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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)**

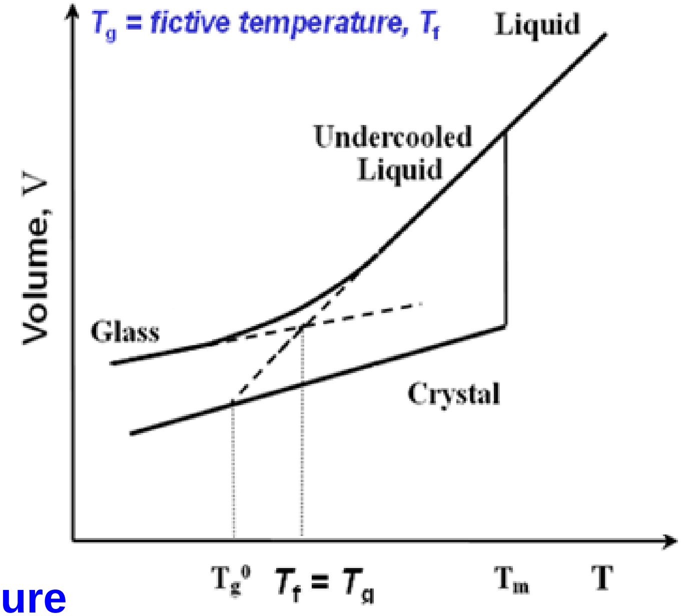
$$\boxed{S = \int C_P d \ln T}$$

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

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

($\because$ very slow cooling rate → longer relaxation time → crystallization

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)

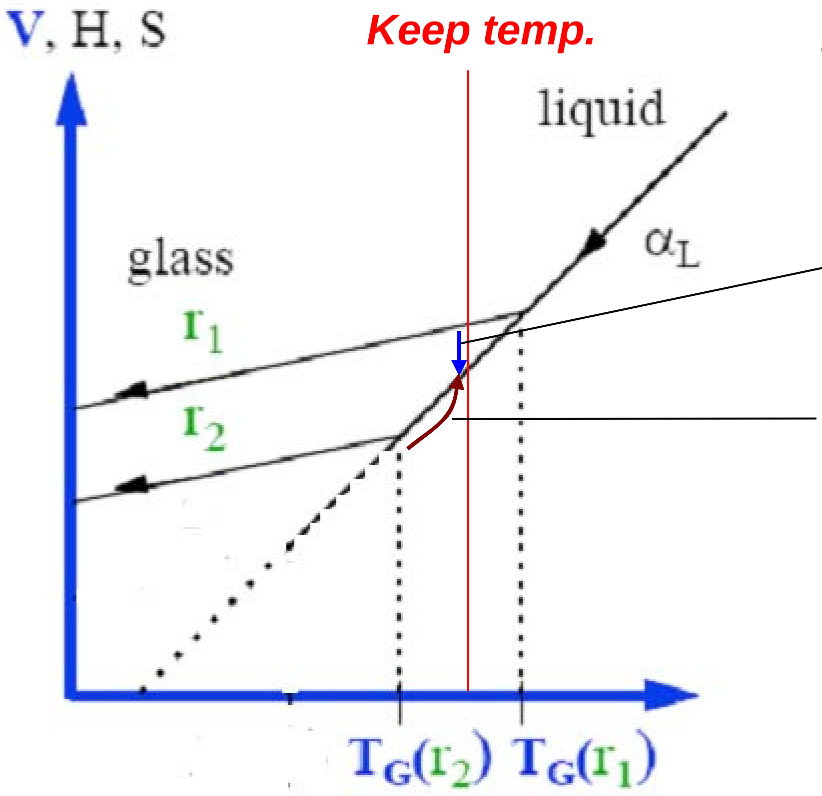
→ understanding of glass transition from viewpoints of relaxation

C. Relaxation behavior

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

*** Process of relaxation behavior: stabilization**

(equilibrium amorphous structure) ⟶ closely related to glass property



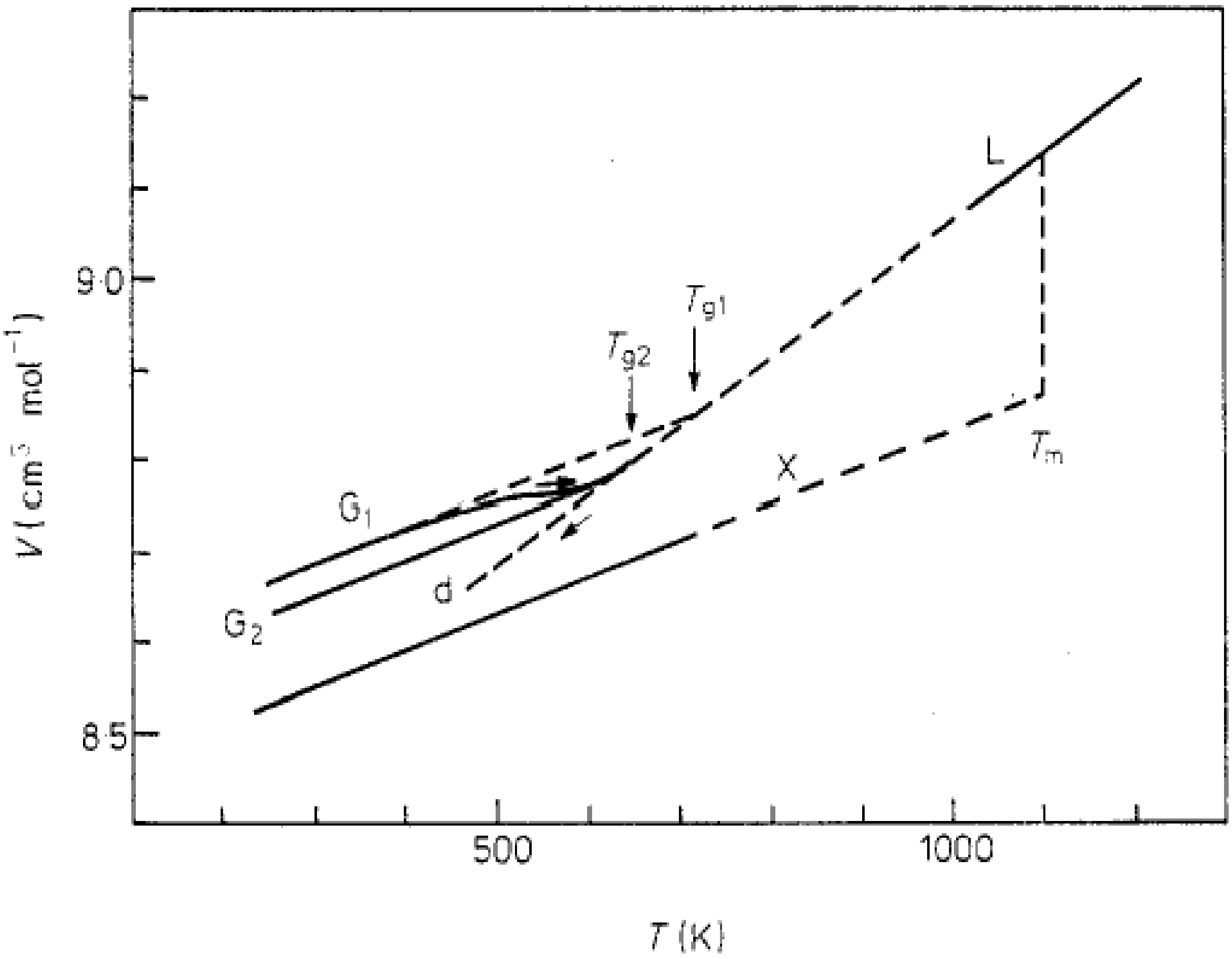
Keep temp.

smaller volume

larger volume

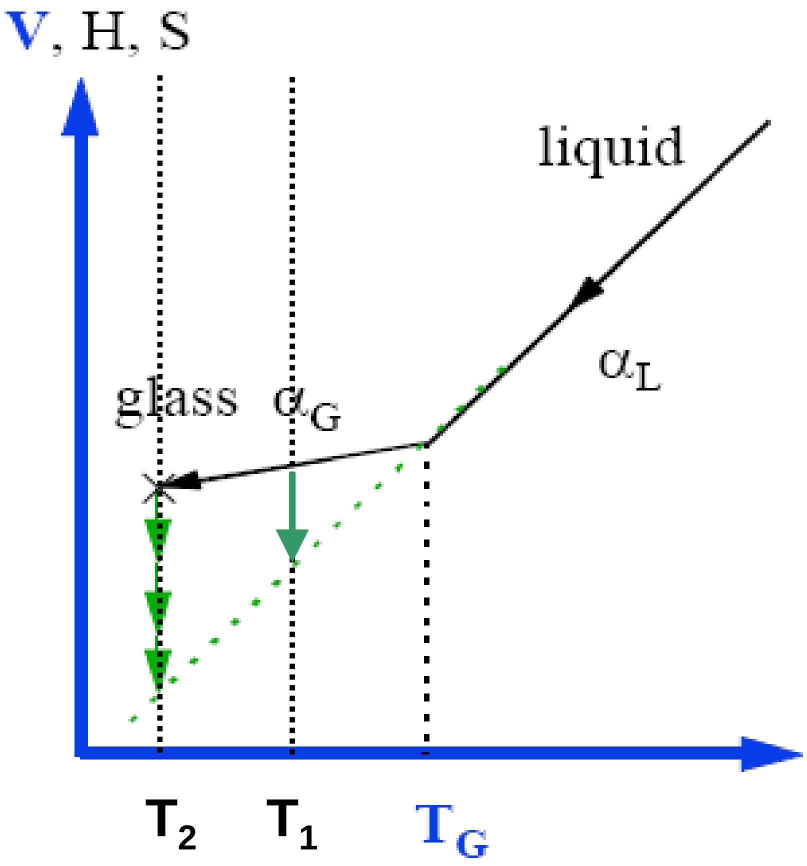
- **depending on cooling rate,**
  specific volume ↑ **or** ↓

C. Relaxation behavior



<Specific volume of PdCuSi>

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)**

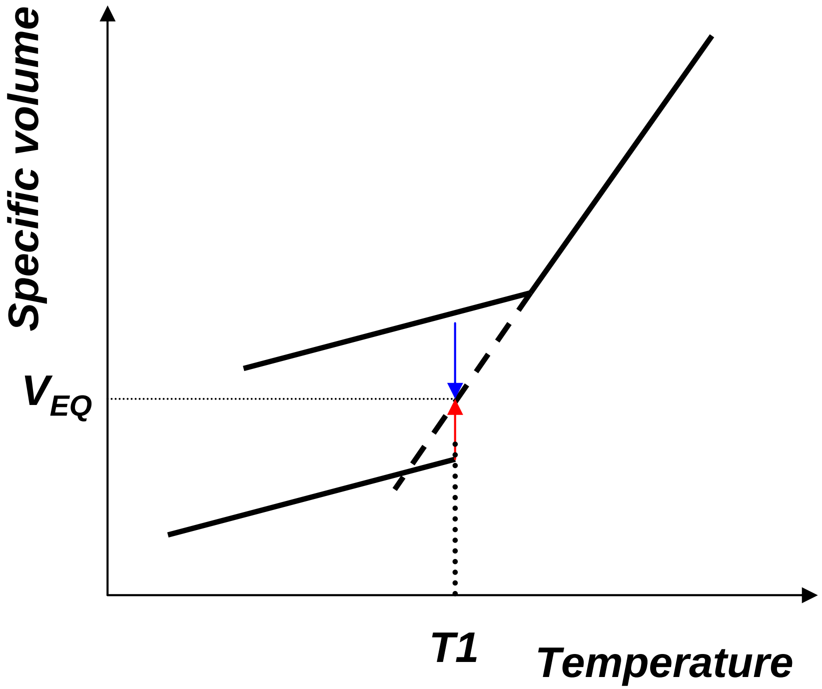
⟶ Kinetics for stabilization: small

⟶ Initial departure: large

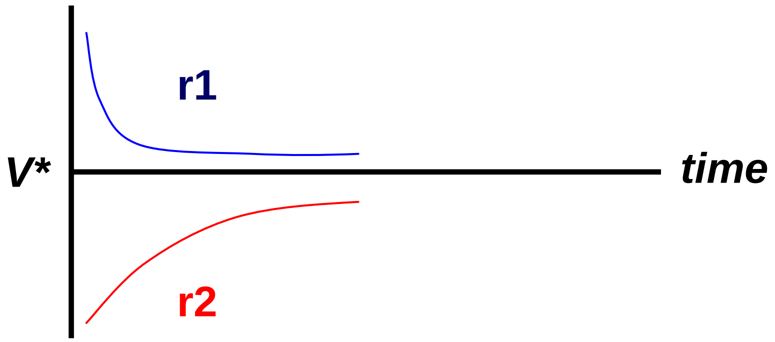
➡ relatively very small degree of (R)

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

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**

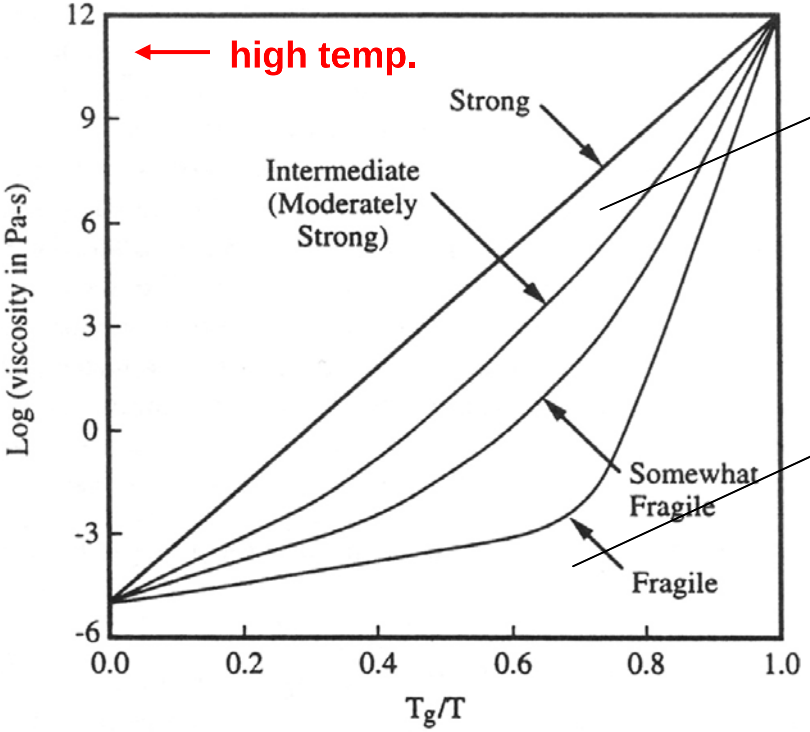
r1 > r2

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***

d. viscosity

*** How do we describe viscous flow?**

→ Several atomistic model

- absolute rate model
- free volume model
- excess entropy model

1) Absolute rate model

→ atom/molecular rearrangement by stress

→ $$\eta = \frac{\tau \exp(\Delta E / kT)}{a_0 \sinh(\tau V_a / 2kT)}$$

τ : shear stress
A_0 : atom jump distance
V_a : flow volume
ΔE : activation energy for flow

→ model describing stress dependence of flow

→ in case of small stress ($\tau V_a / 2kT << 1$)

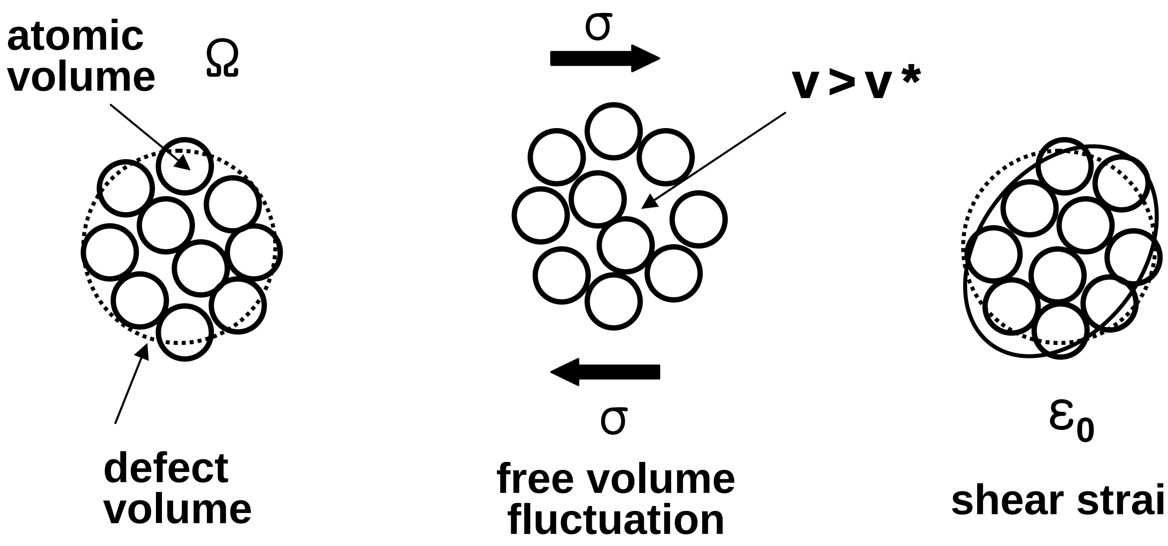
→ Arrhenius temp. dependence for the viscosity

→ $\log \eta$ vs 1/T : linear ← $\eta = \eta_0 \exp(\Delta E / kT)$

→ for many glass, at limited temp. range

2) Free volume model

Free volume → **excess volume originated from thermal expansion without phase change in liquid**



Probability $\exp(A\frac{v^*}{v_f})$

average free volume

- V* : **activated volume for molecular movement** → **crucial role for flow**

➡ Critical step in flow = opening of void of some critical vol. 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.)**

* Is it possible to observe glass transition through free volume?

- if free volume decreases under critical value,

  - hard sphere model $\eta_p = 0.516$

  - M.D. simulation $\eta_p = 0.56$

  $\longrightarrow$ hard sphere dense random packing: $\eta_p = 0.636$

- Qualitative analysis with temp. change
  - expansion coeff.: α_{Tl} , α_{Tg}
  - expansion coeff. of free volume: $\Delta\alpha_T = \alpha_{Tl} - \alpha_{Tg}$

  - Vol at T=0

    V_{occ} (T=0) = $V_g - V_g \alpha_{Tl} T_g$ **(extrapolation of total volume of liquid)**

    (V_g = total volume at T_g)

  - Total vol. at glass (T=0)

    $V = V_g - V_g \alpha_{Tg} Tg$

  - free volume at T=0

    $V_f = V - V_{occ} = V_g (\Delta\alpha_T) T_g$

2) Free volume model

→ by Doolittle (1951)

→ flow of hydrocarbon liquids in the range of high fluidity by empirical relation

$$\eta \approx \eta_0' \exp(\gamma V_0 / V_f)$$

V_0 : van der Waals volume of the molecule
V : molecular volume at given temp.
V_f : free volume (V_f = V-V_0)
ɣ : constant

→ temp. dependence of η → temp. dependence of V_f

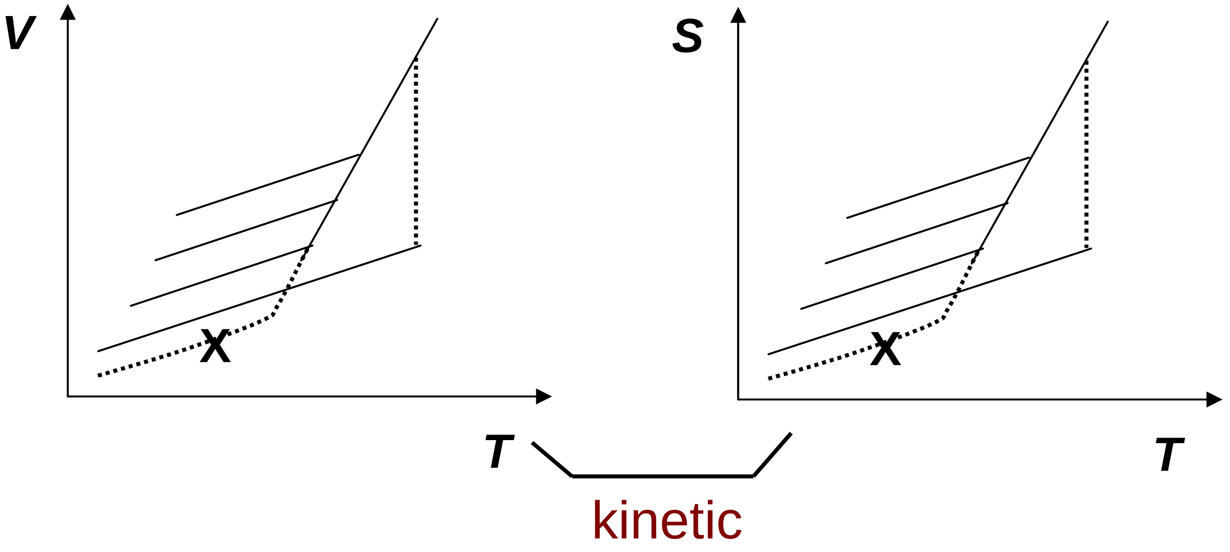
→ Viscosity near T_g by Williams Landel and Ferry (1955)

→ glass transition/ viscosity

$$\eta \approx \eta_0' \exp\left[\frac{b}{f_g + \Delta\alpha(T - T_g)}\right]$$

$f_g = (V_f/V)_{Tg}$: fractional free volume
$\Delta\alpha$: difference between the thermal expansion coeff. of liquid and glass
b = constant

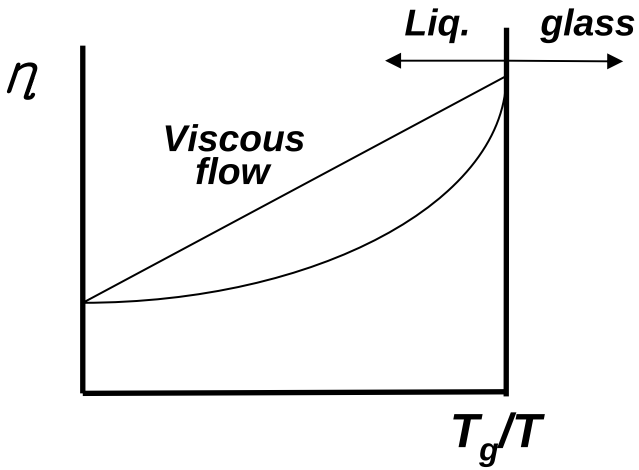
3) Excess entropy model: thermodynamic viewpoint



- decrease of configurational entropy with temp. change → viscosity

by Gibbs $$\eta \approx \eta_0''\exp(c/T\cdot S_c)$$

c: const (potential energy barrier for atom movement)
Sc: configurational entropy



Viscous – fragile – configuration

→ connection