2010 Spring

"Amorphous Materials"

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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)**

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

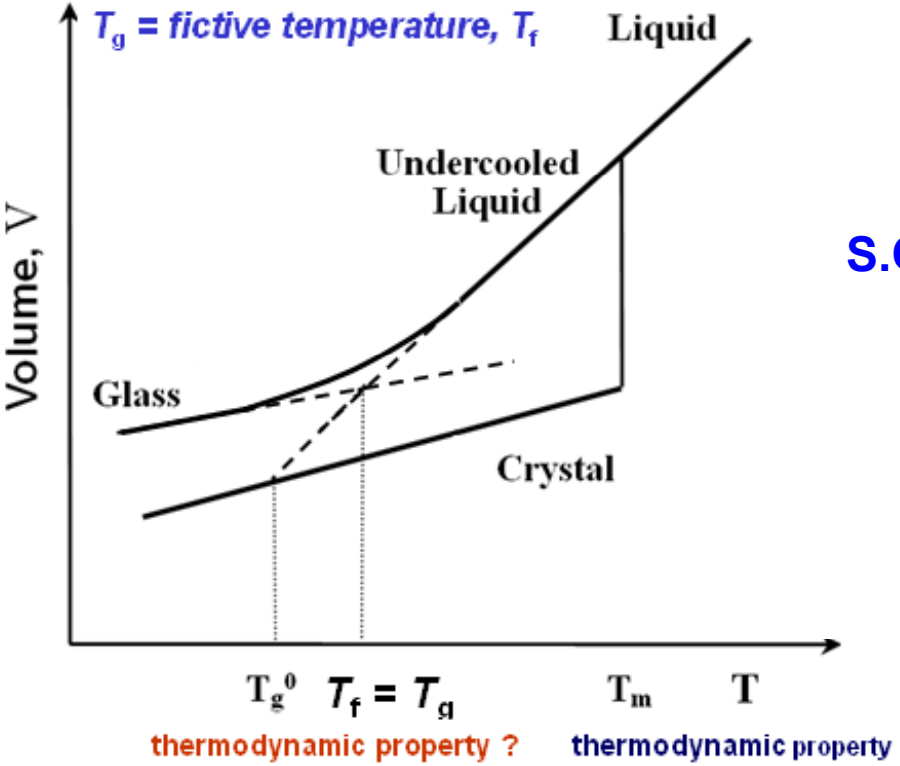
→ The slow cooling rate, the lower T_g → T_K or T_g^0

→ Measurement of Kauzmann temp. is almost impossible.

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

Theories for the glass transition

C. Relaxation behavior



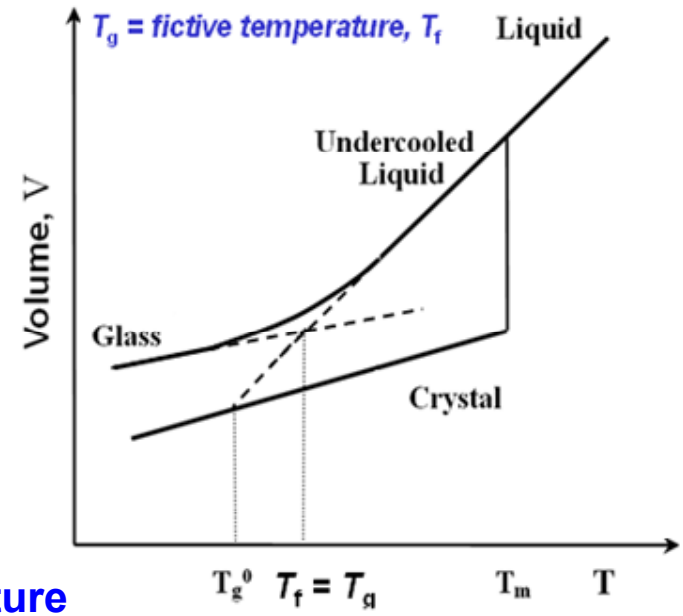
Liquid: enough time scale for atomic redis-tribution with respect to temp. change
→ equilibrium state

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)

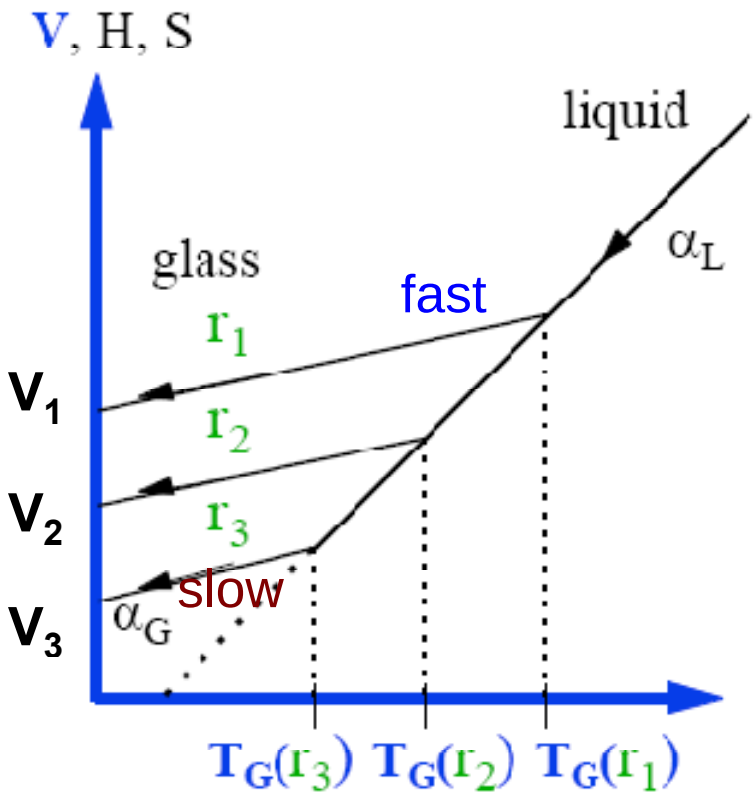
→ If (1) > (2) ➡ liquid // (1)~(2) ➡ glass transition// (1) < (2) ➡ glass

(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"**

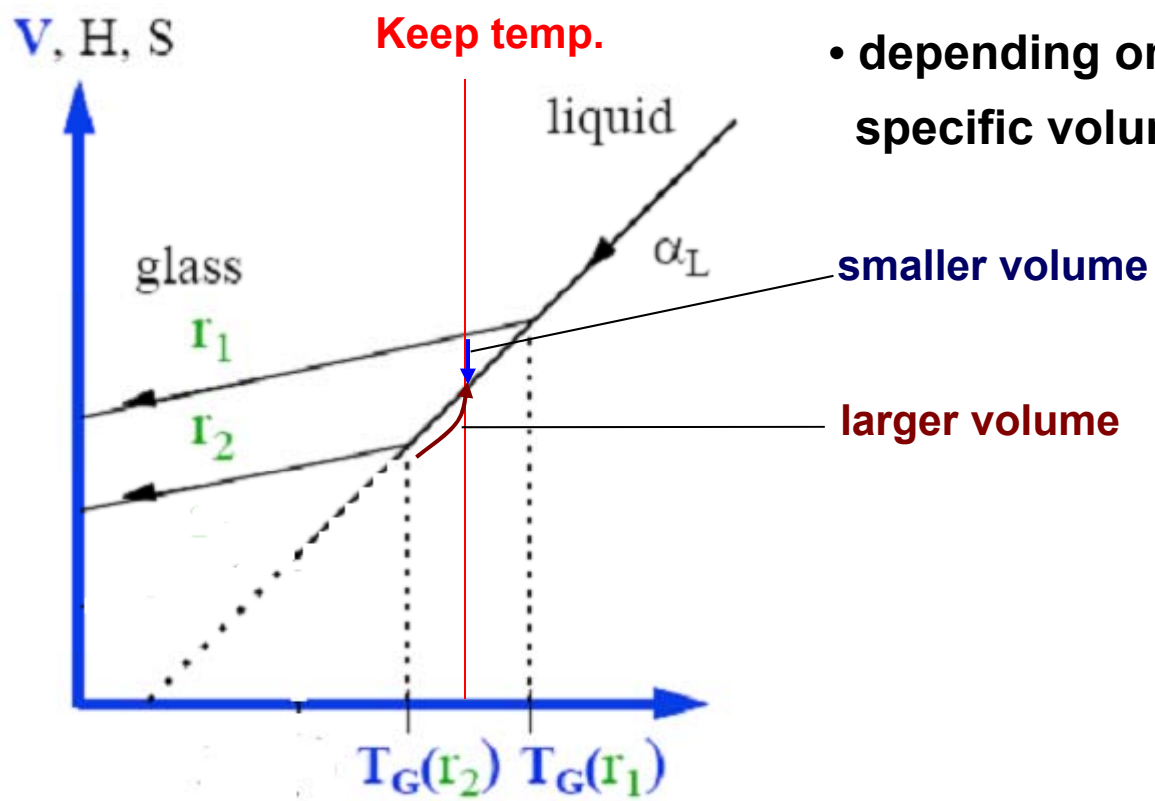
In fact, many properties of glass changes depending on relaxation behavior.

C. Relaxation behavior

- In glass transition region, properties change with time.

* Process of relaxation behavior: **stabilization**

(equilibrium amorphous structure) → closely related to glass property



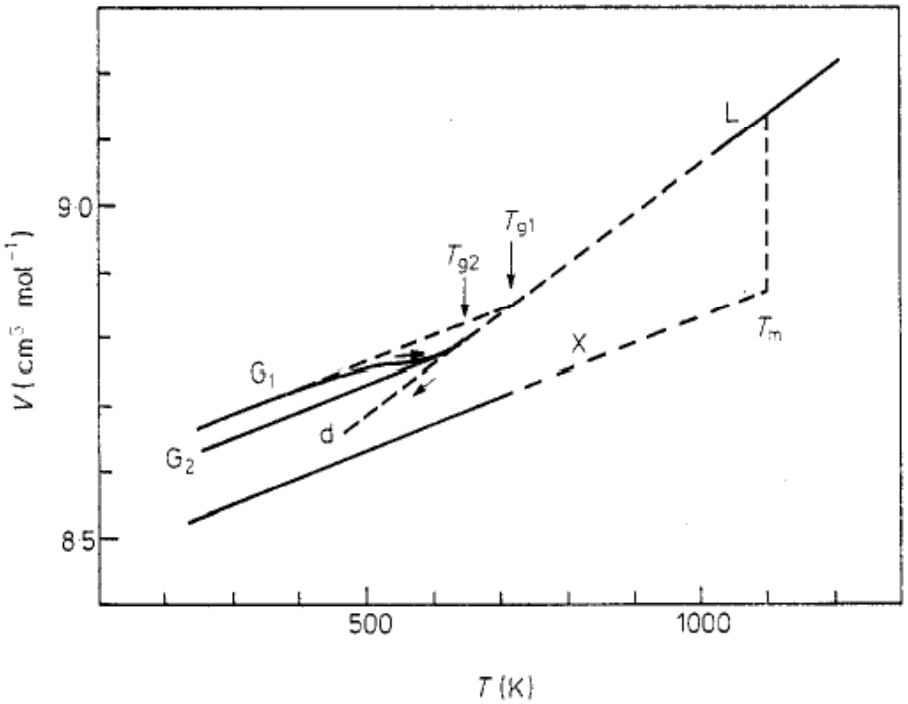
- depending on cooling rate, specific volume ↑ or ↓

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



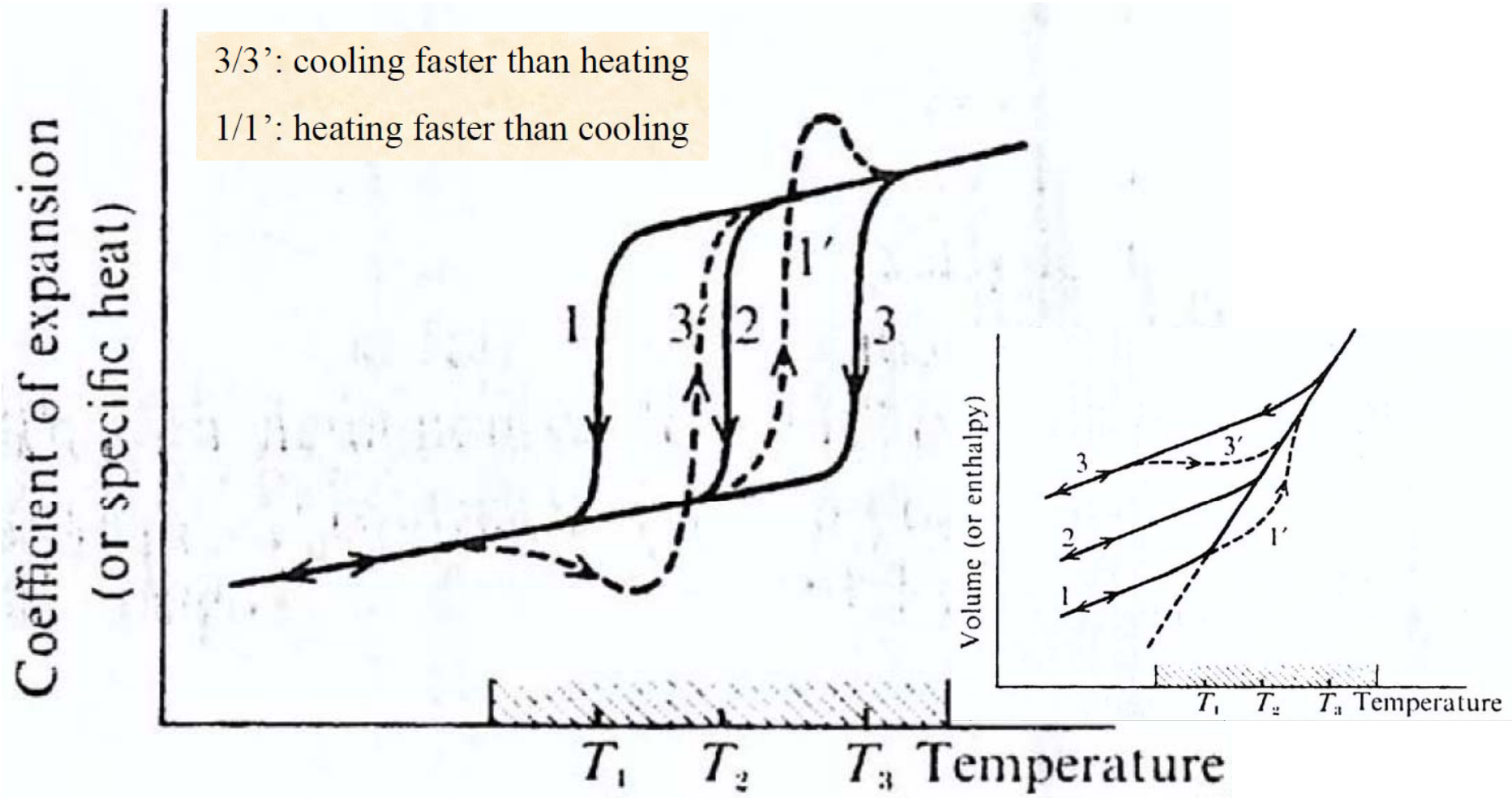
<Specific volume of PdCuSi>

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

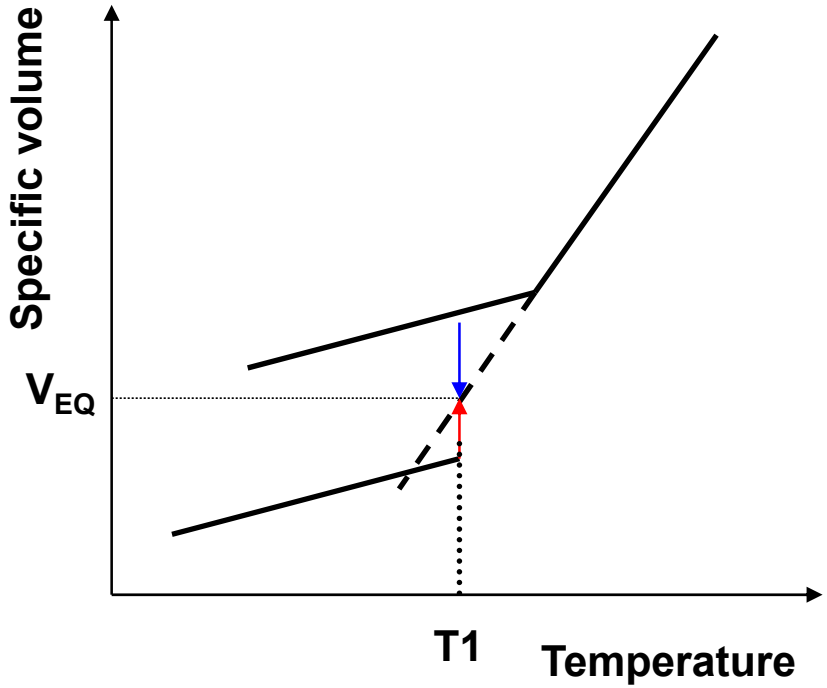
- relaxation ($G_1 \rightarrow G_2$)

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

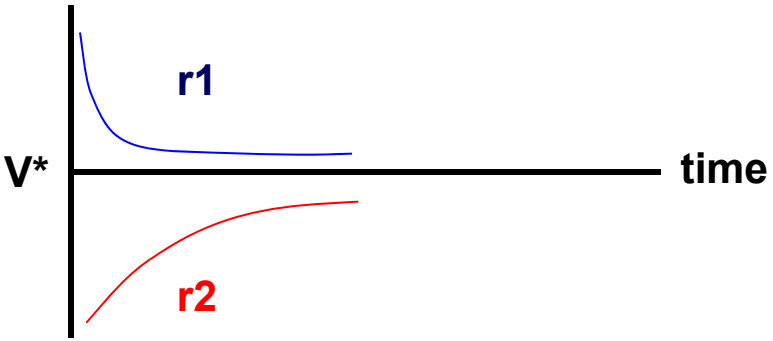
Complex relaxation effect in the transition region



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**

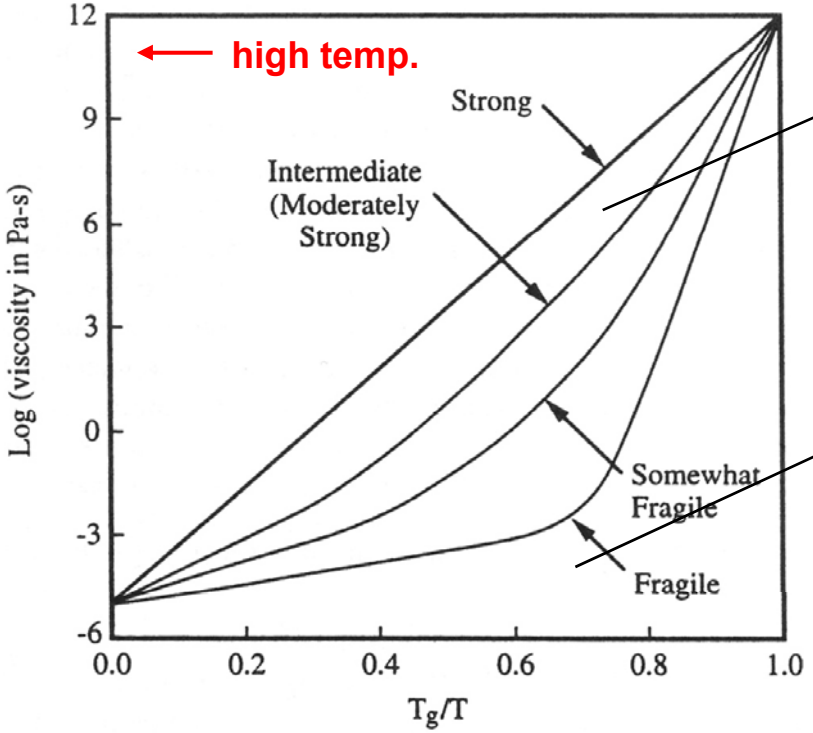
  r1 > r2

d. viscosity

*** Another definition of glass transition;**

- Viscosity ($10^{12\text{-}13}$ poise)
- 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**