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“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)**

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

→ 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

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**

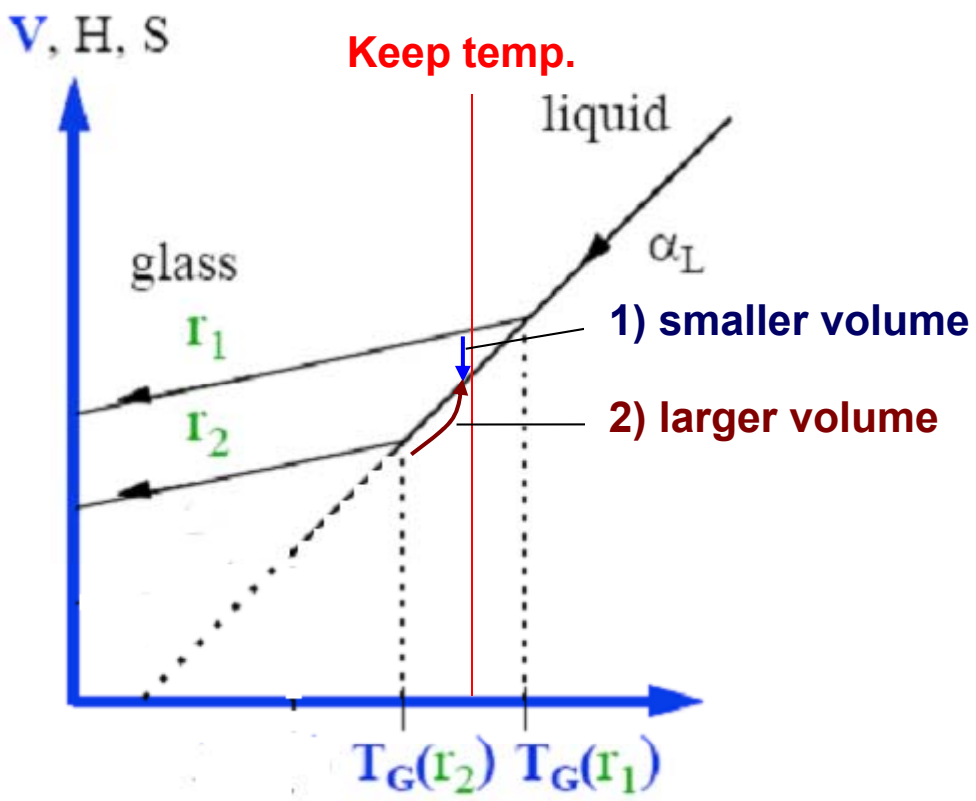
(A concept of glass transition based on kinetic view point)

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

➡ understanding of glass transition from viewpoints of relaxation

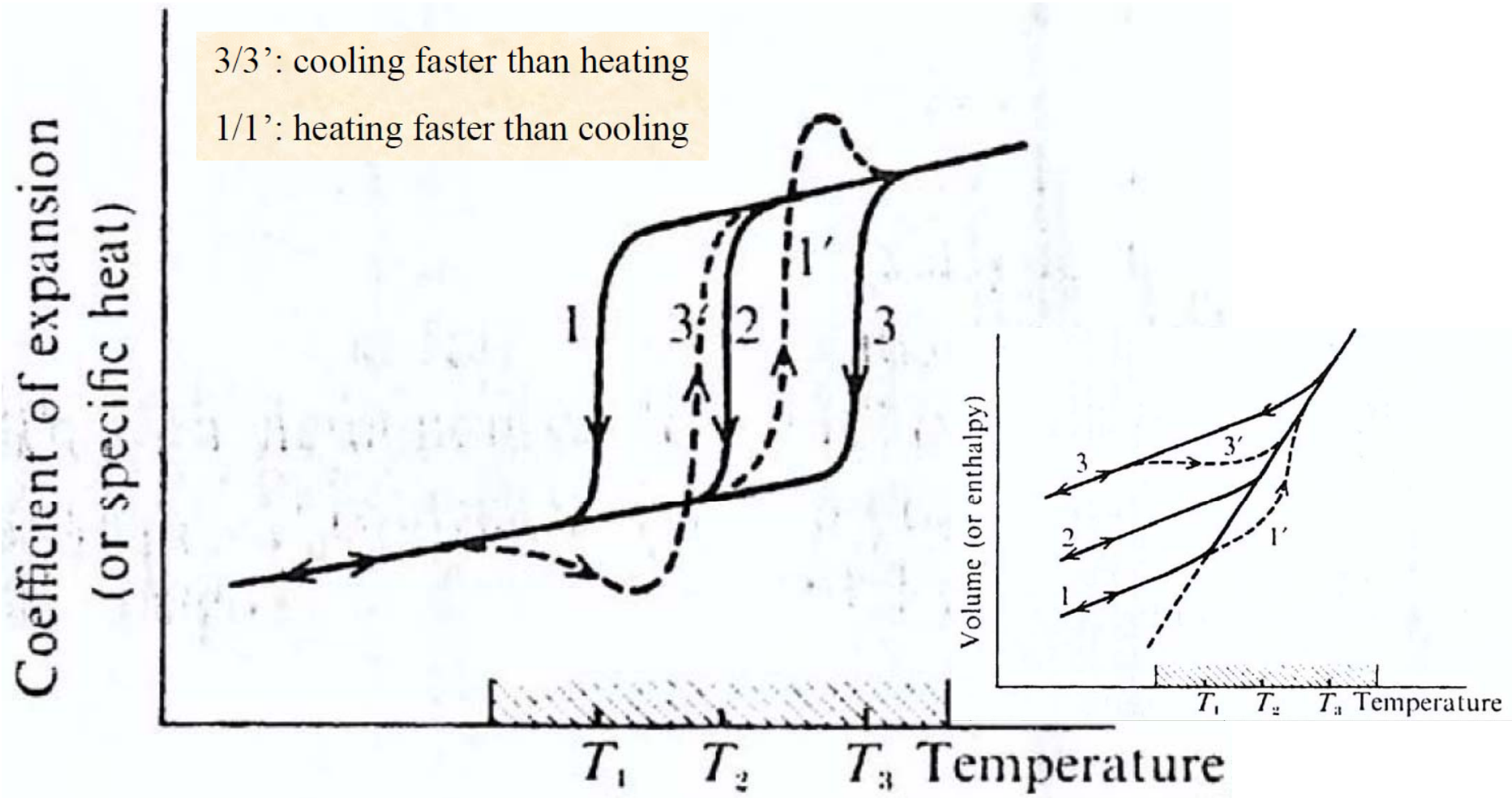
C. Relaxation behavior

- **equil. liquid structure** in supercooled liquid
- glass → configurational change →
  keep the temp. near T_g → **stabilization**



- **depending on cooling rate,**
  specific volume ⬆ **or** ⬇

Complex relaxation effect in the transition region

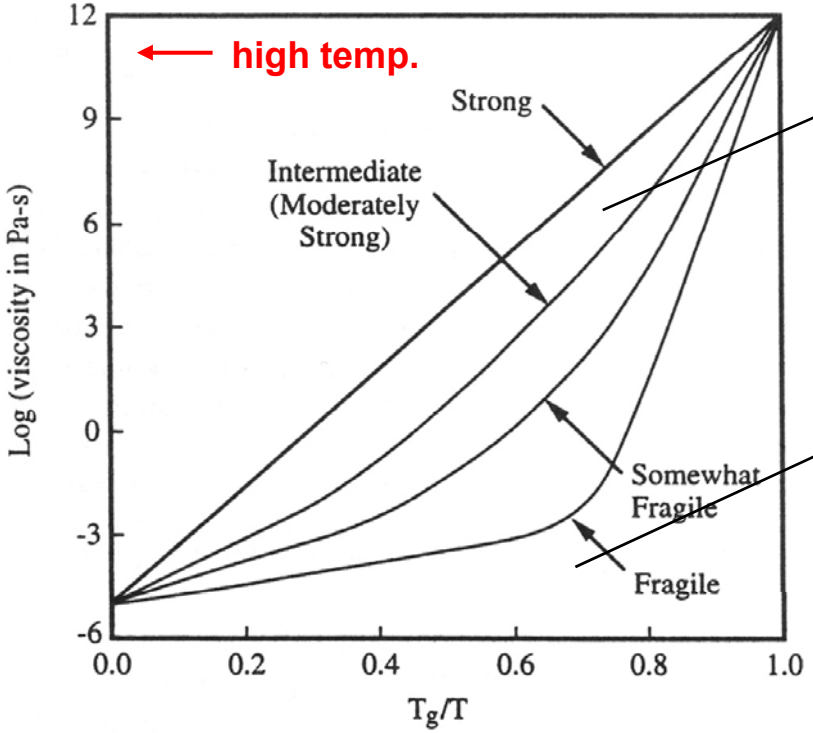


d. viscosity

*** 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 ($\tau V_a / 2kT << 1$)

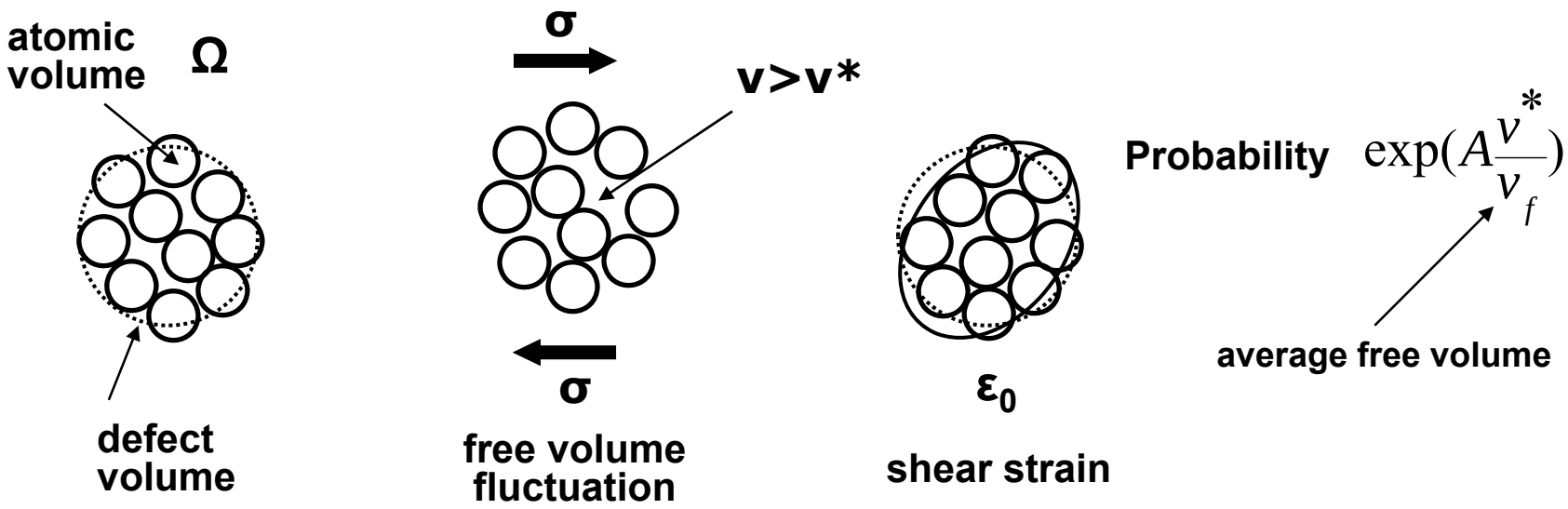
→ Arrhenius temp. dependence for the viscosity

→ $\log \eta$ 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**



- 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

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

Quantitative approach for V_f

→ α_{Tl}, α_{Tg} **Expansion of occupied vol. & free volume**

→ Expansion of free vol.: $\Delta\alpha = \alpha_{Tl} - \alpha_{Tg}$

Expansion of occupied vol.

- occupied vol. at T=0

→ **Extrapolate volume of liquid**

$V_{occ}(T=0) = V_g - V_g \cdot \alpha_{Tl} \cdot \alpha_{Tg}$ (V_g: total vol. of glass at T_g)

- Total vol. of glass at T=0

$V = V_g - V_g \cdot \underline{\alpha_{Tg}} \cdot T_g$ (glass frozen-in V_f)

V_g → occ.: total vol., V_{tot} at T=0

V_g → occ. & free: occ. Vol., V_{occ} at T=0

- free vol. at T=0 $V_f = V_{tot} - V_{occ}$

$= -V_g\alpha_{Tg}T_g + V_g\alpha_{Tl}T_g = V_g \cdot T_g \cdot \Delta\alpha_T$

Fraction of free volume: $\frac{V_f}{V_g} = T_g \cdot \Delta\alpha_T$ (at T=0) (at T=T_g) $\left(\frac{V_f}{V_{tot}} = \frac{V_g \cdot T_g \cdot \Delta\alpha_T}{V_{tot}}\right)$ (at T=0) (at T=0)

2) Free volume model

As mentioned previously, viscous flow: free volume model

→ free volume model ⟷ viscosity

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

$$\eta \approx A \exp(B V_{occ} / V_f)$$ **by Doolittle**

here, $V_f = V_{fg} + V_g \Delta\alpha_T (T - T_g)$ at $T > T_g$

(at T=0)

- Williams-Landel-Ferry equation

$$\ln\left(\frac{\eta_g}{\eta}\right) = \frac{c(T - T_g)}{D + (T - T_g)}$$ **(C, D: empirical const.)**

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 ($V_f = V - V_0$)
γ : constant

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

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

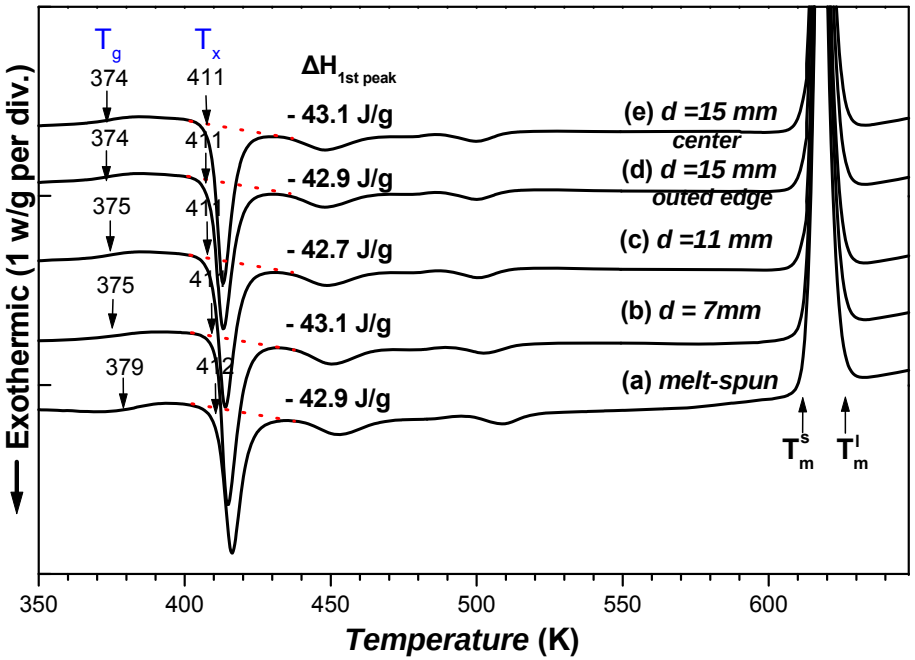
→ glass transition/ viscosity

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

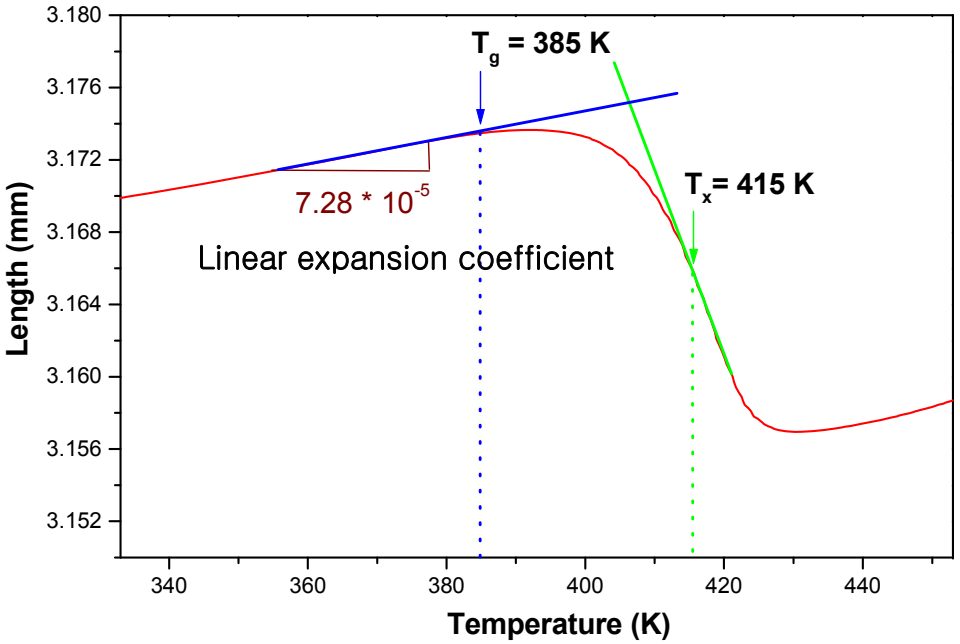
$f_g = (V_f/V)_{Tg}$: fractional free volume
$\Delta\alpha$: difference between the thermal expansion coeff. of liquid and glass
b = constant

Measurement of Glass Transition Temperature (Tg)

Thermal analysis curve (DSC)

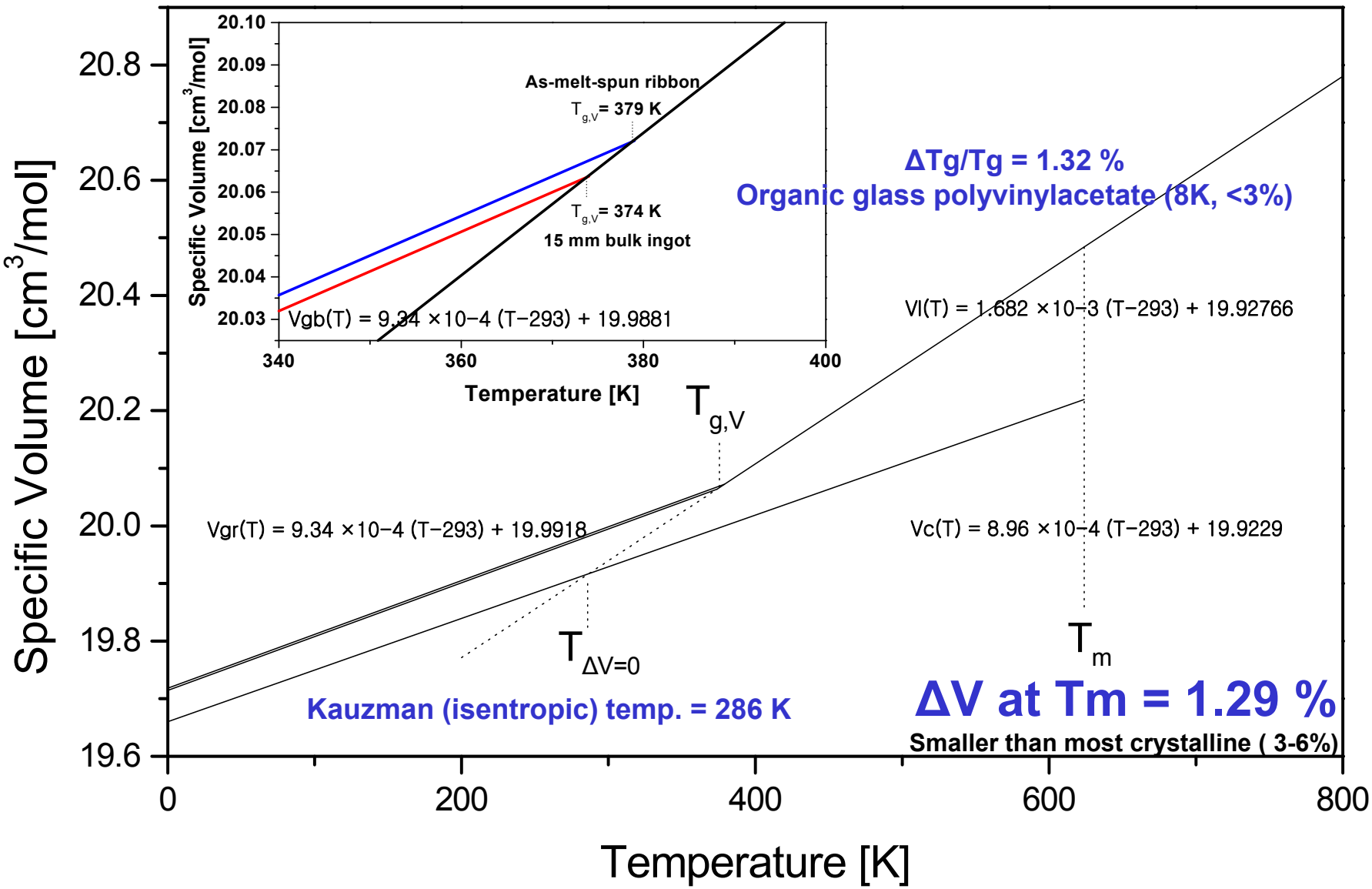


Thermal expansion curve (TMA)



Tg in As-spun (10^5 /s Rc) = 379 K ⇔ Tg in 15mm bulk (2*10 /s Rc) = 374 K

	Amorphous		Crystal	Δ (discrepancy)
	ribbon	15 mm		
Density (g/cm^3)	2.1396	2.140	2.147	$[(\rho_{cryst.}-\rho_{amor.})/\rho_{cryst.}]$ at 293 K 0.327 %
Specific volume (cm^3/mol)	19.9918	19.9881	19.9229	$[(V_{cryst.}-V_{amor.})/V_{cryst.}]$ at 624 K 5.02 %


Specific Volume [cm3/mol]
Temperature [K]
20.8
20.6
20.4
20.2
20.0
19.8
19.6
0
200
400
600
800
Specific Volume [cm3/mol]
Temperature [K]
20.10
20.09
20.08
20.07
20.06
20.05
20.04
20.03
340
360
380
400
As-melt-spun ribbon
Tg,V= 379 K
Tg,V= 374 K
15 mm bulk ingot
Vgb(T) = 9.34 ×10−4 (T−293) + 19.9881
ΔTg/Tg = 1.32 %
Organic glass polyvinylacetate (8K, <3%)
Vl(T) = 1.682 ×10−3 (T−293) + 19.92766
Tg,V
Vgr(T) = 9.34 ×10−4 (T−293) + 19.9918
Vc(T) = 8.96 ×10−4 (T−293) + 19.9229
TΔV=0
Tm
Kauzman (isentropic) temp. = 286 K
ΔV at Tm = 1.29 %
Smaller than most crystalline (3-6%)

Kauzman (isentropic) temp. = 286 K
,where the excess entropy of the liquid vanishes

Assumption : the free volume in liquid Vf(T) disappears at Tk

The free volume in the equilibrium liquid above Tg

$$V_f(T) = V_0 \int_{T_K}^{T} (\beta_l - \beta_g)\,dT \quad \text{with } V_0 = V_l(T_K),$$

where β_l and β_g are the coefficients of the volume expansion of liquid and glass

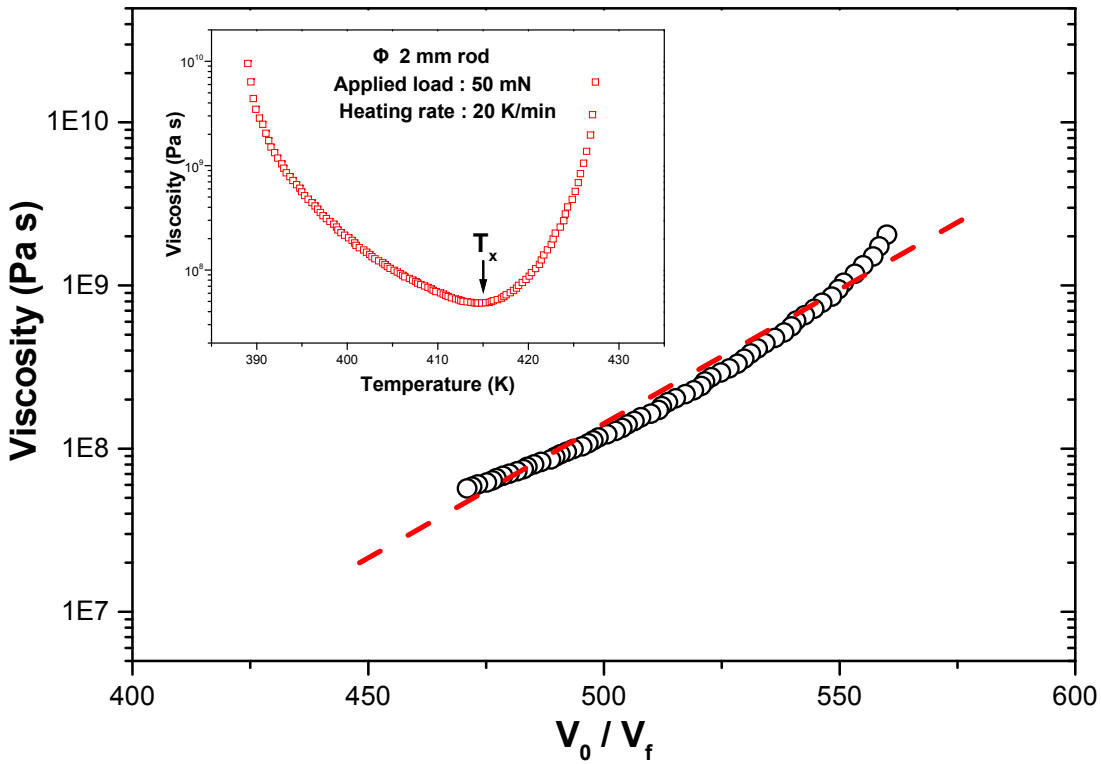
- In the case of constant coefficient, as obtained for the alloy, the fractional free volume depends linearly on the temperature.

With the Doolittle equation , the viscosity of a liquid, η, can be interpreted in terms of its fractional free volume :

$$\eta = \eta_0 \exp\left\{A \frac{V_0}{V_f}\right\}.$$

- From the two eqs., the Doolittle equation leads to the Vogel-Fulcher-Tamman relation, which is commonly used to describe the viscous behavior of glas-forming liquids near Tg.

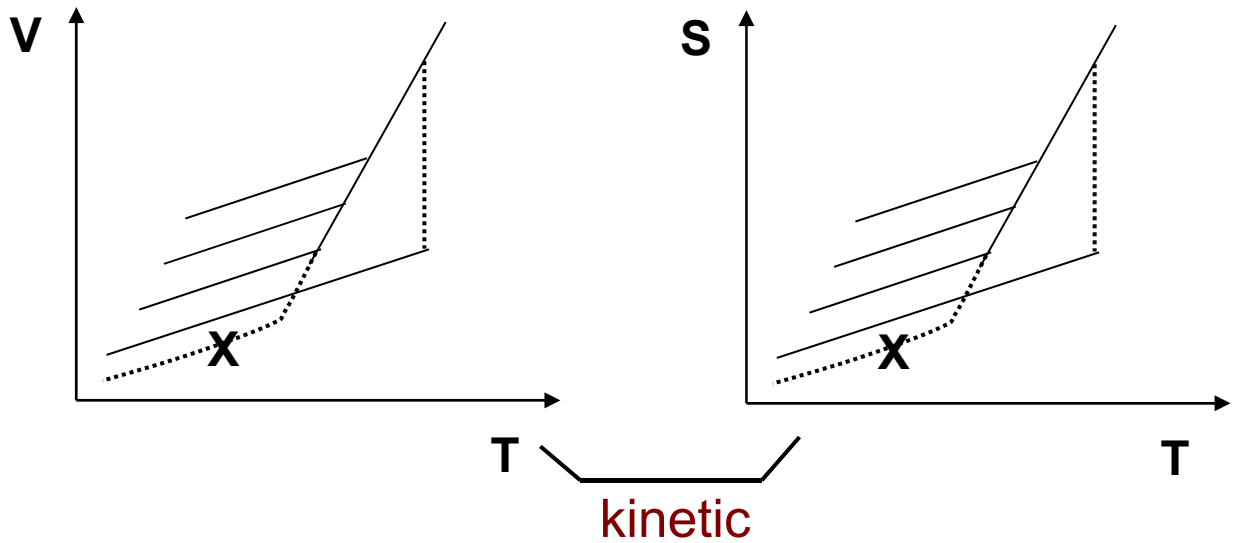
The correlation between the viscosity measured in this study on the supercooled melts and the fractional free volume following from the volumetric experiments



The correlation between log η and V0/Vf postulated by Doolittle's eq. can be demonstrated for the metallic glass former Ca65Mg15Zn20 in the investigated temperature range.

-> Viscosity strongly correlates with the change of free volume in the system

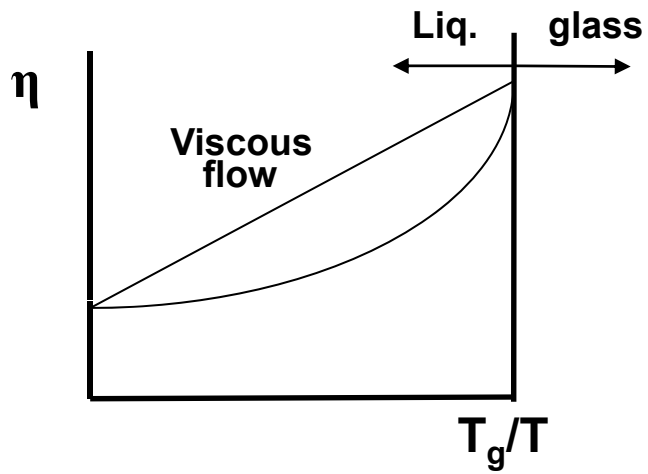
3) Excess entropy model: thermodynamic viewpoint



- 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