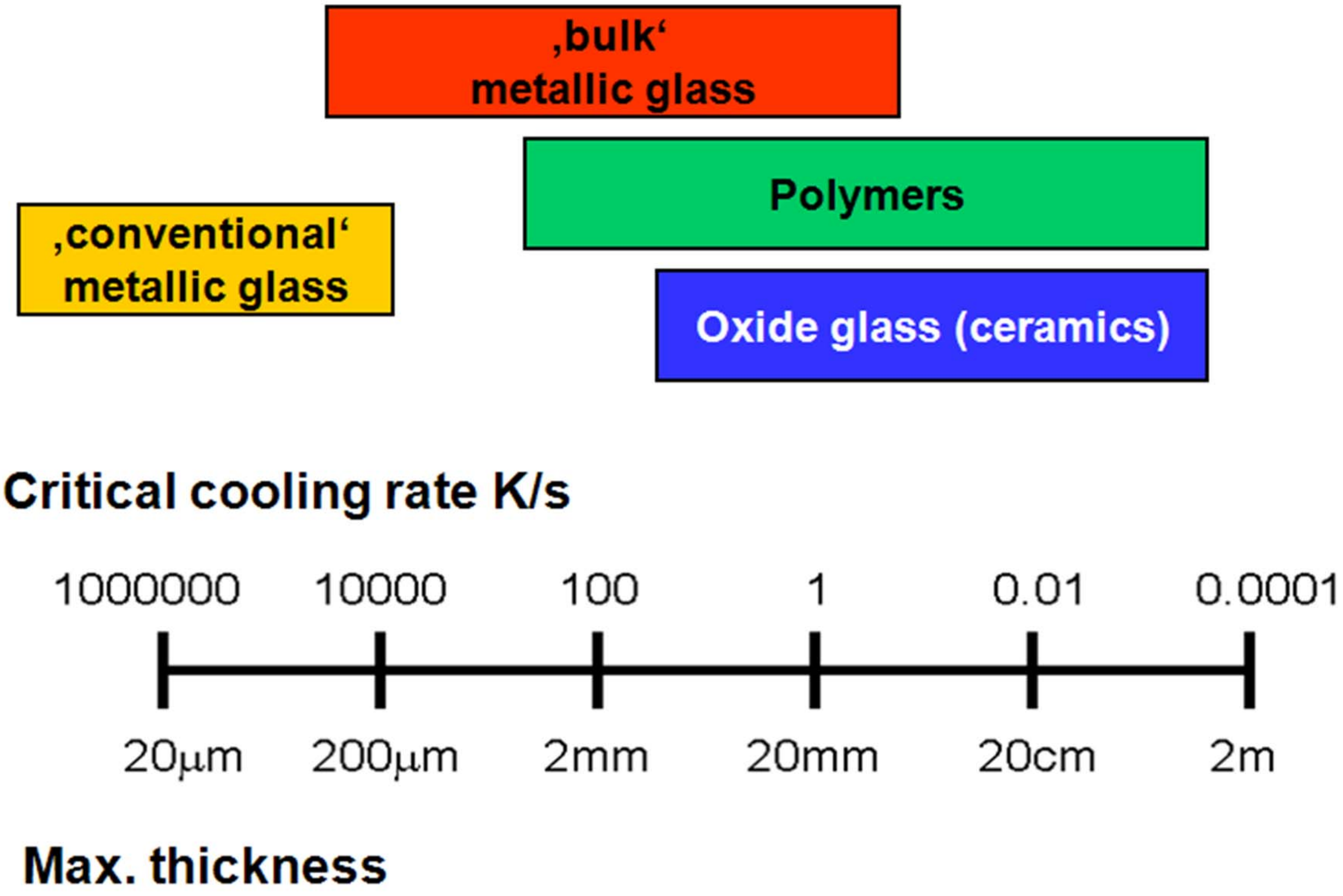


at KRISS



10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
R_c/ K·s^{-1}
$Fe_{80}P_{13}C_7$
$Pd_{82}Si_{18}$
$Pd_{77}Cu_6Si_{17}$
Fe-Al-Ga-P-C-B
$Pd_{40}Cu_{40}P_{20}$
$Pt_{60}Ni_{20}P_{20}$
$La_{55}Al_{25}Ni_{20}$
$Zr_{60}Al_{15}Ni_{25}$
Fe-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



‚bulk‘ metallic glass

Polymers

‚conventional‘ metallic glass

Oxide glass (ceramics)

Critical cooling rate K/s

1000000	10000	100	1	0.01	0.0001
20µm	200µm	2mm	20mm	20cm	2m

Max. thickness

Critical Cooling Rates for Various Liquids

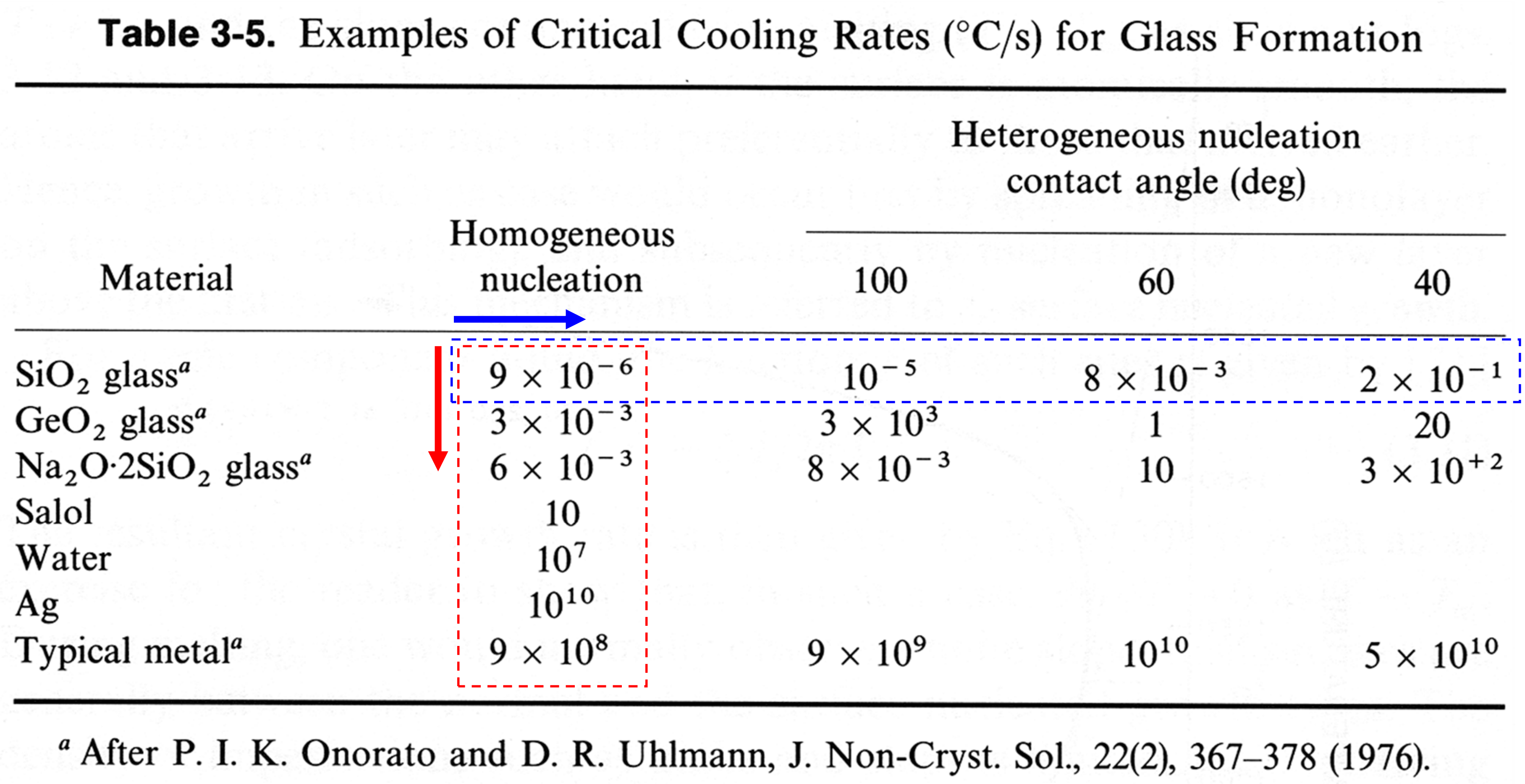


Table 3-5. Examples of Critical Cooling Rates (°C/s) for Glass Formation

		Heterogeneous nucleation contact angle (deg)		
Material	Homogeneous nucleation	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

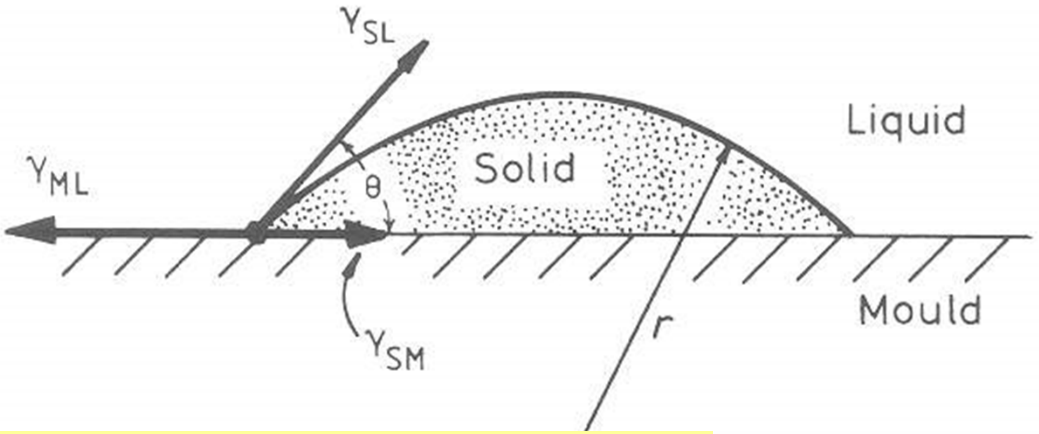
From $$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

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

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

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

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



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

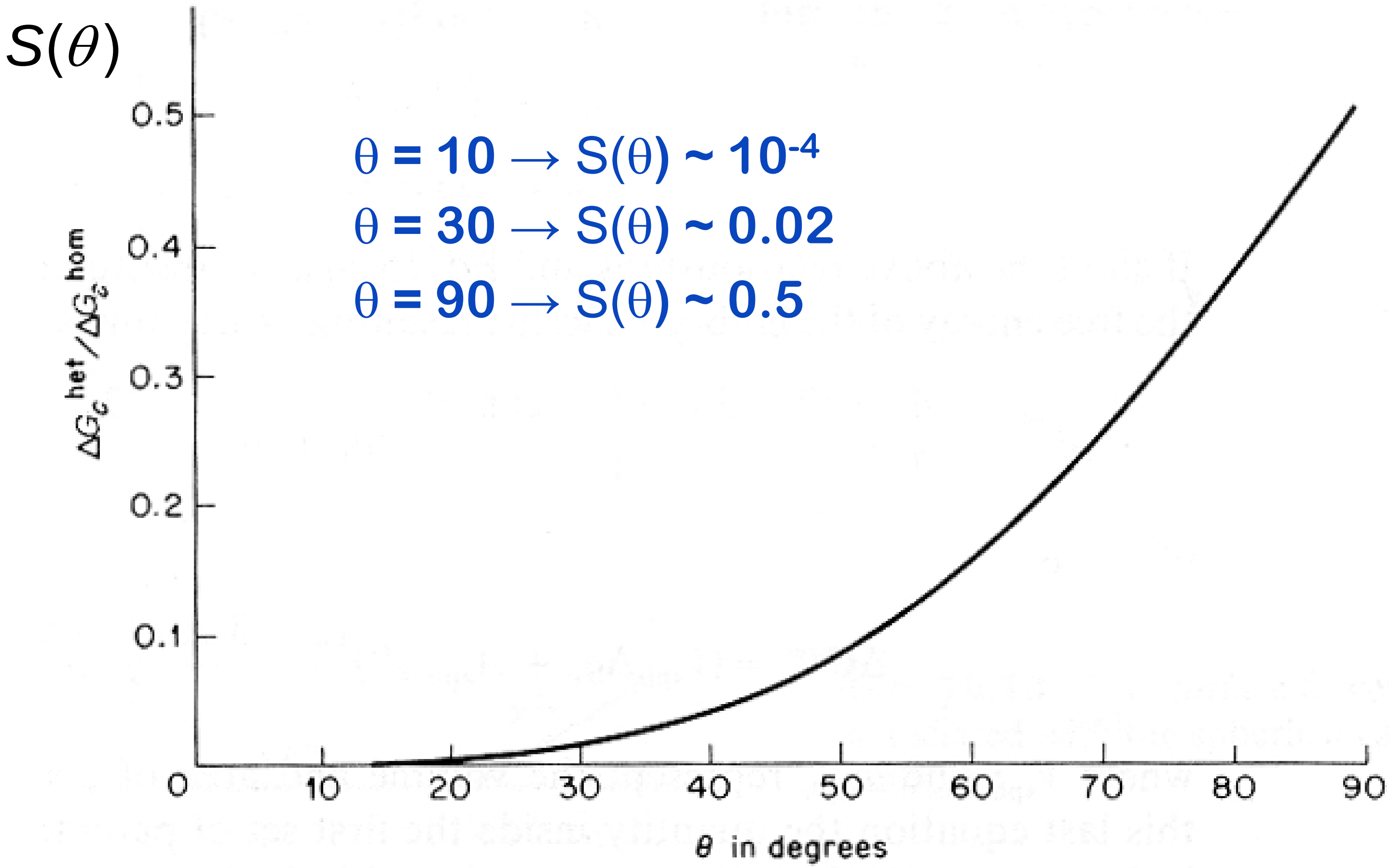
In terms of the wetting angle (θ) and the cap radius (r) (Exercies 4.6)

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

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)

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



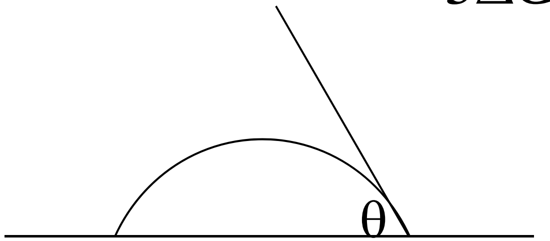
θ = 10 → S(θ) ~ 10^{-4}

θ = 30 → S(θ) ~ 0.02

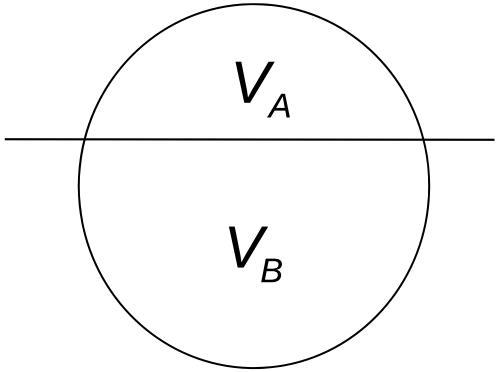
θ = 90 → S(θ) ~ 0.5

Barrier of Heterogeneous Nucleation

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



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



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

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

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

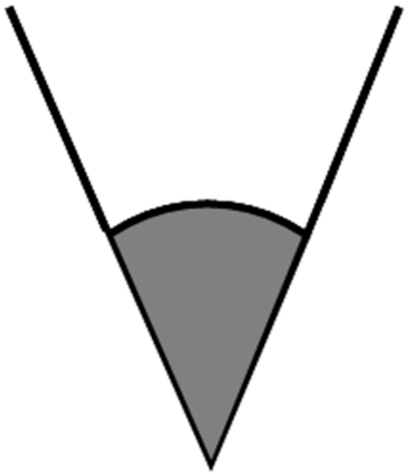
Nucleation Barrier at the crevice

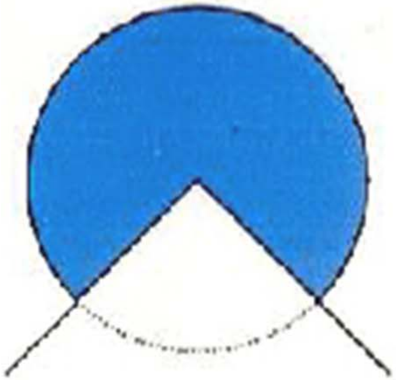
What would be the shape of nucleus and the nucleation barrier for the following conditions?

contact angle = 90

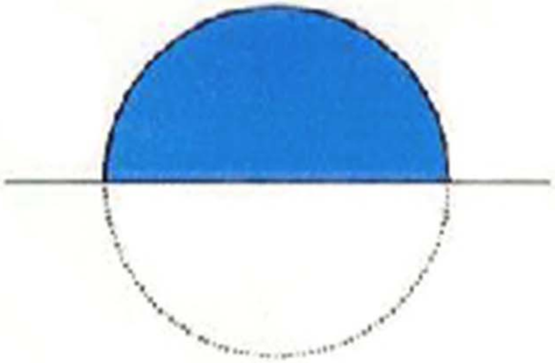
groove angle = 60

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





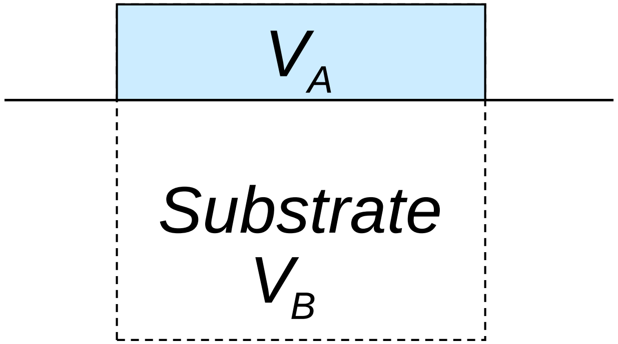
$$\frac{3}{4}\Delta G^*_{\text{homo}}$$



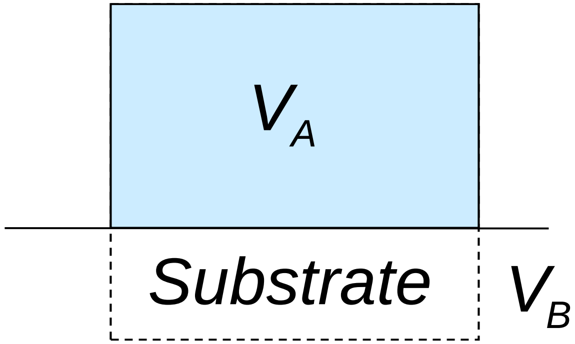
$$\frac{1}{2}\Delta G^*_{\text{homo}}$$

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

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