2009 spring

Advanced Physical Metallurgy

"Amorphous Materials"

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Theories for the glass transition

A. Thermodynamic phase transition

- ***Glass transition***

  H , *V* , *S* : *continuous* $C_p\ a_T\ K_T$: *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.**

B. Entropy

- ***Heat capacity*** → **dramatic change at Tg**
- ***Description of glass transition by entropy*** **(Kauzmann)**

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

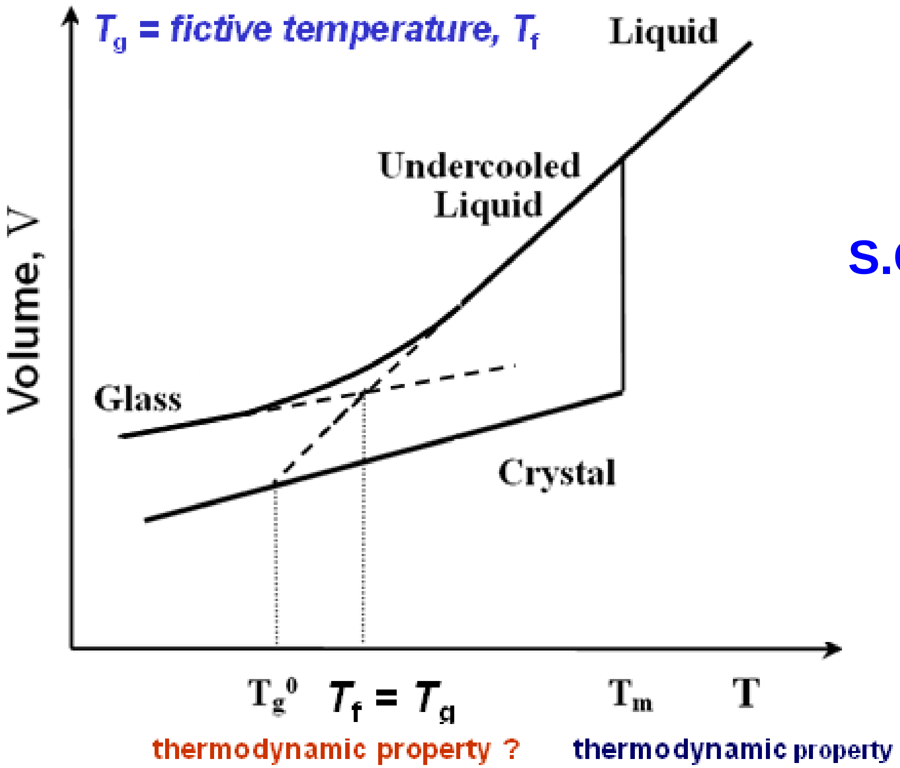
→ ***The slow cooling rate, the lower T_g*** → T_K *or* T_g^0

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

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

Theories for the glass transition

C. Relaxation behavior



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

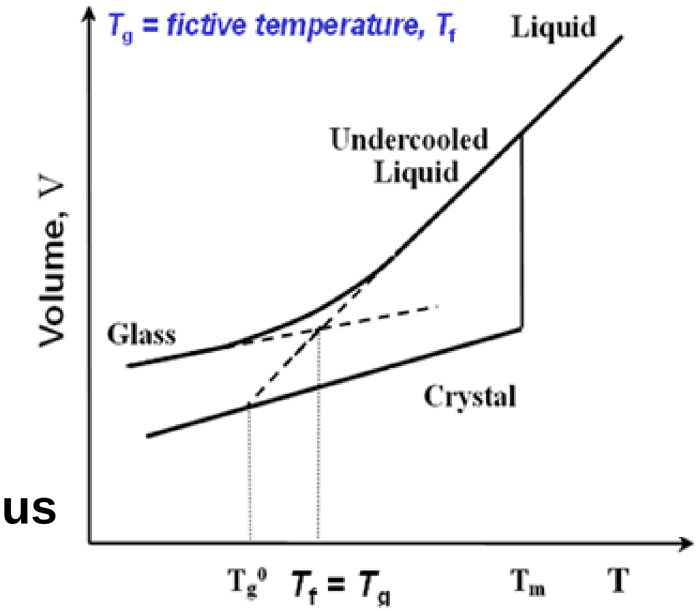
S.C.L: thermodynamically metastable with respect to crystalline
⟶ considering atomic configuration, enough time scale for atomic redistribution
⟶ equilibrium state

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).

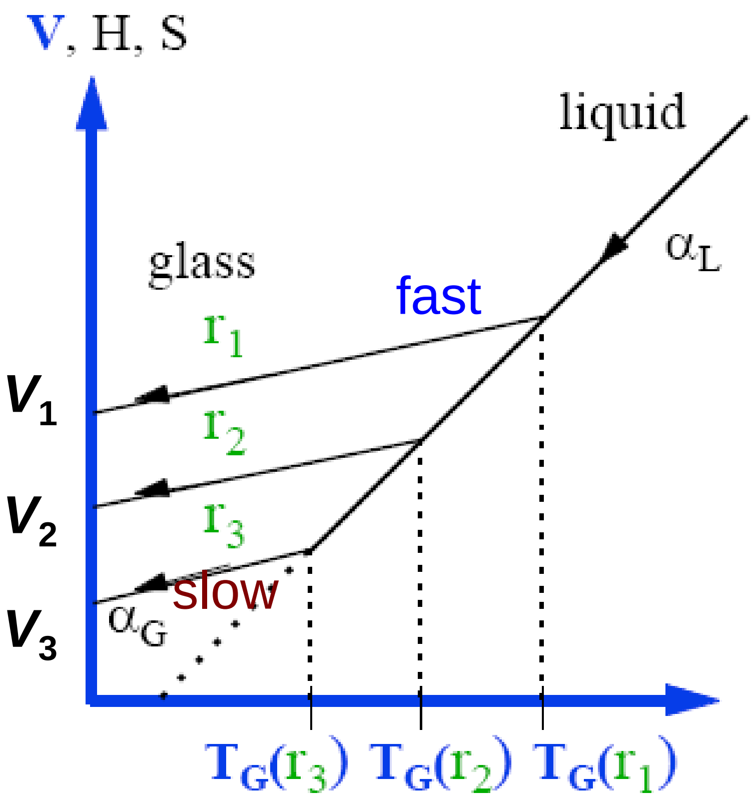
Below glass transition: frozen-in liquid

→ **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/ (1)~(2) ➡ glass transition**

(A concept of glass transition based on kinetic view point)

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, its configuration will change toward equil. amorphous structure.**

➡ "Relaxation behavior"

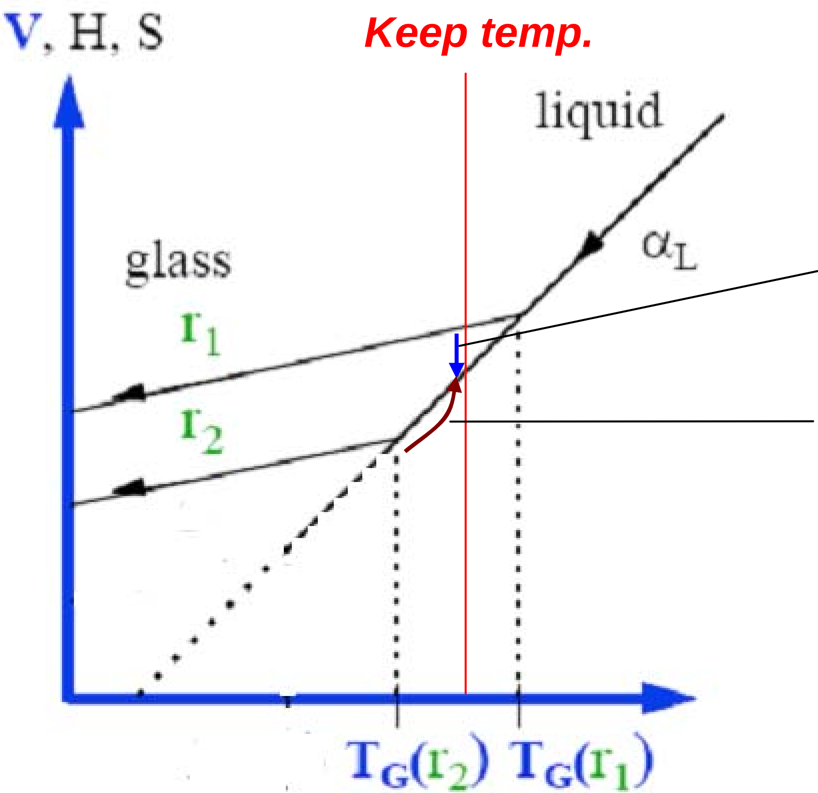
In fact, many properties of glass changes depending on relaxation behavior.

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 ↓

smaller volume

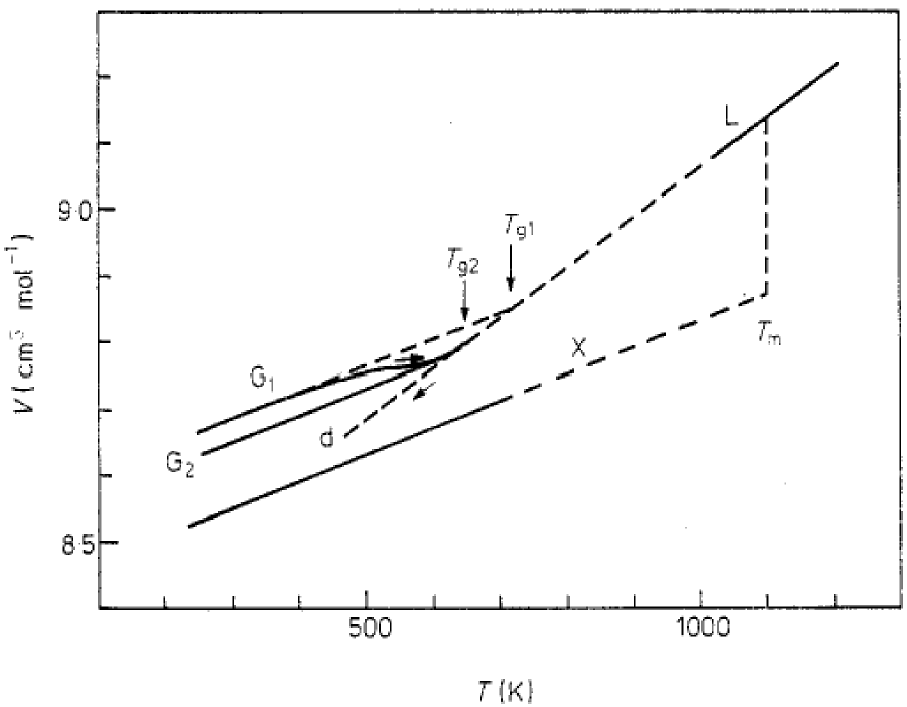
larger volume

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



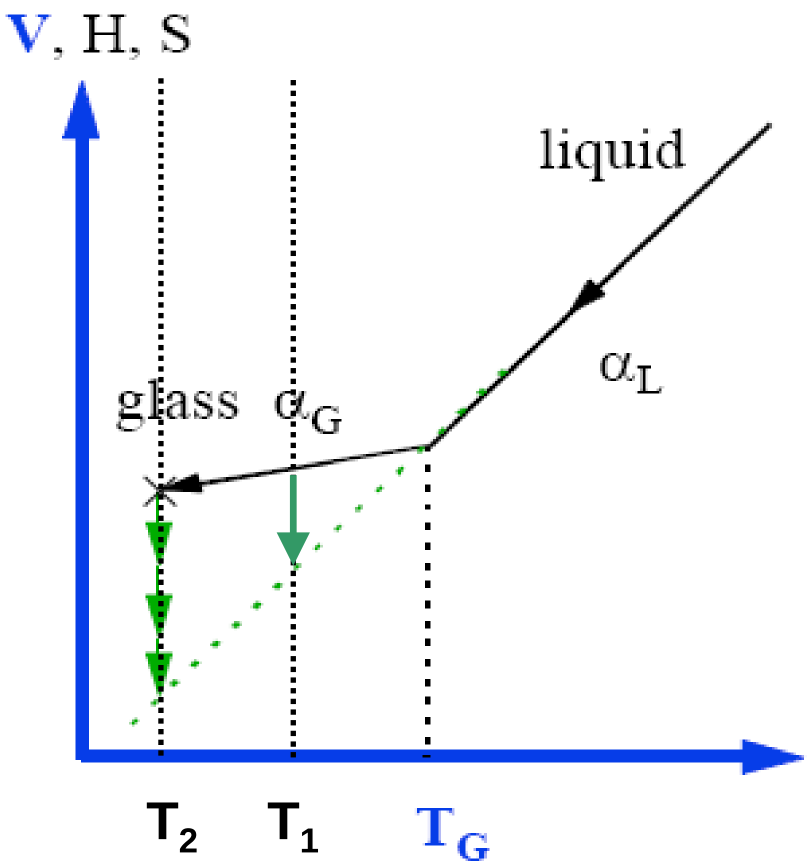
<Specific volume of PdCuSi>

- **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

C. Relaxation behavior : rate of relaxation behavior



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

- **high temp. (T1)**
  - → Kinetics for stabilization: large
  - → Initial departure from equil. amor. structure: small
  - ➡ Total change in property: small
- **low temp. (T1)**
  - → Kinetics for stabilization: small
  - → Initial departure: large
  - ➡ relatively very small degree of (R)

➡ At intermediate temp. kinetics relaxation behavior (property change) may be largest.

C. Relaxation behavior

*** Property change for observation of relaxation behavior (by experiment)**

- Stress relaxation: stress, pressure, voltage
  → strain, volume, polarization
- Creep: constant strain → stress
- driven oscillation
- damped free oscillation: decay of free oscillation of displacement

➡ Stress relaxation, volume relaxation, enthalpy relaxation, creep

C. Relaxation behavior

*** Glass transition**

- experimental observation time (t_0) • structural relaxation time (τ_r)

→ $t_0 > \tau_r$: liquid-like structure (S.C.L)

$t_0 < \tau_r$: solid-like structure (glass)

→ $t_0 \approx \tau_r$: glass transition → liquid equilibrium amor. structure

(time scale is comparable)

(property of liquid-like structure suddenly changes to that of solid-like structure)

➡ understanding of glass transition from viewpoints of relaxation

ex) heat capacity

cf) Kauzmann paradox → Change of C_p in thermodynamic viewpoint

- **As temp. decreased, decoupling of vibration mode from relaxation mode**