2014 Spring

"Advanced Physical Metallurgy"
- Bulk Metallic Glasses -

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Office: 33-313
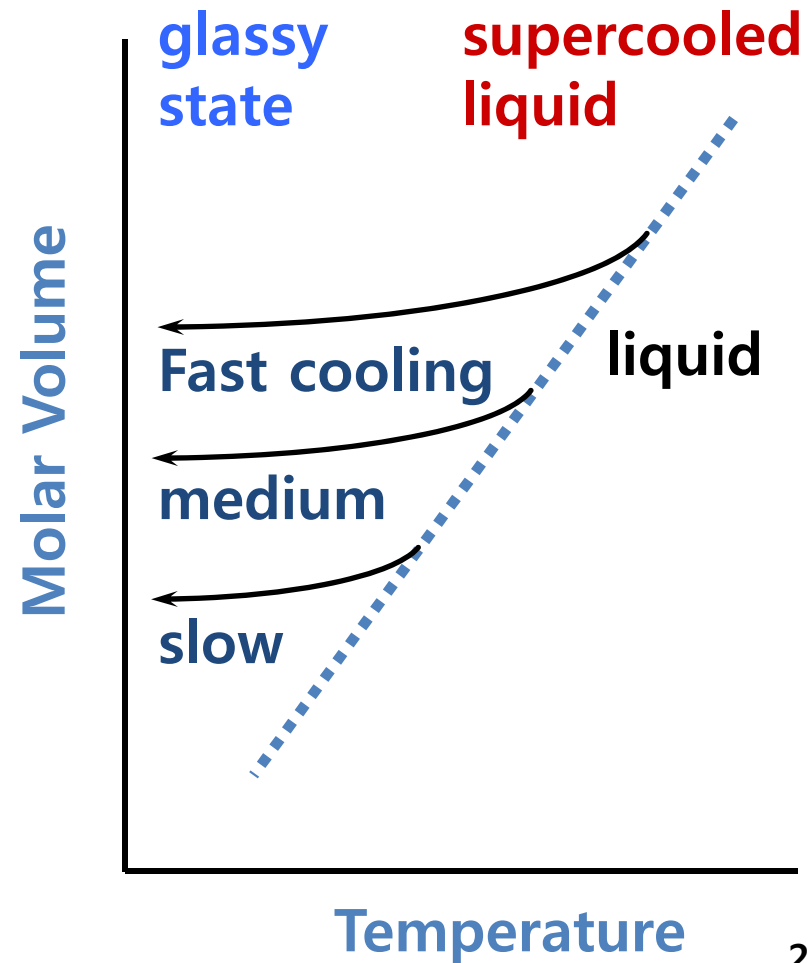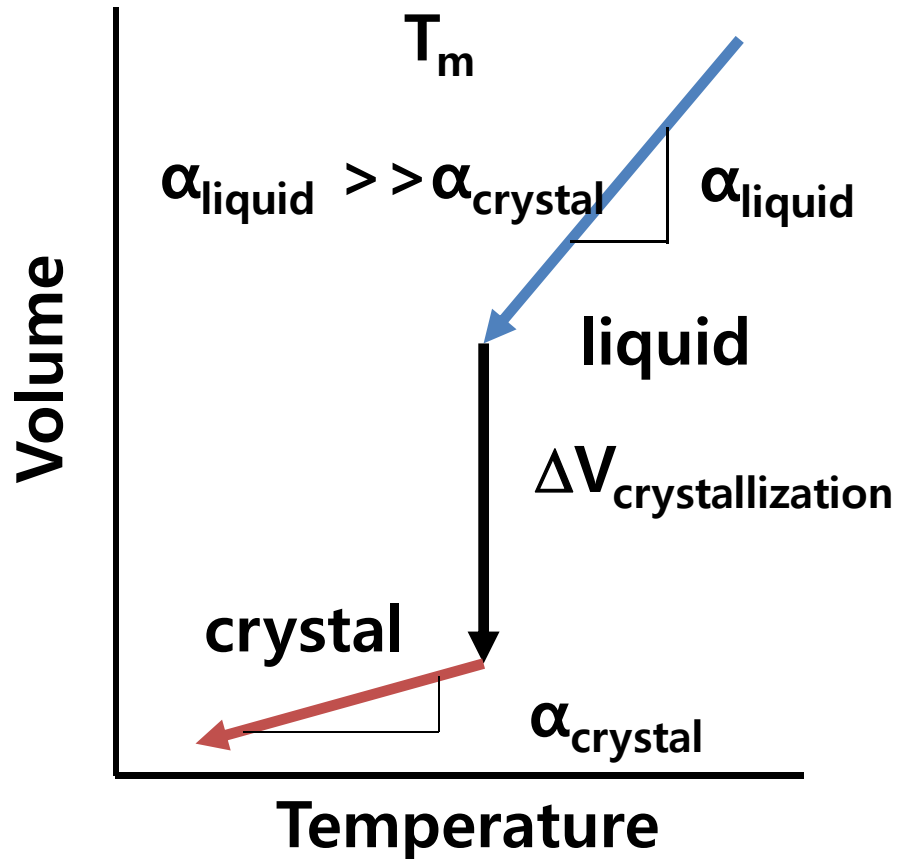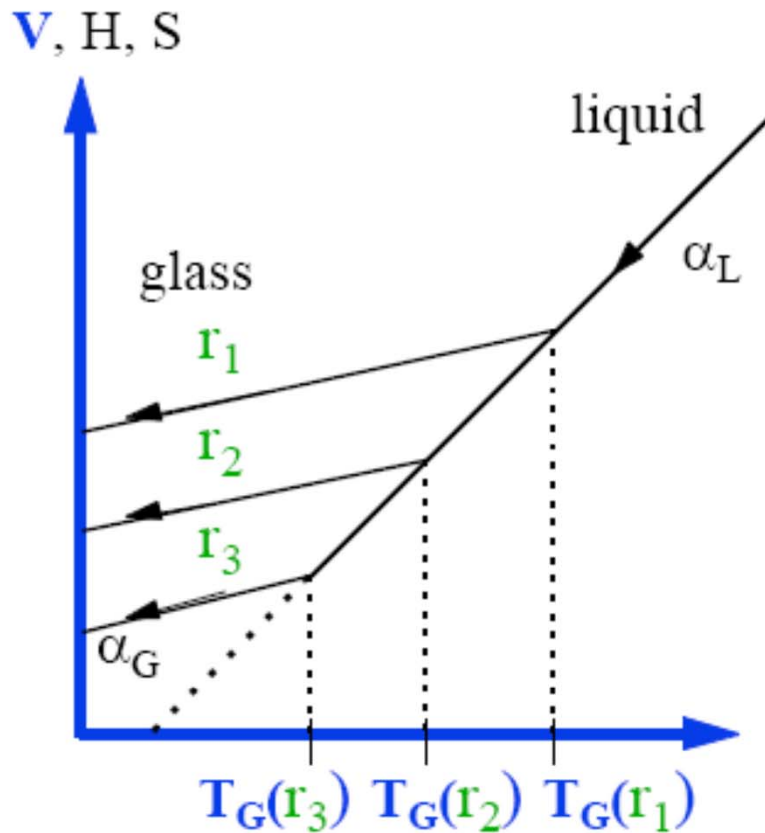Telephone: 880-7221
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* Fundamentals of the Glass Transition

- **Melting and Crystallization are Thermodynamic Transitions**

- **The Glass Transition is a Kinetic Transition**

* Kinetic Nature of the Glass Transition

V, H, S

liquid

glass

r_1

r_2

r_3

α_L

α_G

$T_G(r_3)$ $T_G(r_2)$ $T_G(r_1)$

V, H, S

liquid

glass α_G

α_L

Ideal glass

T_G

Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$
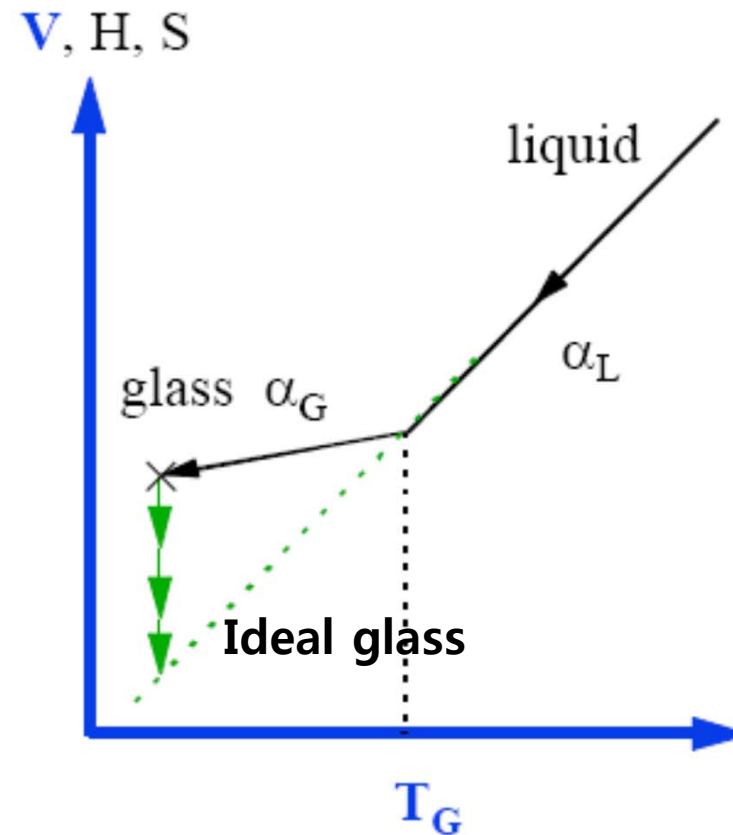
Specific Volume (density) of the glass depends on the time at a given $T < T_g$

* Glass → exited state –(sufficient time)→ relax and eventually transform to crystalline ground state

Glasses can be formed by one of the major types of bonding interactions found in solids.

: covalent, ionic, metallic, van der waals, hydrogen bond

"Phase Transition" $\Delta G = \Delta H - T\Delta S = 0$

Thermodynamically: what is possible!
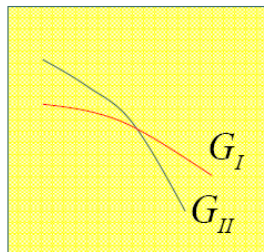
Kinetics: speed/rate of the transition

Thermodynamic classification: **first order** **&** **second order**

a discontinuity occurs in the first derivative of the free energy with respect to T and P.
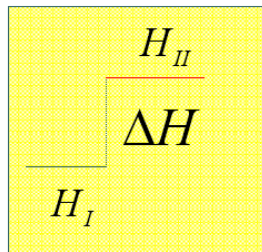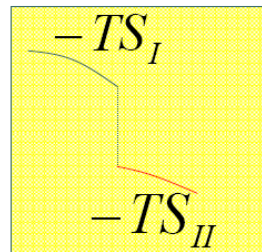
Discontinuities in the second derivatives of the free energy, i.e. heat capacity, thermal expansion, compressibility

: order-disorder transition
i.e. β-brass (Cu-Zr alloy), isotopic-nematic transition in liquid crystals, Ferromagnetic -paramagnetic transition

G_I

G_{II}

T_C

H_{II}

ΔH

H_I

T_C

$-TS_I$

$-TS_{II}$

T_C

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- **Thermodynamics for <u>glass transition</u>**

~ 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 <u>continuous</u> at T_T

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

→ *α_T C_P K_T changes discontinuously.*

– Second derivatives of G (α, β, C_p) are <u>discontinuous</u> 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 free energy
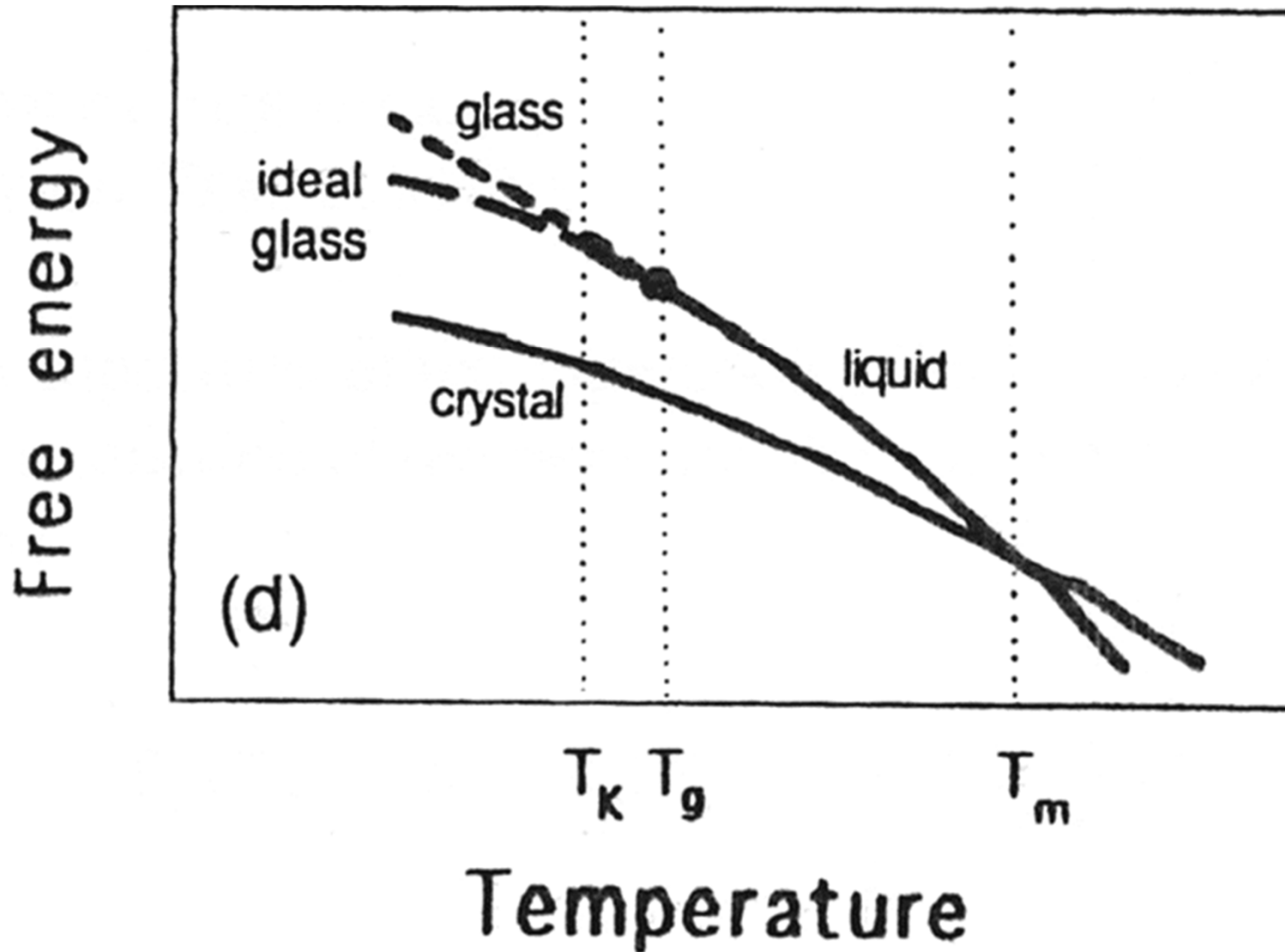
2.5.1 Thermodynamic Stability

The thermodynamic stability of a system at constant temperature and pressure is determined by its Gibbs free energy, G, defined as

$$G = H - TS$$

H is the enthalpy
T is the absolute temperature
S is the entropy

Using the above concepts, it may be stated that a glass becomes more "stable" when the free energy of the glassy phase is lower than that of the competing crystalline phase(s). In other words, the change in free energy, ΔG (= $G_{glass} - G_{crystal}$) becomes negative. Mathematically expressed:

$$\Delta G = \Delta H_f - T\Delta S_f$$

where

the Δ symbol represents the change in these quantities between the final and initial states

H_f and S_f represent the enthalpy of fusion and entropy of fusion, respectively

1) multi component system: $\Delta S\uparrow$_high order alloy → easy

2) low chemical potential due to ① low enthalpy ② large interfacial E between liquid and solid phase :
$\Delta H_f\downarrow$ _constituents with large negative heat of mixing → solid/liquid interface E ↑
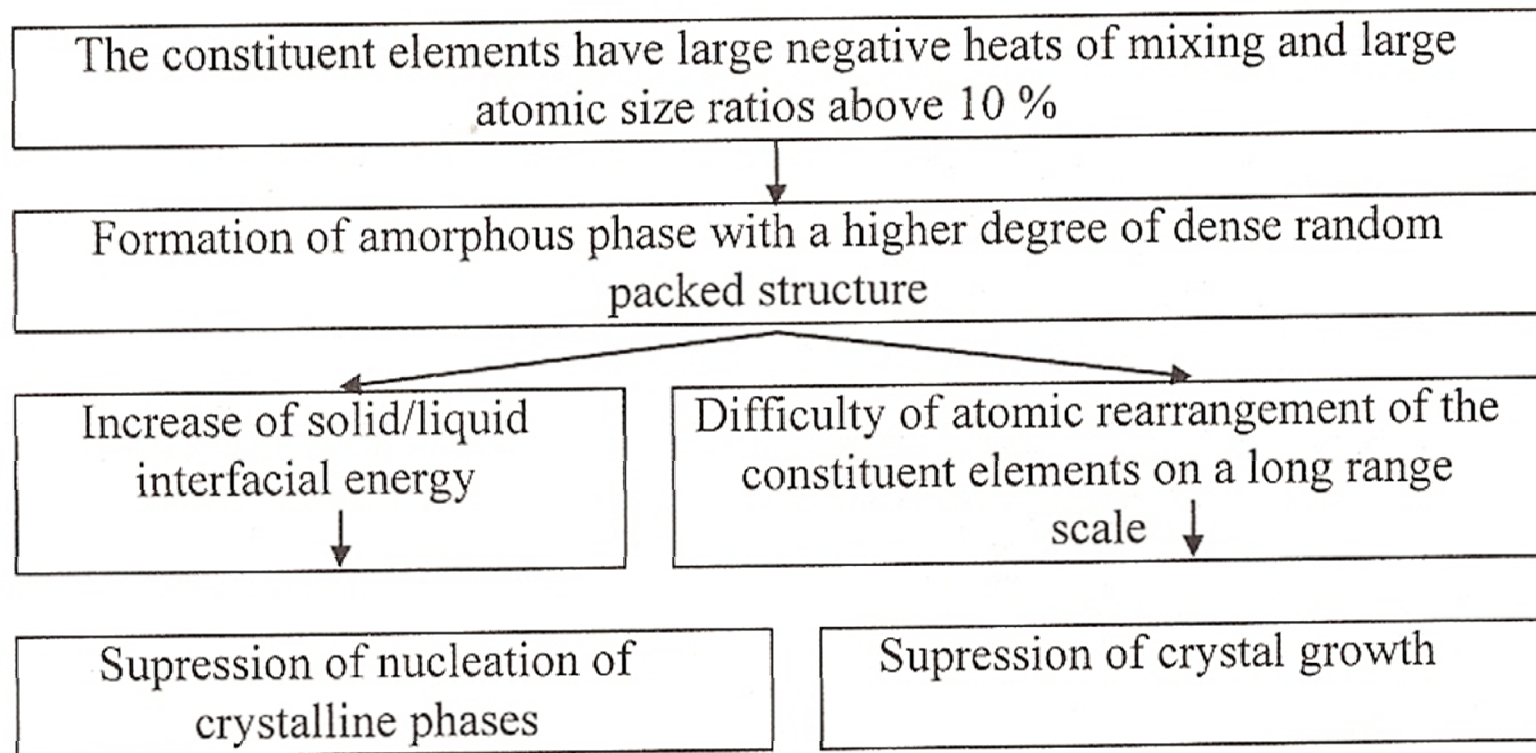
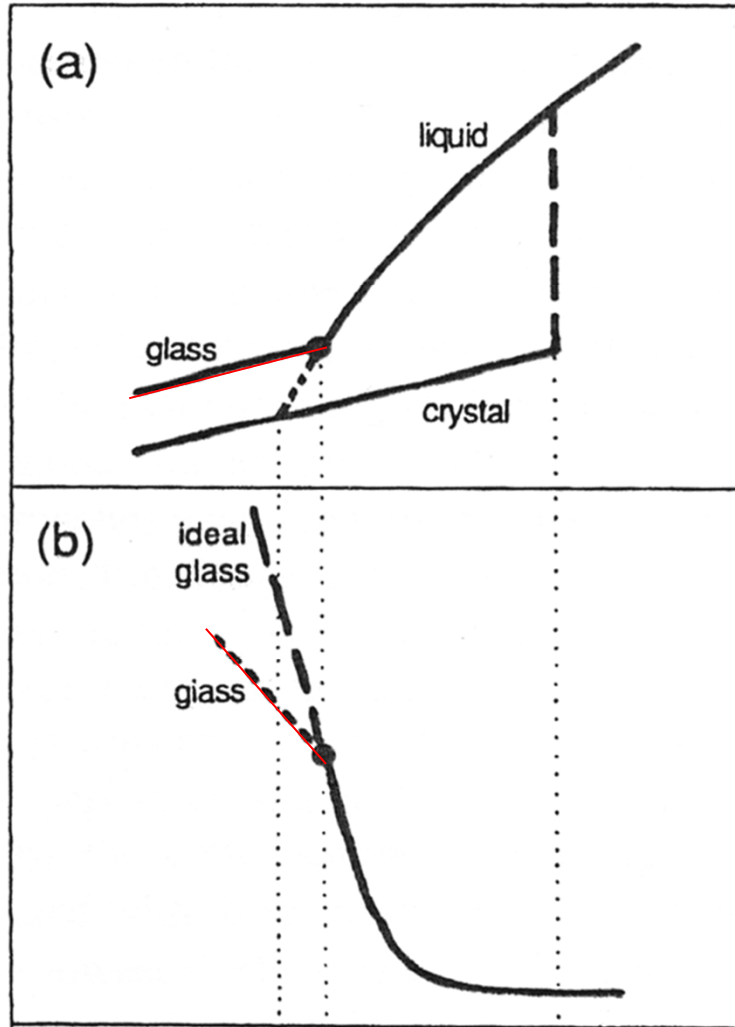**Fig. 5.** *Summary of the reasons for the achievement of the high glass-forming ability for some ternary alloy systems such as Ln-Al-TM, Mg-Ln-TM and Zr-Al-TM, etc. (Ln=lanthanide metal, TM=transition metal).*

continuous   **discontinuous**
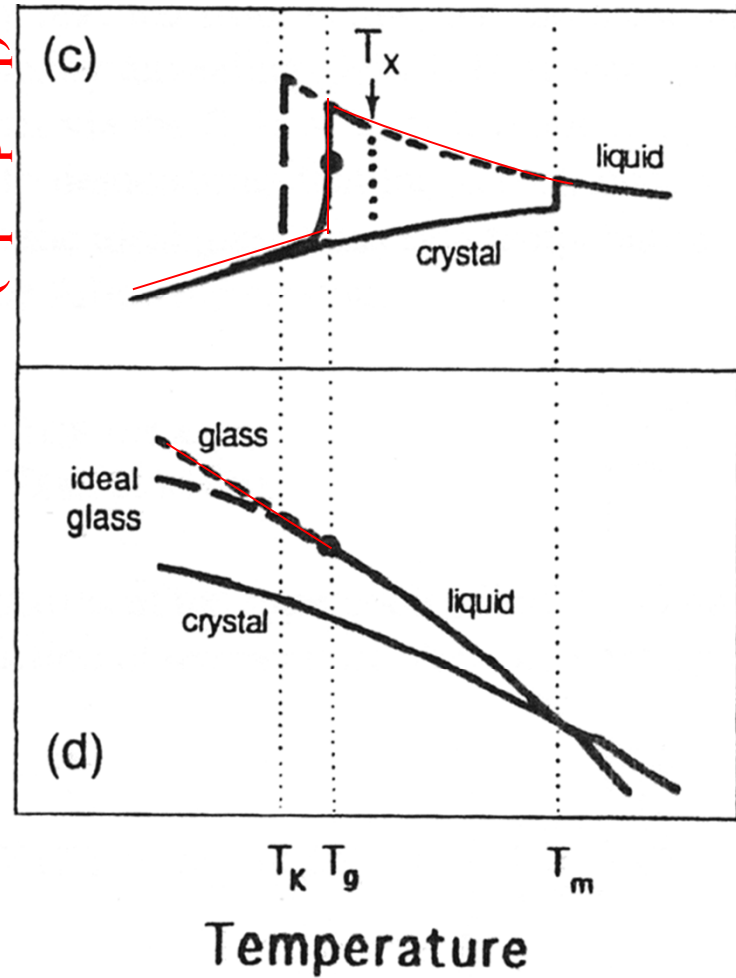
Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

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- **derivative of thermodynamic properties**

  → *discontinuous* (C_p, α_T, K_T)

C_P

liquid

~ **dramatically decrease C_p near T_g during cooling**

$C_{P\,(L)} - C_{P\,(G)}$

glass

~ **dramatically increase C_p near T_g during heating**

→ **Experimental observation during heating**
because the monitoring is very difficult during cooling

T

T_G

<u>**Glass transition**</u>**: heat** → **endothermic**

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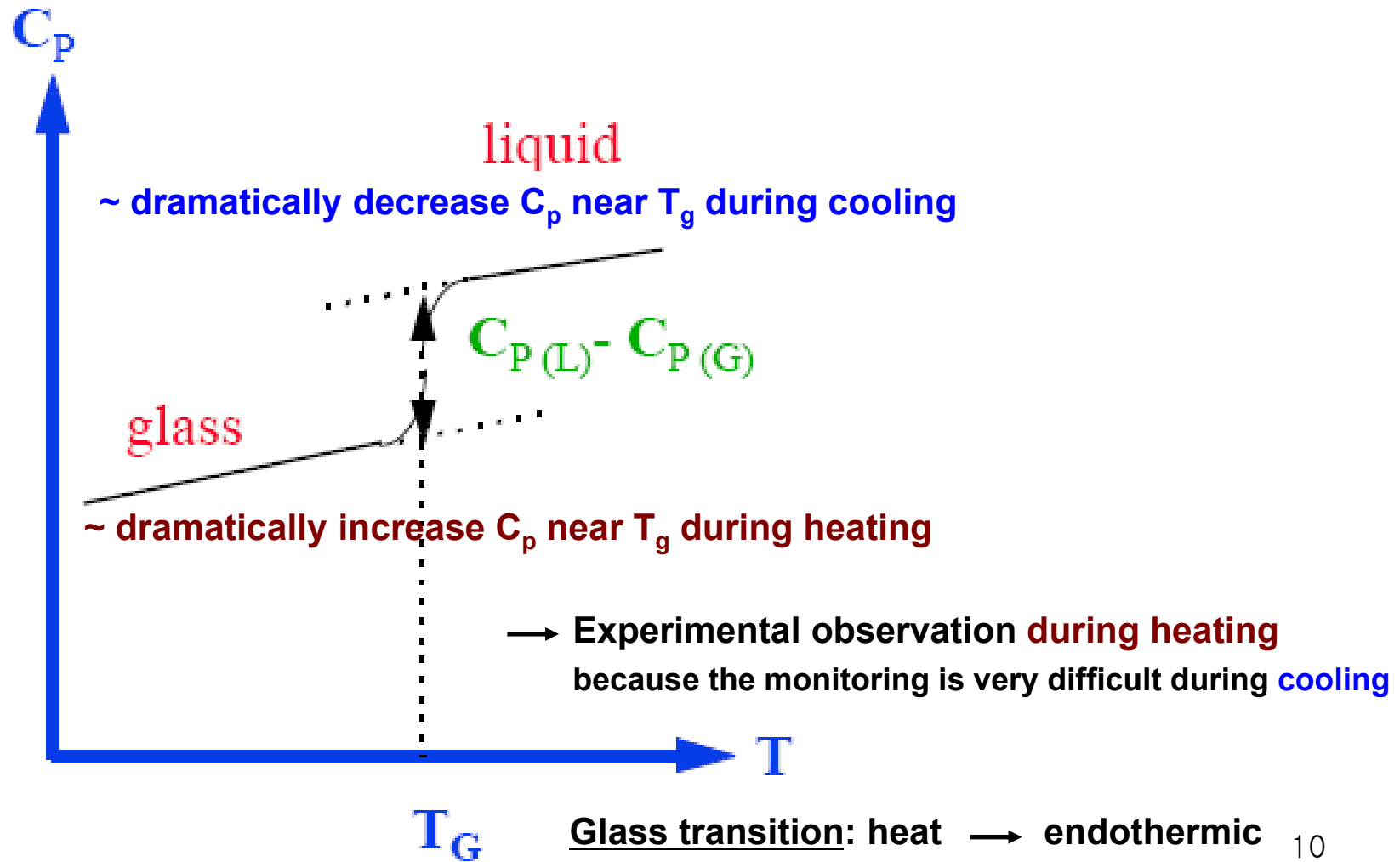
Theories for the glass transition

A. Thermodynamic phase transition

- *Glass transition*

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

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

But,   *1) Tg is dependent on thermal history of sample.*
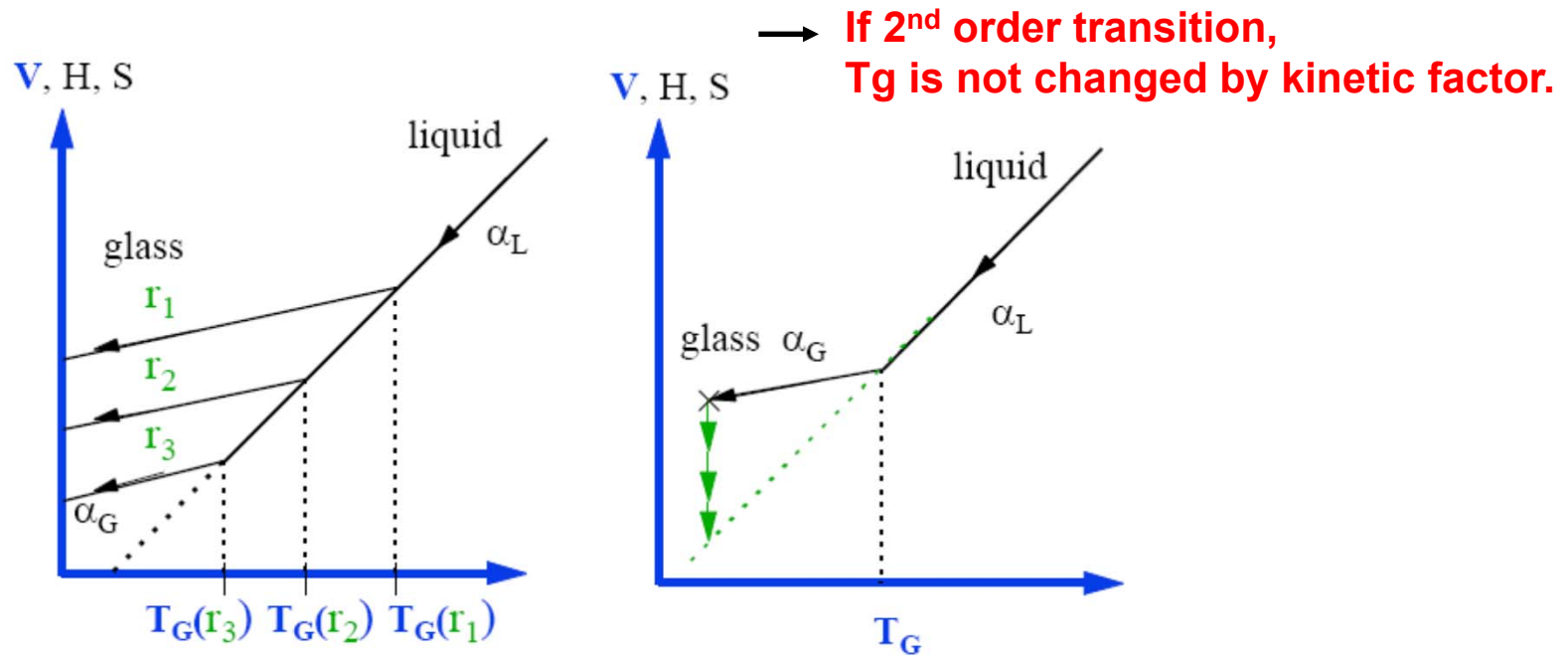
→ **If 2nd order transition,**
Tg is not changed by kinetic factor.

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

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Volume structural relaxation

(a) slow cool; fast reheat
(b) medium cool; medium reheat
(c) fast cool; slow reheat
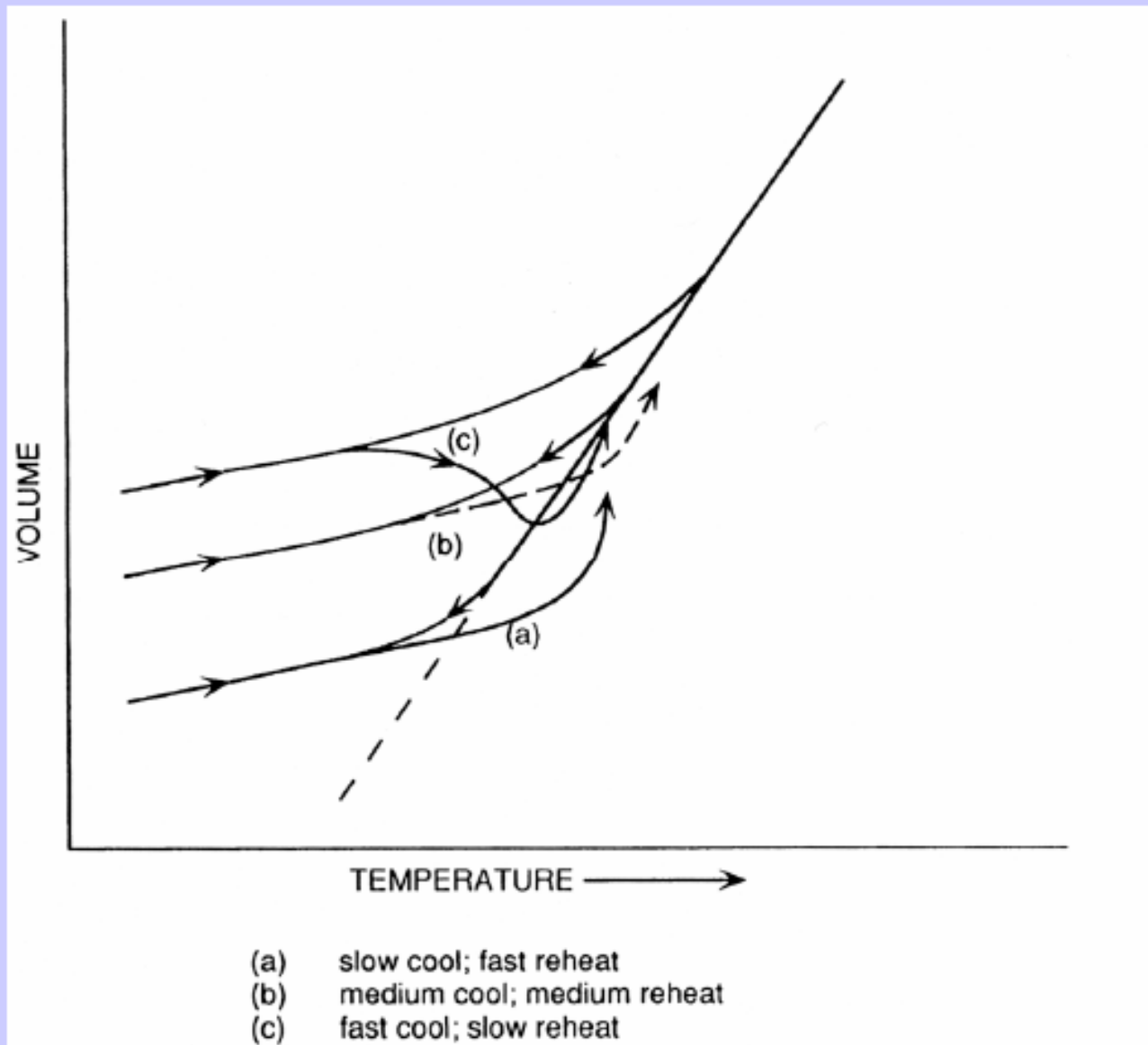
Volume changes in glass upon varying cooling and reheating rates.

Kinetic Nature of the Glass Transition (cont.)

- The glass transition is not a true second order transition but only a "pseudo" second order phase transition
  - 1) the glass is not an equilibrium phase (i.e. its properties depend on time)
  - 2) the glass transition temperature depends on the rate at which it is measured. The glass transition will therefore be defined over a range of temperatures and pressures.

- An approximate but useful relationship is $T_G = (2/3) \, T_M$

- What is the origin of the kinetic nature of T_G ?
  The answer to this question is associated with the time scale for "relaxation of the structure" (return to equilibrium after a perturbation is communicated to the material: change in T or P). It is therefore related to whether or not the material properties (e.g density) can preserve their equilibrium value during the perturbation.

* *Formation of glass during cooling*

- At high T, molecular motion in the liquid is very fast and a change in T can lead to rapid ("instantaneous") molecular rerrangements. During cooling at high temperatures, the system's average free energy is always minimum (i.e. the liquid is at equilibrium at all times during cooling).

- At lower T, the rate of molecular motion becomes lower. The material preserves equilibrium properties during cooling as long as the rate of molecular rearrangement (required by the change in T) is larger than the rate at which the perturbation is exerted on the material (i.e. cooling rate).

- At some temperature (which we will denote as T_g), molecular motions become slower than the rate at which the temperature is changed. The material has no longer sufficient time during cooling to remain in equilibrium (i.e. to exhibit the equilibrium properties, e.g. specific volume) : the relaxation time scale is larger than the experimental time scale, the material does not respond instantaneously to the perturbation.

Definition of a glass ?

$$\tau_{micro} \ll \tau_{exp} \ll \tau_{relax}$$

Time scale separation between microscopic, experimental, relaxation; the system is out of equilibrium on the experimental time scale.
(cf. S.K. Ma, Statistical Physics)

Microscopic time: time for events at sub-atomic distance and duration

- The above statements explain the dependence of the measured glass transition temperature on the rate of cooling.

- A similar discussion can be applied to the effect of pressure.

- The fact that the rate of molecular motion decreases with temperature can be qualitatively explained on the basis of free volume concepts* (molecular motion is afforded by the existence of empty spaces between molecules). The higher the temperature, the higher the specific volume of the material (for a given number of molecules), the higher the free volume in the material, the higher the rate of molecular motion.

- The fact that the material is not in equilibrium below Tg because it did not have sufficient time to reach the equilibrium configuration (S) and density, therefore energy or enthalpy (H) during cooling explains why the specific volume decreases with time at a given $T < T_G$ (phenomenon of physical aging of glasses)
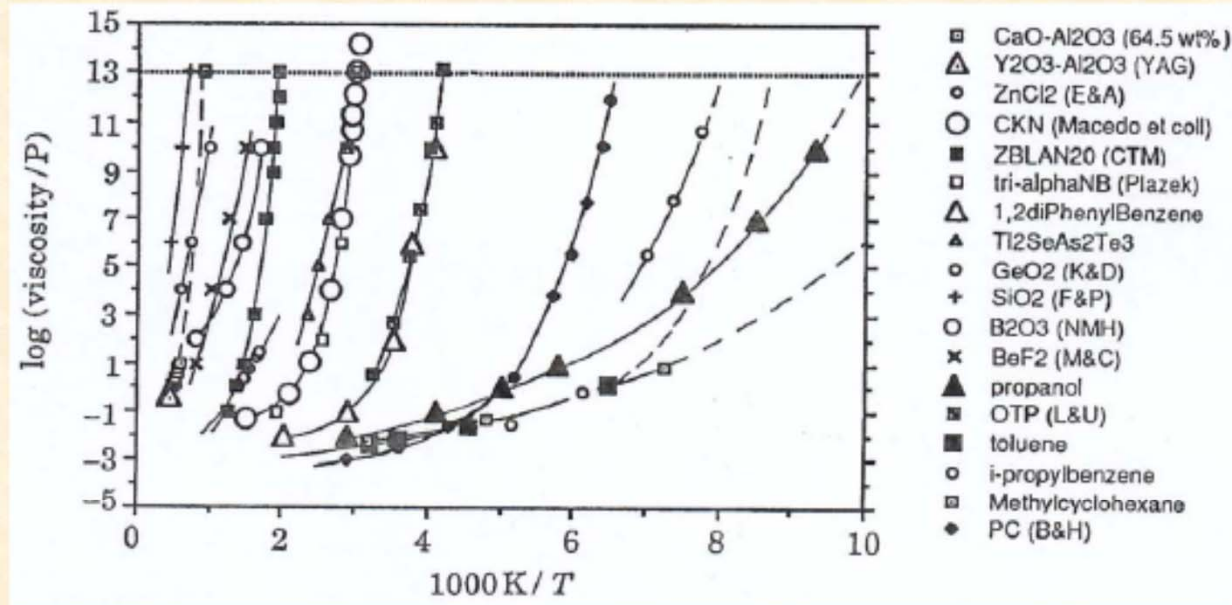
Temperature Dependence of Liquid Viscosity
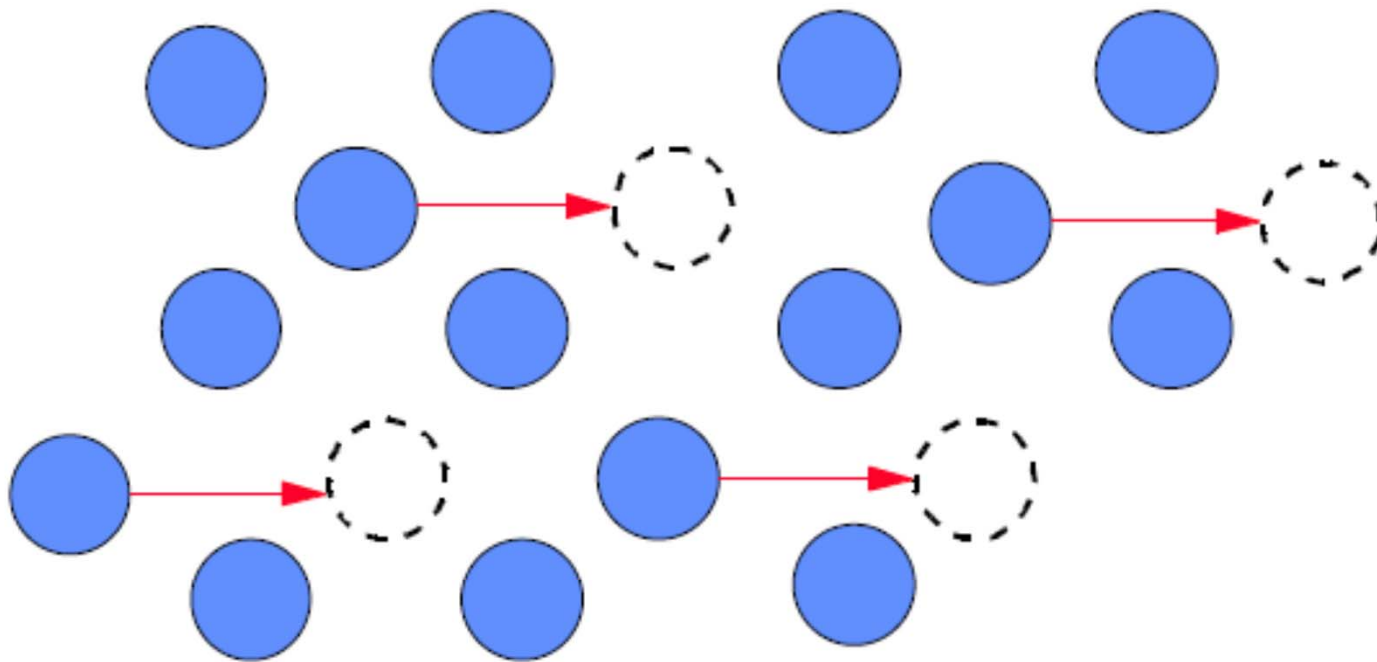
Viscosity is a measure of the resistance to flow. The higher T, the larger the average size of the holes and the larger the energy of the molecules, the easier the molecule move past oneanother, the lower the resistance to flow.

Glass transition defined by typical viscosity η. Arbitrary but convenient

Arrhenius plot: log(time) or log(viscosity) versus 1/T.

Similar behaviour for relaxation times obtained using different methods (dielectric relaxation, NMR). α relaxation time τ_α

Fragility

- **Fragility** ~ ability of the liquid to withstand changes in medium range order with temp.

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

< Classification of glass >

Strong network glass : Arrhenius behavior

$$\eta = \eta_0 \exp[\frac{E_a}{RT}]$$

Fragile network glass : Vogel-Fulcher relation

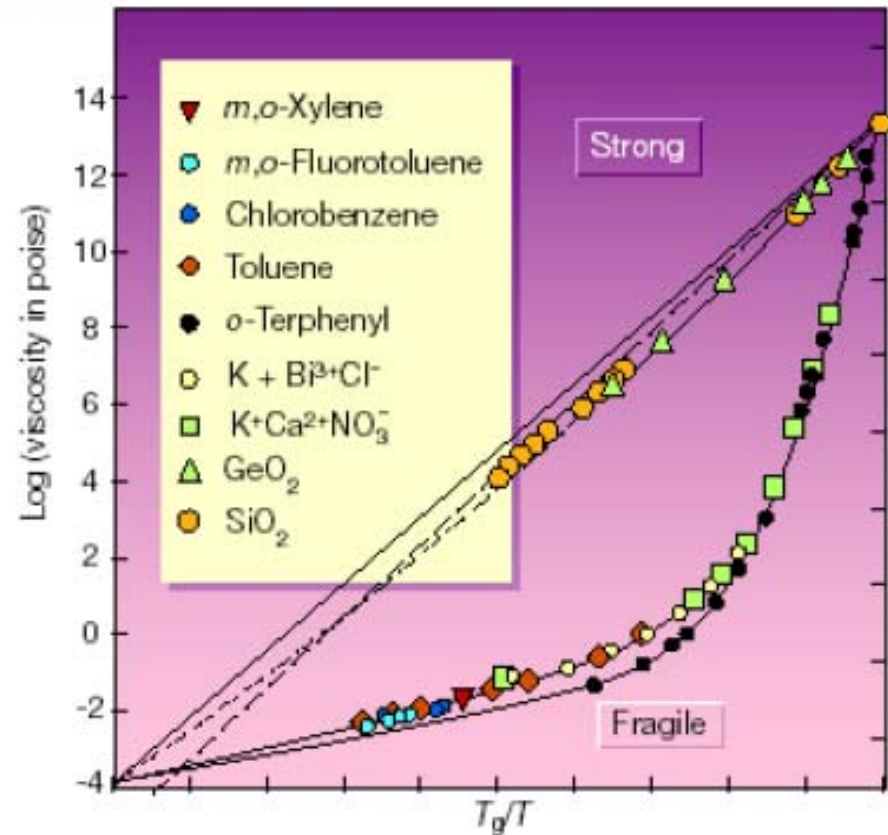$$\eta = \eta_0 \exp[\frac{B}{T - T_0}]$$

< Quantification of Fragility >

$$m = \frac{d\log\eta(T)}{d(T_{g,n}/T)}\bigg|_{T=T_{g,n}} = \frac{d\log\tau(T)}{d(T_g/T)}\bigg|_{T=T_g}$$

Angell-plot (Uhlmann)

- ▼ *m,o*-Xylene
- ◐ *m,o*-Fluorotoluene
- ● Chlorobenzene
- ● Toluene
- ● *o*-Terphenyl
- ○ K + Bi^{3+}Cl$^-$
- □ K$^+$Ca^{2+}NO$_3^-$
- △ GeO$_2$
- ● SiO$_2$

Slope of the logarithm of viscosity, η (or structural relaxation time, τ) at T_g
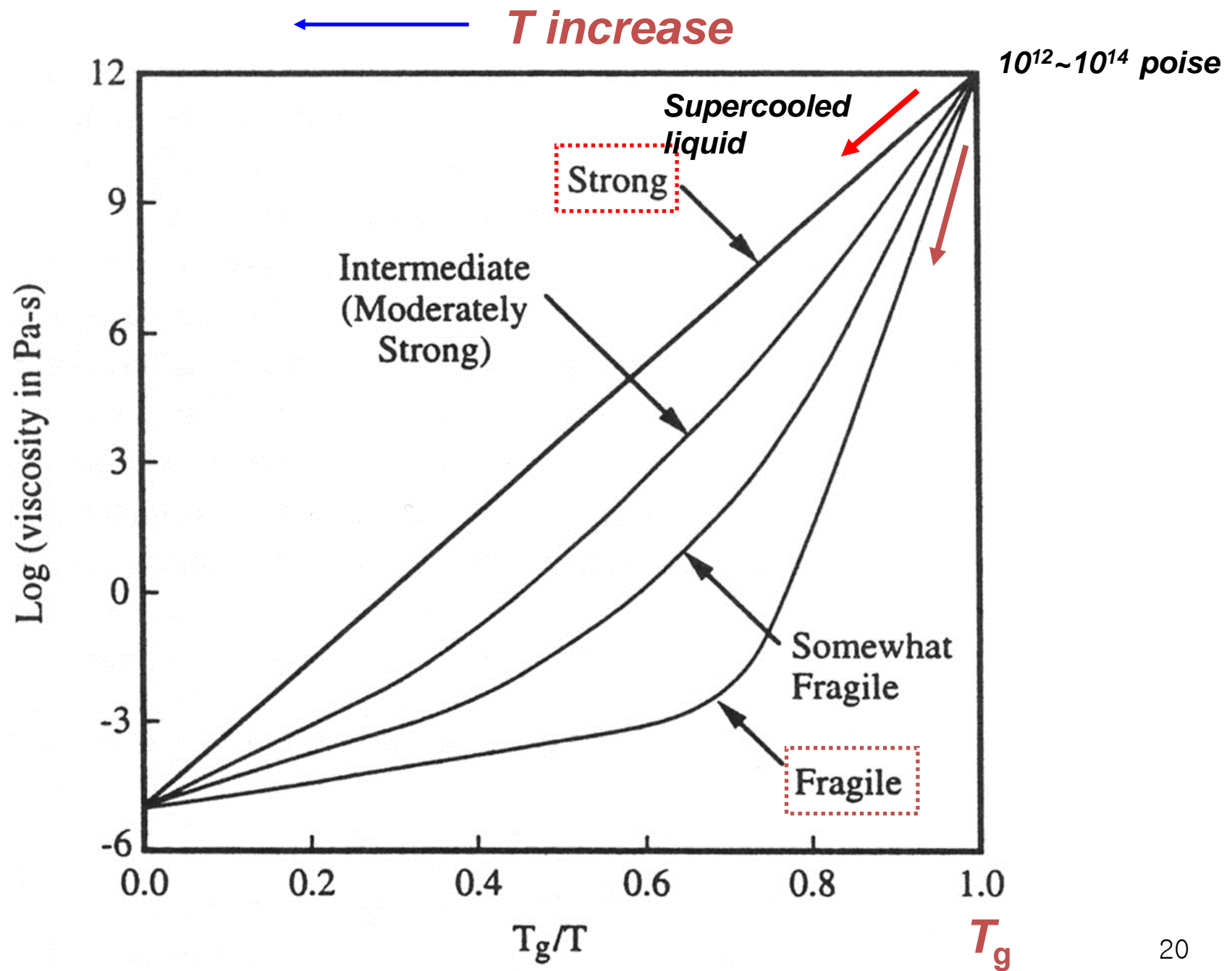
Fragility

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**
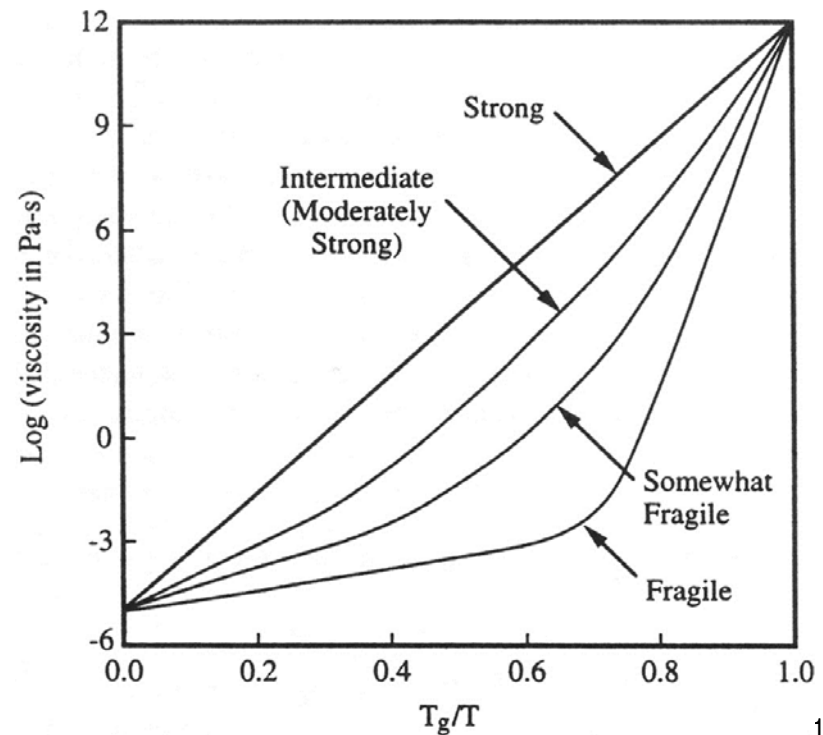 (*small difference of structure*)

  ⟶ **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**

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- **Thermodynamics for <u>glass transition</u>**

~ 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 <u>continuous</u> at T_T

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

→ *α_T C_P K_T changes discontinuously.*

  – Second derivatives of G (α, β, C_p) are <u>discontinuous</u> 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**.

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

measureable

$$\therefore \frac{dT_g}{dP} = \frac{\Delta\kappa_T}{\Delta\alpha_T} \qquad \textbf{(2)}$$

→ **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 :** $\dfrac{dT_g}{dP} < \dfrac{\Delta\kappa_T}{\Delta\alpha_T}$

→ **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

" <u>The specific volume V_g of the glass depends</u> not only on the **temperature**,
being continuous through the transition, but also on the **pressure of formation**"

Jäckle (1989) has shown that

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

Additional consequence of the experimental verification,
" **Glasses prepared under high pressures have <u>higher than normal densities</u>
but normal entropies or enthalpies.** "

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