

2014 Spring

**“Advanced Physical Metallurgy”
- Bulk Metallic Glasses -**

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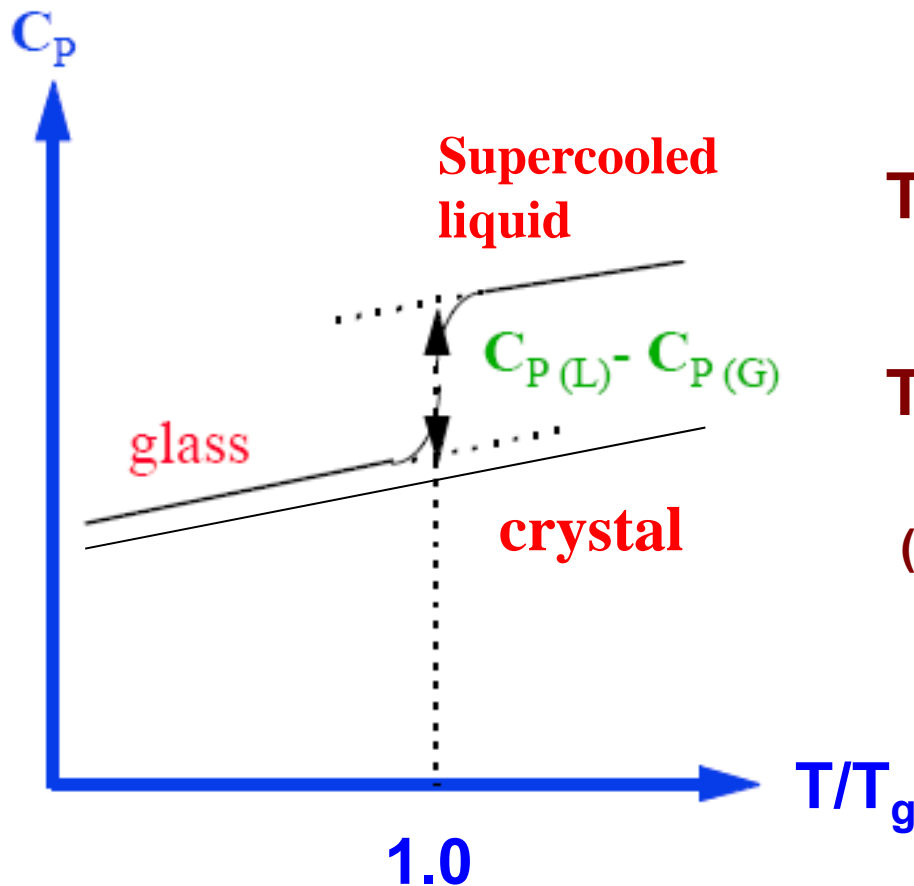
Theories for the glass transition

B. Entropy

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

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

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



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

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

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

Theories for the glass transition

B. Entropy

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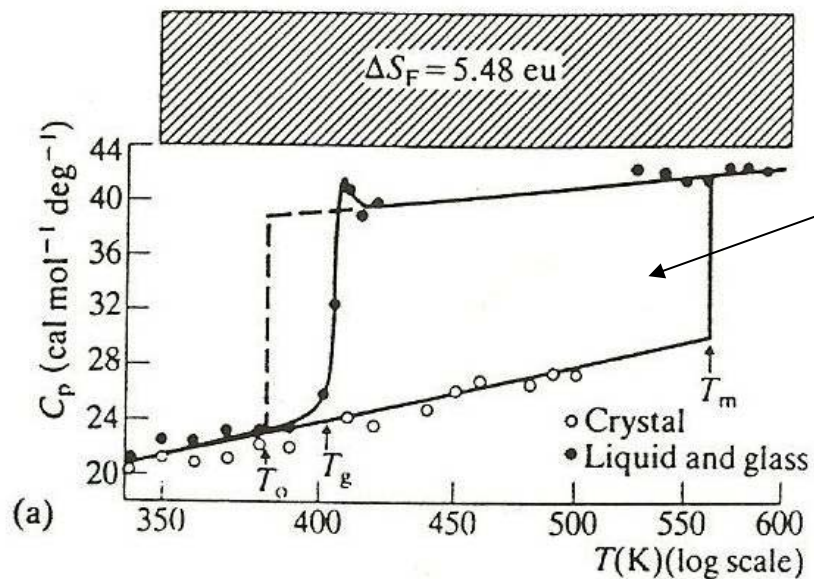
2) The slow cooling rate, the lower T_g

→ **ideal glass transition temperature exist?**

→ **YES**

Glasses

Entropy of fusion



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

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.

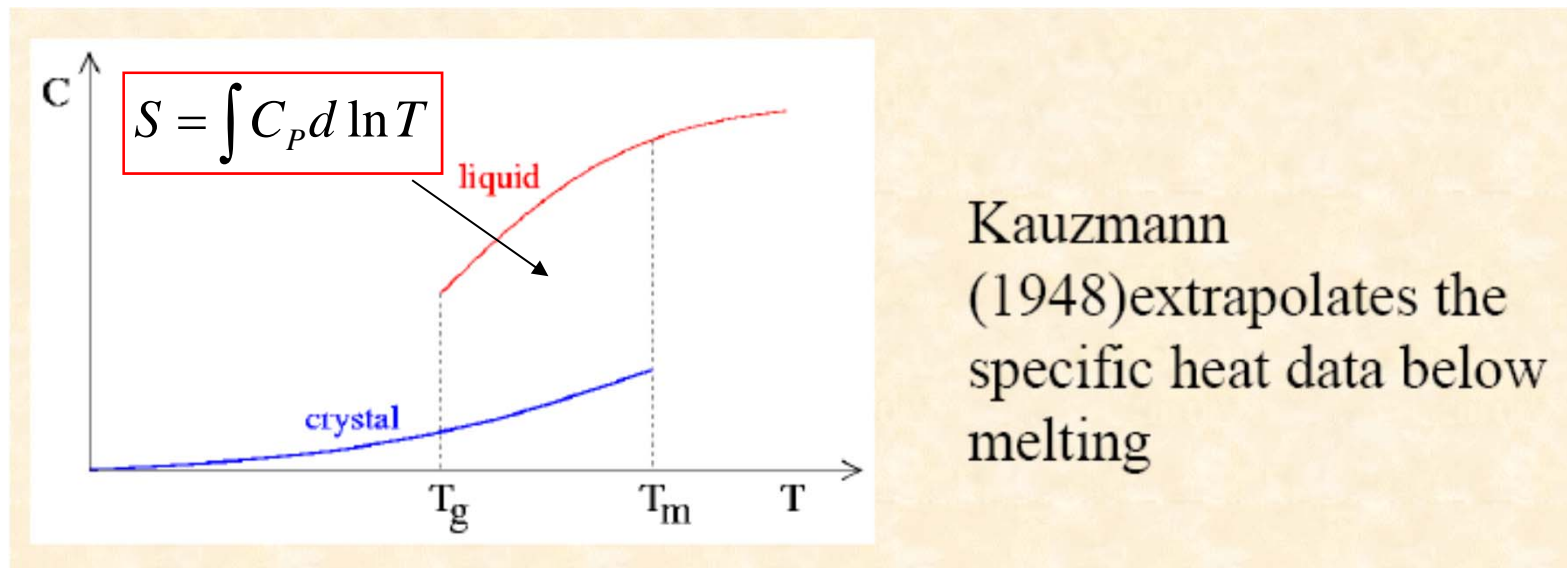
Heat capacities of glassy, liquid and crystalline phases of lithium acetate

Theories for the glass transition

B. Entropy

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

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



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

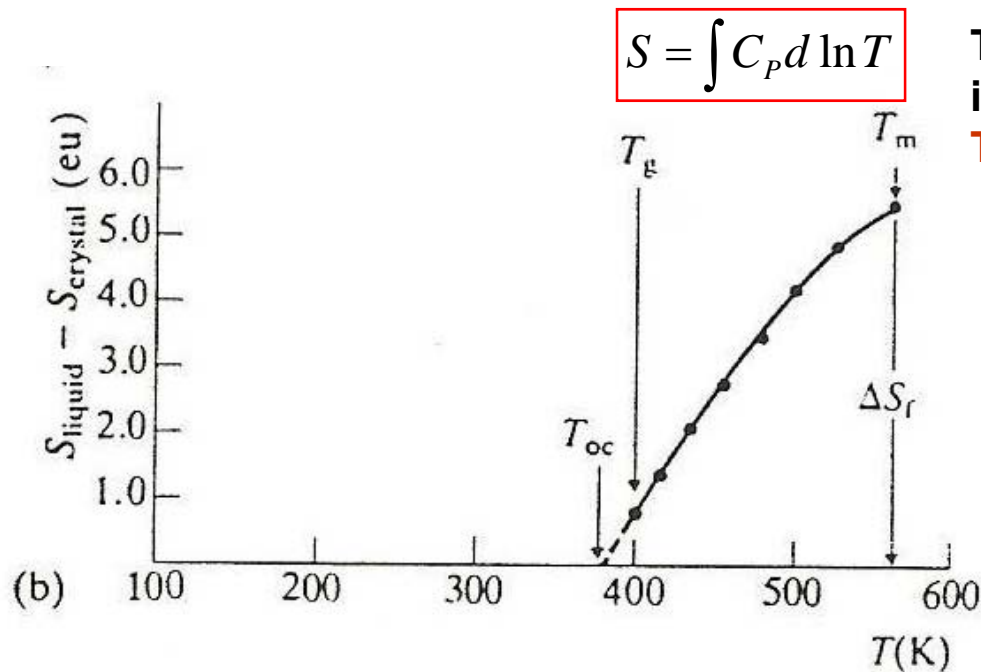
$C_{\text{liquid}} > C_{\text{crystal}}$: *entropy in the liquid decreases faster with T than in the crystal.*

Theories for the glass transition

B. Entropy

- Description of glass transition by entropy (Kauzmann)

2) The slow cooling rate, the lower T_g



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

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

➔ If $T_g < T_{oc}$, $S_{liquid} < S_{crystal}$

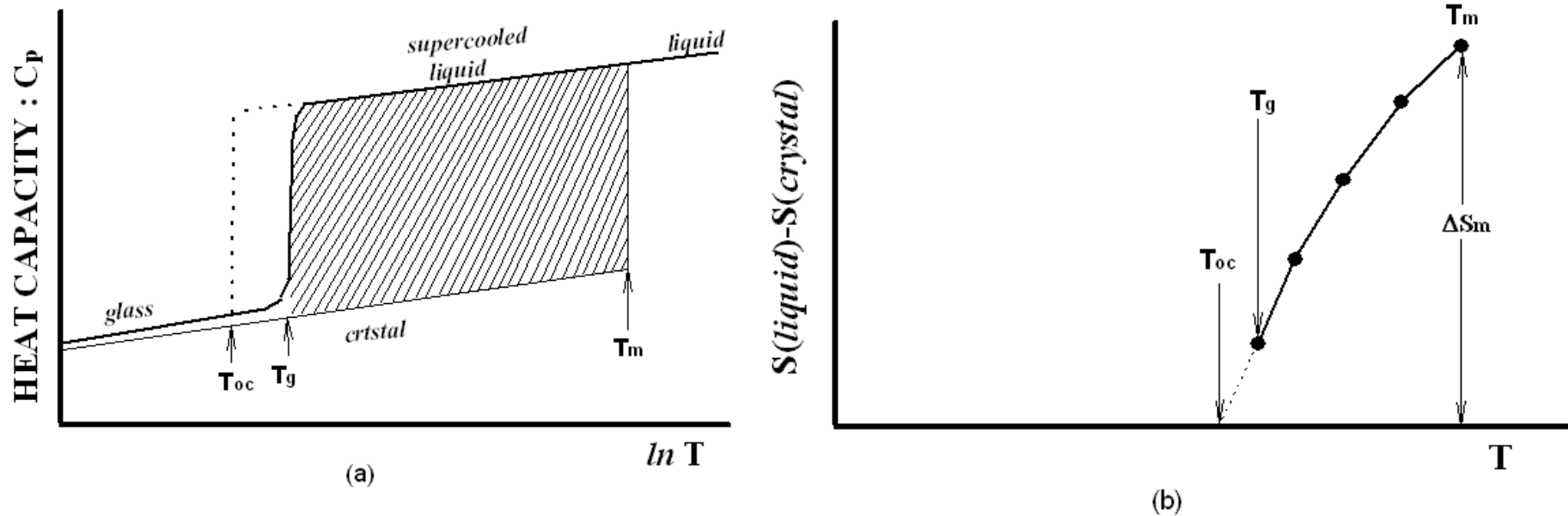
violating third law of thermodynamics

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

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

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

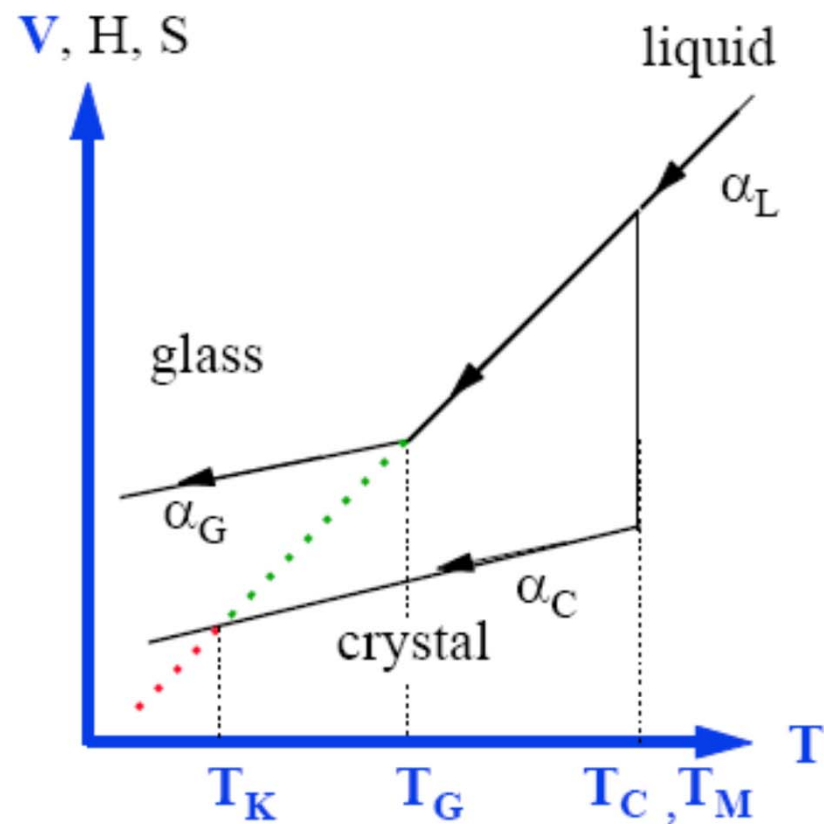


Variation of (a) C_p and (b) excess entropy, S depending on temp. for glass, crystal and liquid. Ideal glass transition temp, T_{oc} . is the temperature when excess entropy is disappeared.

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:

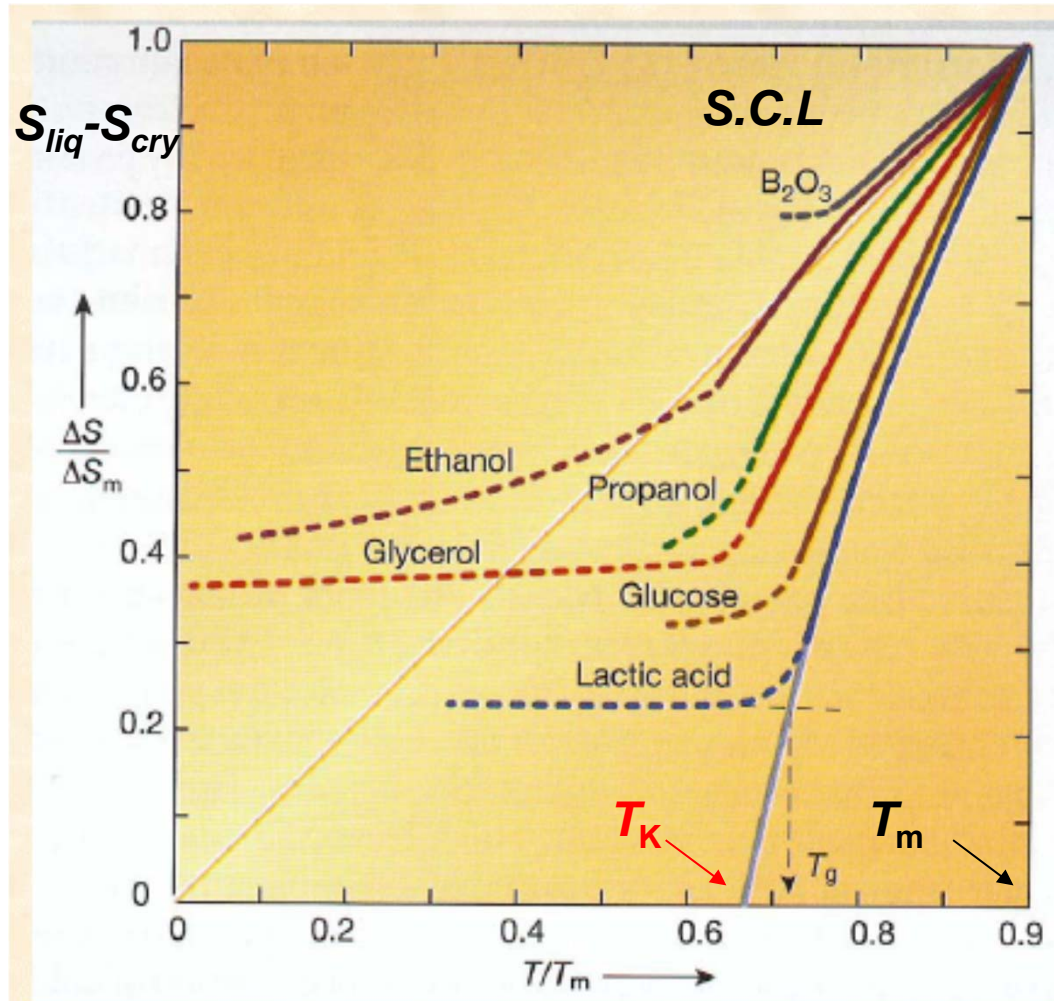
1) at some temperature (T_K), there is a true 2nd order phase transition between the liquid and the glass or 2) the extrapolation to temperatures far below T_G is not valid. So far no one has found the answer !!



* **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.

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

IH: TK에 가장 가까이간 물질로 보고된 것은 무엇인지? (PPT로 제출)

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!!!



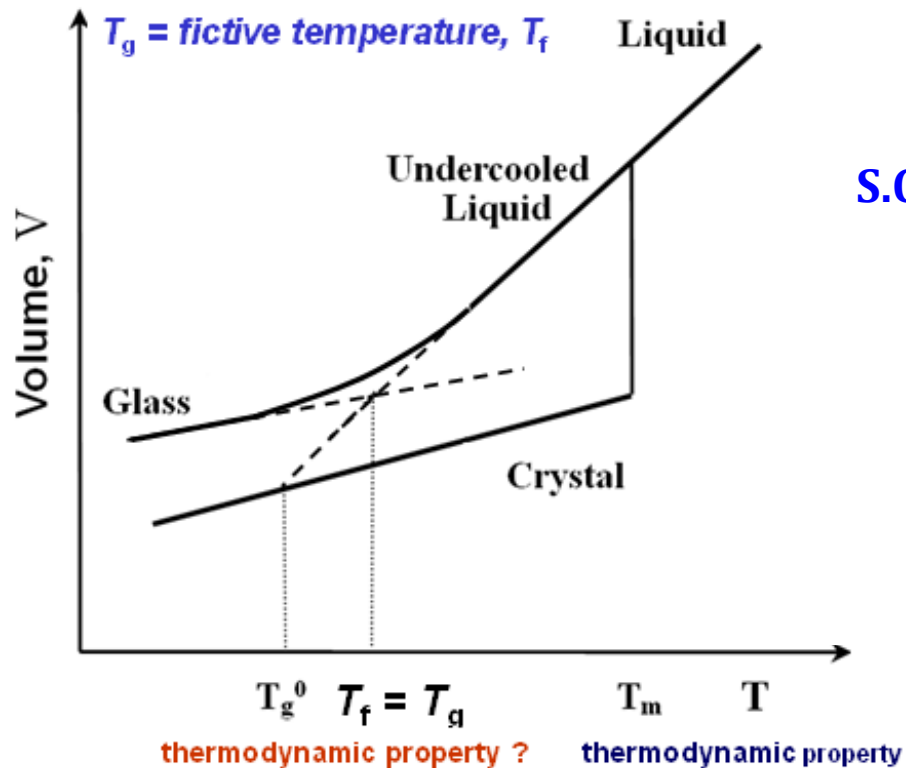
There is a driving force for diamond to convert to graphite but there is (huge) nucleation barrier.

How long it will take is the problem of **kinetics**.

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

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.**

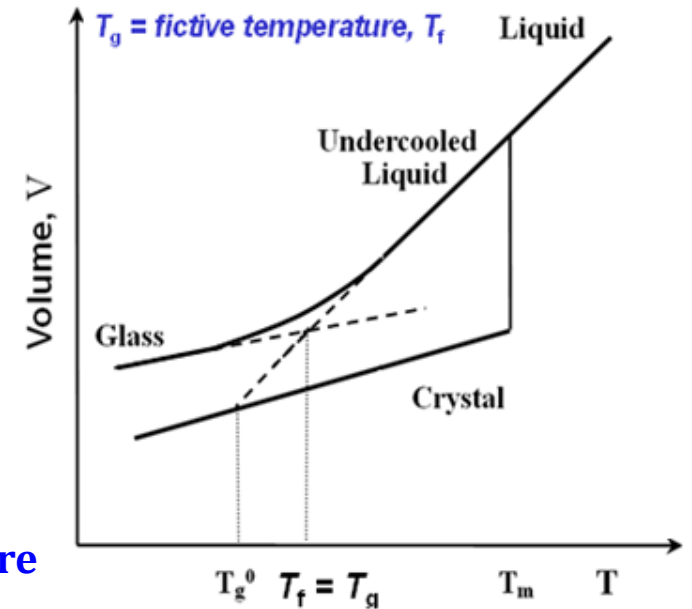
Atomic configuration of glass
: try to move to equilibrium state
→ **relaxation behavior**

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)

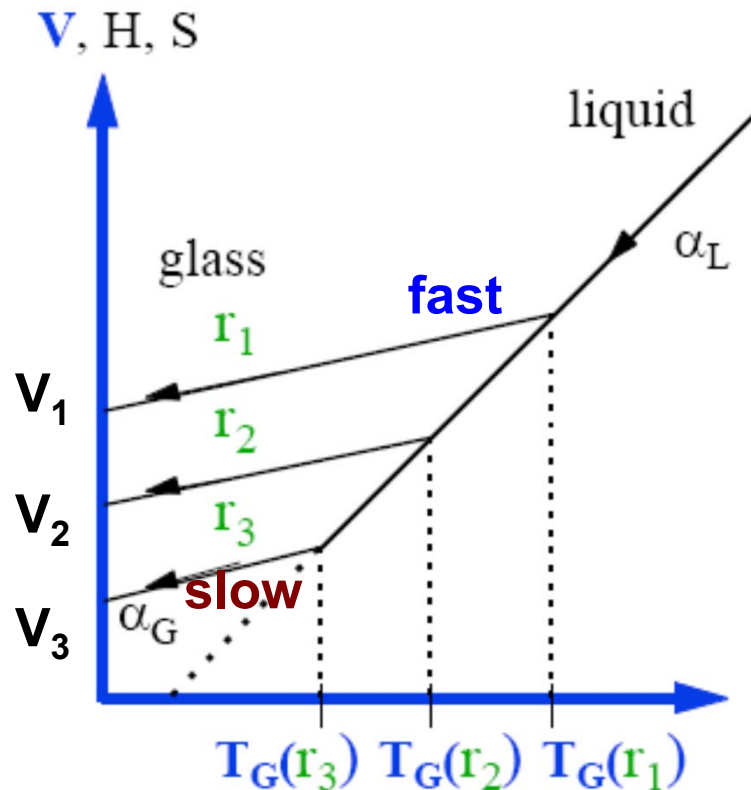
→ If (1) > (2) ⇒ liquid // (1)~(2) ⇒ **glass transition** // (1) < (2) ⇒ glass

(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 → 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”

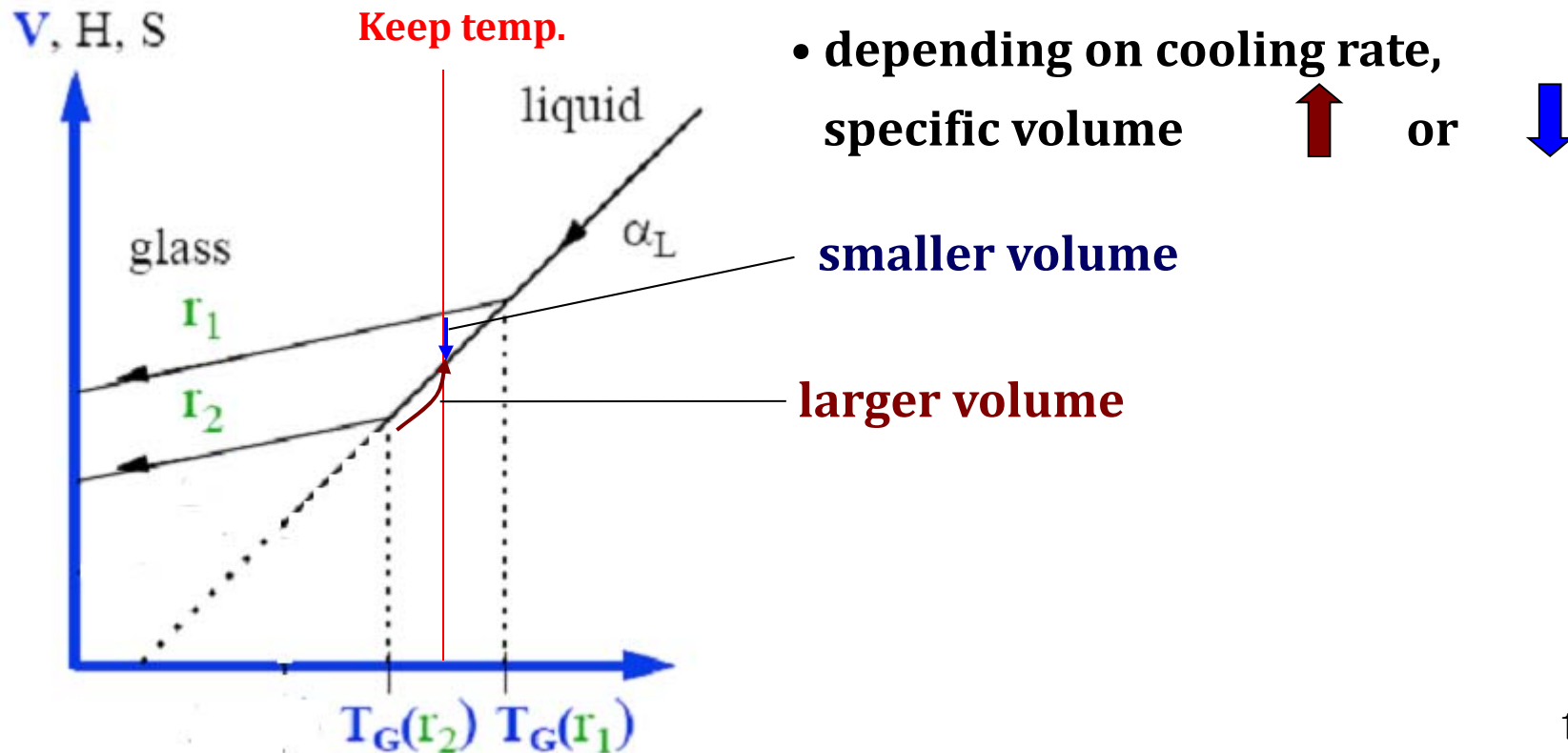
In fact, many properties of glass changes depending on relaxation behavior.

C. Relaxation behavior

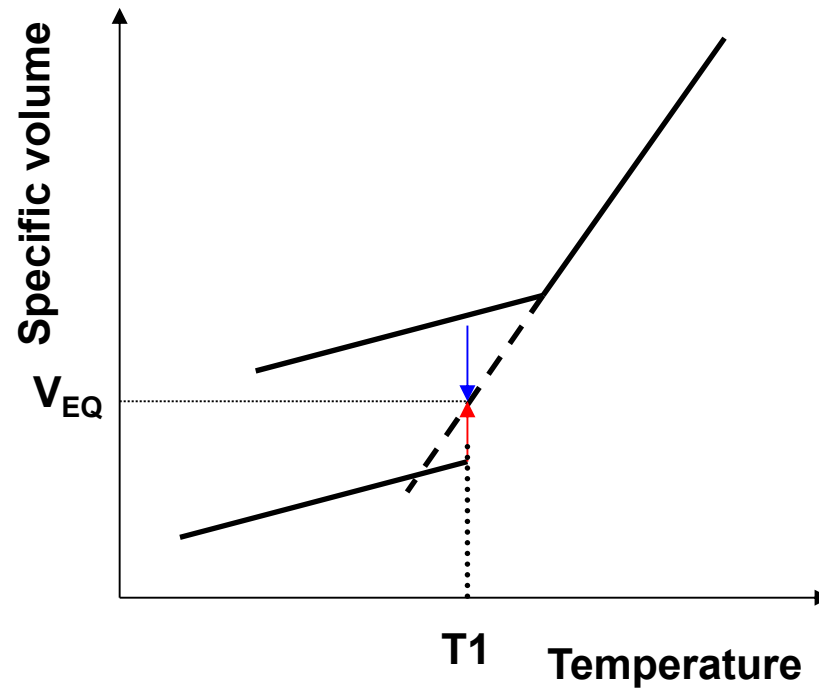
- In glass transition region, properties change with time.

* Process of relaxation behavior: **stabilization**

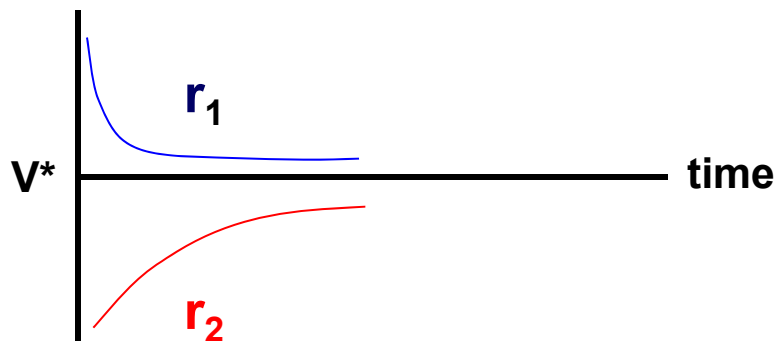
(equilibrium amorphous structure) → **closely related to glass property**



Relaxation from initial volumes above and below the equilibrium volume



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



• relaxation kinetics

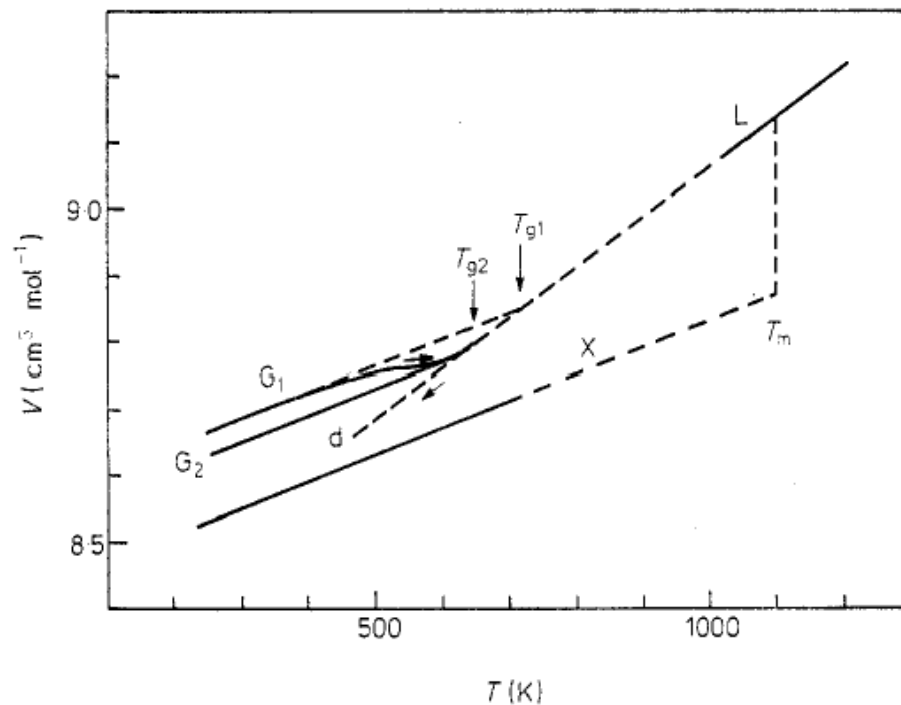
$$r_1 > r_2$$

C. Relaxation behavior

✦ Correlation between structural relaxation time and cooling rate

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

$q = -dT/dt$: 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

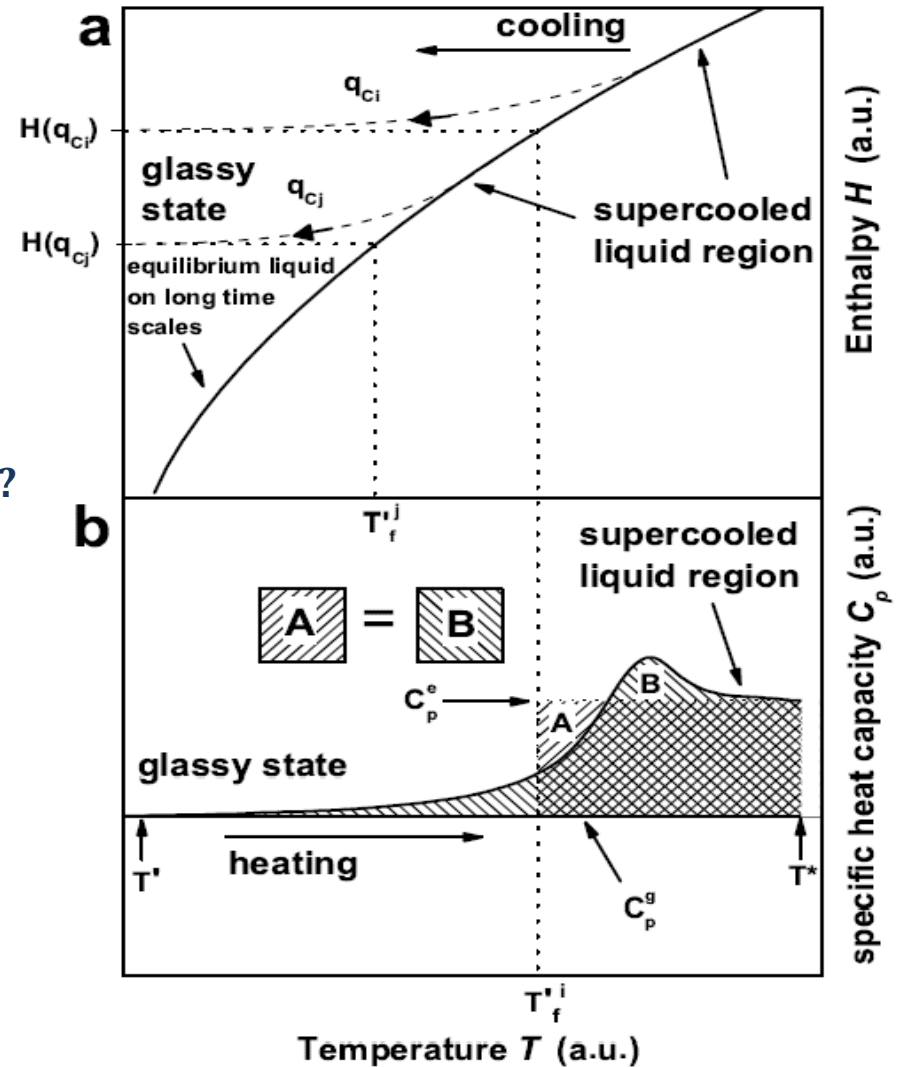
When the kinetics become fast enough to allow the sample to regain metastable equilibrium

Heating rate dominant or cooling rate dominant?

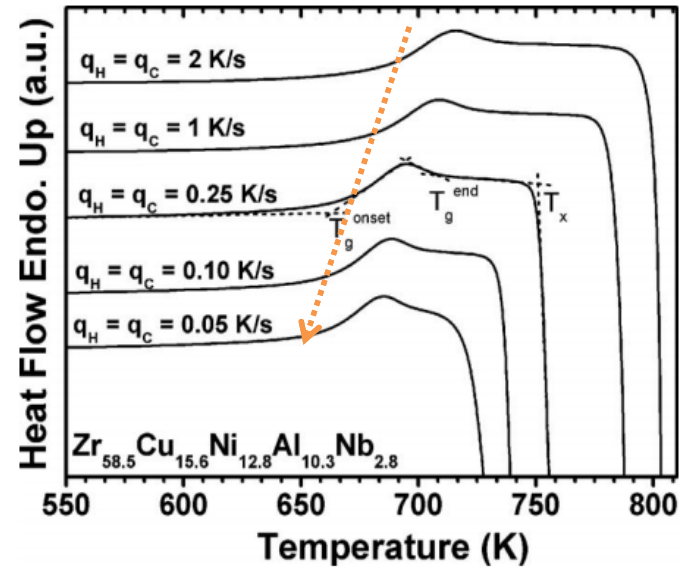
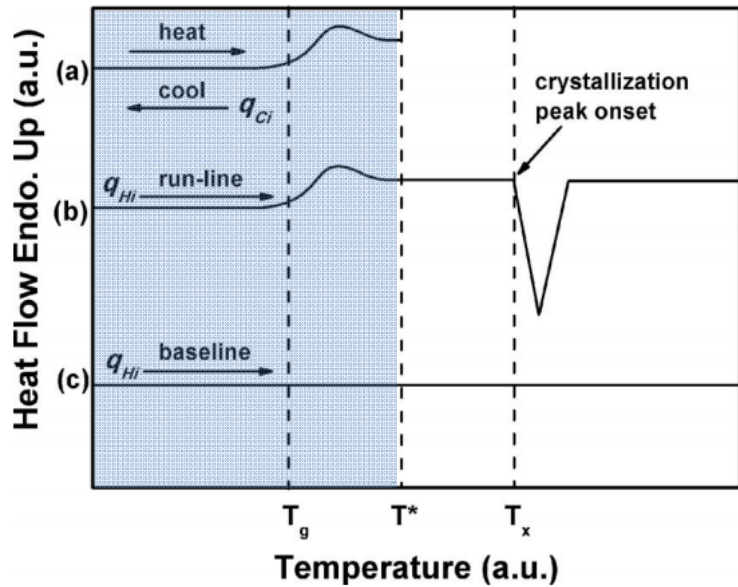
Heating rate > cooling rate \Rightarrow Overshoot \uparrow

Determined from DSC up-scan

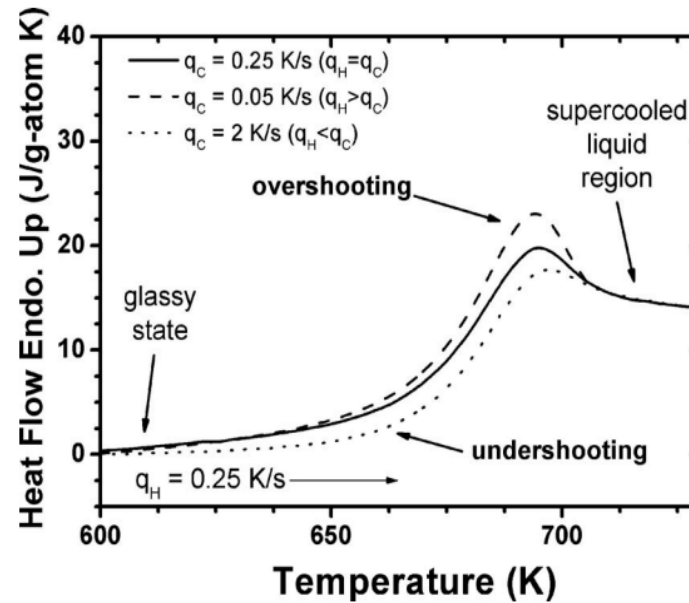
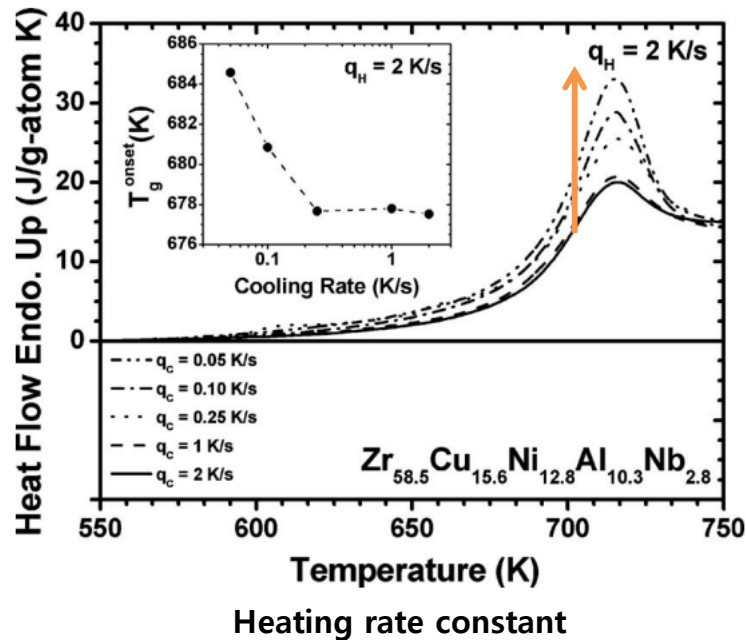
$$\int_{T^*}^{T'_f} (C_p^e - C_p^g) dT_f = \int_{T^*}^{T'} (C_p - C_p^g) dT$$



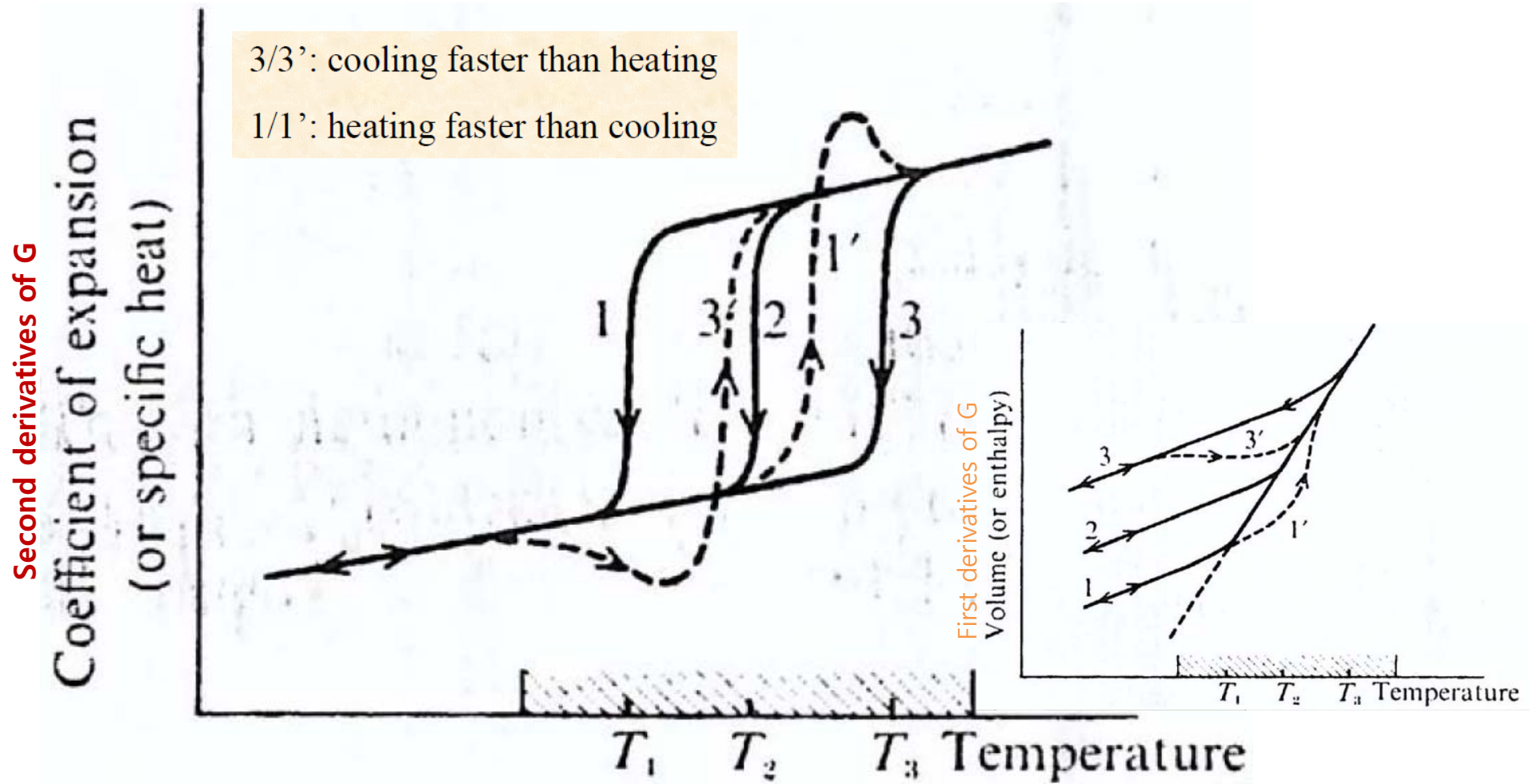
Heating and cooling rate controlled by DSC



Heating rate > cooling rate \Rightarrow Overshoot \uparrow



Complex relaxation effect in the transition region

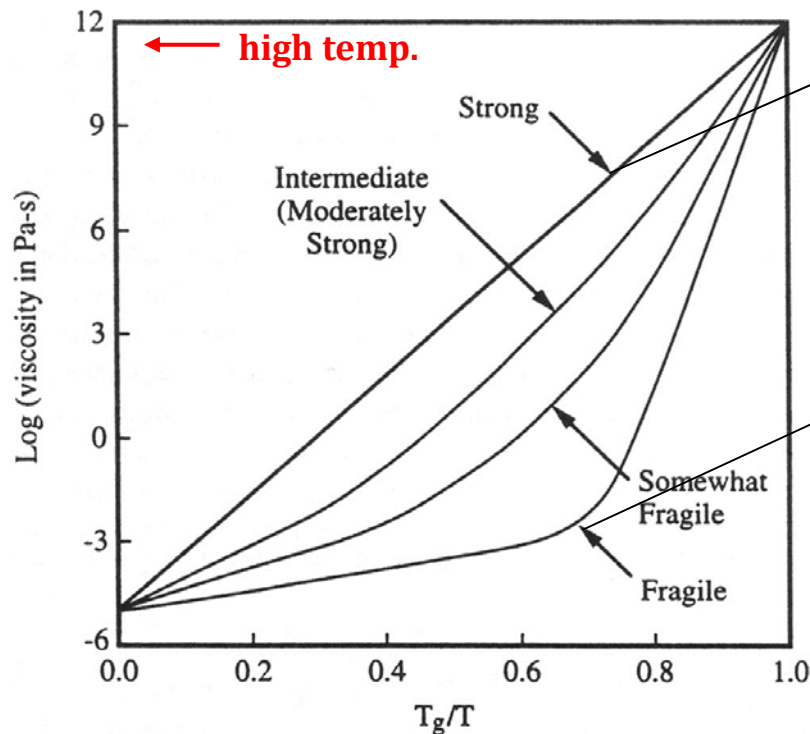


d. viscosity

* 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

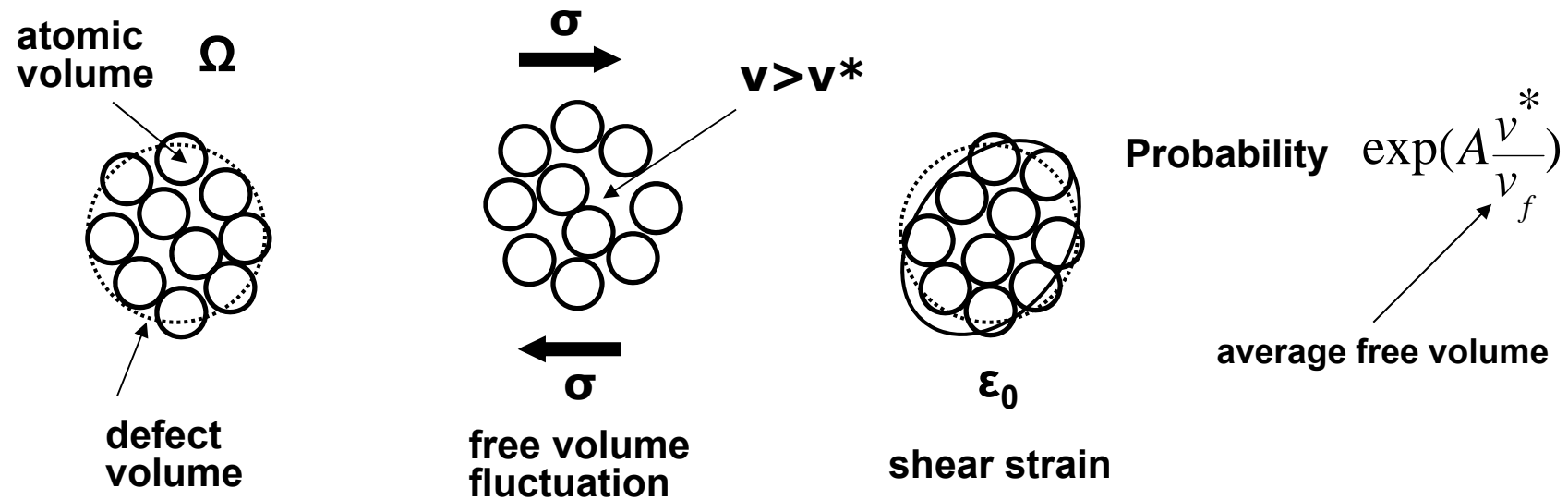
- deviation from simple Arrhenius behavior

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

→ 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)

$S = \int C_P d \ln T$ → **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)

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(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