

2019 Fall

**“Advanced Physical Metallurgy”
- Non-equilibrium Solidification -**

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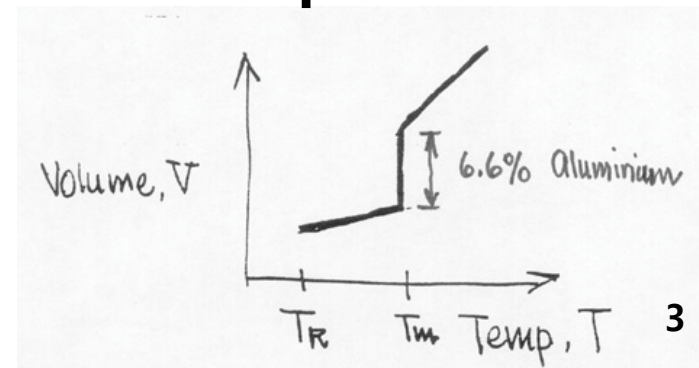
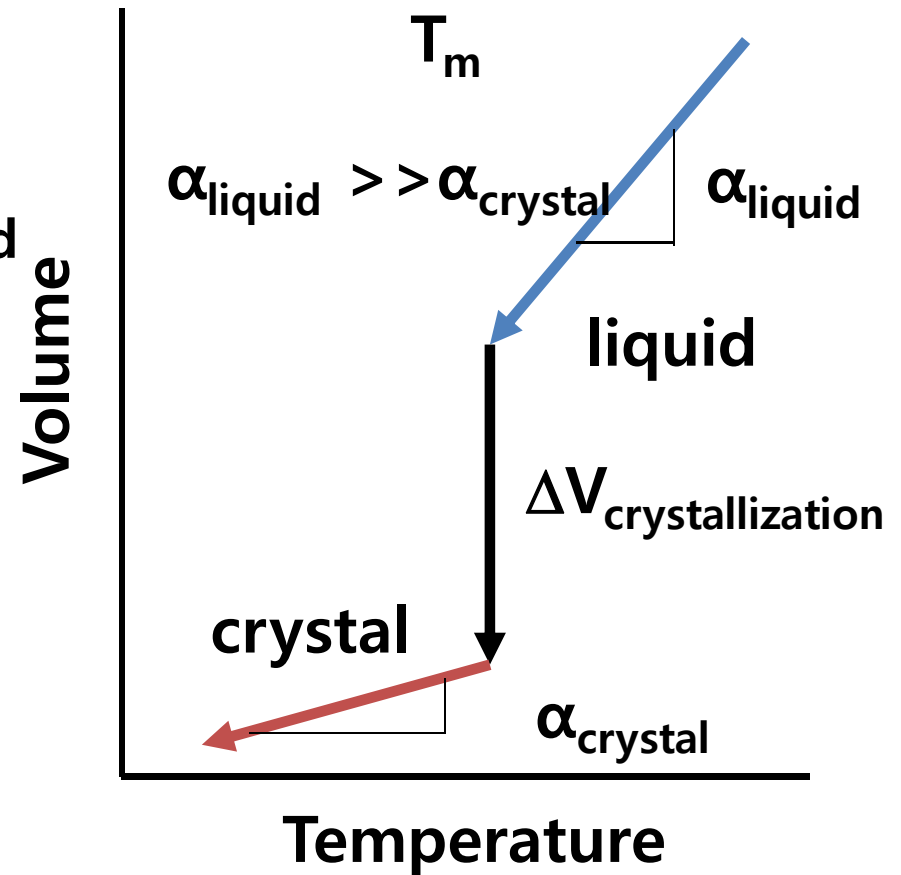
Office hours: by appointment

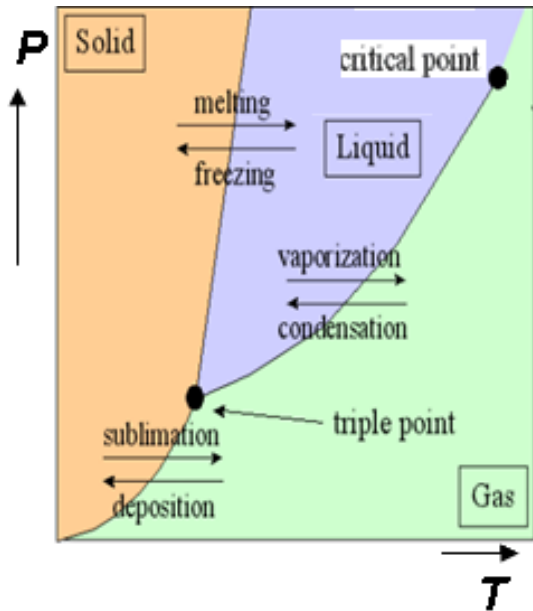
Fundamentals of the Glass Transition

- **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 °C 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

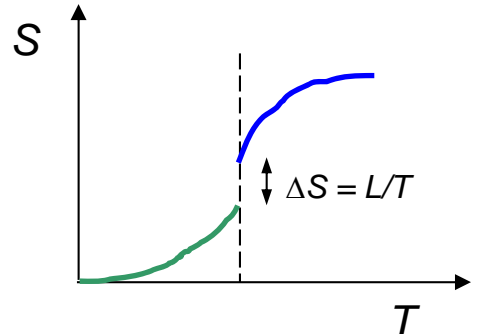
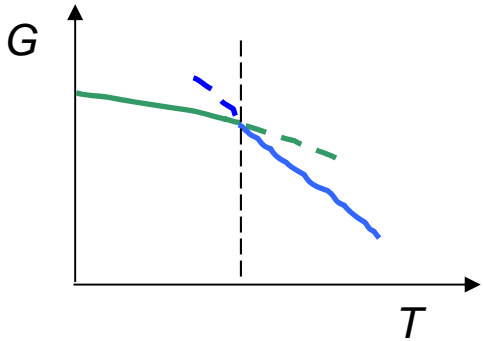
- Volume is high as a hot liquid
- Volume **shrinks** as liquid is cooled
- At the melting point, T_m , the liquid crystallizes to the thermodynamically stable crystalline phase
- More compact (generally) crystalline phase has a smaller volume
- The crystal then shrinks as it is further cooled to room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



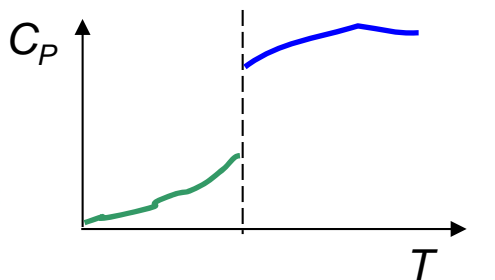


The First-Order Transitions

Latent heat
 Energy barrier
 Discontinuous entropy, heat capacity



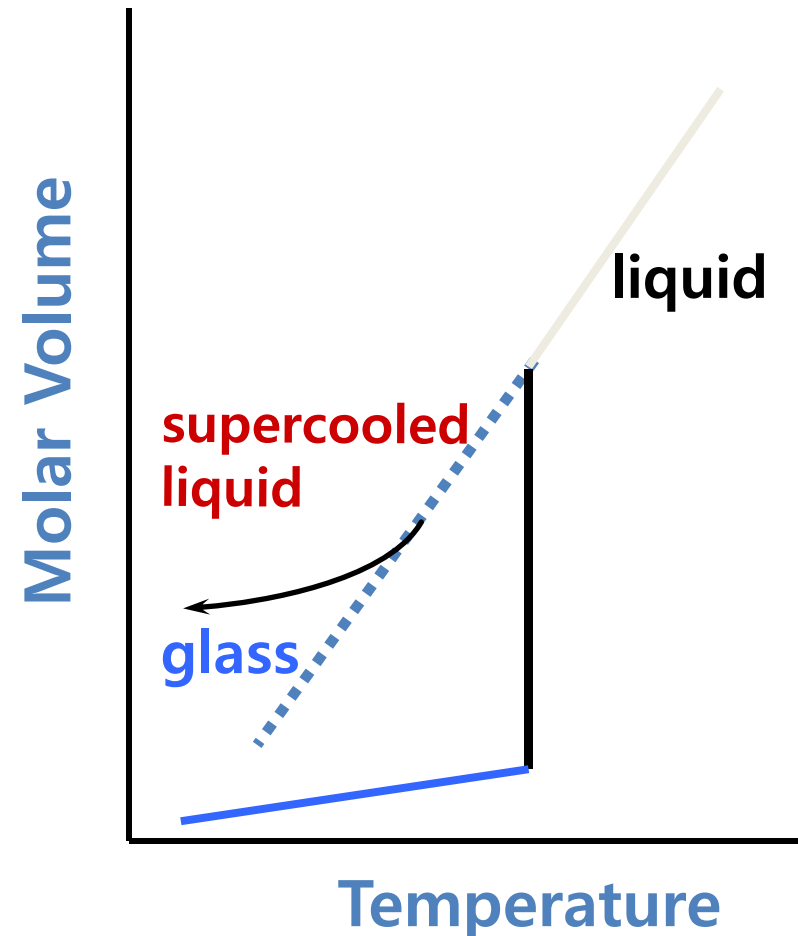
$$C_P = T \left(\frac{\partial S}{\partial T} \right)_{P,N}$$



- 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
- $$V = \left(\frac{\partial G}{\partial P} \right)_T \quad S = - \left(\frac{\partial G}{\partial T} \right)_P \quad H = G - T \left(\frac{\partial G}{\partial T} \right)_P$$
- Second derivatives of G (α , β , C_p) are **discontinuous** at T_T
- $$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \beta = \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$
- Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

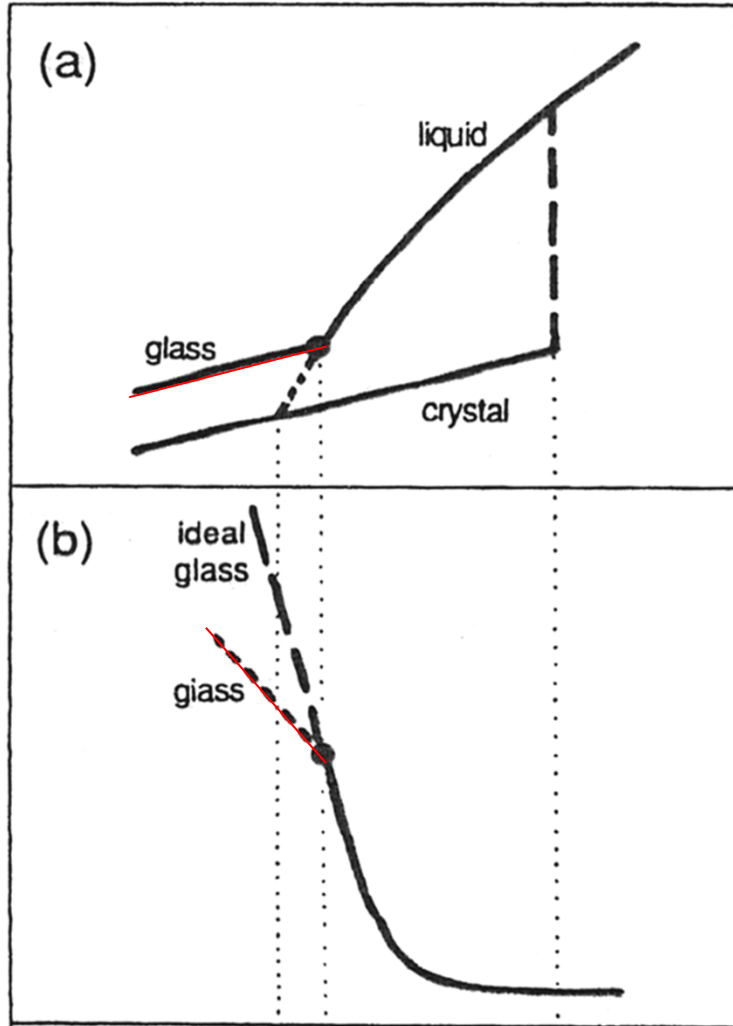
Glass Formation is Controlled by **Kinetics**

- 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



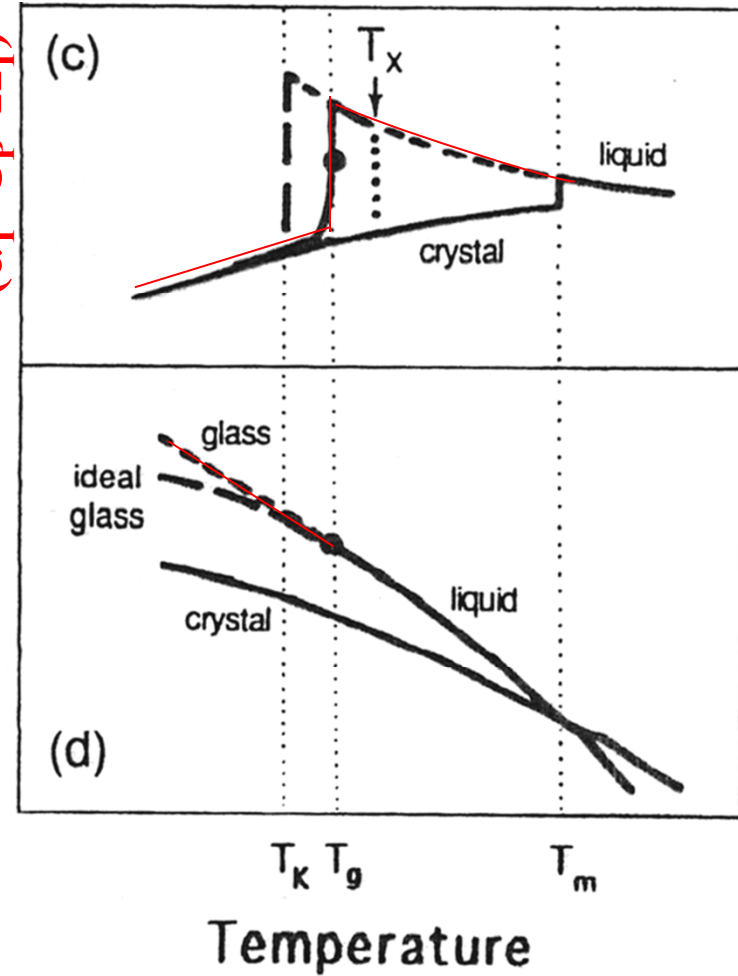
Entropy (V, S, H)

continuous

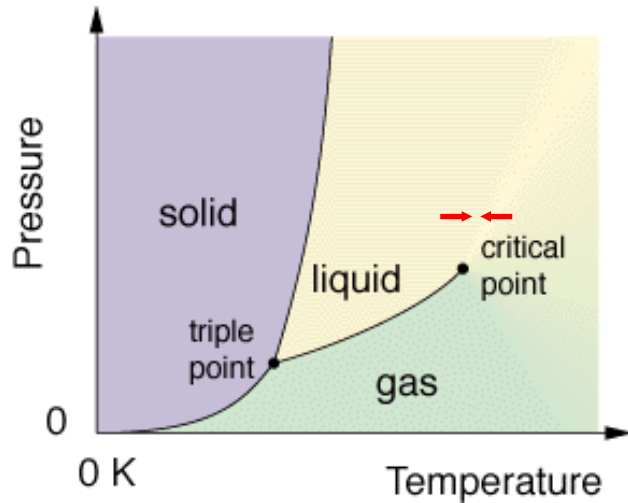


discontinuous

Specific heat
($\alpha_T C_p K_T$)



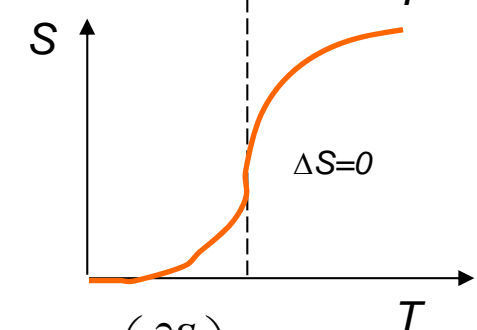
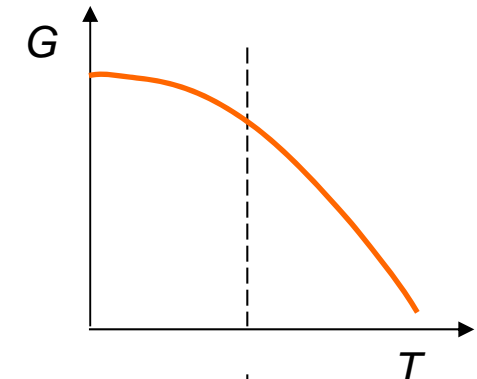
Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.



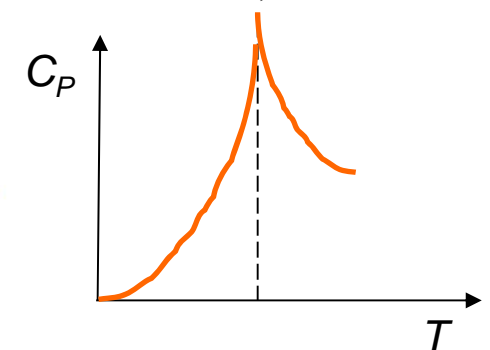
The Second Order Transition

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

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

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

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

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

Theories for the glass transition

A. Thermodynamic phase transition

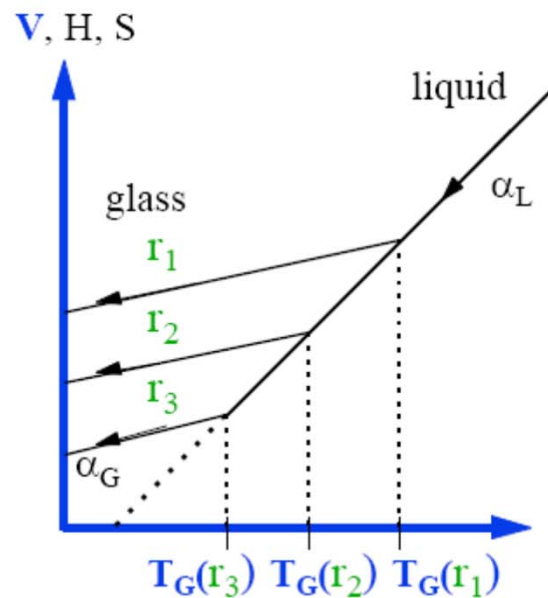
- **Glass transition**

H, V, S : continuous

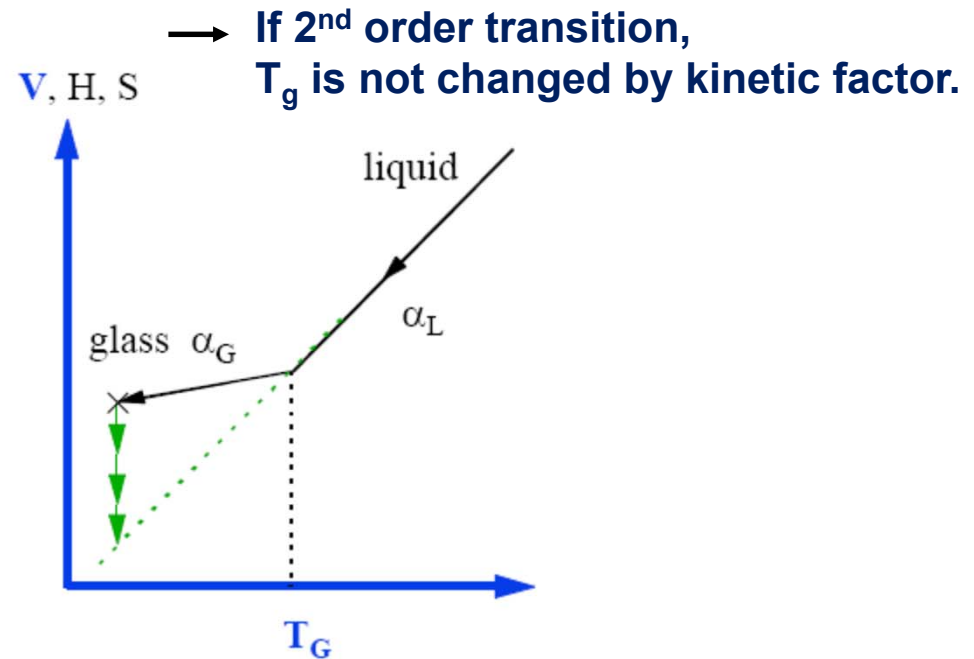
C_p, α_T, K_T : discontinuous

→ by thermodynamic origin, 2nd order transition

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



T_g 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 $T < T_g$

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

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

measurable

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

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

It is found **by measuring the discontinuities** $\Delta\alpha_T, \Delta C_P, \Delta\kappa_T$ 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.”**

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

Prigogine Defay Ratio

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

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. ”

• 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

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

→ α_T, C_P, κ_T changes discontinuously.

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

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

Heat capacity
at constant P or V

Coefficient of
thermal expansion

Compressibility
at constant T or S

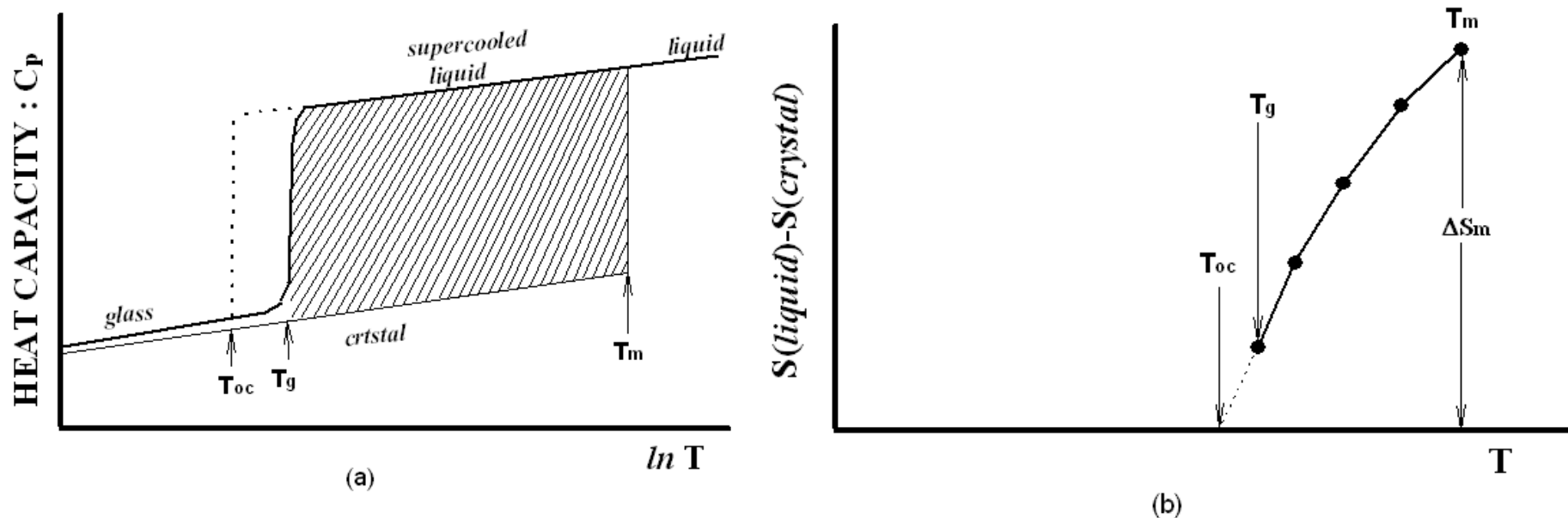
❖ The glass transition is 'pseudo' second-order phase transition.

And the transition depends on **kinetic factors.**

Theories for the glass transition

B. Entropy

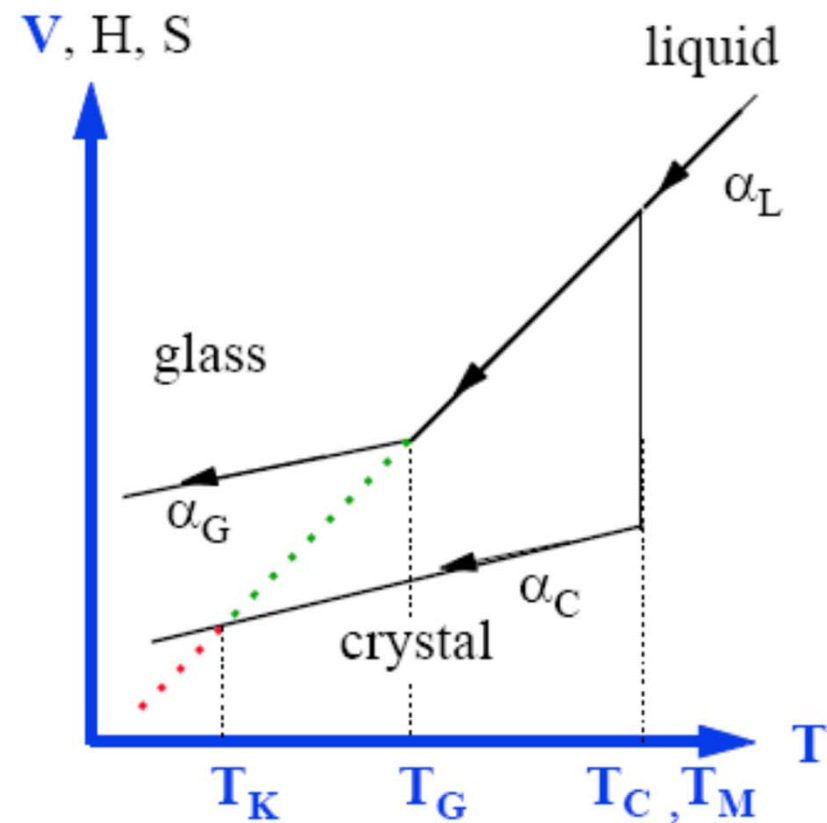
- Description of glass transition by entropy (Kauzmann)
- **Ideal glass transition temperature ($T_{oc} = T_g^0$)**
: lower temperature limit to occur glass transition thermodynamically



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 transition 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 !!

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 $T_G = (2/3) T_M$
- 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 rearrangements. 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 ?

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

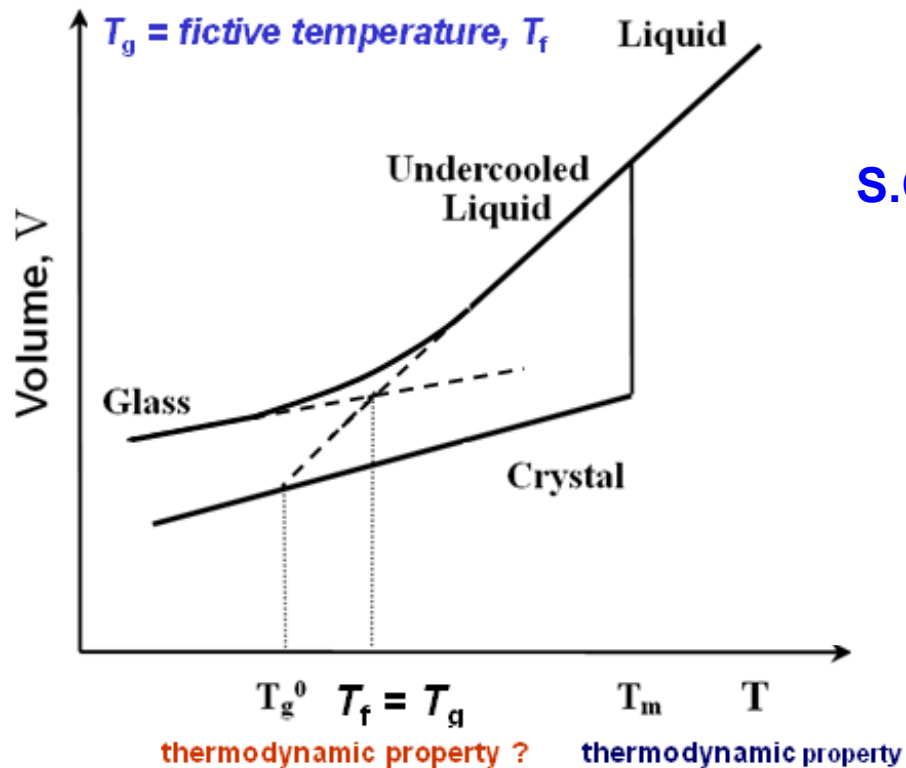
Time scale separation between microscopic, experimental, relaxation; the system is out of equilibrium on the experimental time scale.

(cf. S.K. Ma, Statistical Physics)

- 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 T_g 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.

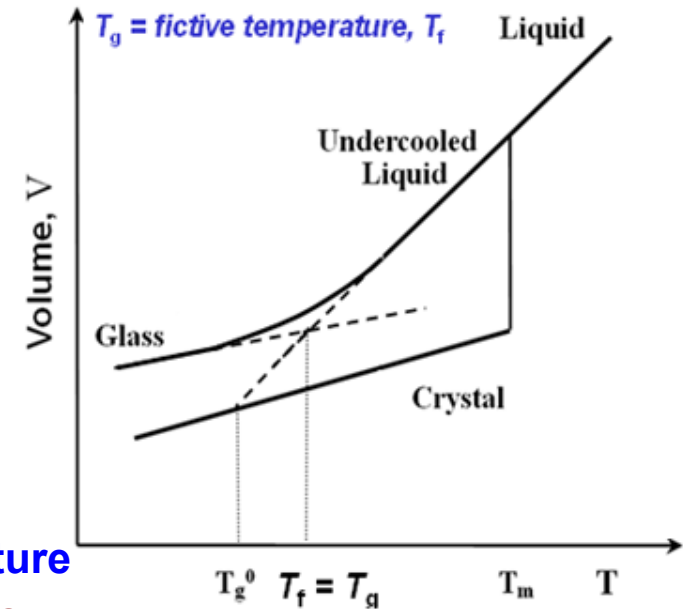
Atomic configuration of glass
 : try to move to equilibrium state
 → **relaxation behavior**

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)**

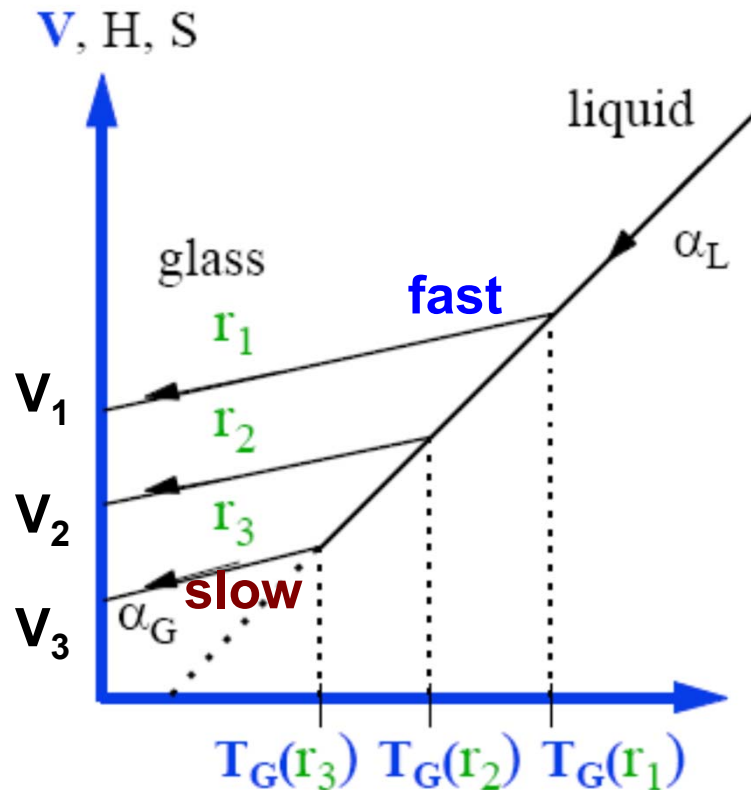
→ If (1) > (2) ⇒ liquid // (1)~(2) ⇒ **glass transition** // (1) < (2) ⇒ glass

(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



T_g 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 \rightarrow lower density structure
 \rightarrow higher transport properties

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

\rightarrow “Relaxation behavior”

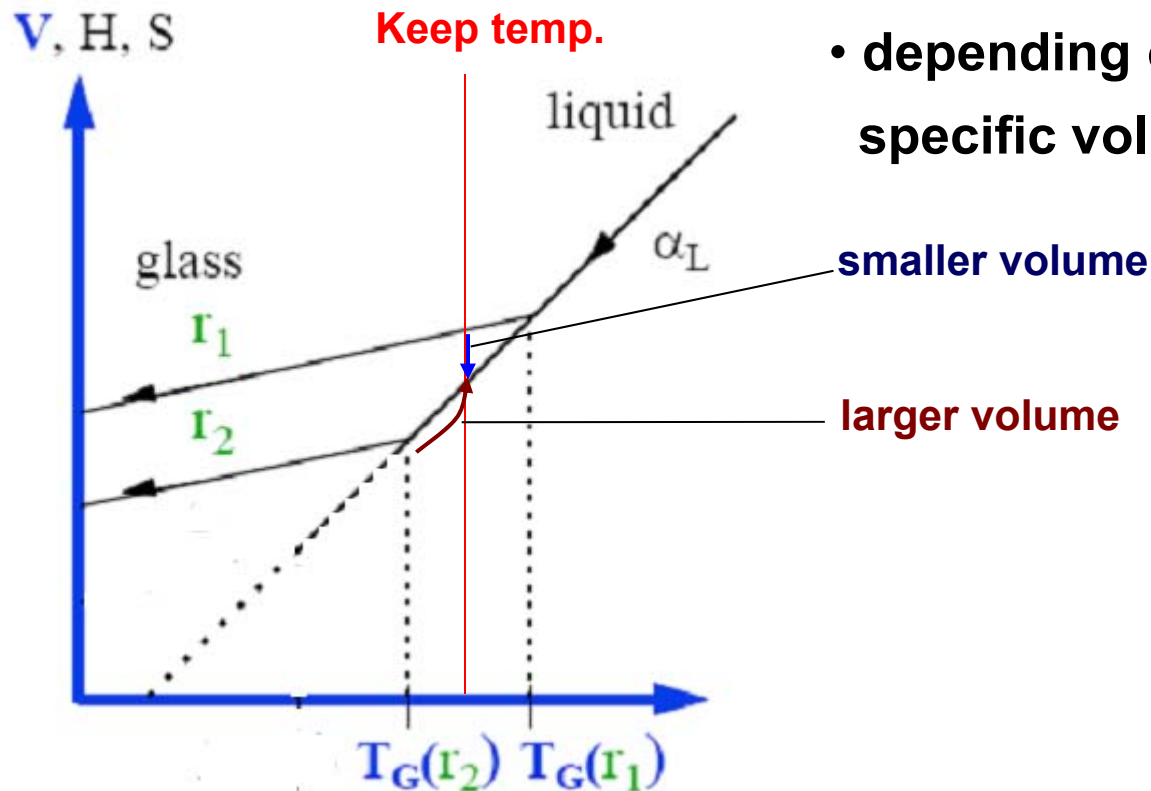
In fact, many properties of glass changes depending on relaxation behavior.

C. Relaxation behavior

- In glass transition region, properties change with time.

* Process of relaxation behavior: **stabilization**

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



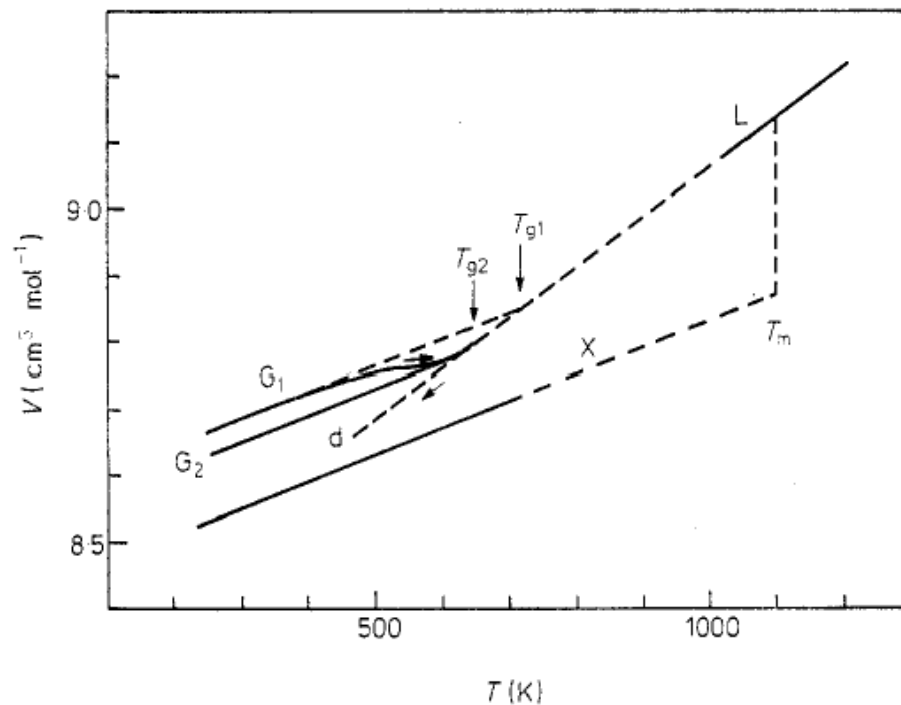
- depending on cooling rate, specific volume **↑** or **↓**

C. Relaxation behavior

✦ Correlation between structural relaxation time and cooling rate

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

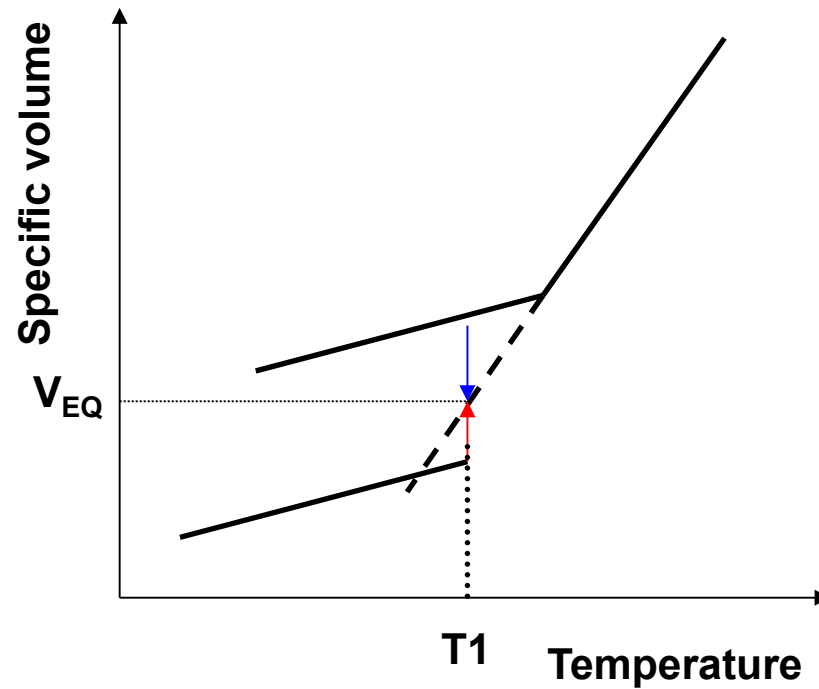
$q = -dT/dt$: cooling rate
 Q : activation energy of viscous flow



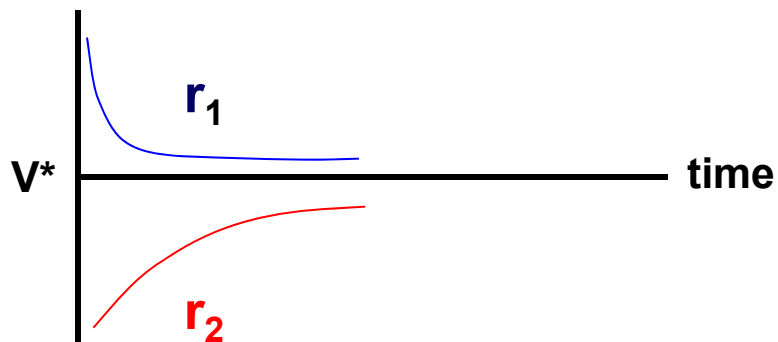
<Specific volume of PdCuSi>

- 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

Relaxation from initial volumes above and below the equilibrium volume



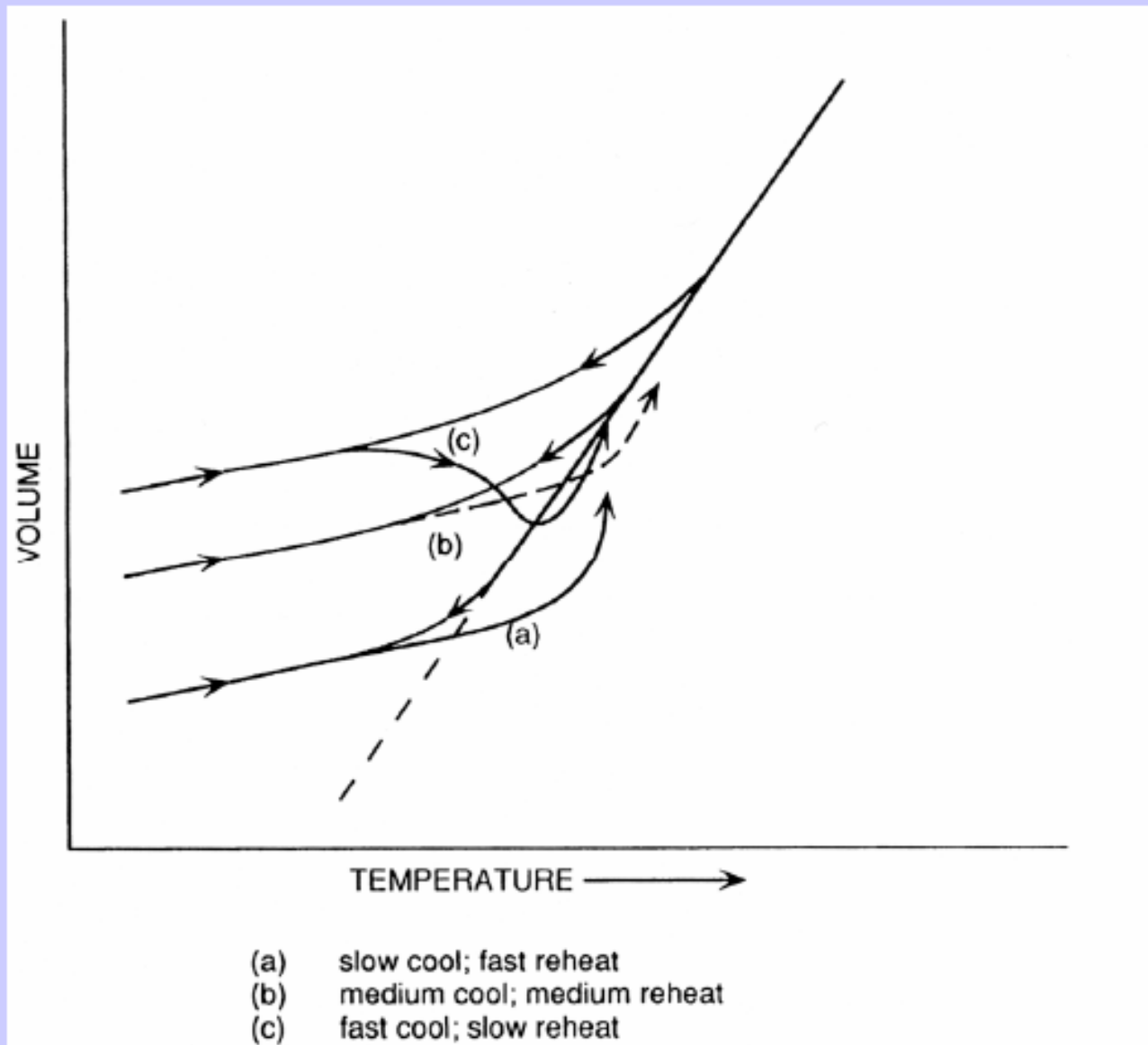
Variation of volume with time form initial volumes above and below the equil. volume



• relaxation kinetics

$$r_1 > r_2$$

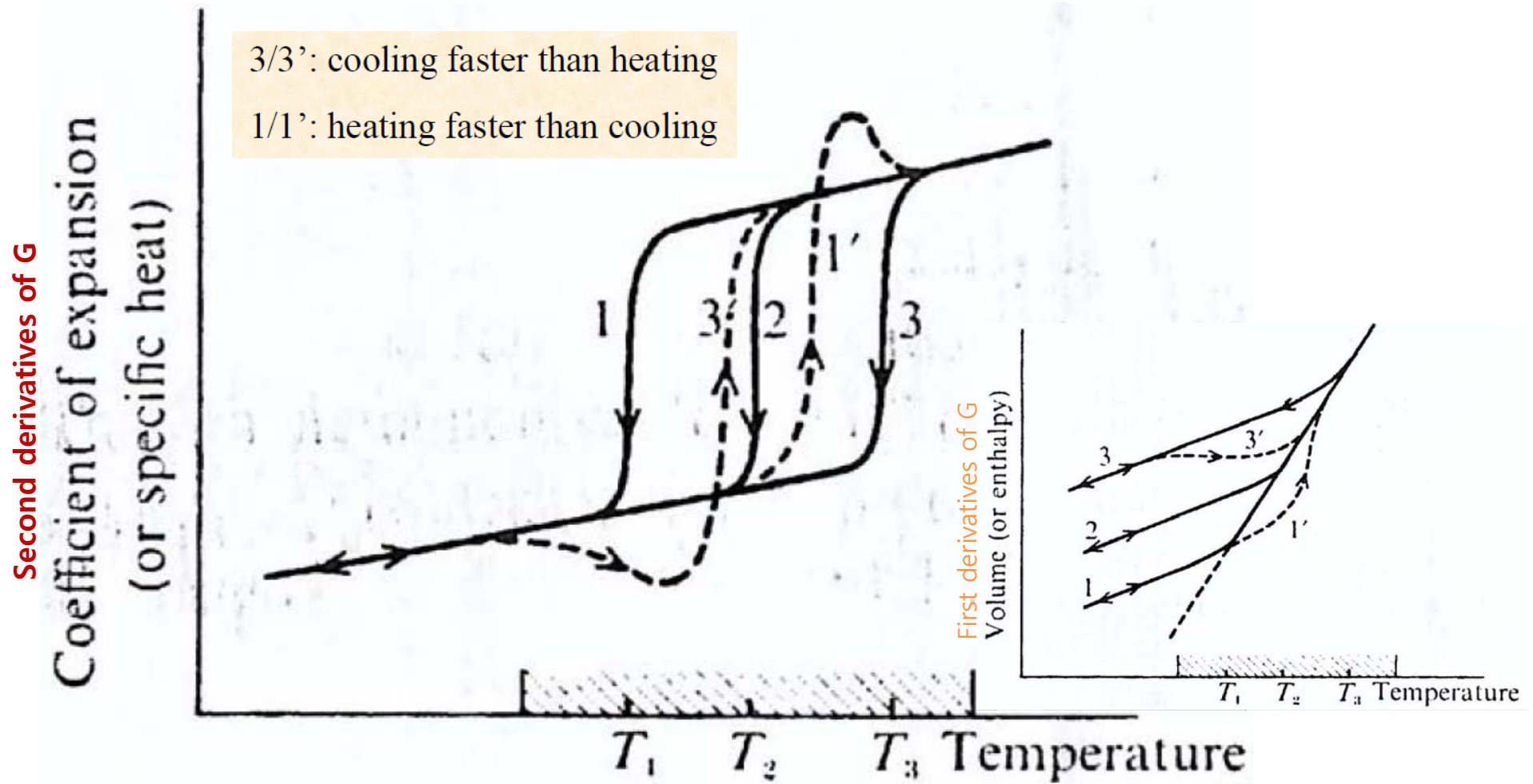
Volume structural relaxation



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



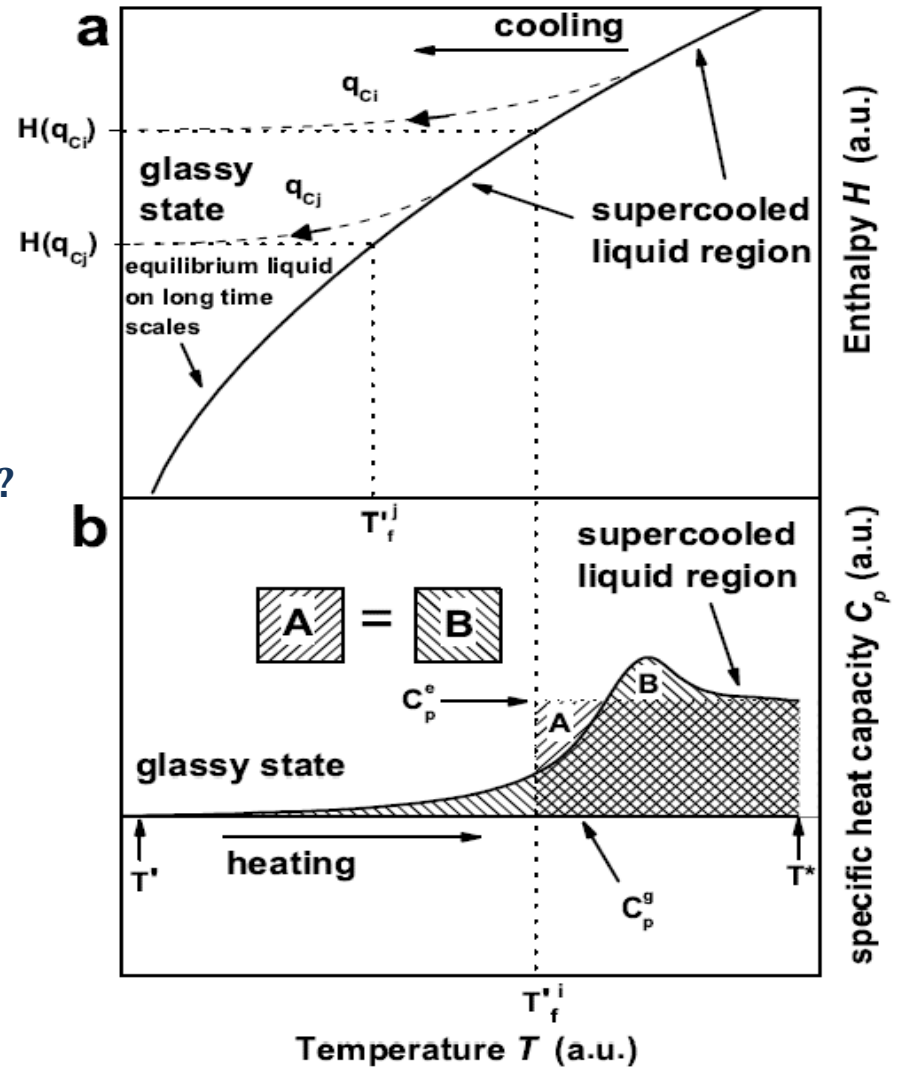
overshoot in heating process

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

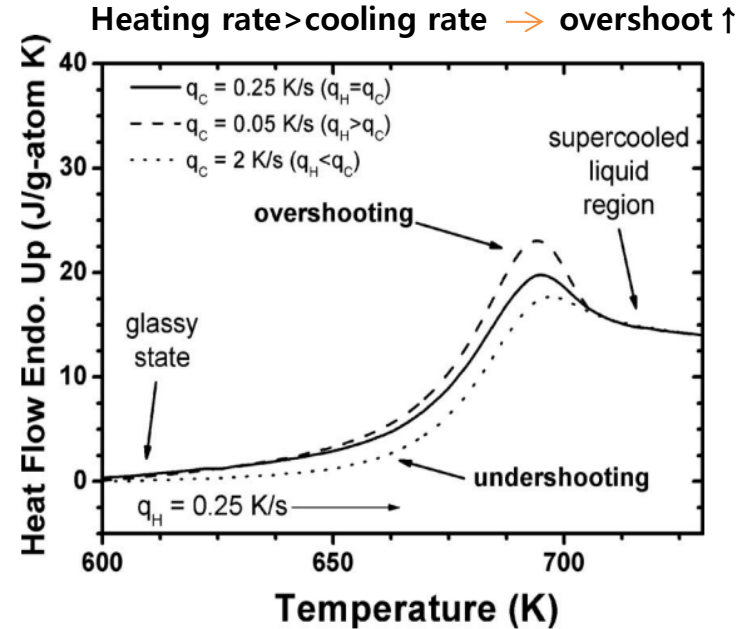
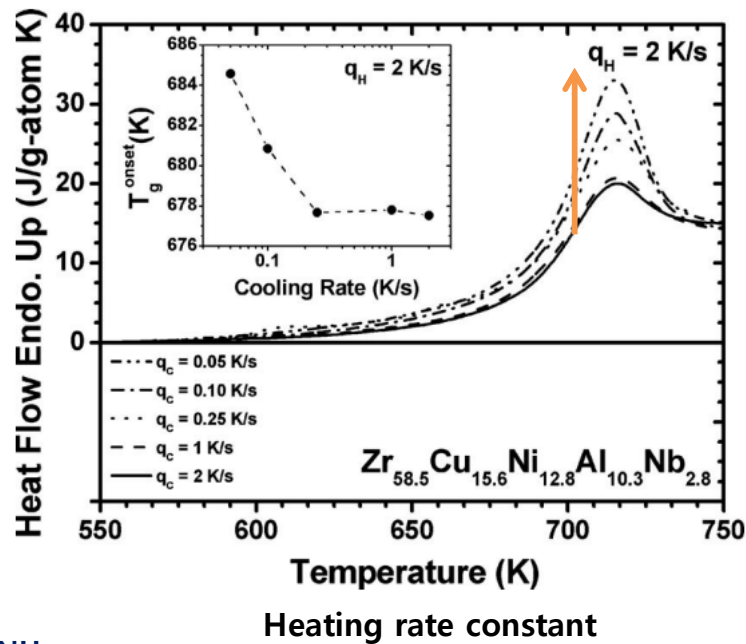
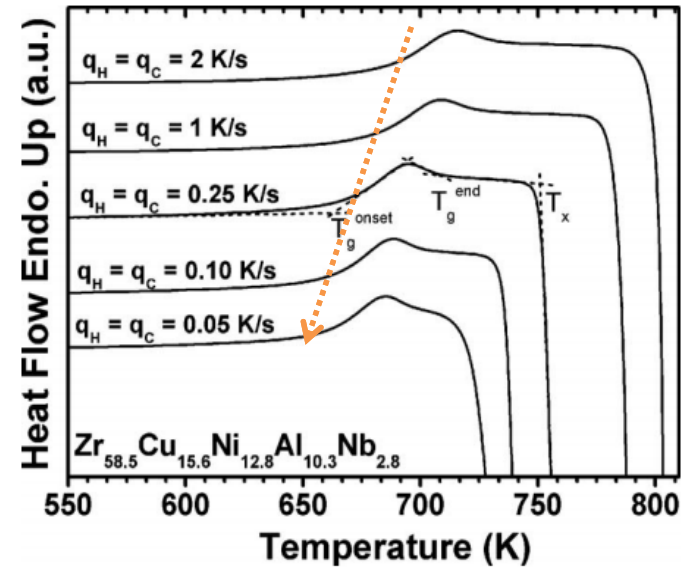
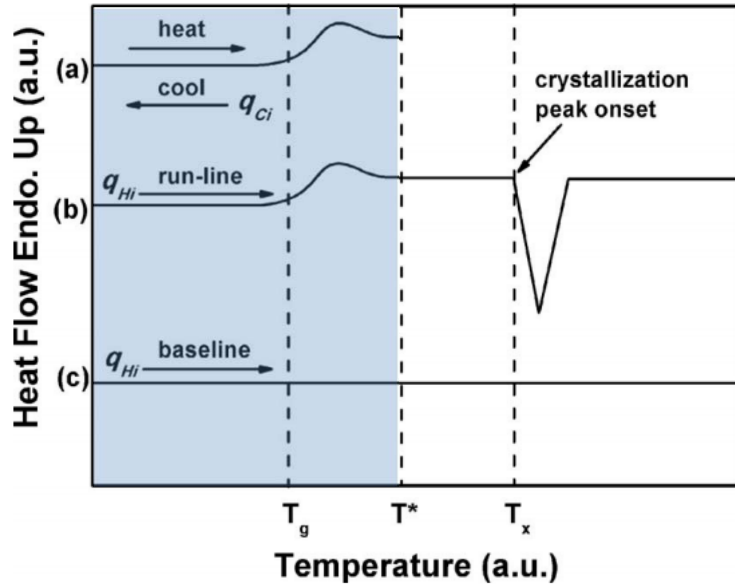
Heating rate dominant or cooling rate dominant?

Determined from DSC up-scan

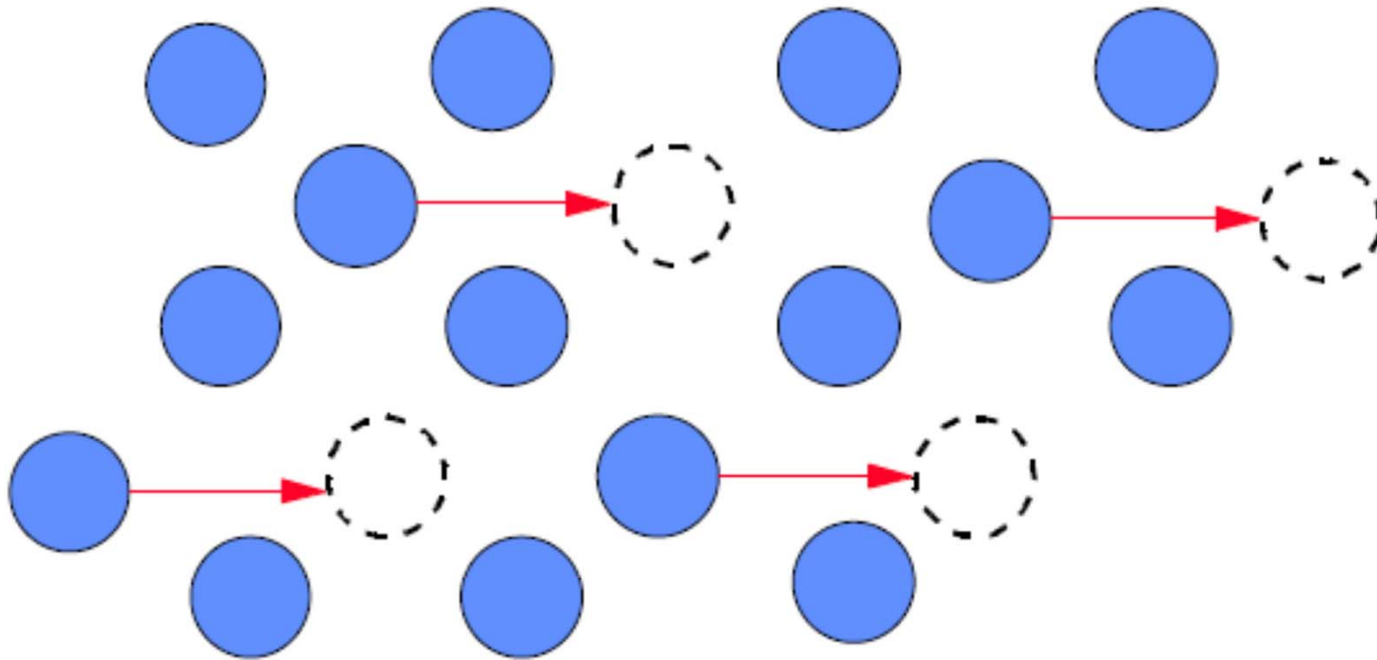
$$\int_{T^*}^{T'_f} (C_p^e - C_p^g) dT_f = \int_{T^*}^{T'} (C_p - C_p^g) dT$$



Heating and cooling rate controlled by DSC

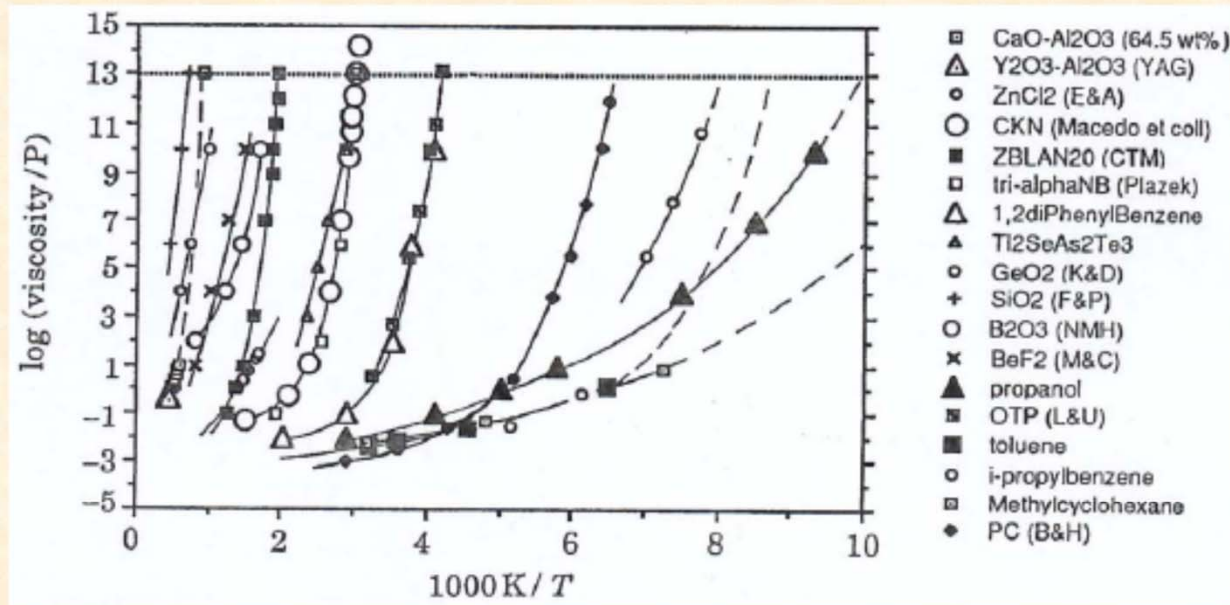


Temperature Dependence of Liquid Viscosity



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 one another, 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

$$\updownarrow \quad \eta = \eta_0 \exp\left[\frac{E_a}{RT}\right]$$

Fragile network glass : Vogel-Fulcher relation

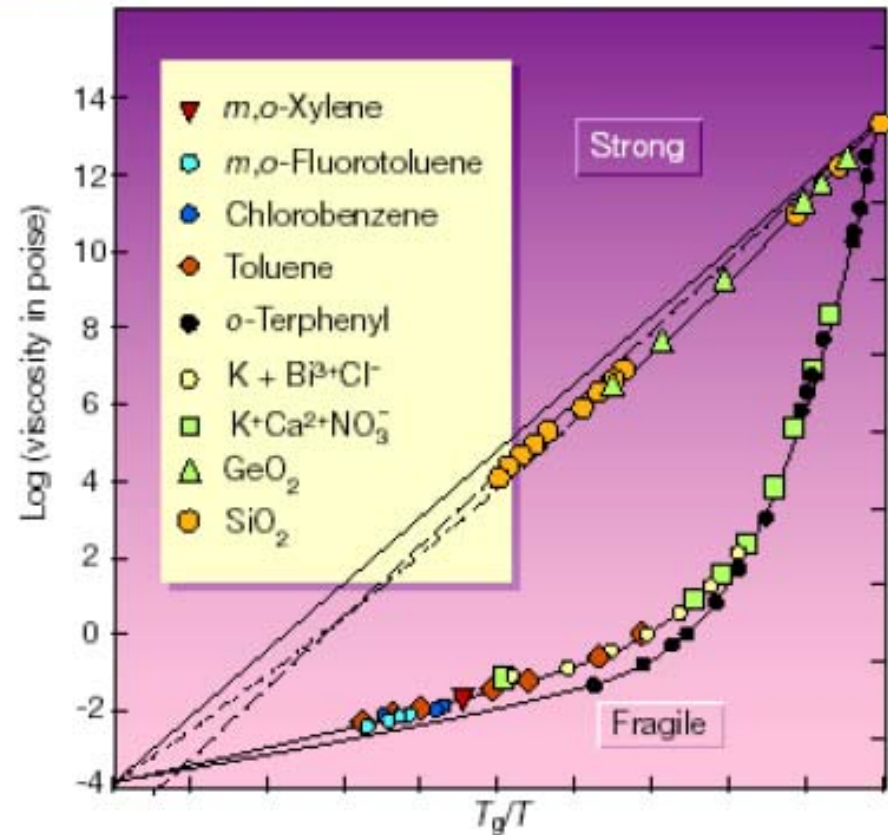
$$\eta = \eta_0 \exp\left[\frac{B}{T - T_0}\right]$$

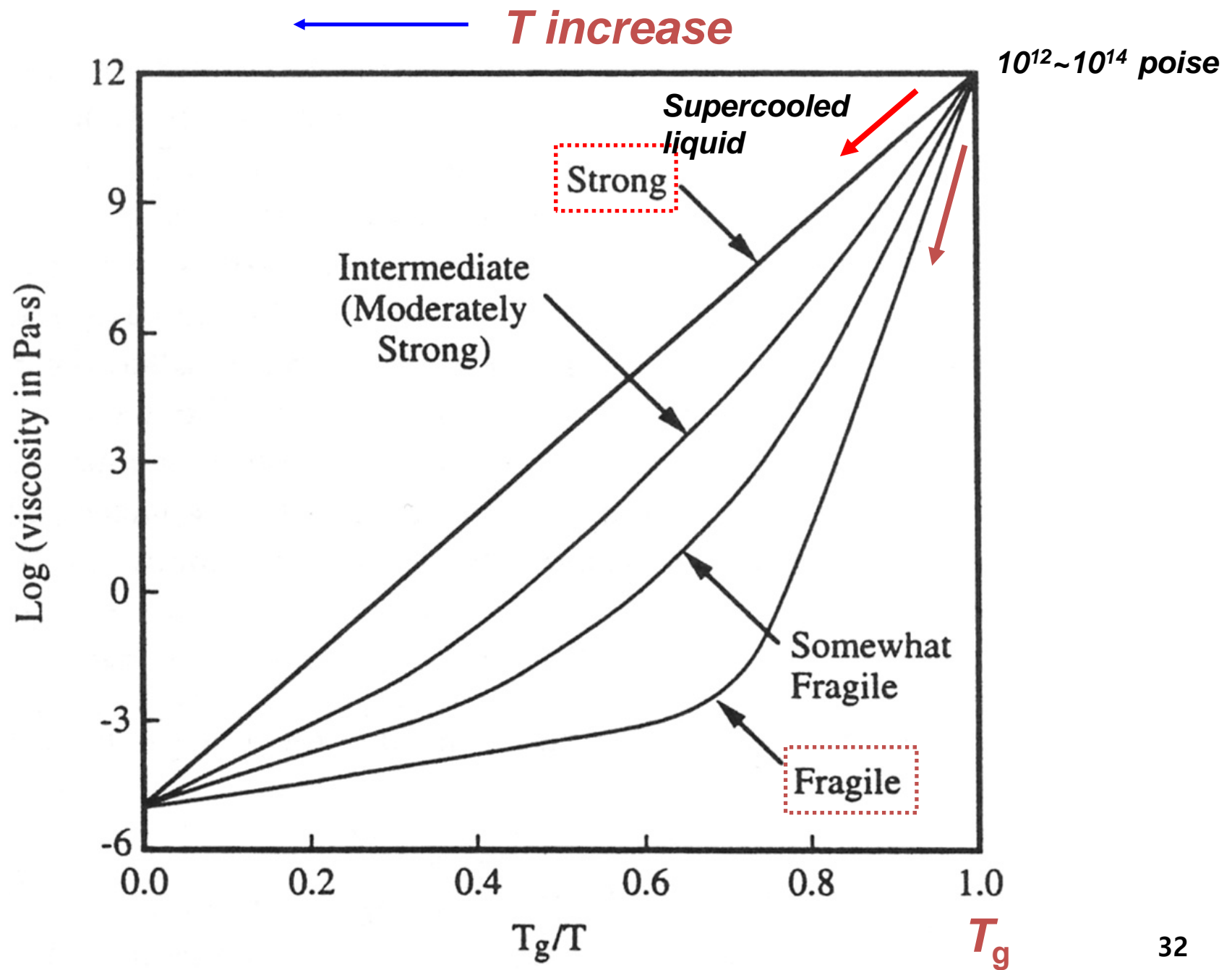
< Quantification of Fragility >

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

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

Angell-plot (Uhlmann)





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)

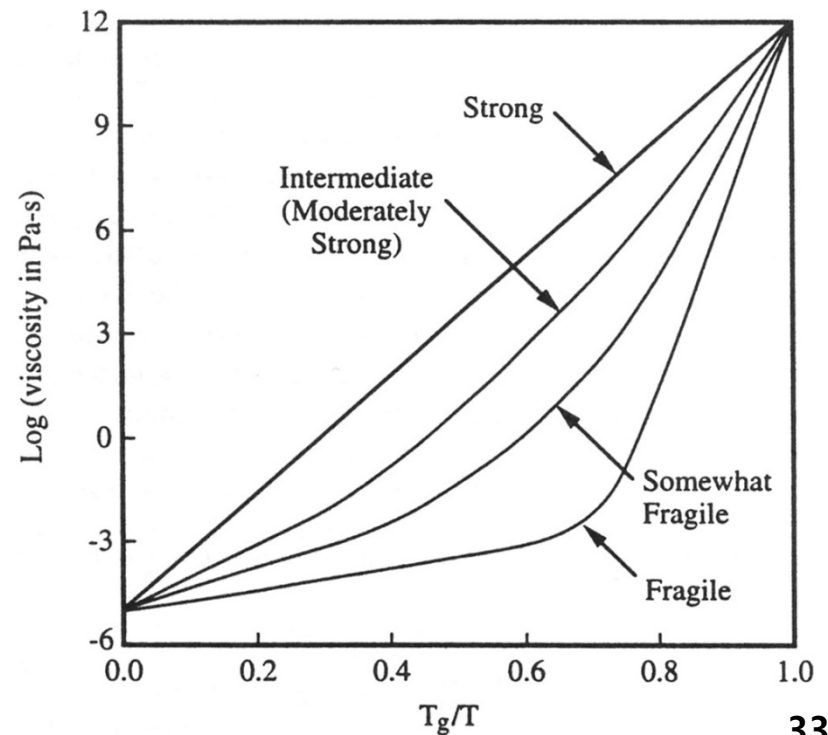
- SCL: relatively low entropy

- **fragile glass-forming liquid**

- non-directional bonding
(Van der waals bonding)

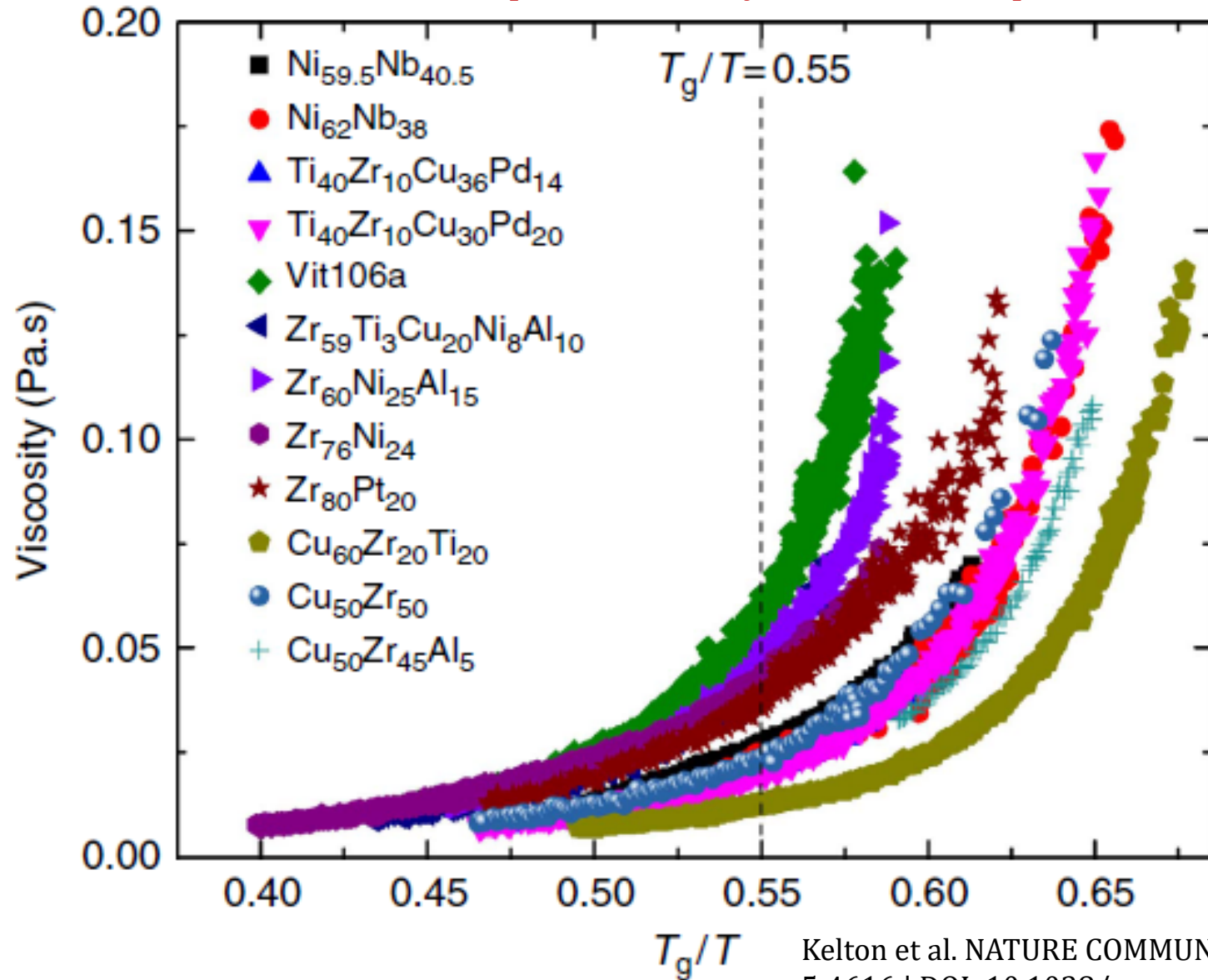
- large difference of C_p at T_g
(relatively large free volume)

- SCL: relatively high entropy



Viscosity variation of liquid during cooling

No clear relationship btw viscosity variation of liquid vs GFA!



Homework :

4) Please explain T_A temperature?

5) How to determine fragility in metallic liquid?

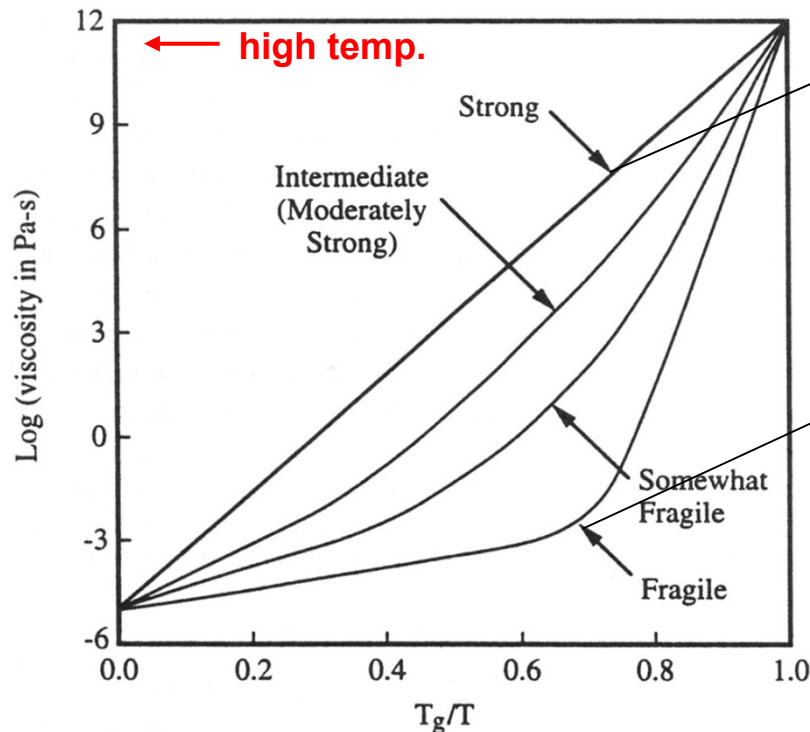
Due date: 15 October 2019

d. viscosity

* Another definition of glass transition;

- **Viscosity (10^{15} centiPoise = 10^{12-13} 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

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

→ Oxide glass ex) SiO_2 , GeO_2

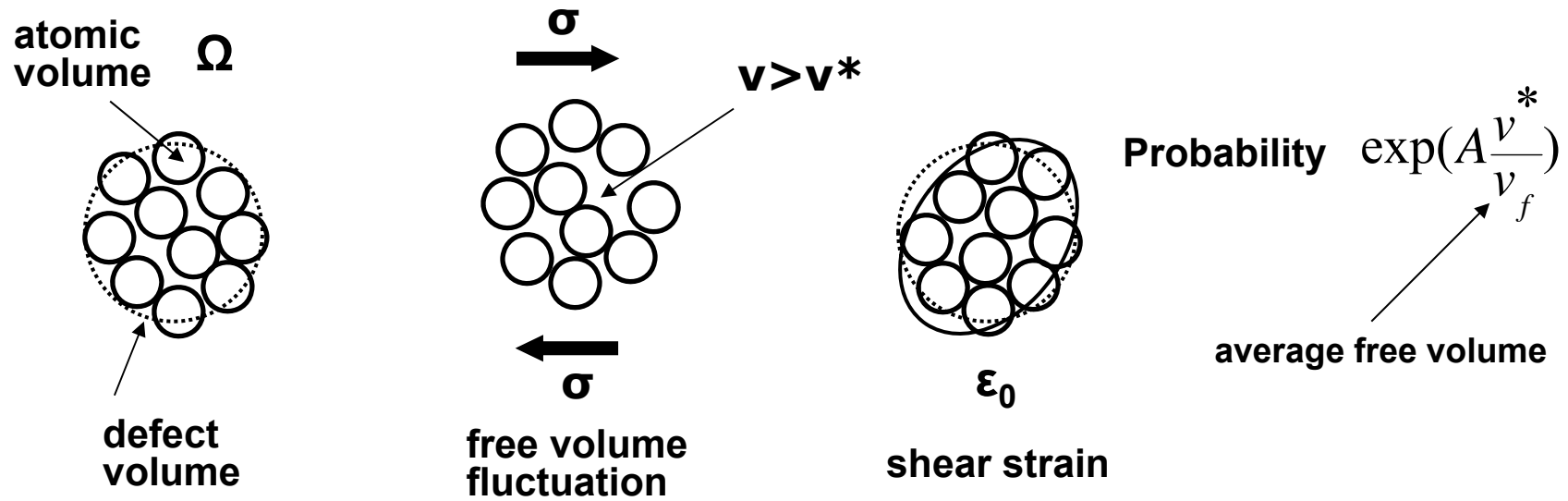
fragile glass : Vogel-Fulcher relation
- deviation from simple Arrhenius behavior

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

→ 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** (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 T_g

- Description of glass transition by entropy (Kauzmann)

$$S = \int C_P d \ln T \rightarrow \text{The slow cooling rate, the lower } T_g \rightarrow T_K \text{ or } T_g^0$$

→ 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^{12-13} 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