2010 Spring

"Amorphous Materials"

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Contents for previous class

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"

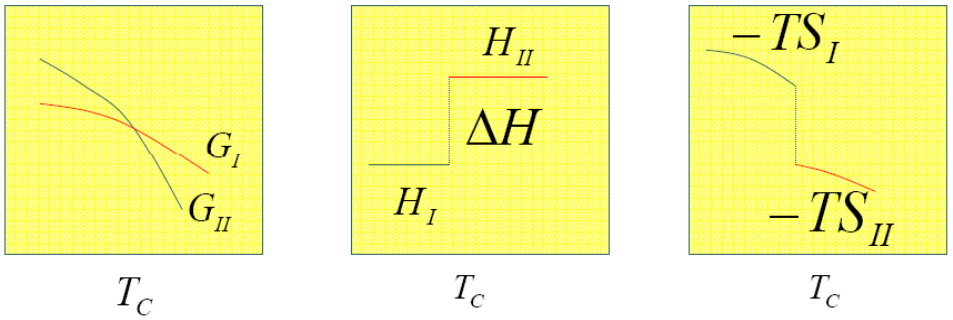
$$\Delta G = \Delta H - T\Delta S = 0$$

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

- **Thermodynamics for glass transition**

~ 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 continuous at T_T

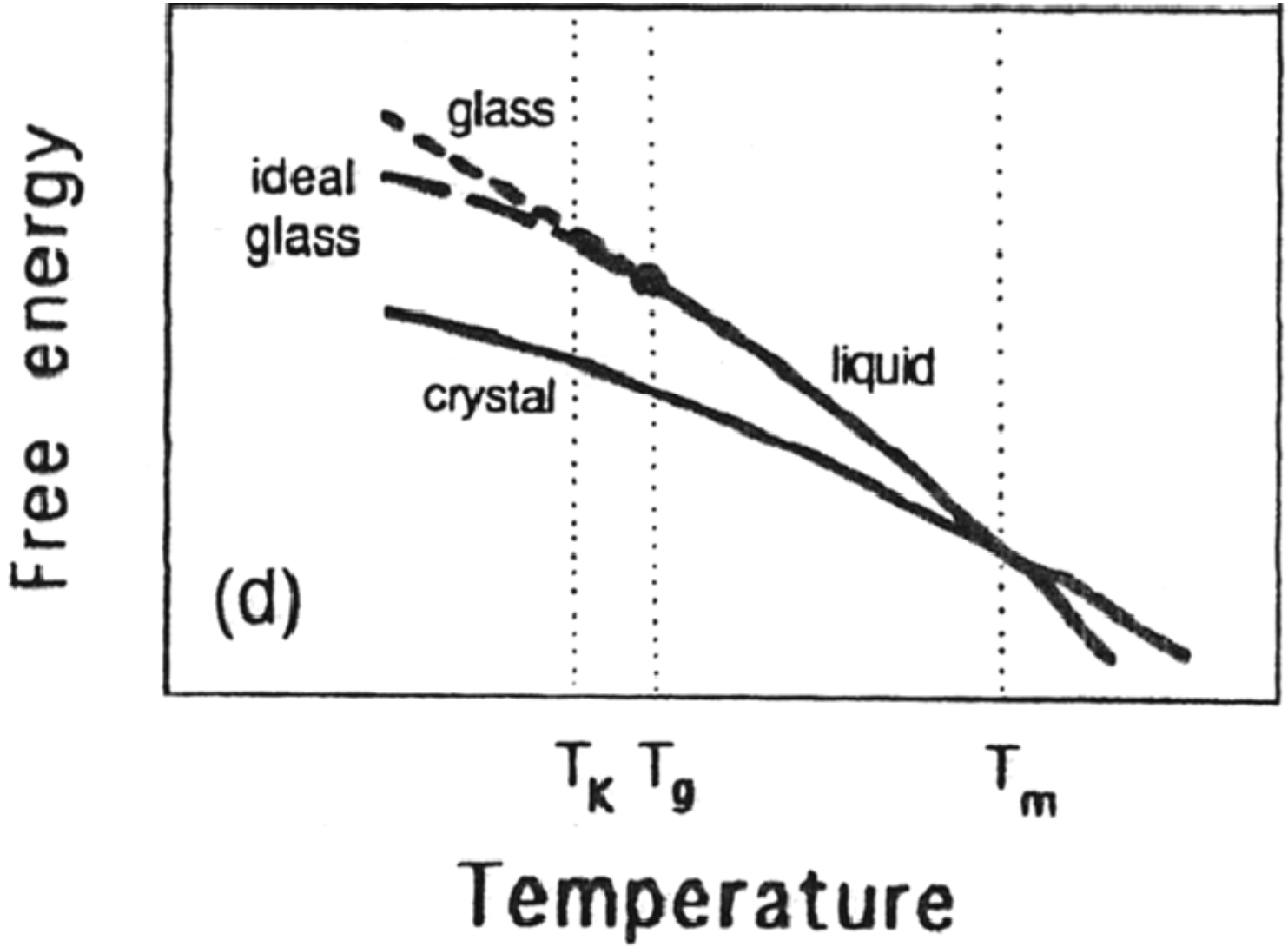
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

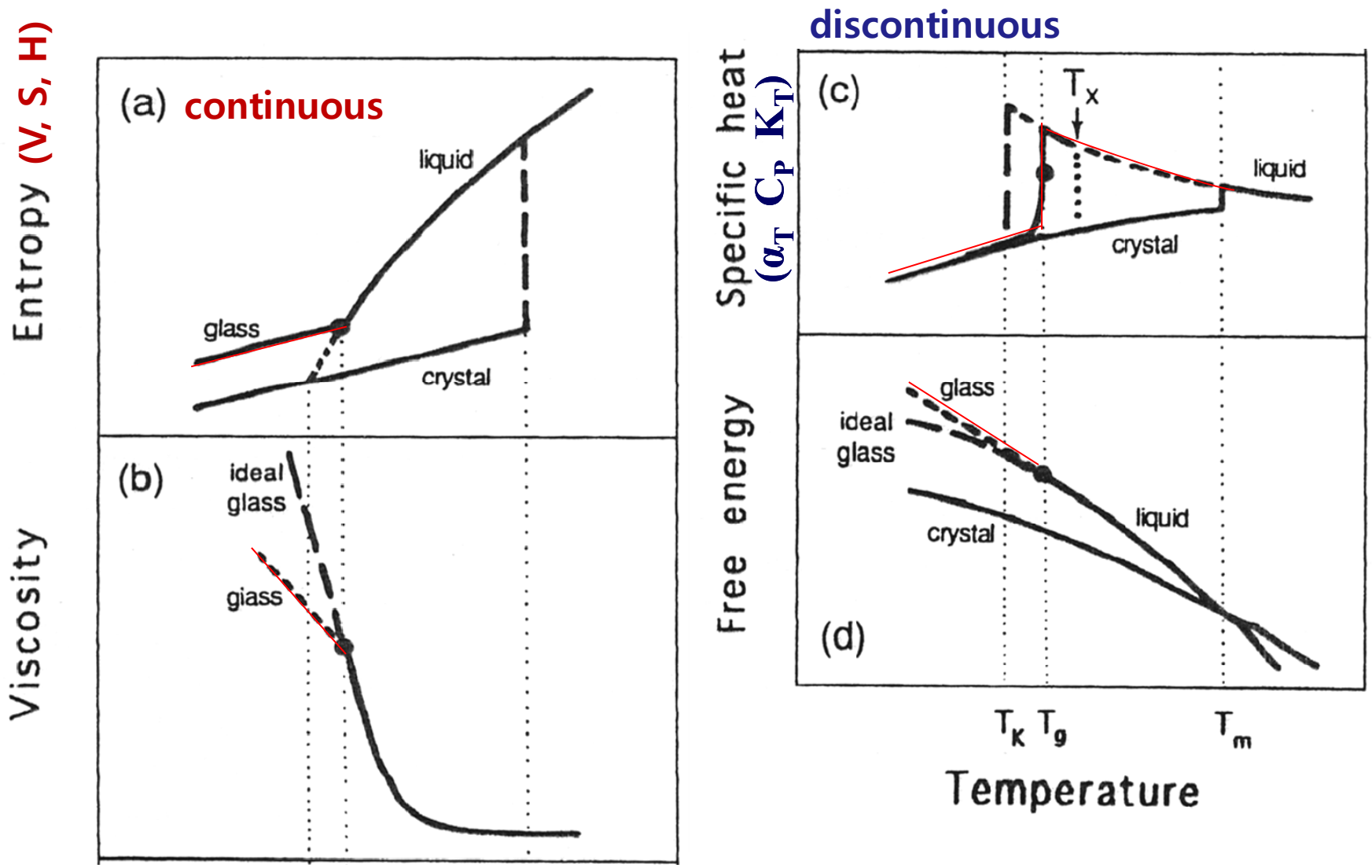
→ α_T C_P K_T changes discontinuously.

– Second derivatives of G (α, β, C_p) are discontinuous at T_T

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Schematic of the glass transition showing the effects of temperature on free energy

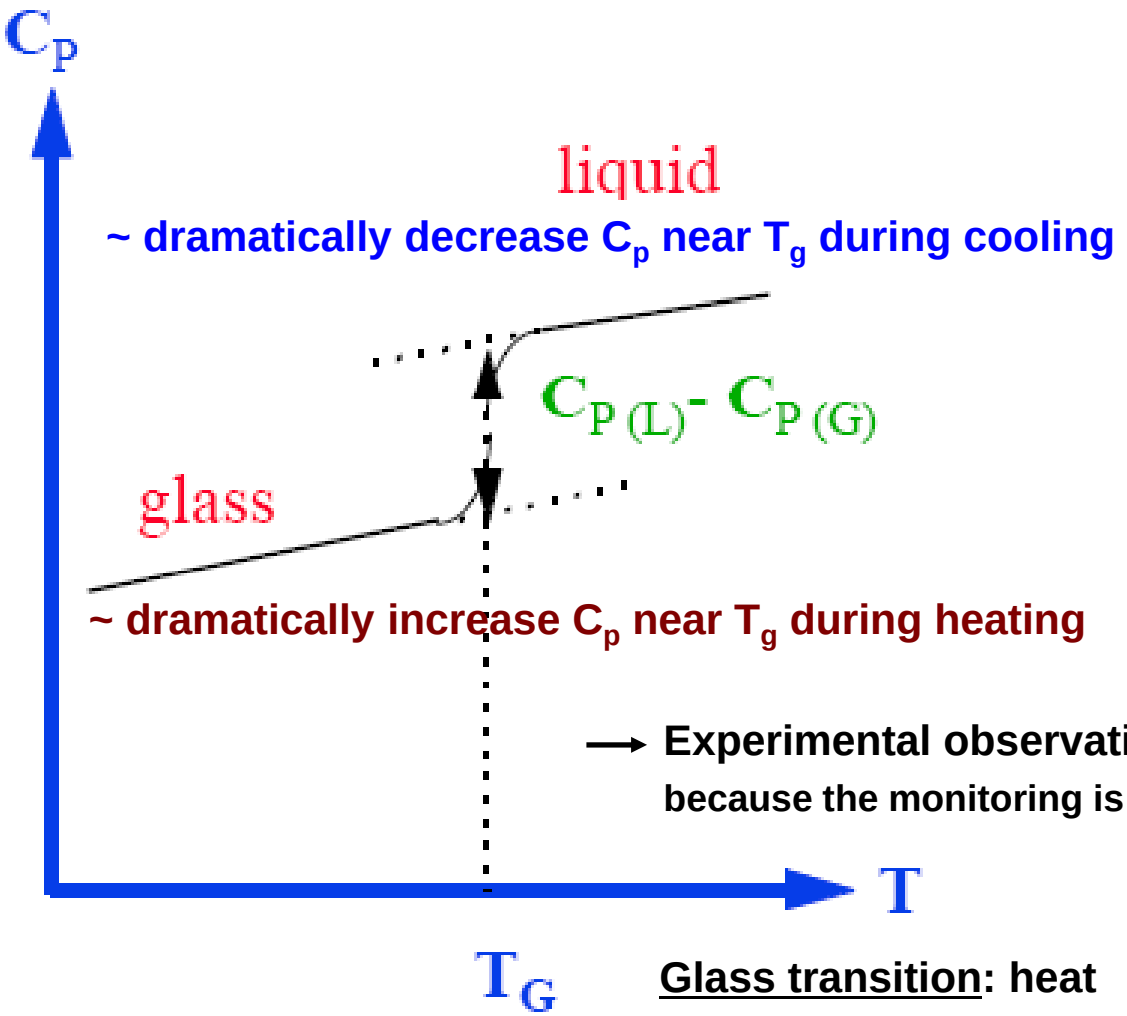




Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization onset temperature.

- **derivative of thermodynamic properties**

  → ***discontinuous*** **(C_p, α_T, K_T)**

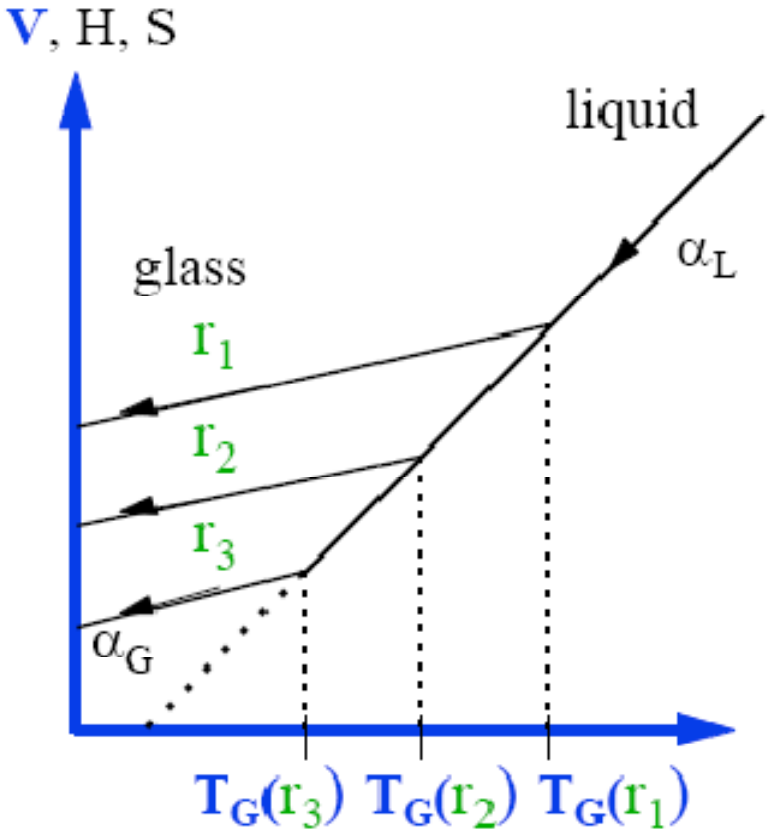


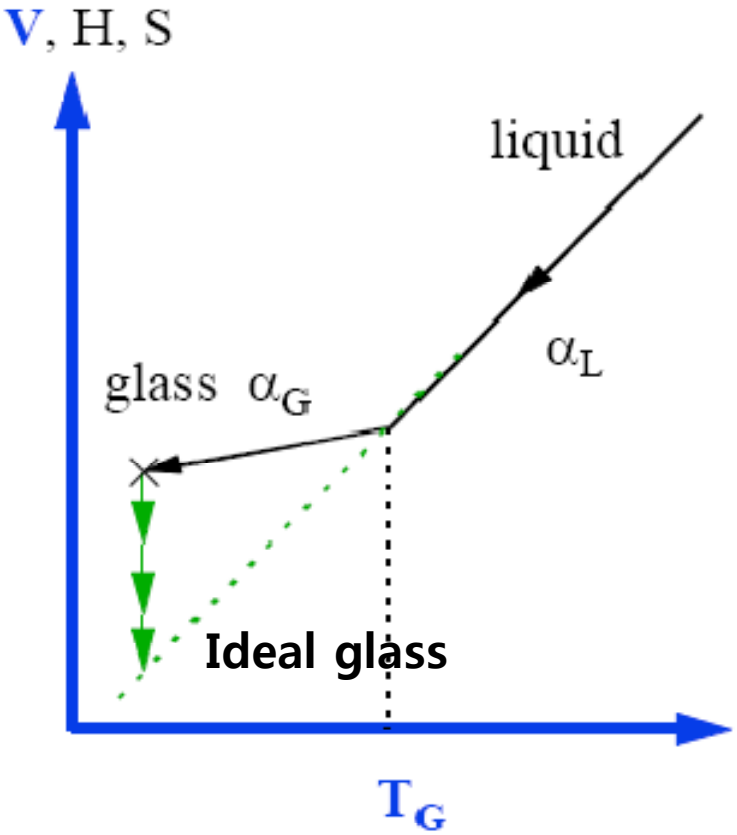
→ **Experimental observation during heating**
because the monitoring is very difficult during cooling

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

2) T_g depends on thermal history.

Kinetic Nature of the Glass Transition

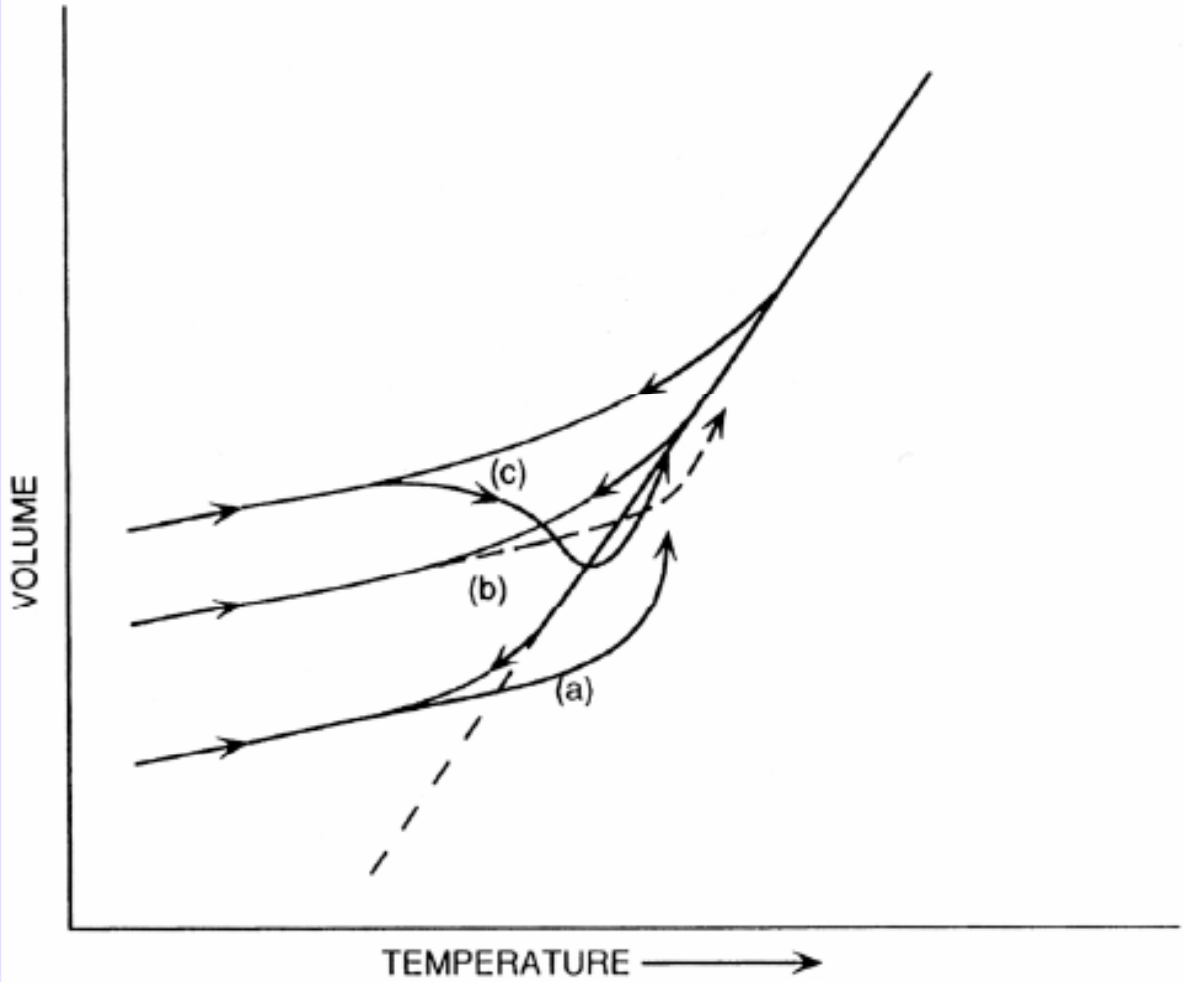




Tg depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$

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

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

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

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)

- 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)