

Materials Engineering Science
MESC. 5025

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Chapter 4.
Amorphous Solids

Introduction:

- The “Amorphous State” of Matter is one where the structure does not exhibit translational order on any significant length scale.
- From a structural viewpoint, amorphous solids (non-crystalline solids, disordered solids, glasses) and liquids are identical. i.e. they are characterized by a non-periodic spatial arrangement of molecular units.
- The above statement is easy to understand for liquids, since Brownian motion at high temperature prevents the orderly packing of molecular units into an ordered crystalline state. What prevents glasses from crystallizing since they exist at lower temperatures than liquids where the state of matter is a-priori determined by intermolecular interactions. From a thermodynamic viewpoint, the crystal phase is the most stable phase below the melting temperature. Glasses will be best defined by discussing both kinetic and thermodynamic concepts.

Liquid to Crystal Transition vs. Liquid to Glass Transition

- Crystallization (liquid to crystal transition) is defined from a thermodynamic standpoint by a number of changes in the materials properties at the transition temperature T_C :
 - a change in enthalpy (a latent heat of crystallization ΔH_C)
 - a change in specific volume or density ($\Delta V_C, \Delta \rho_C$)
 - a change in isobaric coefficient of thermal expansion ($\Delta \alpha_C$)
 - a change in isothermal compressibility ($\Delta \beta_C$)
 - a change in heat capacity $C_{P(A)}, C_{P(B)}$
- Such changes in material properties at a phase transformation is characteristic of what one calls a First Order Phase Transformation.
- Liquid to Glass Transition is also a transition from the liquid to the solid state. What can be said about the characteristic changes in state functions (G or V, H) for the liquid to glass transformation.

Ehrenfest Classification of Phase Transitions

- First Order Phase Transition at T_T :
 - G is continuous at T_T
 - First derivatives of G (V, S, H) are discontinuous at T_T
$$V = \frac{\partial G}{\partial P}_T \quad S = - \frac{\partial G}{\partial T}_P \quad H = G - T \frac{\partial G}{\partial T}_P$$
 - Second derivatives of G (α, β, C_p) are discontinuous at T_T
$$C_p = \frac{\partial H}{\partial T}_P \quad \alpha = \frac{1}{V} \frac{\partial V}{\partial T}_P \quad \beta = \frac{-1}{V} \frac{\partial V}{\partial P}_T$$
 - Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

Experimental Evidence: Dilatometry $V = f(T, P)$

- Second Order Phase Transition at T_T :

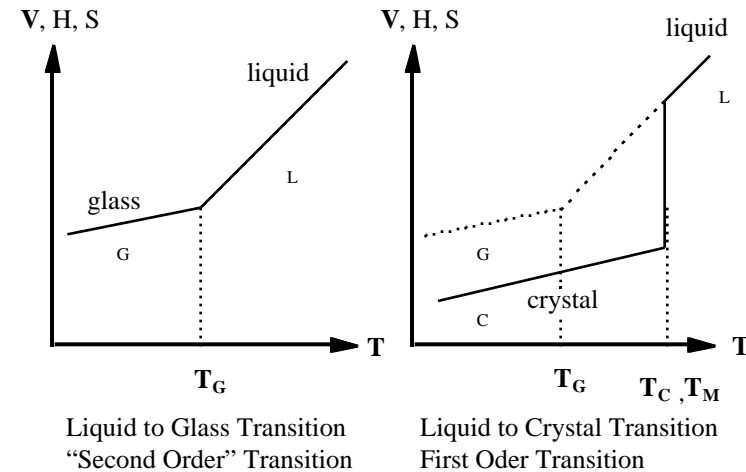
- G is continuous at T_T
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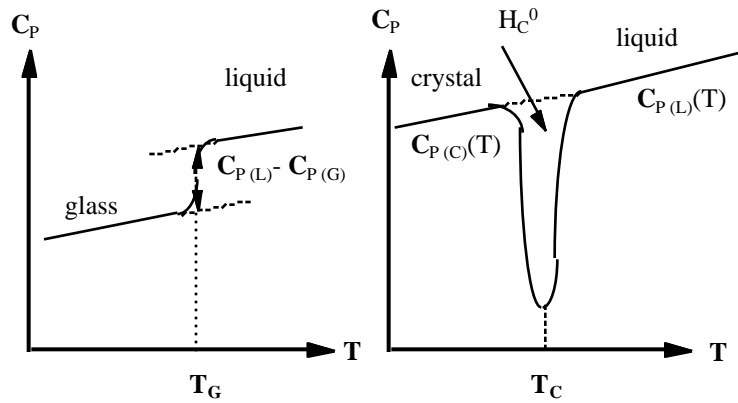
- Second derivatives of G (α, β, C_p) are discontinuous at T_T

$$C_p = \frac{\partial H}{\partial T}_P \quad \alpha = \frac{1}{V} \frac{\partial V}{\partial T}_P \quad \beta = \frac{-1}{V} \frac{\partial V}{\partial P}_T$$

- Examples: Order-Disorder Transitions in Metal Alloys, Onset of Ferromagnetism, Ferroelectricity, Superconductivity.



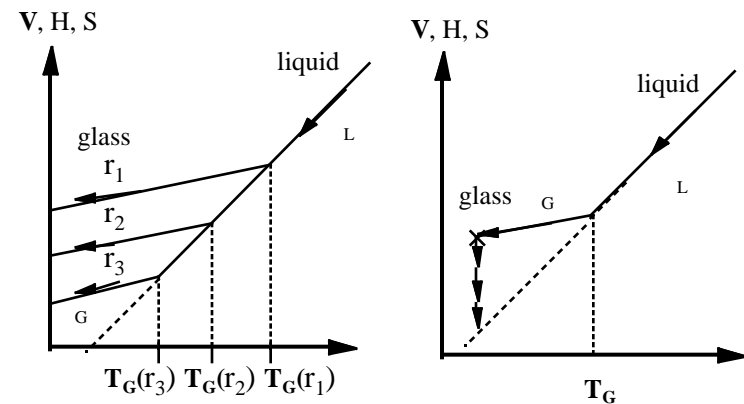
Experimental Evidence: Calorimetry $C_p = f(T)$



Liquid to Glass Transition
"Second Order" Transition

Liquid to Crystal Transition
First Order Transition

Kinetic Nature of the Glass Transition



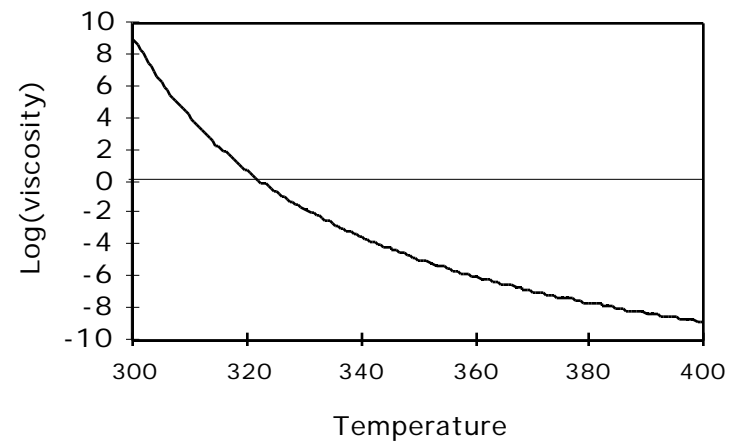
T_g depends on the rate at which the liquid is cooled. $T_G(r_3) < T_G(r_2) < T_G(r_1)$ if $r_3 < r_2 < r_1$

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

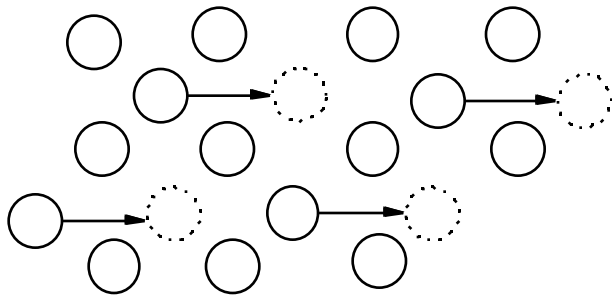
Kinetic Nature of the Glass Transition (cont.)

- 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.

Temperature Dependence of Liquid Viscosity



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 one another, the lower the resistance to flow.

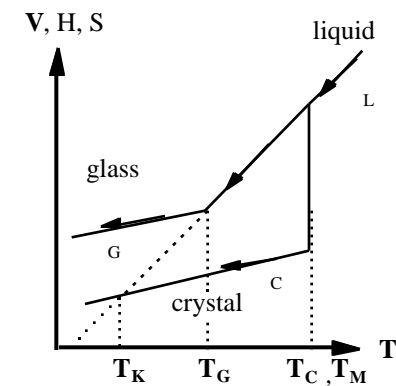
- At high T, molecular motion in the liquid is very fast and a change in T can lead to rapid (“instantaneous”) molecular rearrangements. During cooling at high temperatures, the system’s average free energy is always minimum (i.e. the liquid is at equilibrium at all times during cooling).
- At lower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

- 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 T_g 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)

* free volume theory will be expanded upon later.

Controversies in Amorphous Solids: The Kauzmann Paradox

If we extrapolate the specific volume of the liquid from above T_M to temperatures much below T_G , one must accept that at some temperature T_K well above 0 K, the specific volume, the enthalpy and the entropy of the equilibrium liquid would become lower than that of the crystal... Since the above statement is not possible (Kauzmann paradox), two solutions are possible:



1) at some temperature (T_K), there is a true 2nd order phase transition between the liquid and the glass or 2) the extrapolation to temperatures far below T_G is not valid. So far no one has found the answer !!

Value of the Prigogine Defay Ratio: R

- Continuity conditions for G or μ at a first order phase transition allowed us to derive the Clapeyron equation $\frac{dP}{dT} = \frac{S}{V} = \frac{H}{TV}$
- If T_G is a second order transition, continuity of V and S at T_G leads to two similar relations between materials parameters and state variables.

$$\begin{aligned} V_G &= V_L & dV_G &= dV_L \\ dV_G &= \alpha_G V_G dT - \kappa_G V_G dP & \Rightarrow & \\ dV_L &= \alpha_L V_L dT - \kappa_L V_L dP & \frac{dP}{dT} &= \frac{C_p}{VT \alpha} \end{aligned}$$

$$\begin{aligned} S_G &= S_L & dS_G &= dS_L \\ dS_G &= (C_p^G/T)dT - \alpha_G V_G dP & \Rightarrow & \\ dS_L &= (C_p^L/T)dT - \alpha_L V_L dP & \frac{dP}{dT} &= \frac{\alpha}{\kappa} \end{aligned}$$

The Prigogine-Defay ratio, R, defined by:
must be equal to unity.

$$R = \frac{C_p \kappa}{VT(\alpha)^2}$$

Crystallization vs. Glass Transition

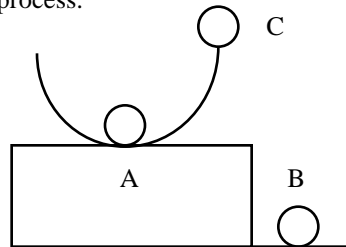
Why some liquids can form both glasses and crystals !!!

- So far, we have treated crystallization and glass transition as separate events which do not interfere with one another. A number of materials, when cooled from the liquid state undergo a liquid to glass transformation, others always crystallize, while some can do both depending on the conditions.
- To understand the origin of these observations, we will discuss in fairly idealized terms the process of crystal nucleation.
- We will consider a pure material having a crystal phase (C) and a liquid phase (L). The equilibrium conditions between these two phases is given in terms of the pressure P and the melting temperature T_M by the Clapeyron equation. The Gibbs rule of phase indicates that for a fixed pressure P, the liquid phase is stable above T_M , while the crystal phase is stable below T_M . As a liquid is cooled below T_M , the phase transformation should occur spontaneously on thermodynamic grounds ($G < 0$ for $T < T_M$)

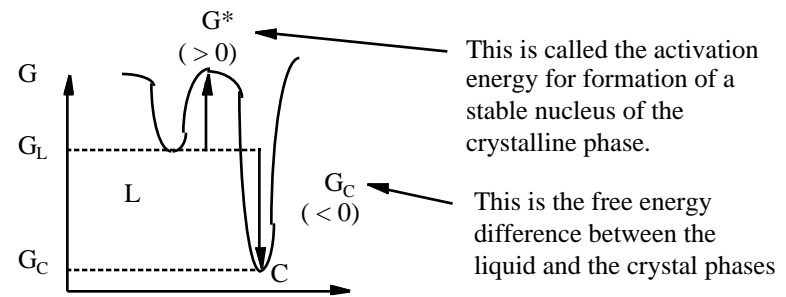
Kinetic Control of Phase Transformations

- However, experience tells us that extremely pure liquids do not undergo crystallization as they are supercooled below the melting temperature. Supercooled liquid often exist in a metastable state. Their crystallization is an activated process.

Considering the following analogy helps understand this concept: Ball A is in a local equilibrium (metastable) state. This state is not as stable as B (i.e. potential energy of A is higher than that of B), but is stable towards small fluctuations in height. If a sufficient push (over the barrier) is given to A, ball A will join ball B.



Ball A is in a metastable state
 Ball B is in a equilibrium state
 Ball C is in an unstable state



- If we apply the concepts developed by Eyring (rate theory) to this process, the rate of nucleation (i.e. the number of nuclei formed per unit time and per unit volume of the liquid phase) is written as:

$$\dot{N} = \frac{dN_v}{dt} = \frac{kT}{h} \exp \left(-\frac{G^*}{kT} \right) = \frac{kT}{h} \exp \left(-\frac{G_N^* + G_T^*}{kT} \right)$$

G_N^* and G_T^* are the activation free energies for nucleus formation and for atomic or molecular transport to the crystal/liquid interface.

Calculation of the Activation Free Energies

- Let us consider the formation of a “spherical” nucleus of the crystal phase from the liquid phase. We will denote by:
 - $G_c(R, T)$: the free energy difference between the crystal nucleus of radius R and the equivalent liquid volume at the temperature T
 - $G_c^0(T)$: the free energy difference between the bulk crystal and the bulk liquid at temperature T
 - σ : the crystal - liquid interfacial free energy per unit area

$$G_c(R, T) = \frac{4}{3}\pi R^3 G_c^0(T) + 4\pi R^2 \sigma$$

must be < 0 for crystallization to proceed spontaneously

< 0 if $T < T_M$
 $= 0$ if $T = T_M$
 > 0 if $T > T_M$

is always > 0 as surfaces raise the energy

- We can express the free energy $G_c^0(T)$ in terms of the latent enthalpy of crystallization $H_C^0(T)$ and the entropy change upon crystallization $S_C^0(T)$:

$$G_c^0(T) = H_C^0(T) - T S_C^0(T)$$

This equation can be simplified when T is not far from T_M since::

$$H_C^0(T) = H_C^0(T_M) \text{ and } S_C^0(T) = S_C^0(T_M) \text{ and at } T_M$$

$$G_c^0(T_M) = 0 = H_C^0(T_M) - T_M S_C^0(T_M)$$

$$S_C^0(T_M) = H_C^0(T_M) / T_M \text{ therefore}$$

$$G_c^0(T) = H_C^0(T_M) (1 - T / T_M) = - H_M^0(T_M) (1 - T / T_M)$$

$$G_c(R, T) = 4\pi R^2 \sigma - \frac{4}{3}\pi R^3 H_M^0(T_M) \frac{T}{T_M}$$

The first term is always positive and dominates for sufficiently low values of R while the second term is positive as long as $T < T_M$ and dominates for large values of R . ΔT is known as the undercooling ($\Delta T = T_M - T$)

Free Energy of Nucleation vs. Radius and Undercooling

