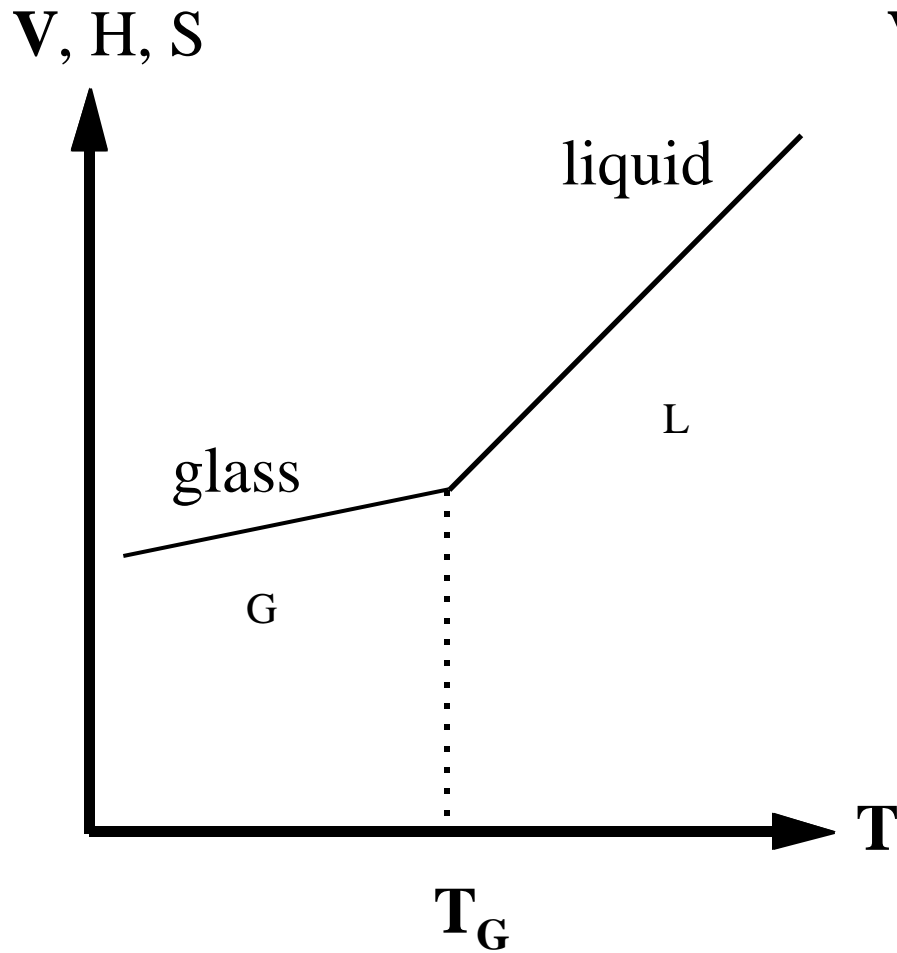


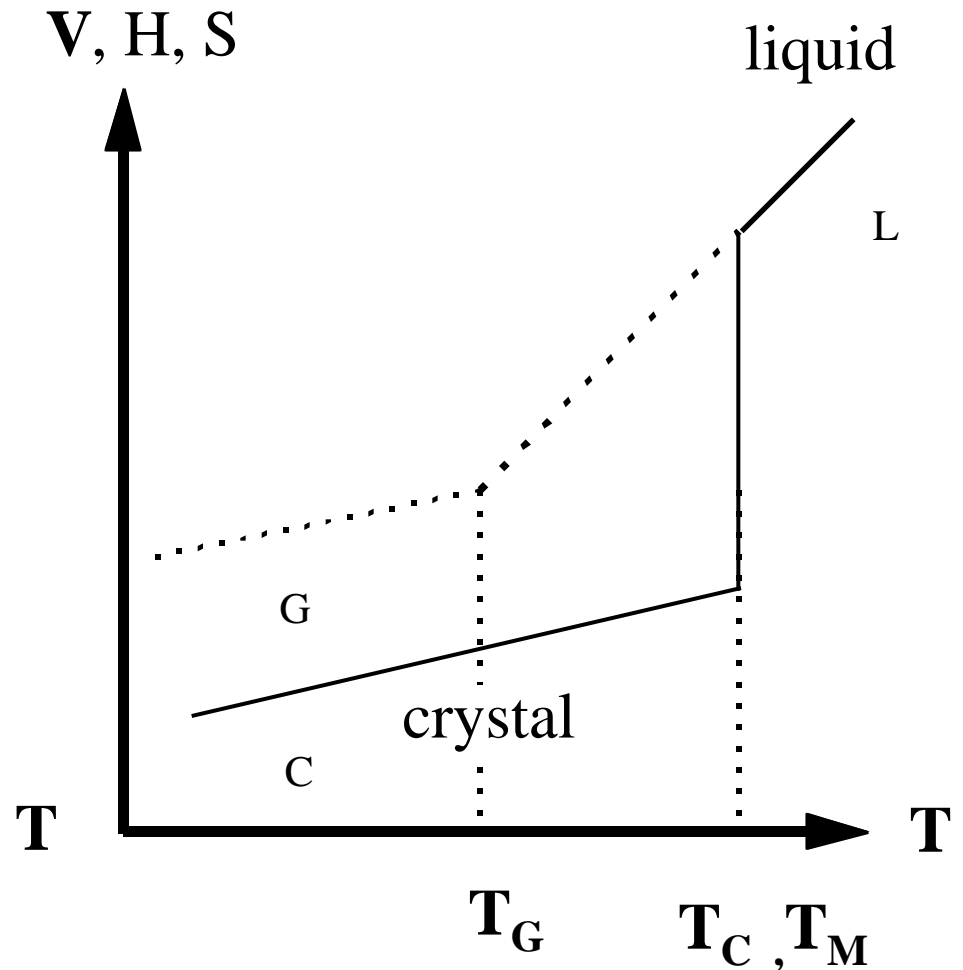
## The Glass Transition and the Glassy State

- 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, glasses) and liquids are identical. i.e. they are characterized by a non-periodic spatial arrangement of molecular units.
- At sufficiently high temperatures, Brownian motion prevents the orderly packing of molecular units into an ordered crystalline state since  $kT \gg$  intermolecular energies (stable states are the liquid and at even higher temperatures, for small molecules, the gas state).
- As a liquid is cooled, in some instances it solidifies by crystallizing, in others it becomes a solid amorphous material.
- The important questions to address are therefore:
  - How do we differentiate liquid to glass from liquid to crystal phase transformations ?
  - What prevents a liquid from crystallizing ?

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

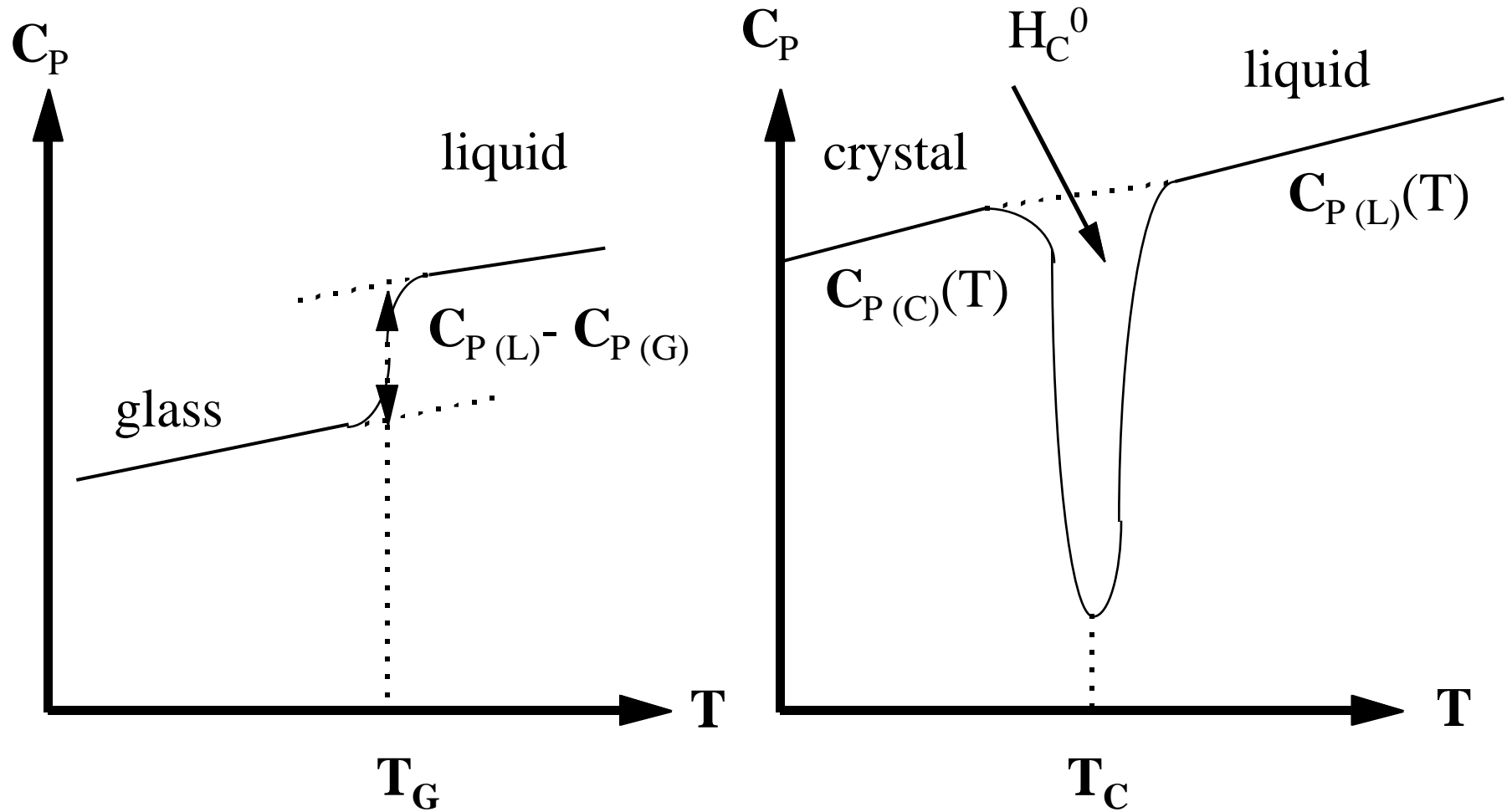


Liquid to Glass Transition  
“Second Order” Transition



Liquid to Crystal Transition  
First Order Transition

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



Liquid to Glass Transition  
"Second Order" Transition

Liquid to Crystal Transition  
First Order Transition

## 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  $H_C$ )
  - a change in specific volume or density ( $V_C, V_A, \rho_A, \rho_C$ )
  - a change in isobaric coefficient of thermal expansion ( $\alpha_C, \alpha_A$ )
  - a change in isothermal compressibility ( $\beta_C, \beta_A$ )
  - 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 ( $\rho$  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  $T_T$

$$V = \left. \frac{\partial G}{\partial P} \right|_T \quad S = - \left. \frac{\partial G}{\partial T} \right|_P \quad H = G - T \left. \frac{\partial G}{\partial T} \right|_P$$

- Second derivatives of  $G$  ( $\alpha$ ,  $\beta$ ,  $C_p$ ) are discontinuous at  $T_T$

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

- Examples: Vaporization, Condensation, Fusion, Crystallization, Sublimation.

- Second Order Phase Transition at  $T_T$ :

- $G$  is continuous at  $T_T$

- First derivatives of  $G$  ( $V$ ,  $S$ ,  $H$ ) are continuous at  $T_T$

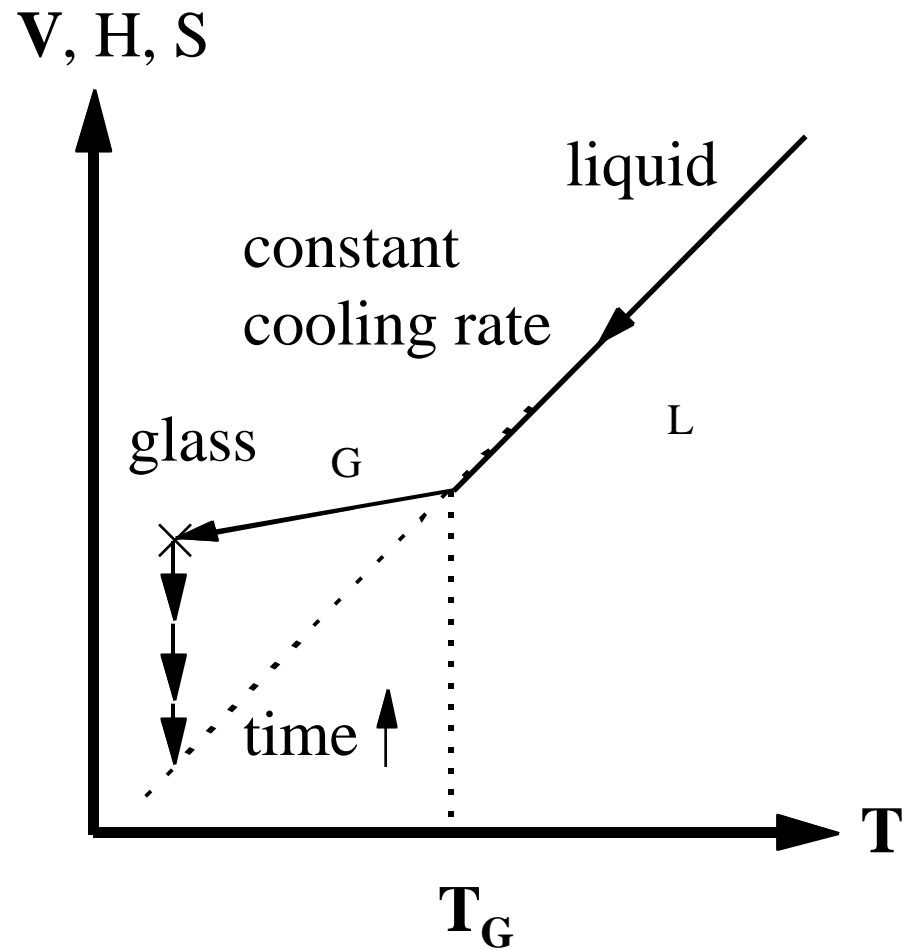
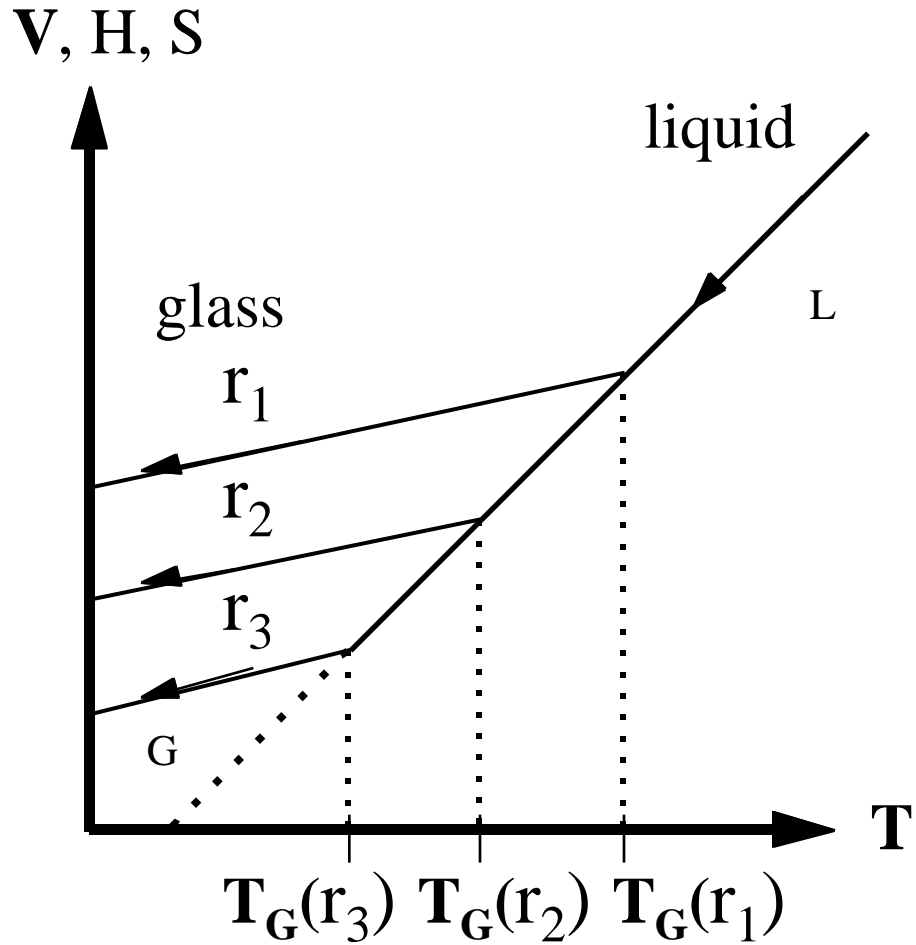
$$V = \left. \frac{\partial G}{\partial P} \right|_T \quad S = - \left. \frac{\partial G}{\partial T} \right|_P \quad H = G - T \left. \frac{\partial G}{\partial T} \right|_P$$

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

# The Glass Transition is not a true second order phase 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

- 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 (cooling for example).

- At high  $T$ , molecular motion in the liquid is very fast and a change in  $T$  can lead to a rapid (“instantaneous”) change in chain conformation, required for the volume to adjust itself to the new temperature. 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  $T$ , conformational changes occur more slowly. The material preserves equilibrium properties during cooling as long as the time scale needed for the change in conformation (required by change in  $T$ ) is less than the time scale over which the perturbation is exerted on the material.
- At some temperature (which we will denote as  $T_g$ ), the rate of conformational changes becomes lower 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 observed glass transition temperature on the rate of cooling.
- The fact that the rate of molecular motion decreases with temperature can be qualitatively explained on the basis of free volume concepts (conformational changes are afforded by the existence of empty spaces between molecules (free volume) and by the ease to overcome the free energy barrier to rotation around single bonds). The higher the temperature, the larger the thermal energy and the higher the free volume in the material, thus, the higher the rate of conformational changes.
- 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 temperature  $T < T_G$  (phenomenon of physical aging of glasses).

## **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.
- If the time scale over which a liquid is cooled is long enough to allow the optimum (most stable) chain conformation to form and to allow these chains to pack with three dimensional translational order, the material will crystallize.
- If the cooling process is so fast that the most stable chain conformation does not have sufficient time to form or if the chain contains too many defects (tacticity, branch points, regio defects or too many different local configurations, etc..) then the polymer will not crystallize upon cooling but will eventually become glassy as the temperature reaches the glass transition temperature.