2014 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses -

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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

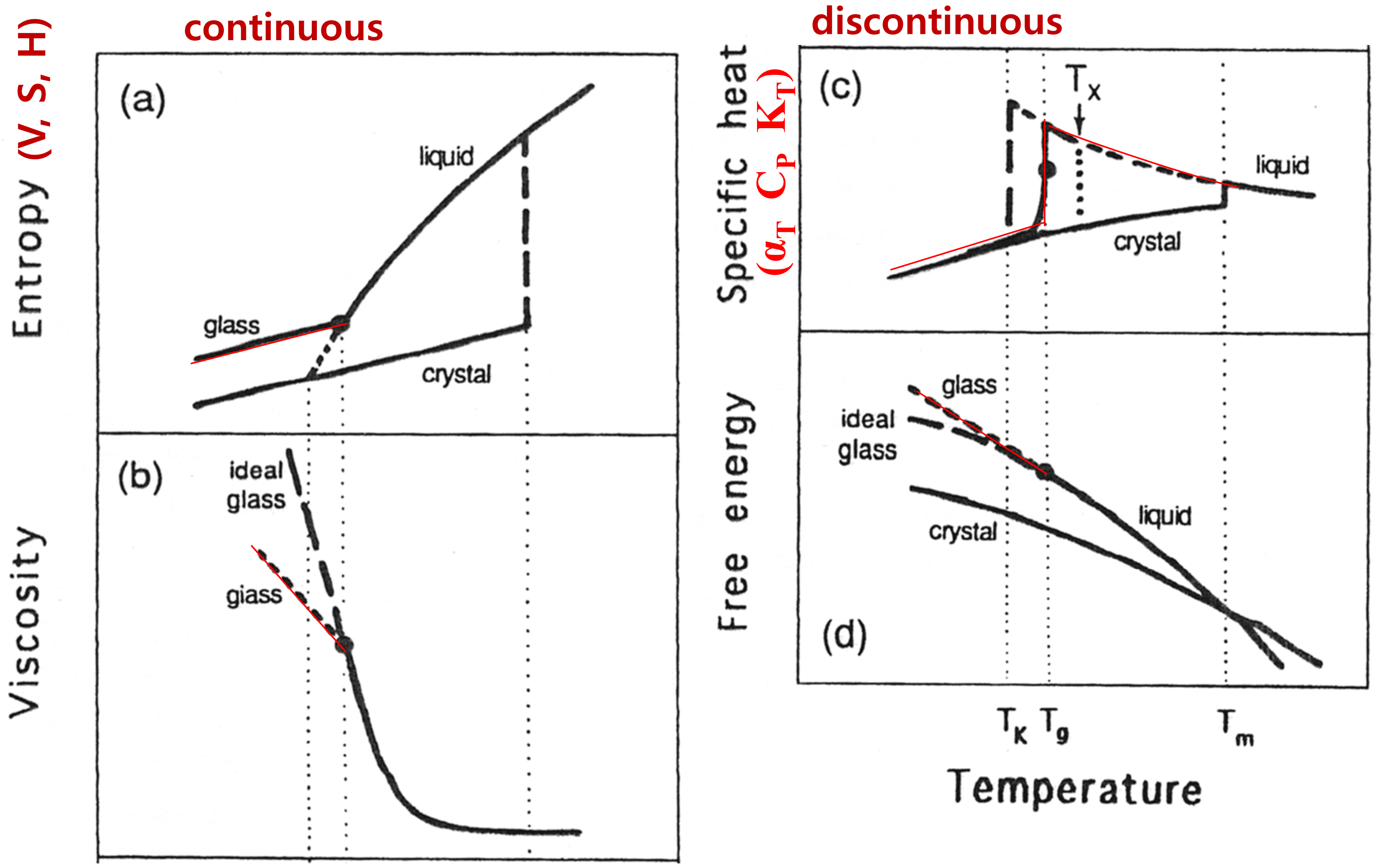
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

→ $\alpha_T\ C_P\ K_T$ *changes discontinuously.*

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

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

❖ **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.

Theories for the glass transition

A. Thermodynamic phase transition

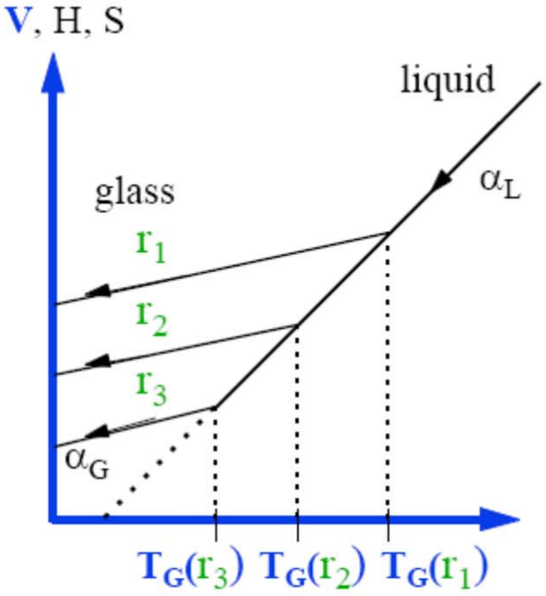
- *Glass transition*

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

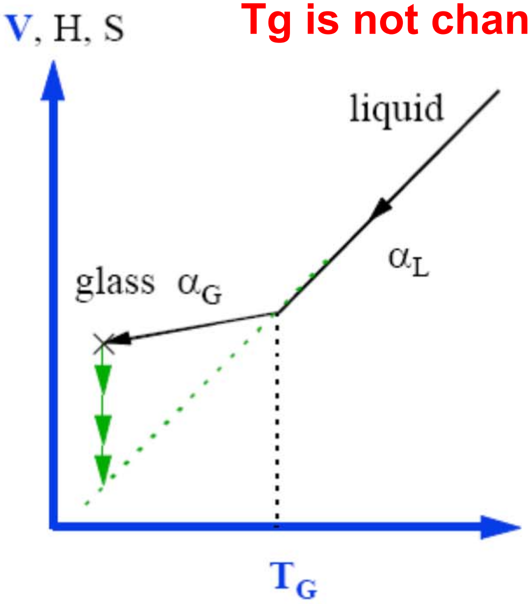
  → **by thermodynamic origin, 2nd order transition**

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

→ **If 2nd order transition,**
Tg is not changed by kinetic factor.

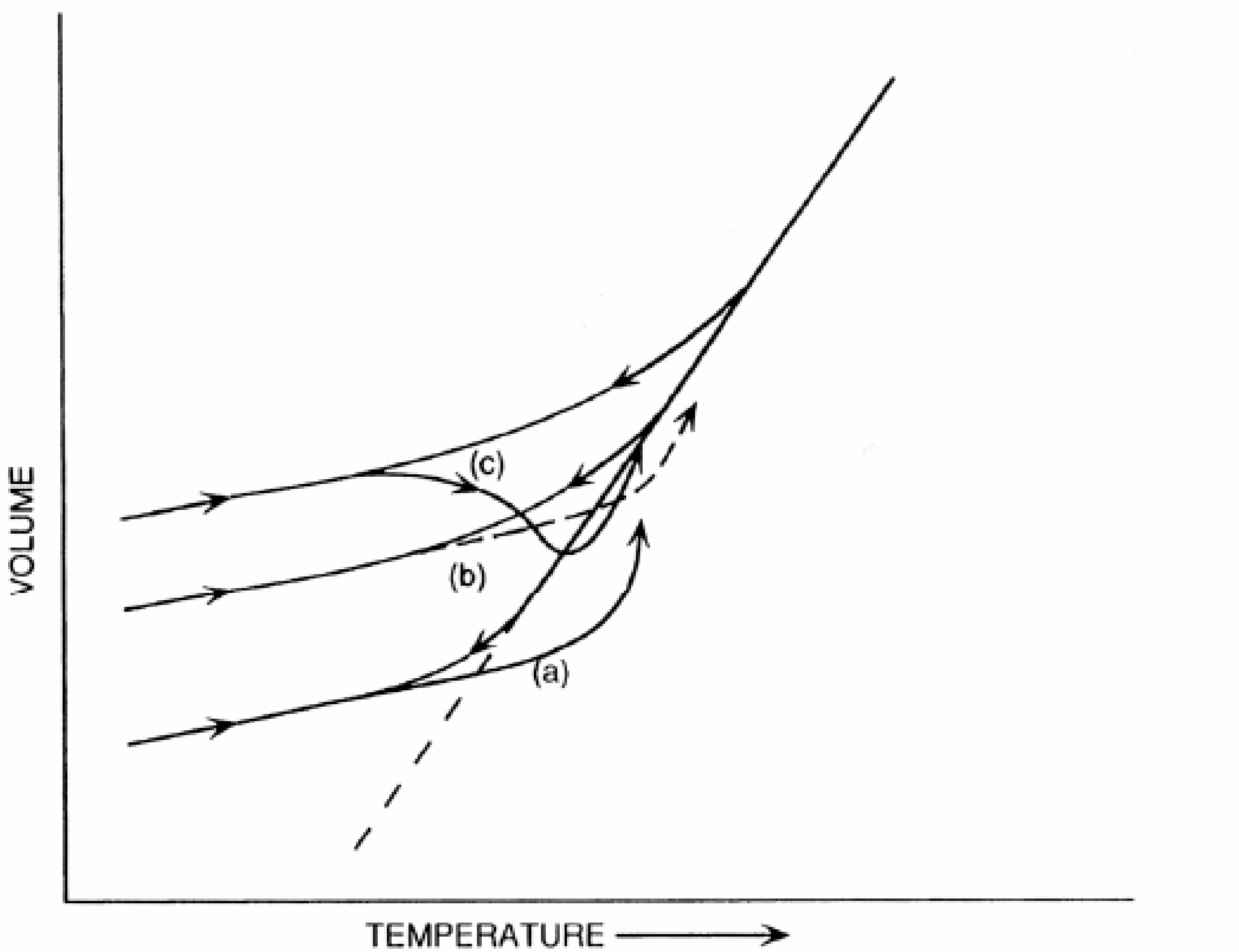


Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$



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

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)

Fragility

~ extensively use to figure out liquid dynamics and glass properties corresponding to "frozen" liquid state

< 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

- ***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)*

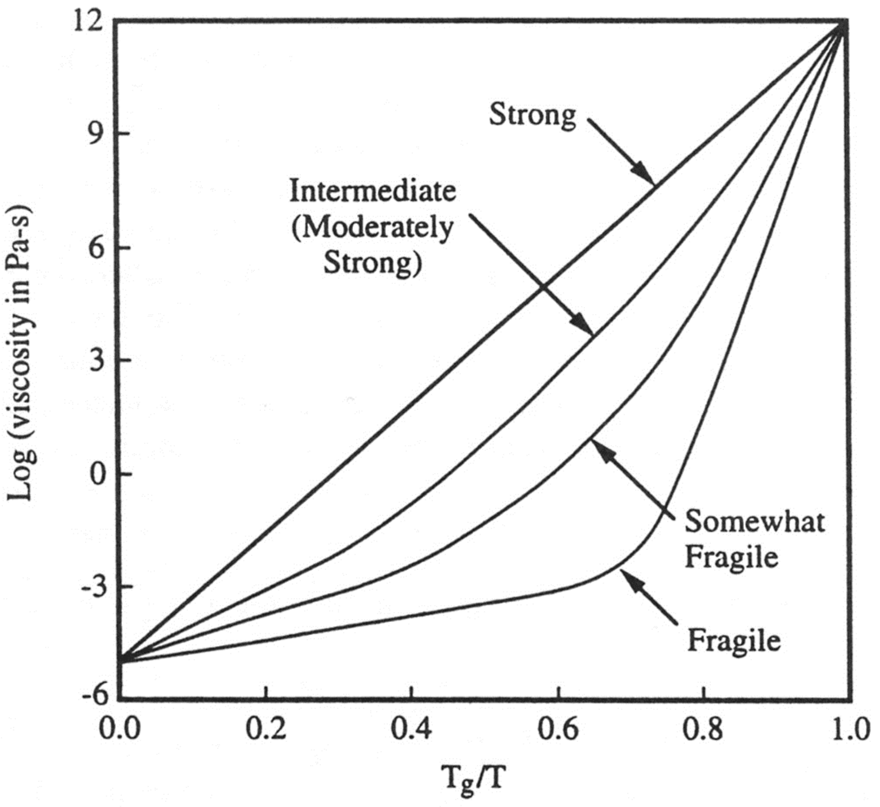
→ SCL: relatively low entropy

• 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



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

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.**

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

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

Additional consequence of the experimental verification,

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

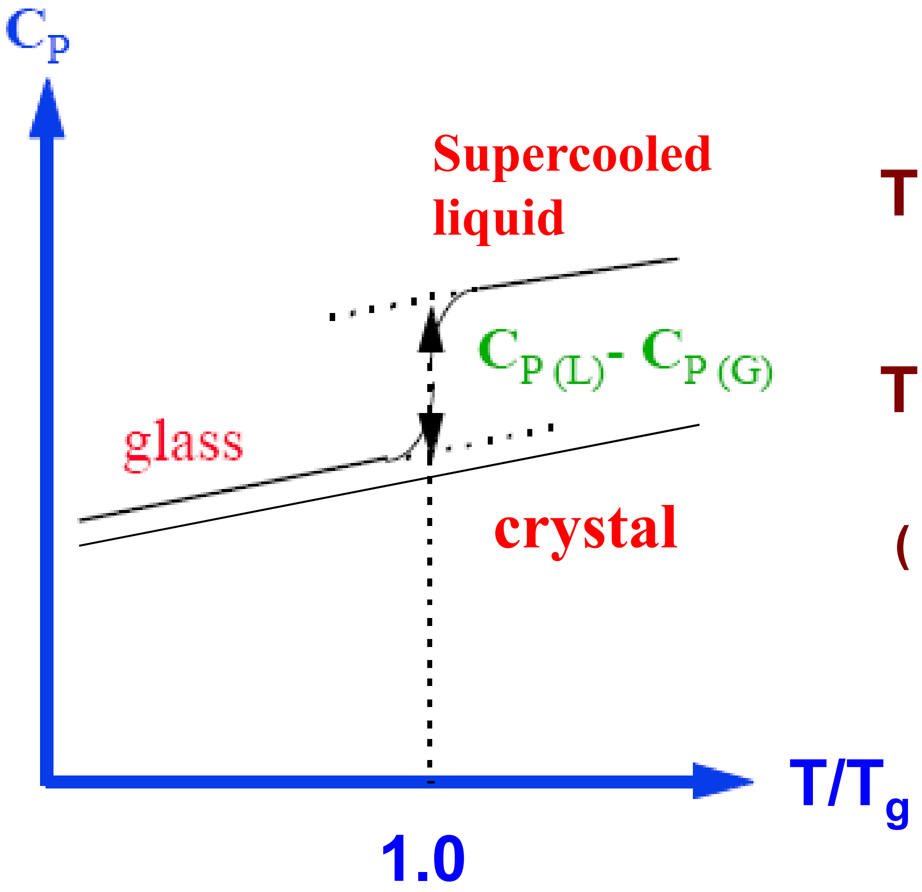
Theories for the glass transition

B. Entropy

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

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

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



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

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

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

Theories for the glass transition

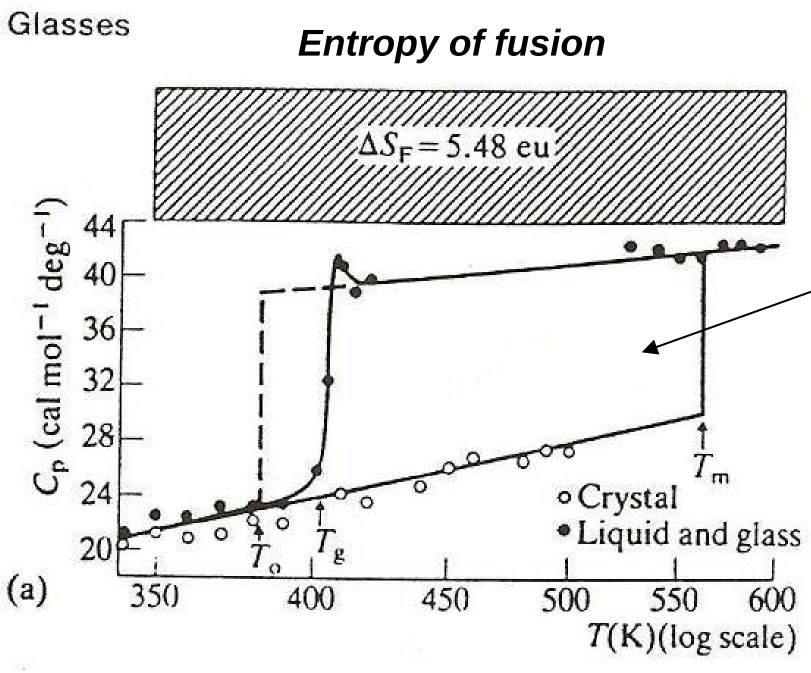
B. Entropy

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

  2) The slow cooling rate, the lower T_g

  → **ideal glass transition temperature exist?**

  → **YES**



Entropy of fusion

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

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

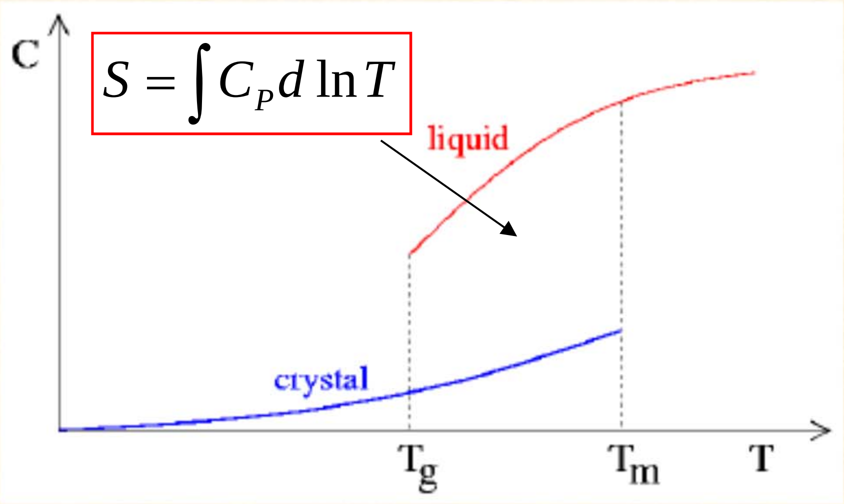
Heat capacities of glassy, liquid and crystalline phases of lithium acetate

Theories for the glass transition

B. Entropy

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

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



Kauzmann (1948)extrapolates the specific heat data below melting

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

$c_{\text{liquid}} > c_{\text{crystal}}$ entropy in the liquid decreases faster with T than in the crystal

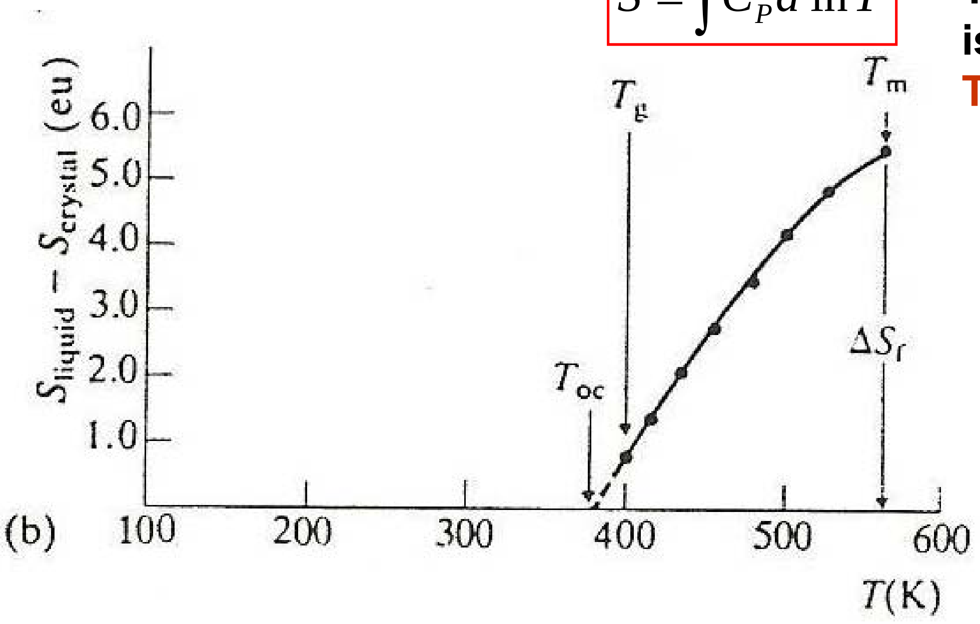
Theories for the glass transition

B. Entropy

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

2) The slow cooling rate, the lower T_g

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



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)

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

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

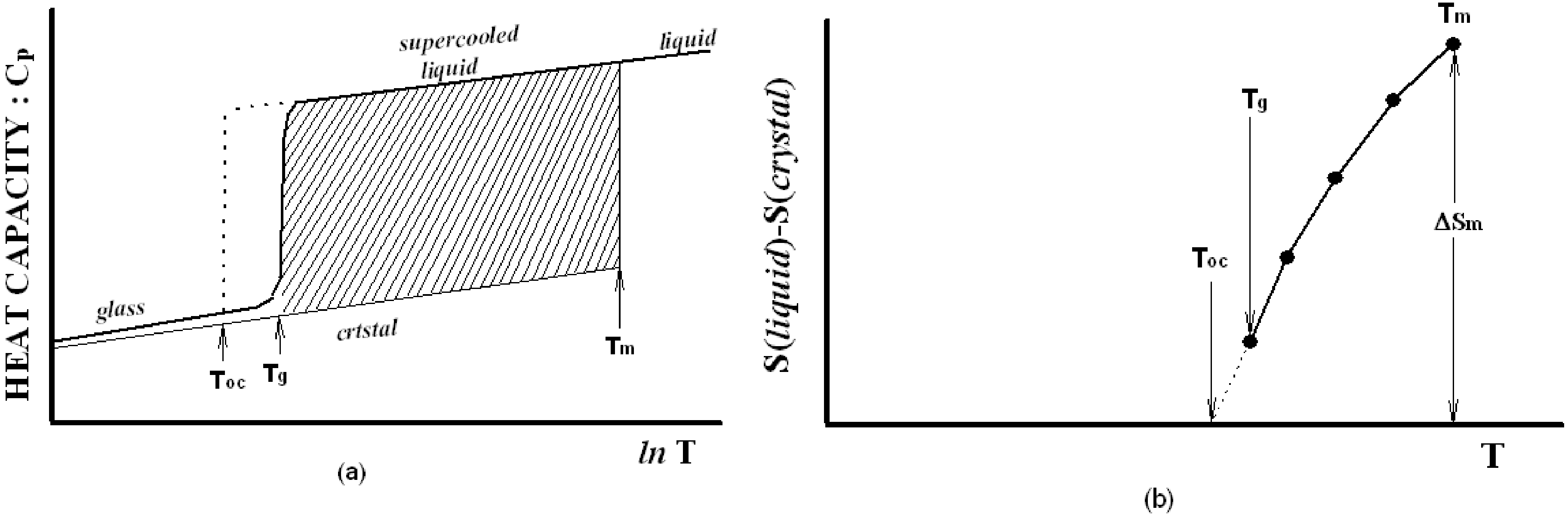
violating third law of thermodynamics

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

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

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

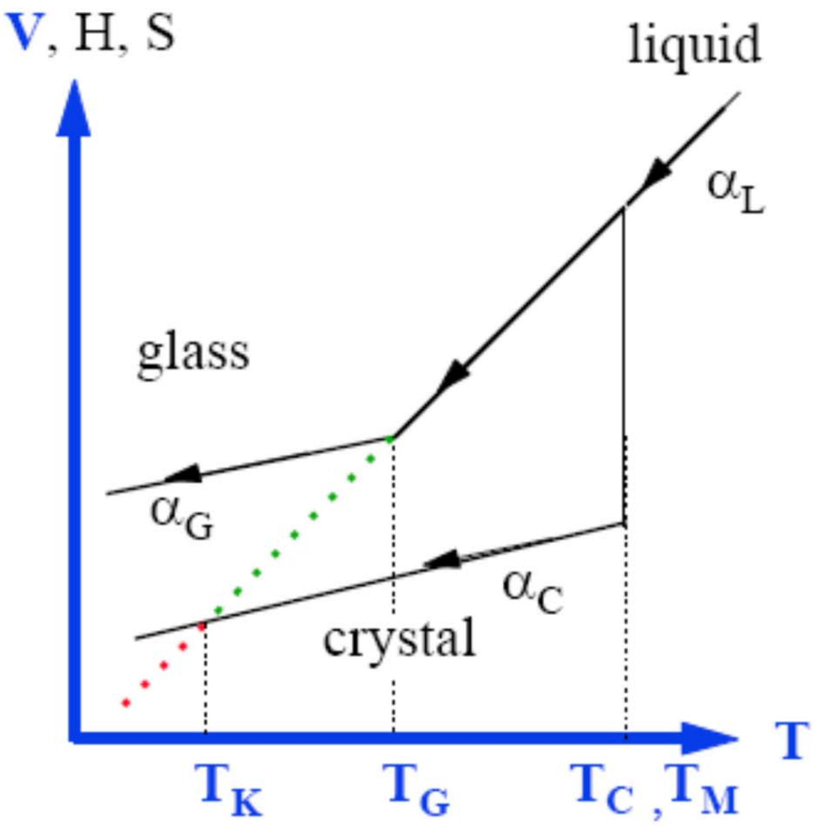
: **lower temperature limit to occur glass transition thermodynamically**



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

Controversies in Amorphous Solids: The Kauzmann Paradox

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

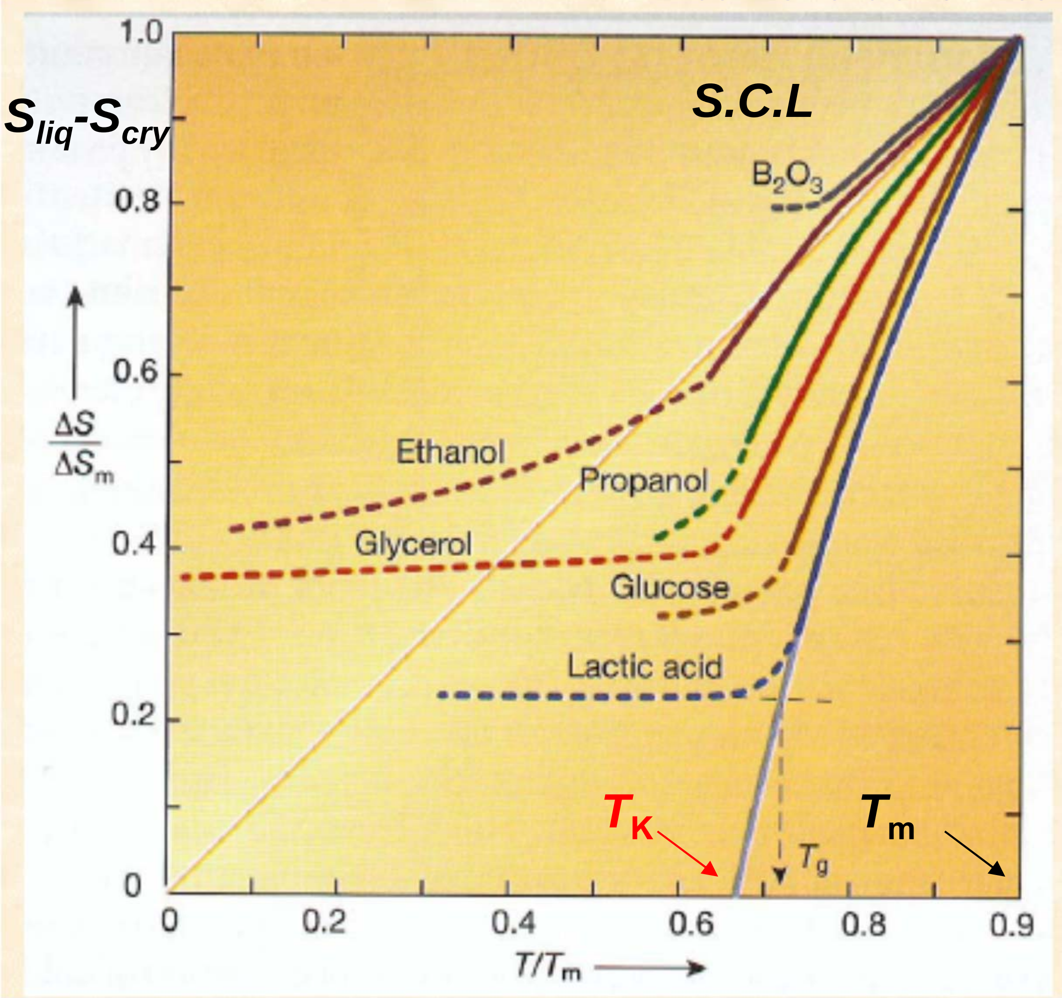


1) at some temperature (T_K), there is a true 2nd order phase tansition between the liquid and the glass or 2) the extrapolation to temperatures far below T_G is not valid. So far no one has found the answer !!

* Kauzmann's paradox

The configurational entropy apparently extrapolates to zero at low temperatures.

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



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!!!

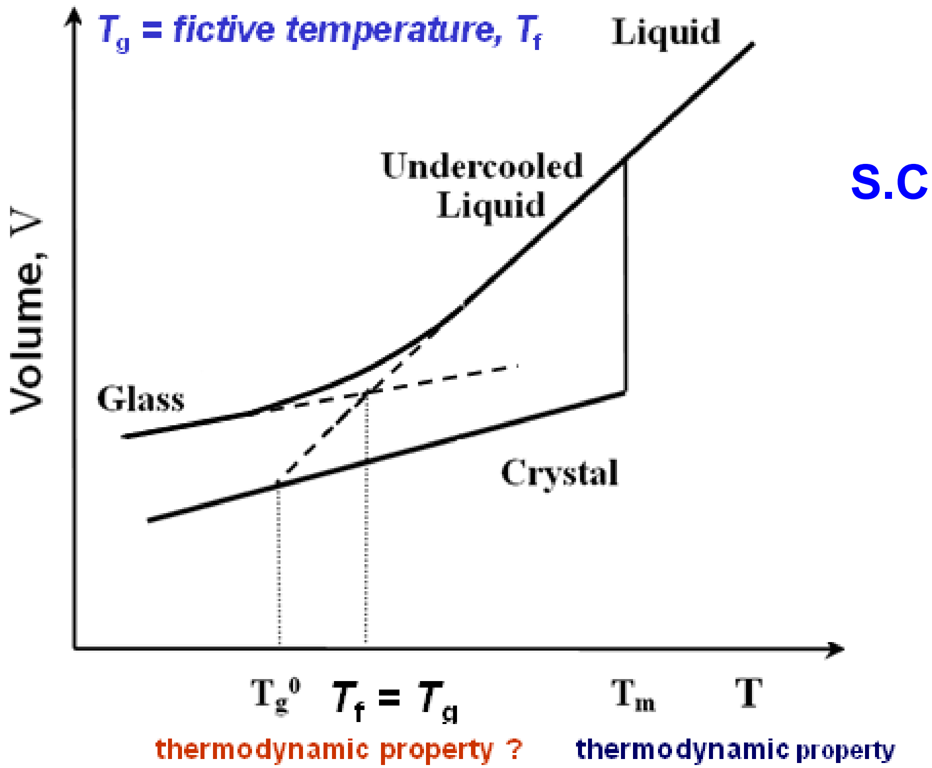
There is a driving force for diamond to convert to graphite but there is (huge) nucleation barrier.

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

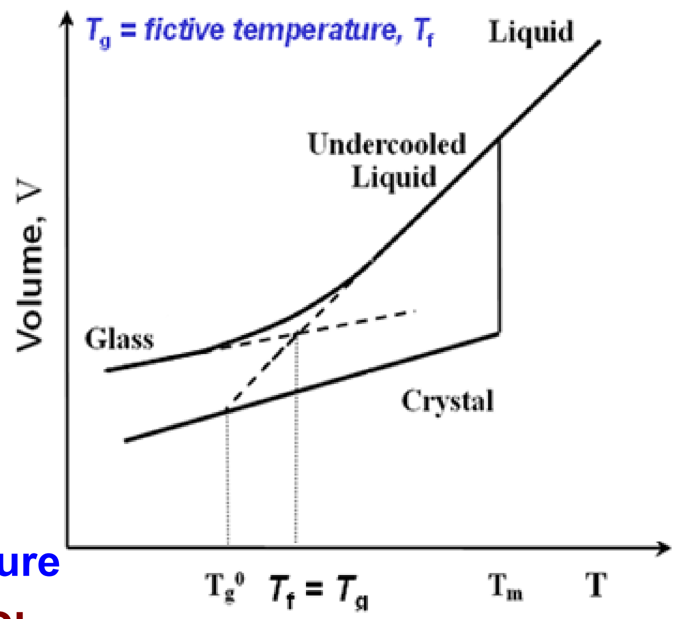
S.C.L: thermodynamically metastable with respect to crystalline
→ considering atomic configuration, enough time scale for atomic redistribution
→ equilibrium state

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)

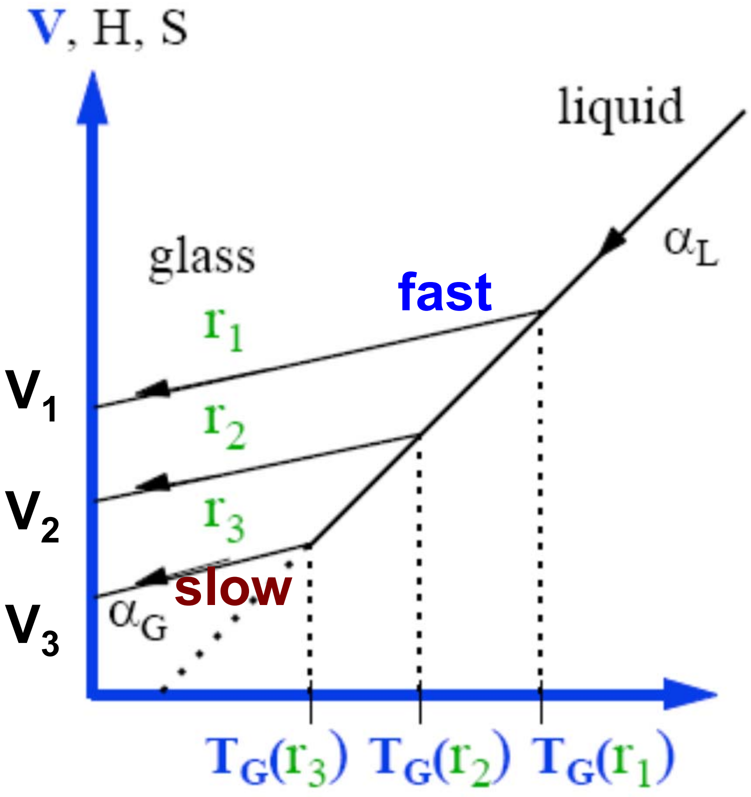
→ If (1) > (2) ➡ liquid // (1)~(2) ➡ glass transition// (1) < (2) ➡ glass

(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



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"

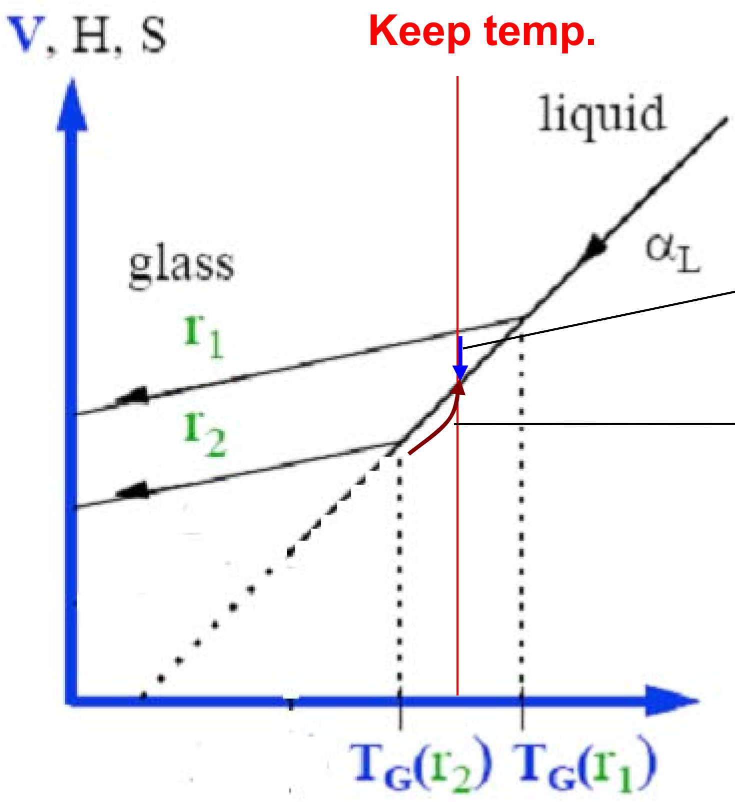
In fact, many properties of glass changes depending on relaxation behavior.

C. Relaxation behavior

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

*** Process of relaxation behavior: stabilization**

(equilibrium amorphous structure) ⟶ closely related to glass property

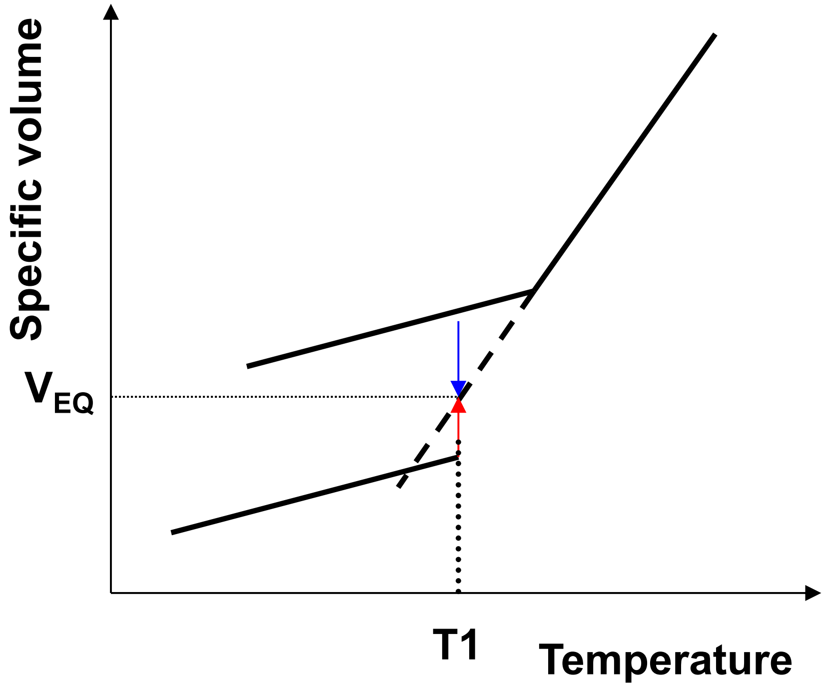


smaller volume

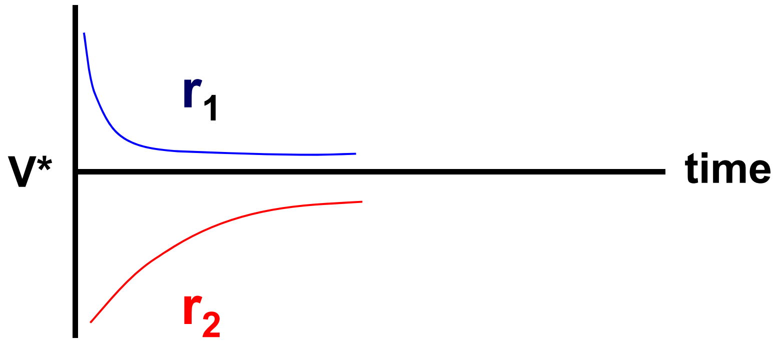
larger volume

- **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

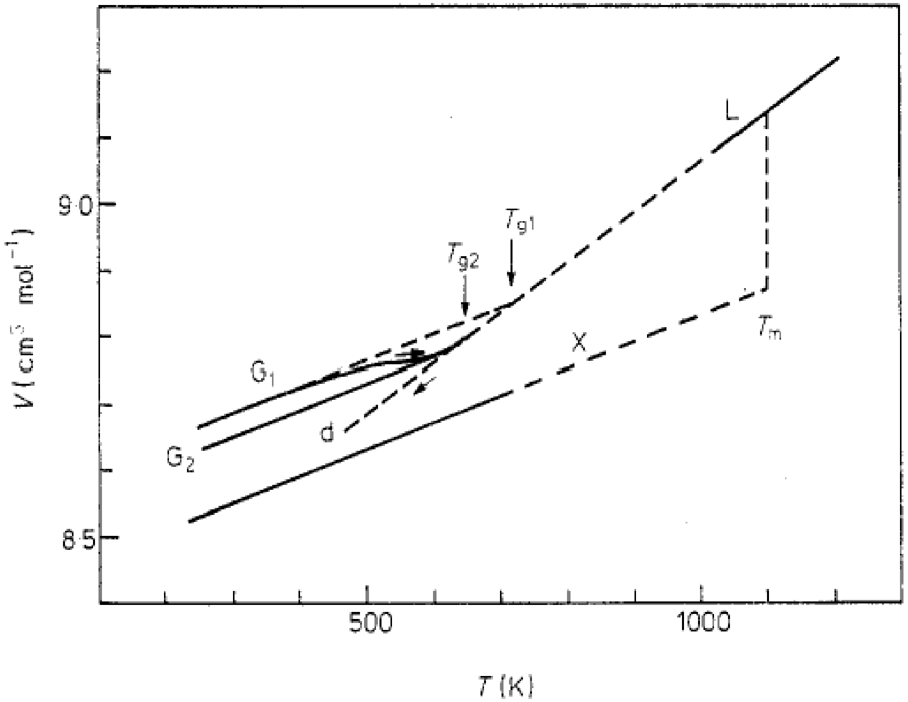
$r_1 > r_2$

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

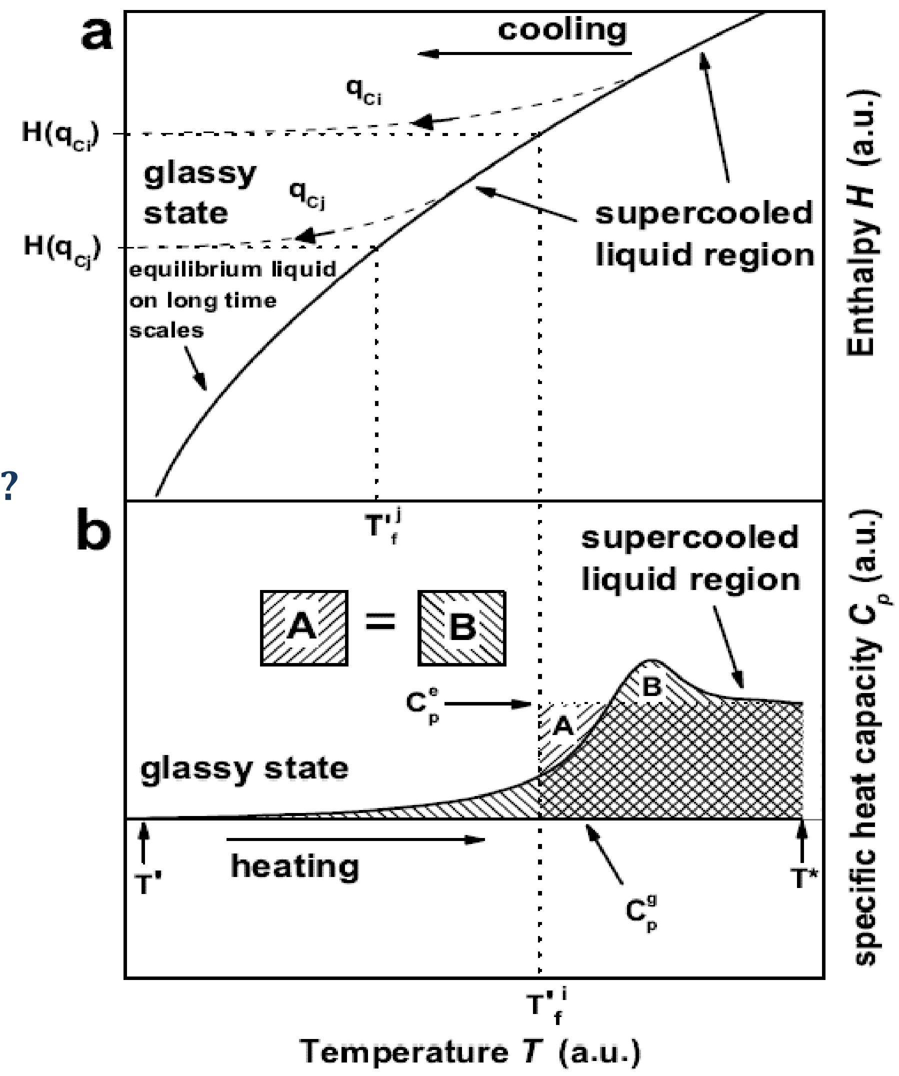
overshoot in heating process

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)

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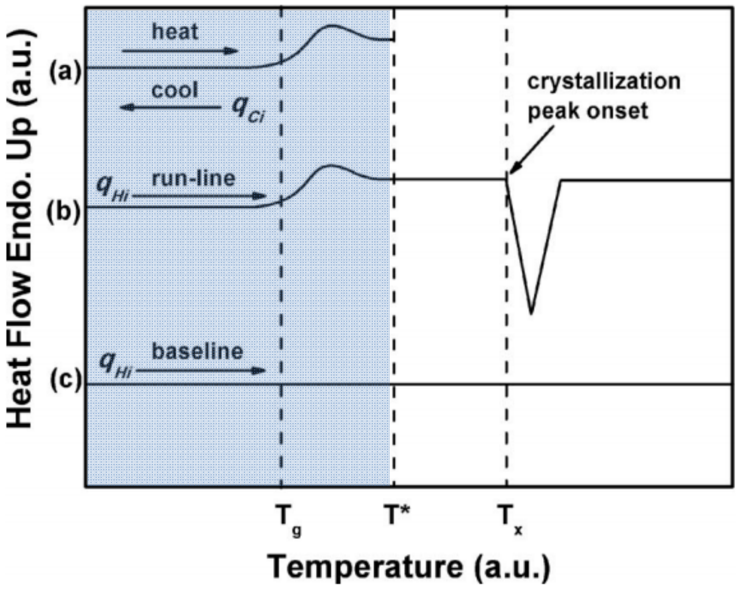
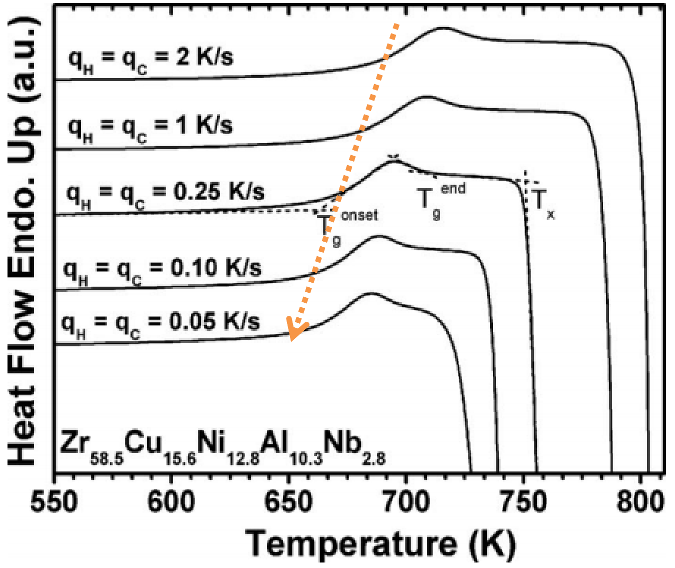
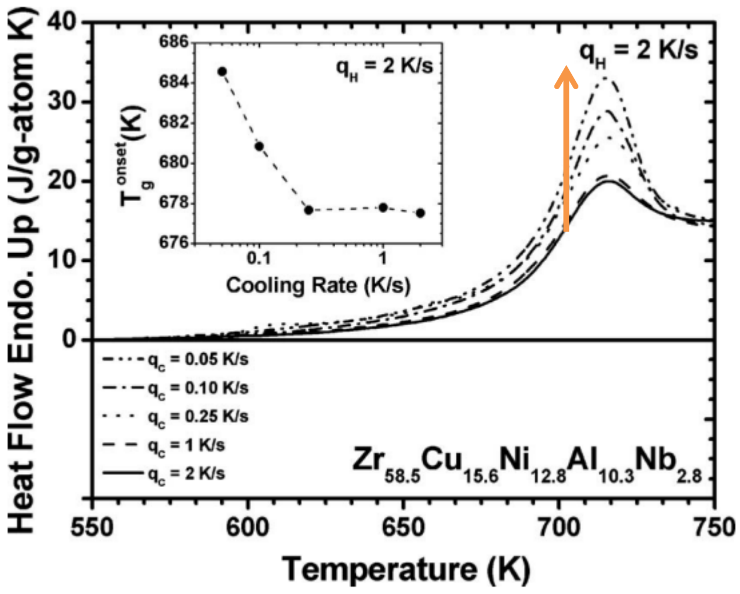
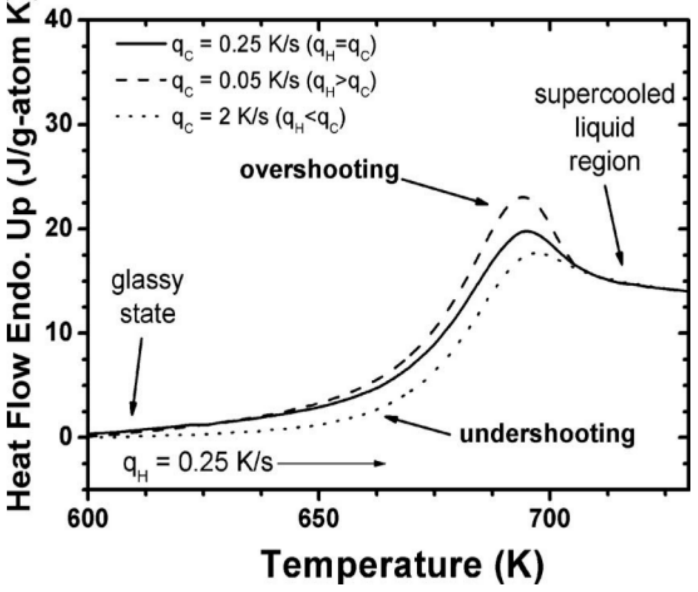
Heating and cooling rate controlled by DSC





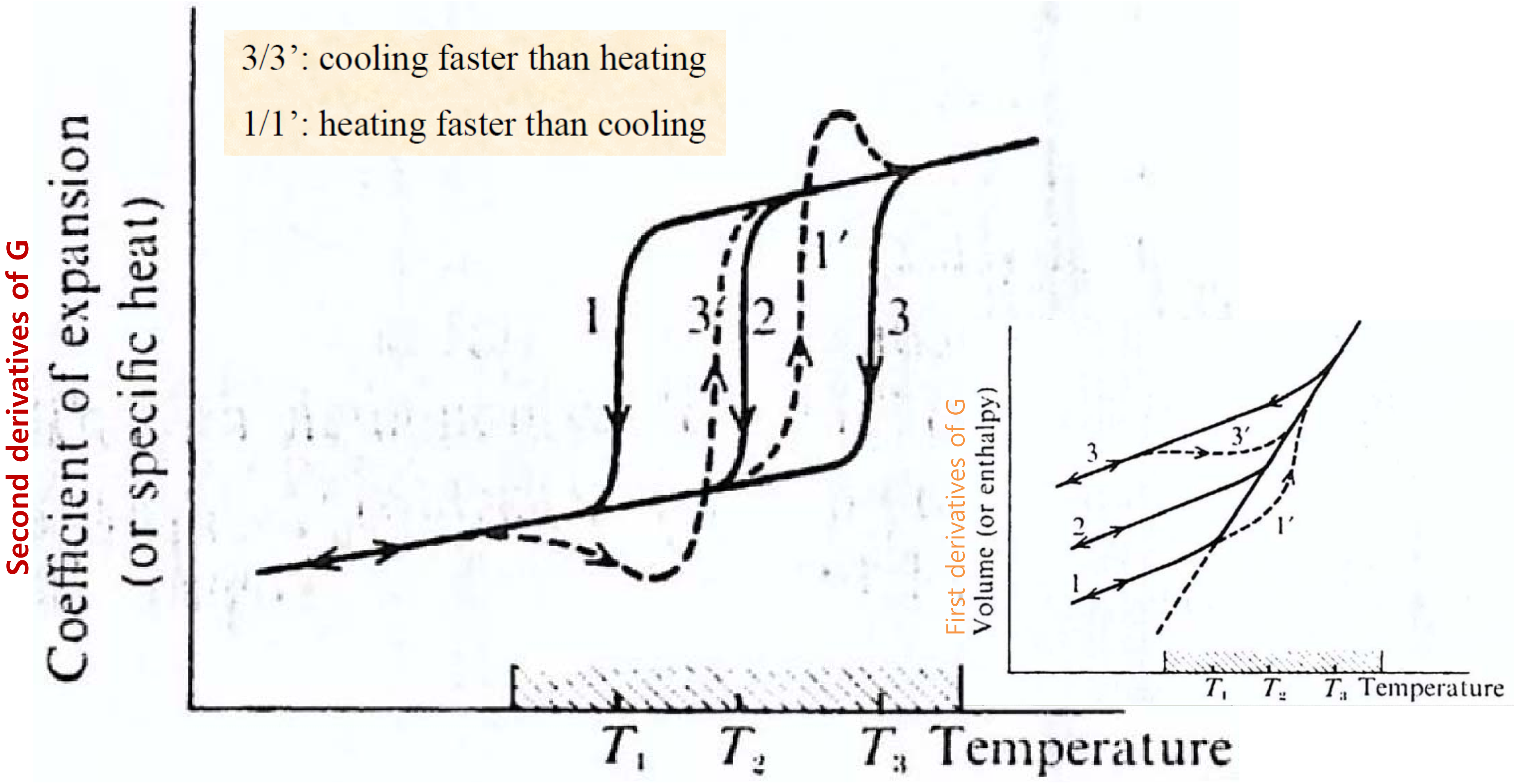
Heating rate>cooling rate → overshoot↑





Heating rate constant

Complex relaxation effect in the transition region



3/3’: cooling faster than heating

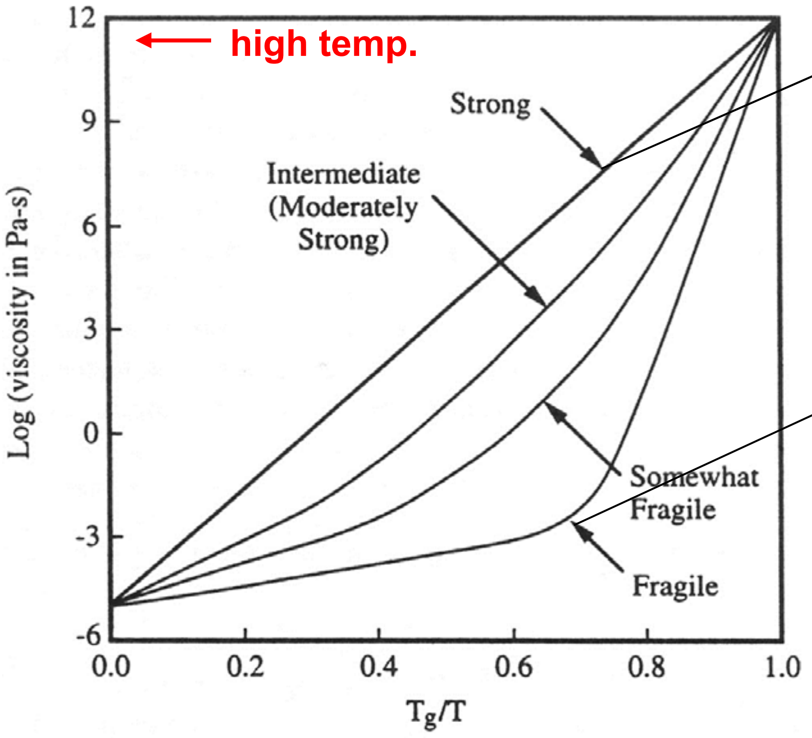
1/1’: heating faster than cooling

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**

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.**

(∵ 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 ($10^{12\text{-}13}$ poise) 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**