2010 Spring

"Amorphous Materials"

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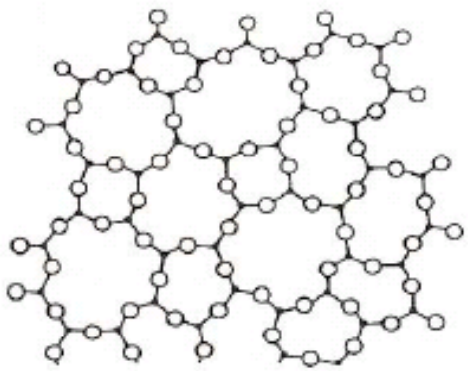
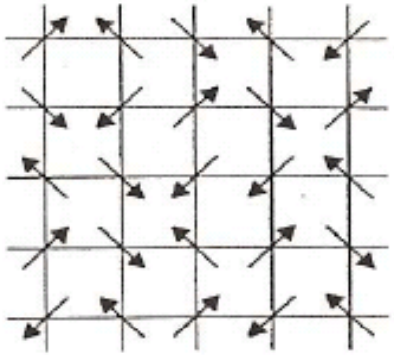
Contents for previous class

- *What kind of randomness exist in amorphous materials?*
- *Crystal - disorder*



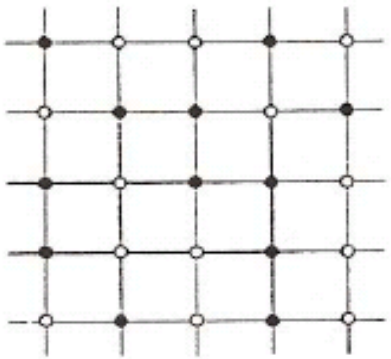
Random atomic structure

(a) Topological disorder

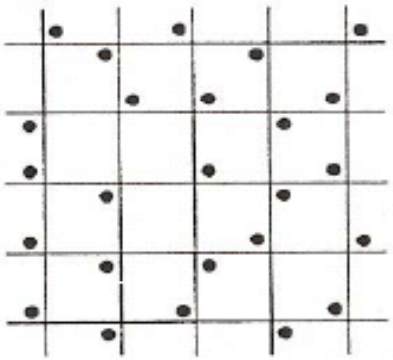


(b) Spin disorder

Crystal lattice



(c) Substitutional disorder



(d) Vibrational disorder

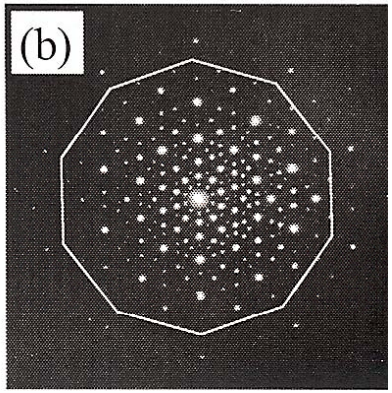
Contents for previous class

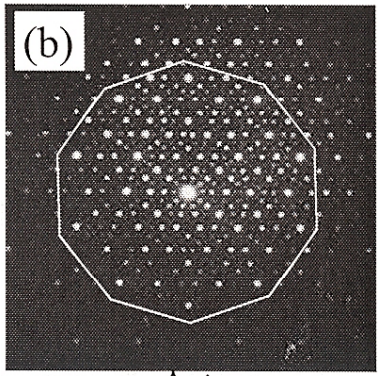
- *Quasicrystal*: orientational order

  long range order: quasiperiodic

  - icosahedral phase (5 fold symmetry)

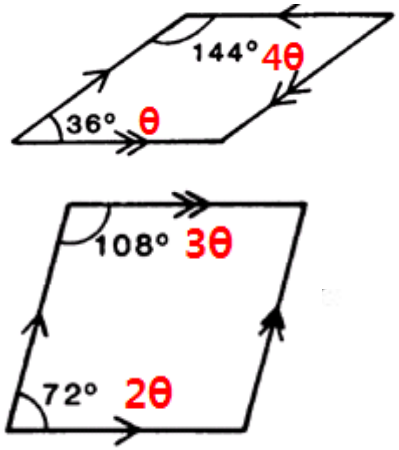
  - decagonal phase (10 fold symmetry)

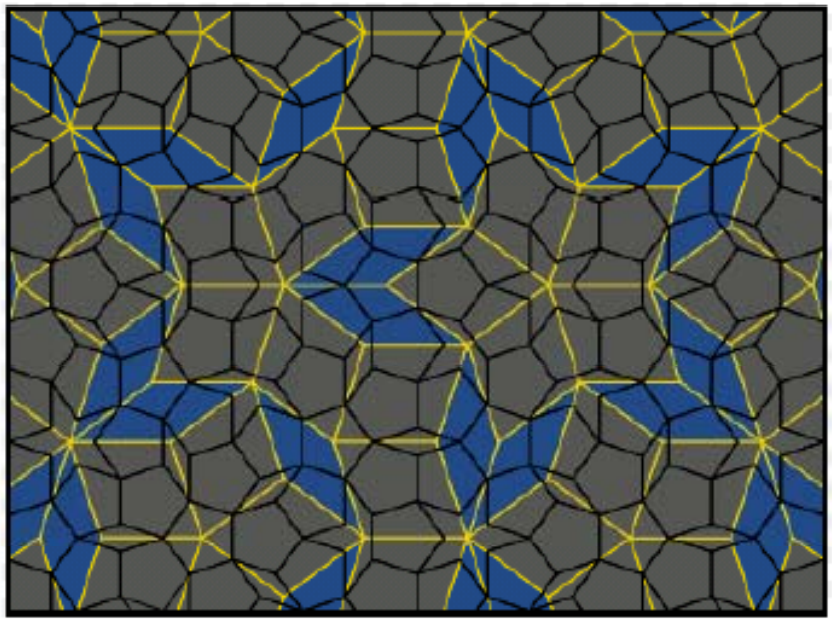




two types of unit cell: acute & obtuse rhombi

Interpretation by penrose tiling





- between crystal & amorphous phases

Contents for previous class

- *Amorphous, non-crystalline, glass*

  amorphous: do not possess long range order
  = non-crystalline
  : no topological ordering (a)

  glass : *amorphous materials which exhibits glass transition*

  → *Formation of glass is not necessarily to be rapid quenching.*

- *What kind of randomness exist in amorphous materials?*

Perfect crystal	→	disorder	→	quasicrystal	→	amorphous
: *unit cell*		: *underlying perfect crystalline lattice* (b, c, d)		ex) *icosahedral phase*		: *no topological ordering* (a)

Contents for today's class

- **Fundamentals of glass transition**
- **Glass: Solid? or liquid?**
- **Free volume**
- **Glass transition**
  - **Classification of phase transition**
- $T_f \geq T_g$ (*T_f = fictive temperature*)

If liquid is cooled, two events can occur.

1) **Crystallization (solidification at $T_{m.p.}$)**

2) **Undercooled below $T_{m.p.}$ (supercooled)** → **More viscous** → **Glass**

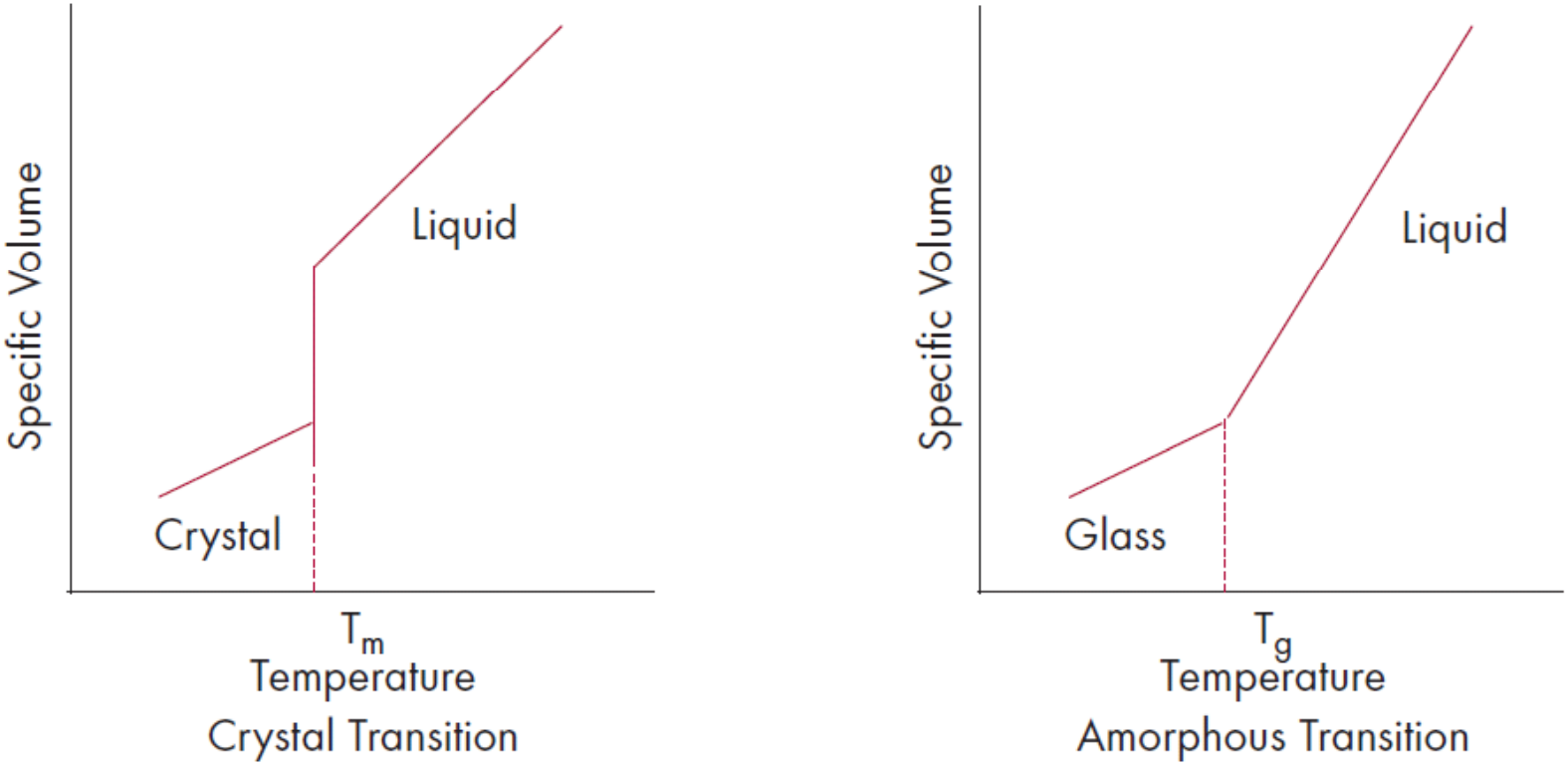


Figure 4. Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).

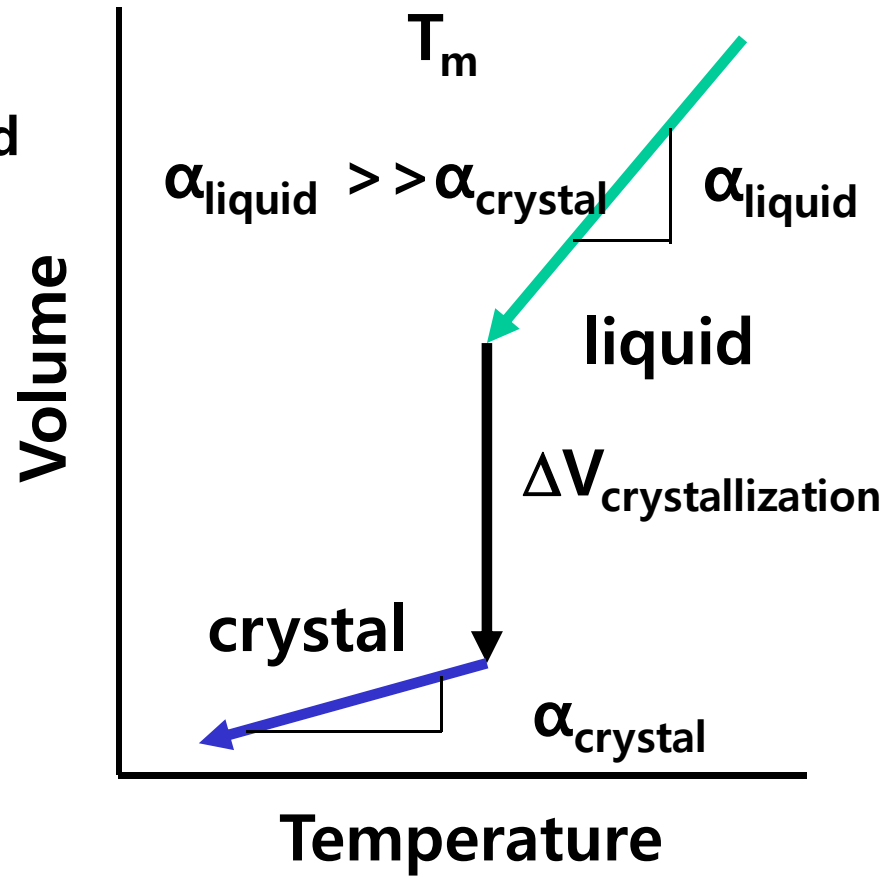
Fundamentals of the Glass Transition

- **Melting and Crystallization are Thermodynamic Transitions**
  - Discontinuous changes in structure and properties and T_m
  - Structures are thermodynamically controlled and described by the Phase Diagram
  - $T_{melting}$ and $T_{liquidus}$ have fixed and specific values, 1710 ^oC for SiO_2, for example

- **The Glass Transition is a Kinetic Transition**
  - Continuous changes in structure and properties
  - Structure and properties are continuous with temperature
  - Structures and properties can be changed continuously by changing the kinetics of the cooled or reheated liquid

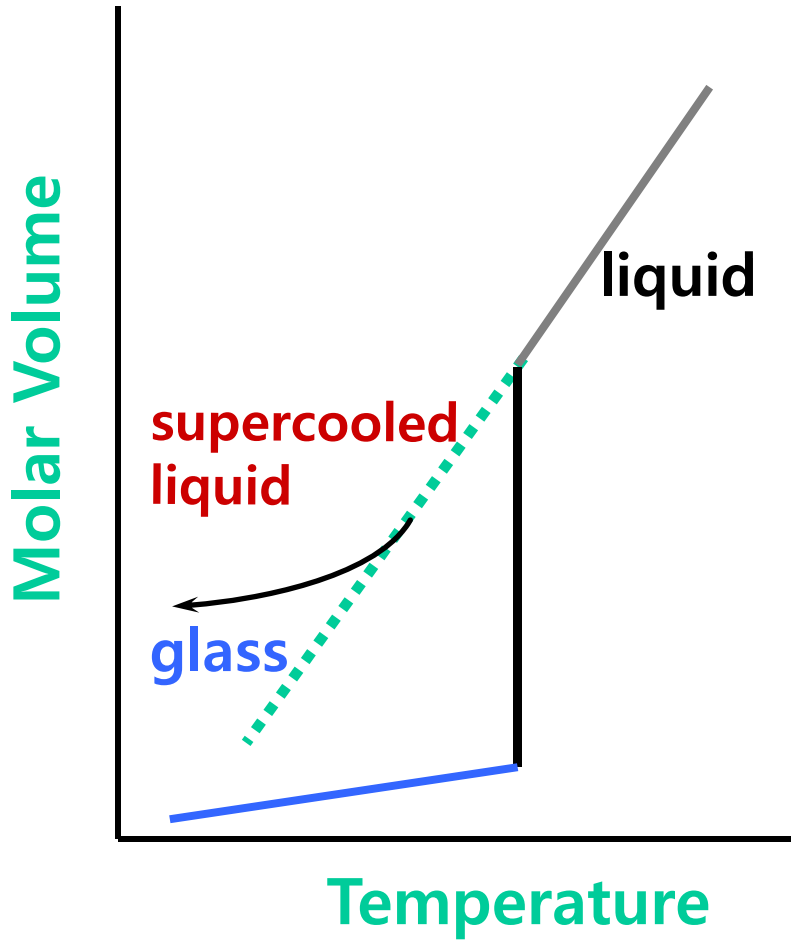
Crystallization is Controlled by Thermodynamics

- Volume is high as a hot liquid
- Volume shrinks as liquid is cooled
- At the melting point, T_m, the liquid crystallizes to the thermodynamically stable crystalline phase
- More compact (generally) crystalline phase has a smaller volume
- The Crystal then shrinks as it is further cooled to room temperature
- Slope of the cooling curve for liquid and solid is the thermal expansion coefficient, α



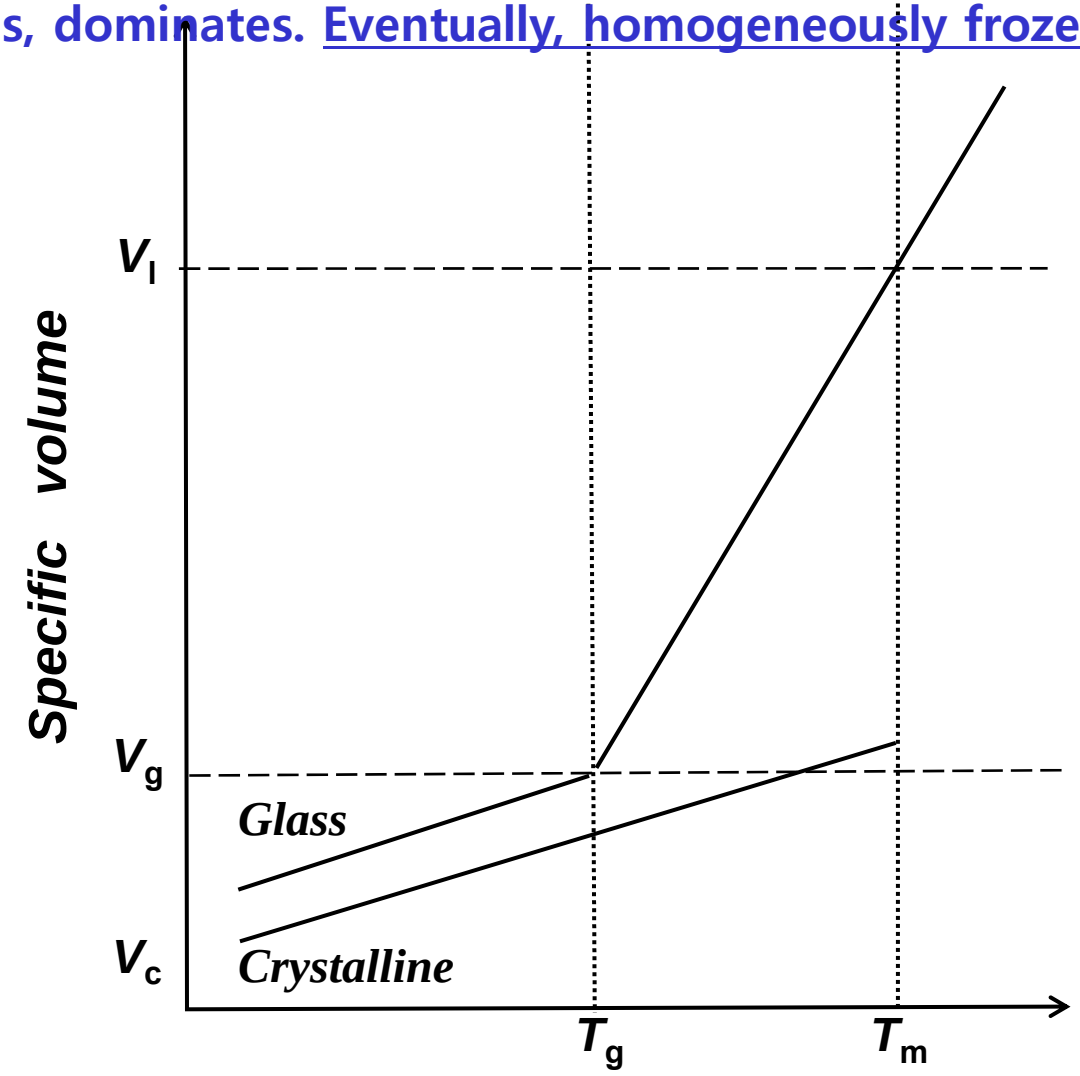
Glass Formation is Controlled by Kinetics

- Glass forming liquids are those that are able to "by-pass" the melting point, T_m
- Liquid may have a high viscosity that makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure
- Liquid maybe cooled so fast that it does not have enough time to crystallize
- Two time scales are present
  - "Internal" time scale controlled by the viscosity (bonding) of the liquid
  - "External" timescale controlled by the cooling rate of the liquid



Glass transition

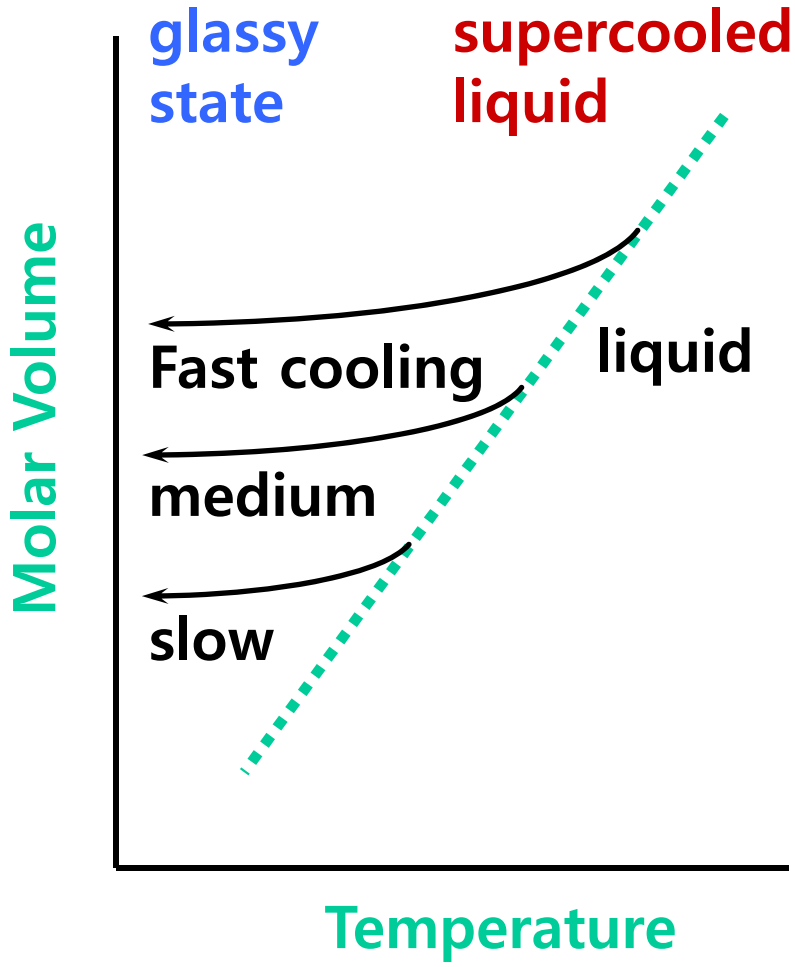
On cooling, although the driving force for nucleation is continually increasing, this is opposed by the rapidly decreasing atomic mobility which, at very high undercoolings, dominates. Eventually, homogeneously frozen at T_g.



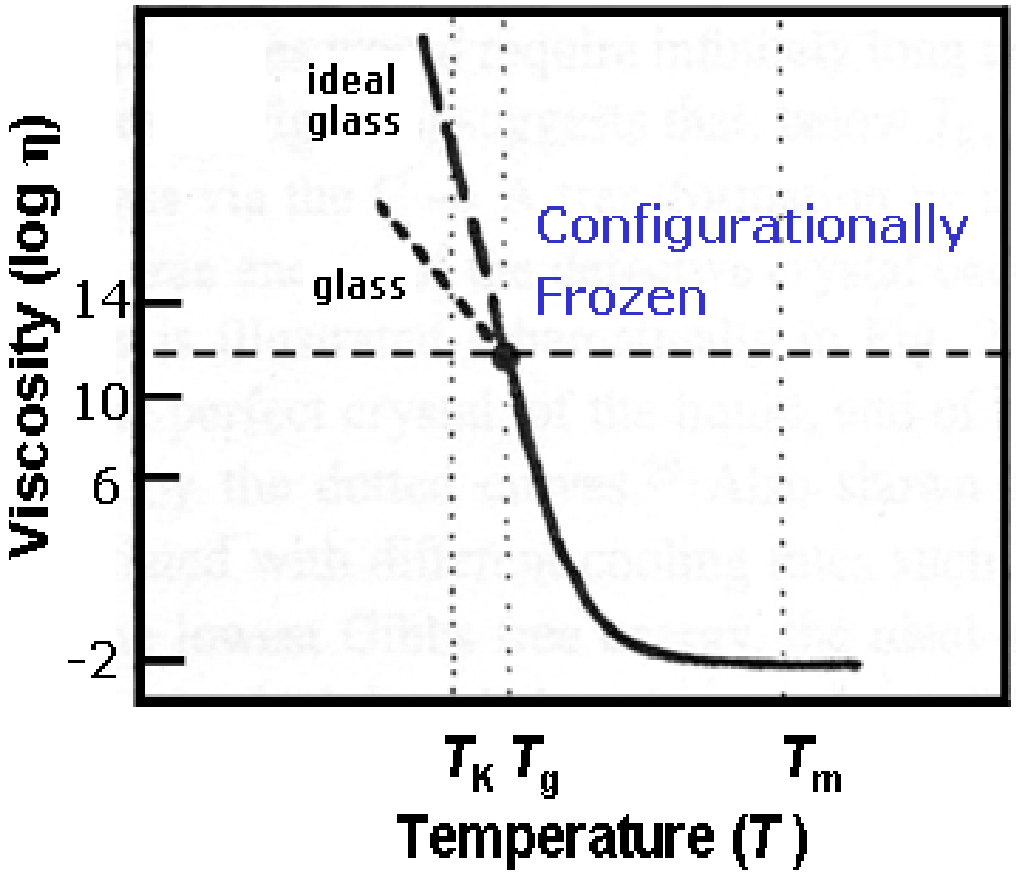
specific volume (volume per unit mass)

The Cooling Rate Affects the Properties of Glass

- Faster cooling freezes in the glass at a higher temperature
- The temperature is lowered so fast that the liquid does not have time to relax to the properties at the next lower temperature, glass is formed at a high temperature
- Slower cooling freezes in the glass at a lower temperature
- The temperature is lowered slowly enough that the liquids can relax to properties at lower and lower temperatures, glass is eventually formed at a lower temperature



Glass : undercooled liquid with high viscosity

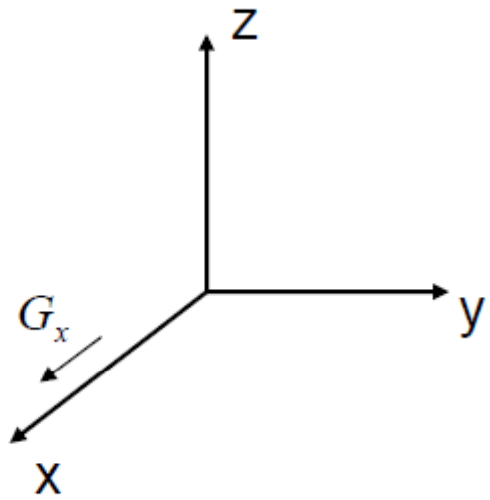


A solid is a materials whose viscosity exceeds $10^{14.6}$ poise

cf) liquid ~*10^{-2} poise*

* Glass: Solid? or liquid?

$$\eta = G_x / (\frac{dv_x}{dz})$$



G_x : *Shear stress in x direction*

→ causing velocity gradient: $\frac{dv_x}{dz}$

dz: thickness of element perpendicular to the applied stress

small stress

ex) *100 N applies for one day to 1 cm³ of material having viscosity of $10^{14.6}$ poise*

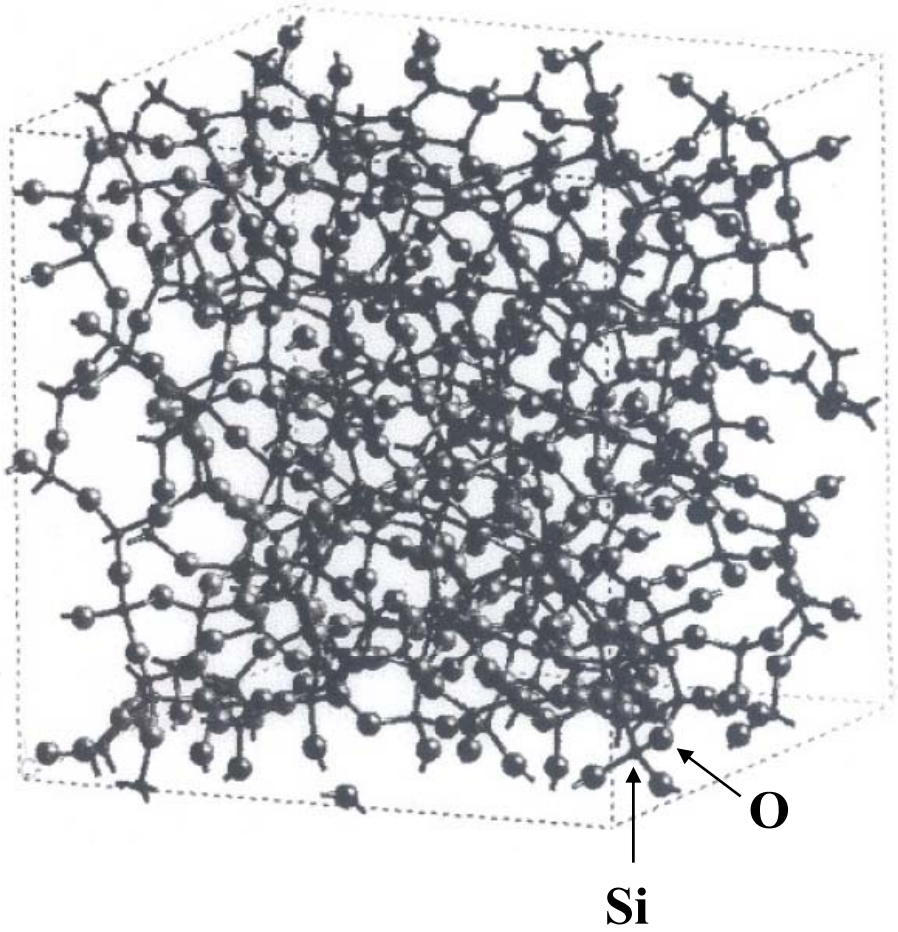
→ *yield deformation of 0.02 mm*

just measurable

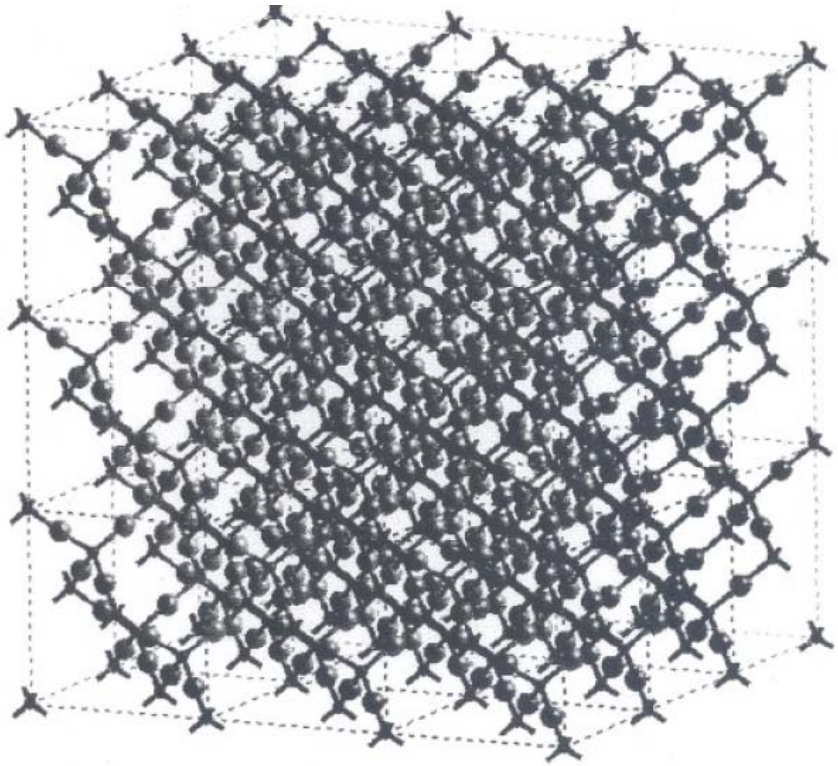
→ ***Solid*** **: application of small force for one day produces no permanent change.**

Silica - SiO_2

Amorphous silica

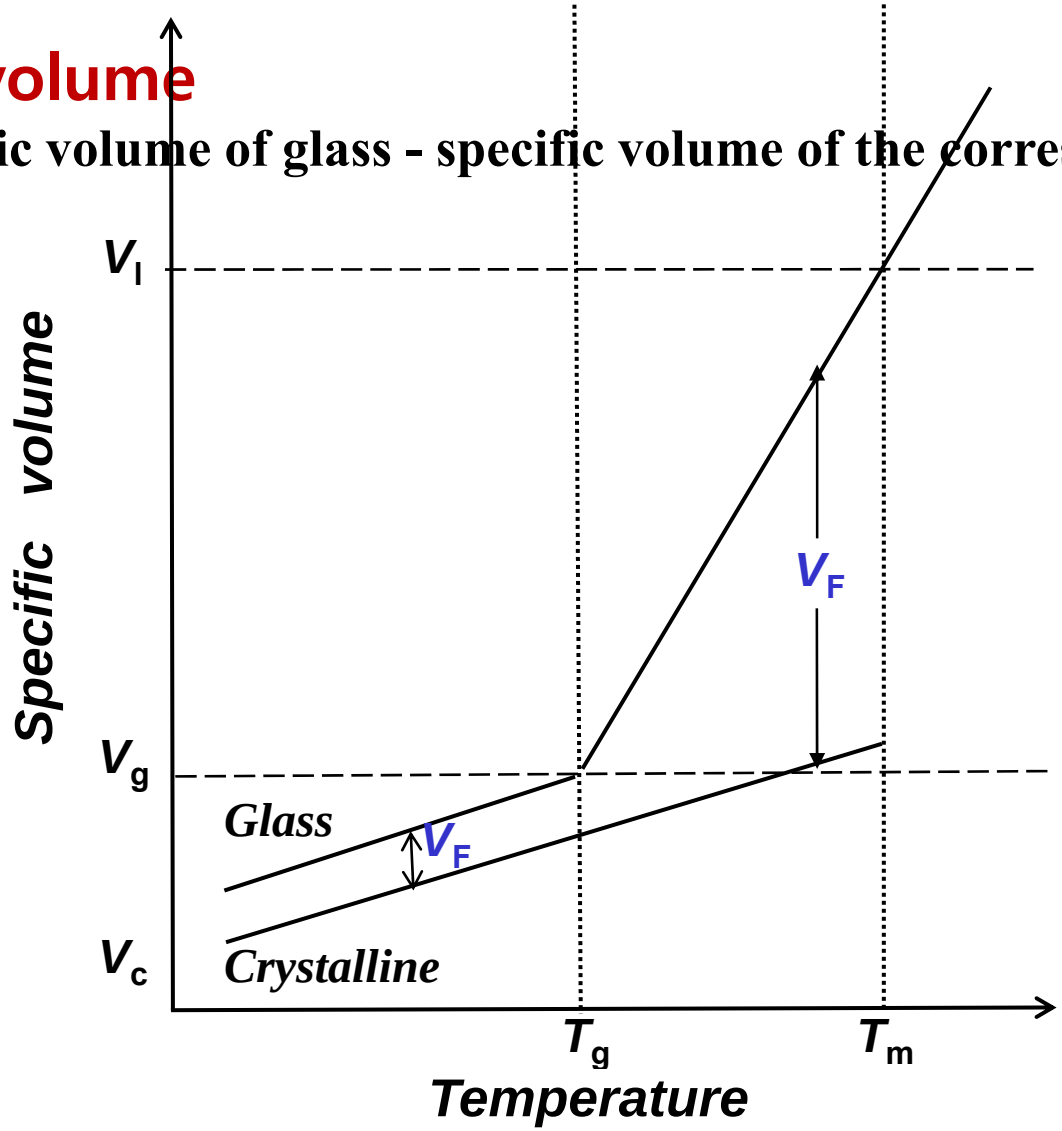


Crystalline SiO_2



Free volume

= specific volume of glass - specific volume of the corresponding crystal



At the glass transition temperature, T_g, the free volume increases leading to atomic mobility and liquid-like behavior.

Below the glass transition temperature atoms (ions) are not mobile and the material behaves like solid

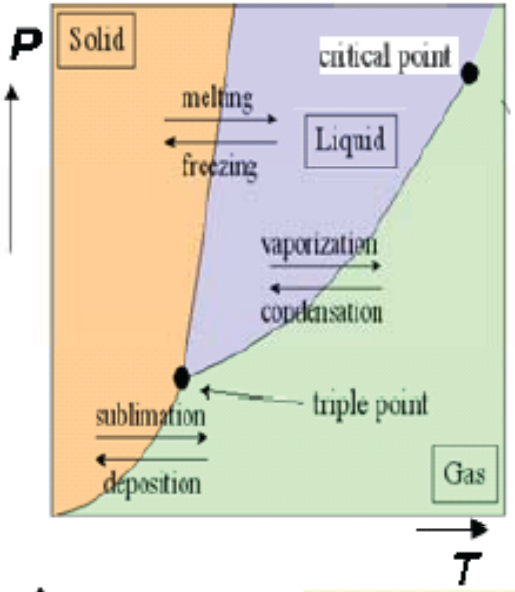
Glass transition

❖ The glass transition is not first order transition (such as melting), meaning there is no discontinuity in the thermodynamic functions (energy, entropy, density).

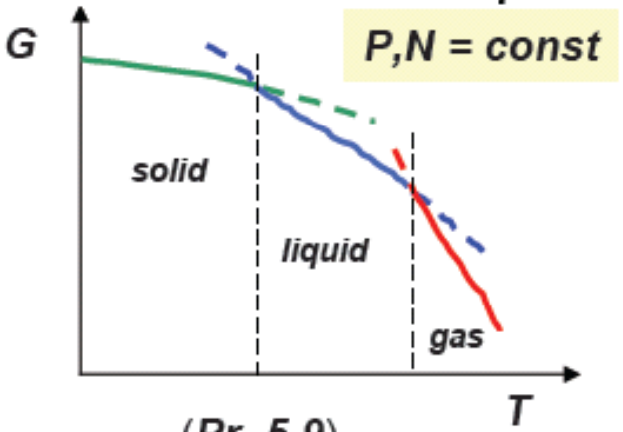
❖ The glass transition is 'pseudo' second-order phase transition. And the transition depends on kinetic factors (cooling rate).

❖ Sometimes the glass transition is a first order transition, most prominently in Si where the structure changes from 4 coordinated amorphous solid to 6 coordinated liquid. And the same applies to water (amorphous ice).

The First-Order Transitions



Latent heat
Energy barrier
Discontinuous entropy, heat capacity



(*Pr. 5.9*).

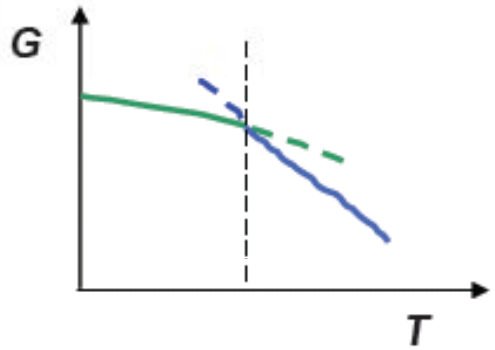
On the graph ***G*(*T*)** at ***P,N*** = const, the slope **d*G*/d*T*** is always negative:

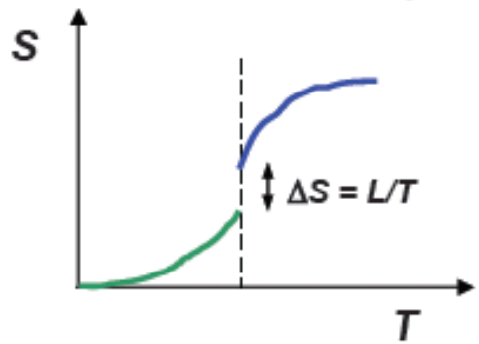
$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$$

In the first-order transitions, the ***G(T)*** curves have a real meaning even beyond the intersection point, this results in ***metastability*** and ***hysteresis***.

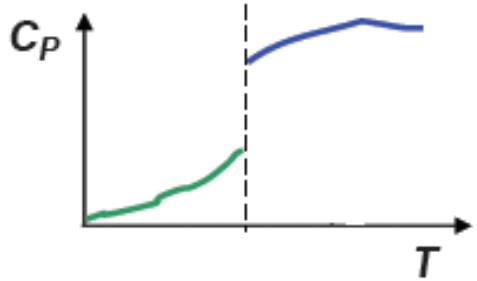
An energy barrier that prevents a transition from the higher μ to the lower μ phase. (e.g., gas, being cooled below T_{tr} does not immediately condense, since surface energy makes the formation of very small droplets energetically unfavorable).

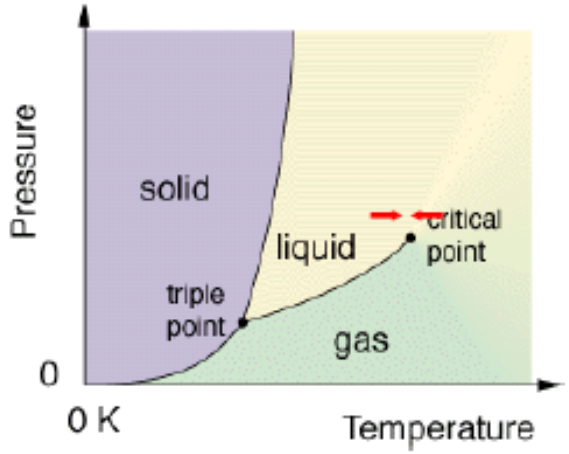
Water in organic cells can avoid freezing down to –20^{0}C in insects and down to –47^{0}C in plants.





$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N}$$

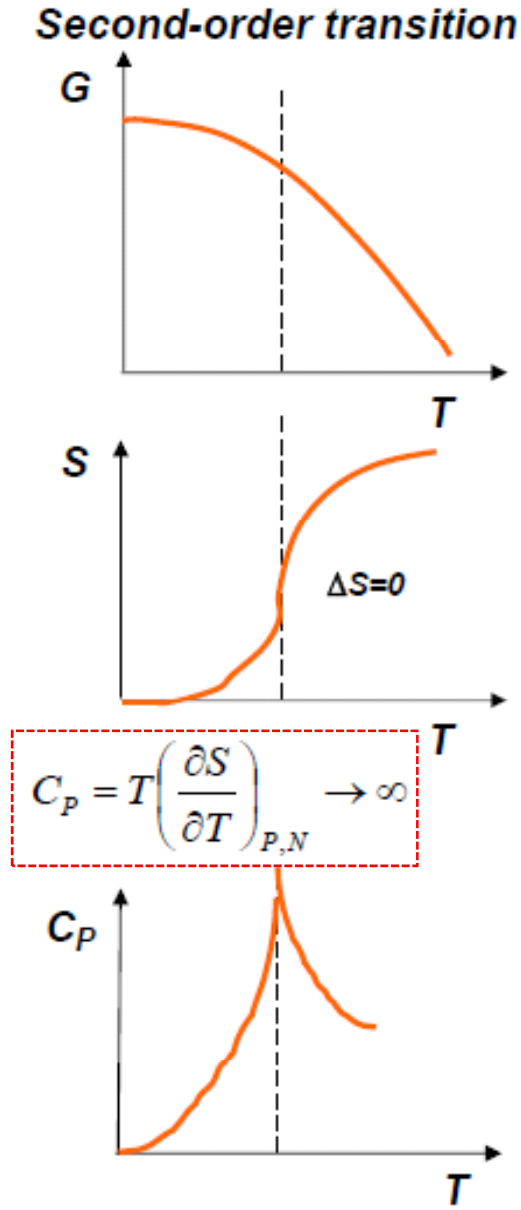




The Second Order Transition

No Latent heat
Continuous entropy

Discontinuous heat capacity



As one moves along the coexistence curve toward the critical point, the distinction between the liquid phase on one side and the gas phase on the other gradually decreases and finally disappears at (T_C, P_C). The T-driven phase transition that occurs *exactly* at the critical point is called a second-order phase transition. Unlike the 1st-order transitions, the 2nd-order transition does not require any latent heat (L=0). In the *second-order transitions* (*order-disorder transitions* or *critical phenomena*) the entropy is continuous across the transition. The specific heat $C_P = T(\delta S/\delta T)_P$ diverges at the transition.

Whereas in the 1st-order transitions the $G(T)$ curves have a real meaning even beyond the intersection point, nothing of the sort can occur for a 2nd-order transition – the Gibbs free energy is a continuous function around the critical temperature.

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

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

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

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

  - 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

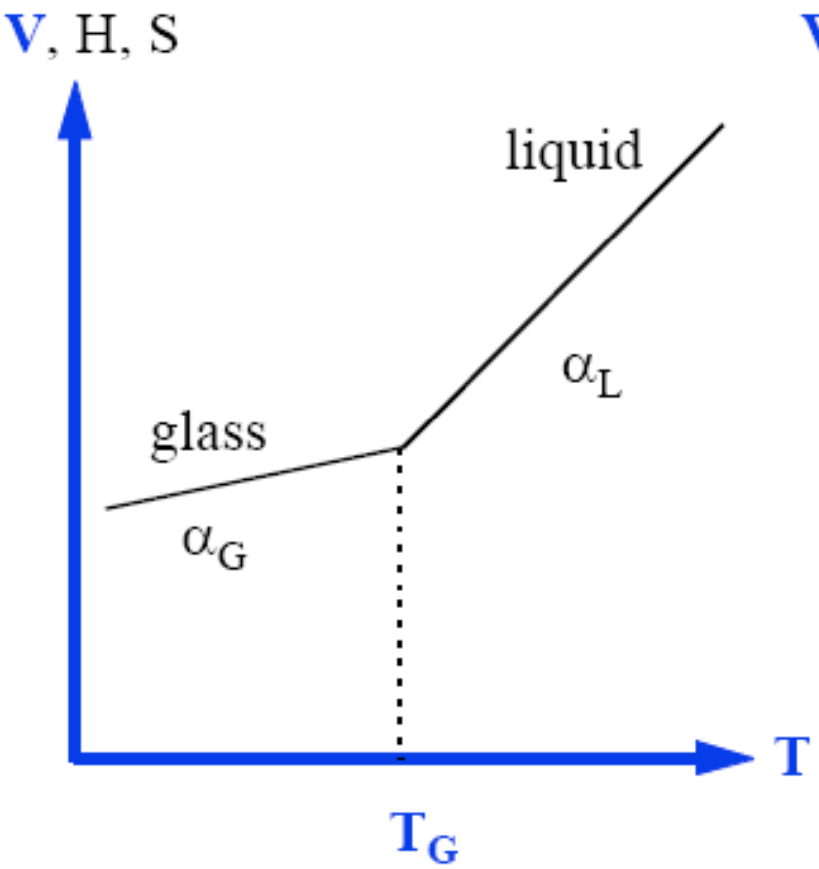
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

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

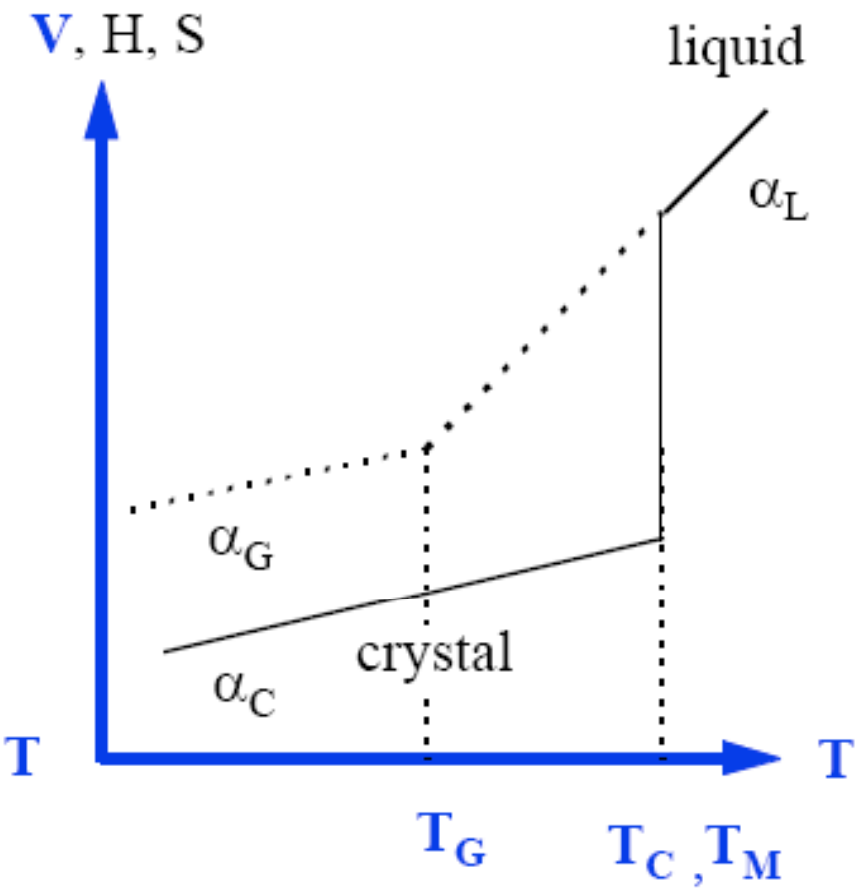
$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

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

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



Liquid to Glass Transition
"Second Order" Transition



Liquid to Crystal Transition
First Oder Transition

- 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

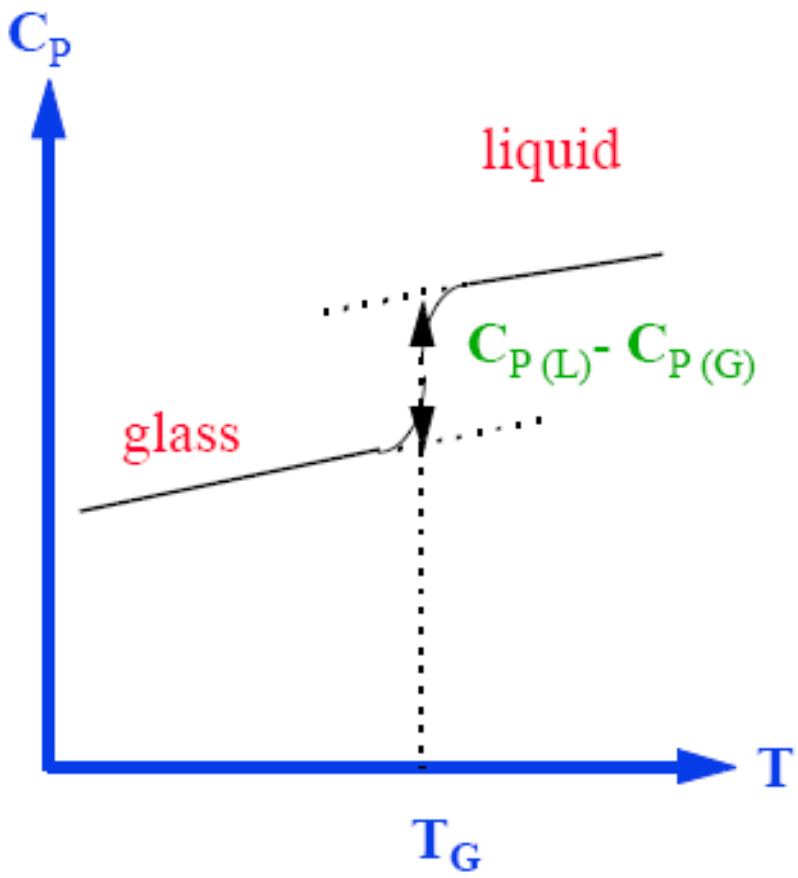
$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

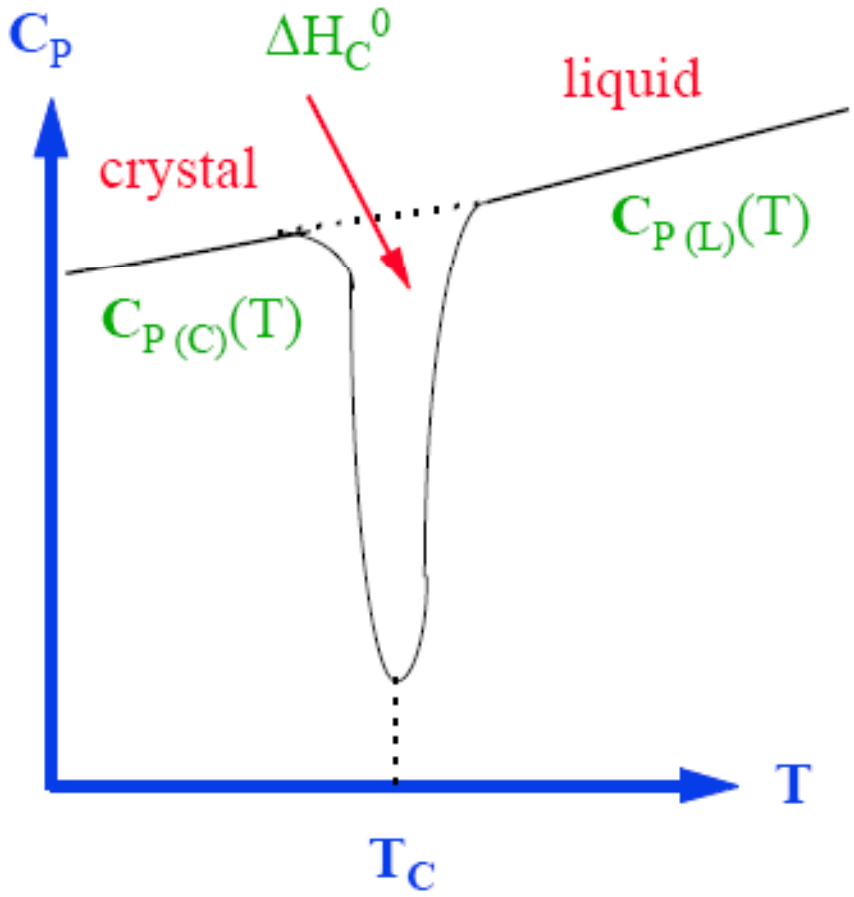
  - Second derivatives of G (α, β, C_p) are discontinuous at T_T

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

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

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

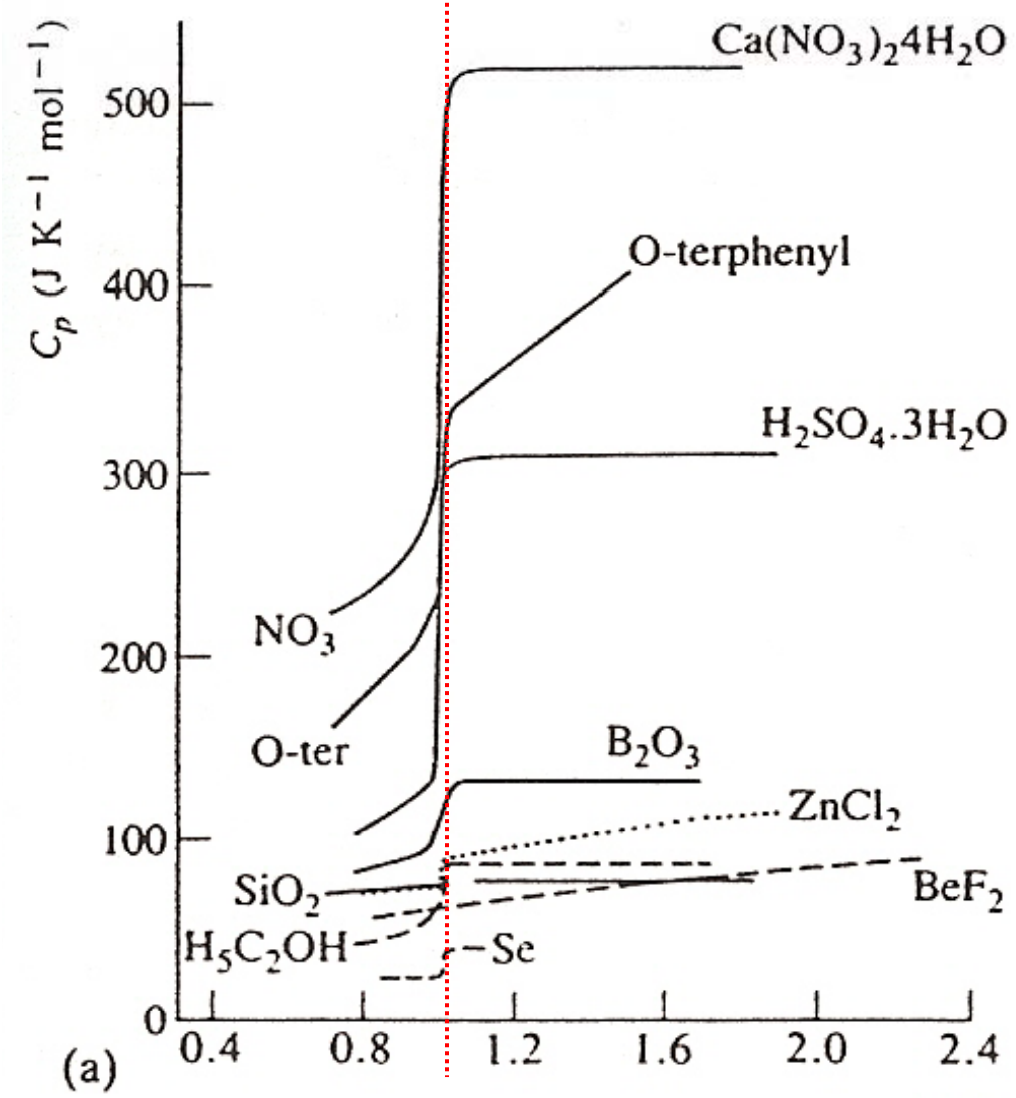




Liquid to Glass Transition
"Second Order" Transition

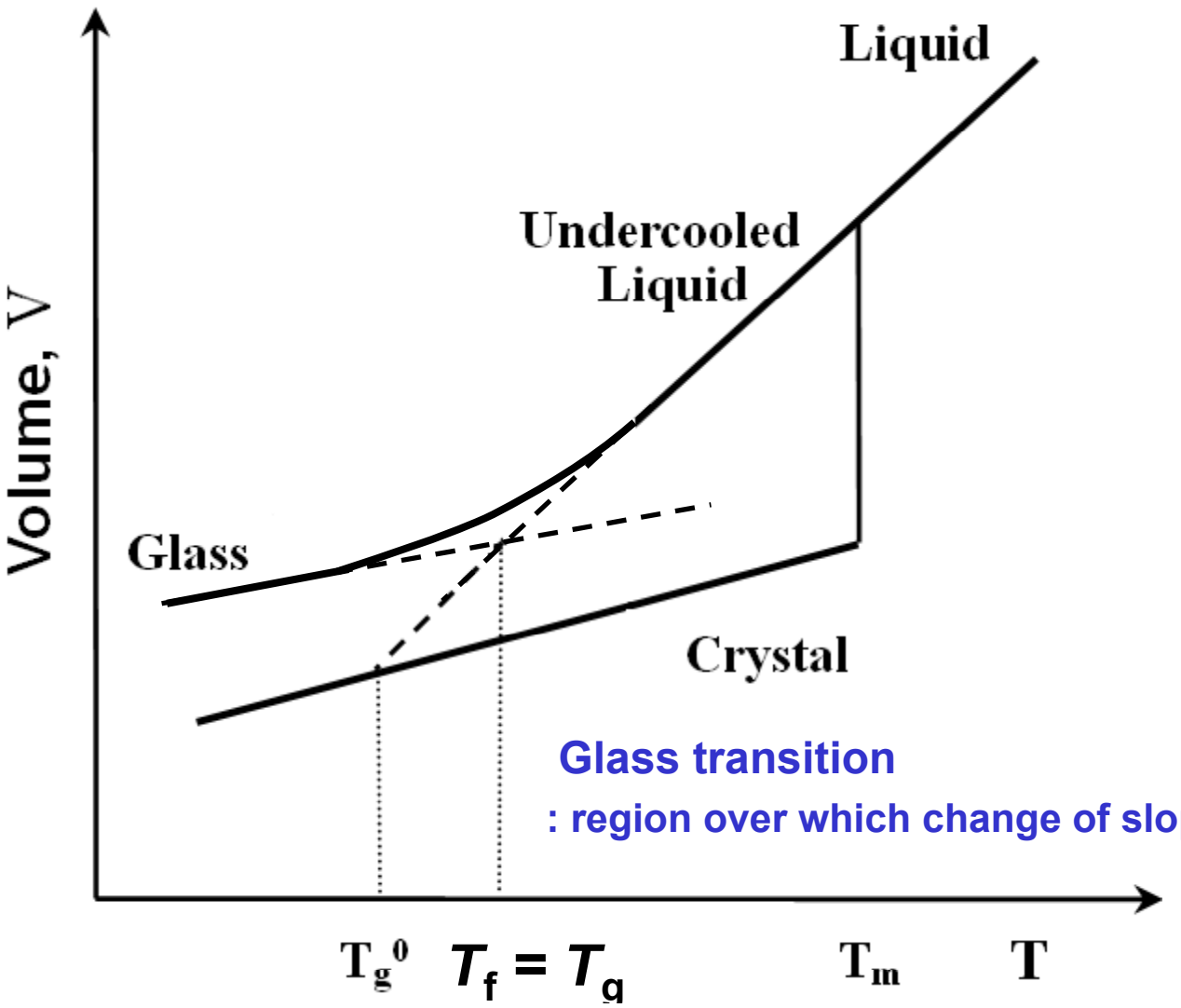
Liquid to CrystalTransition
First Order Transition

Difference of C_p at T_g depending on materials



Normalizing as T_g

T_g = *fictive temperature*, T_f



Glass transition

: region over which change of slope occurs

thermodynamic property ?

thermodynamic property

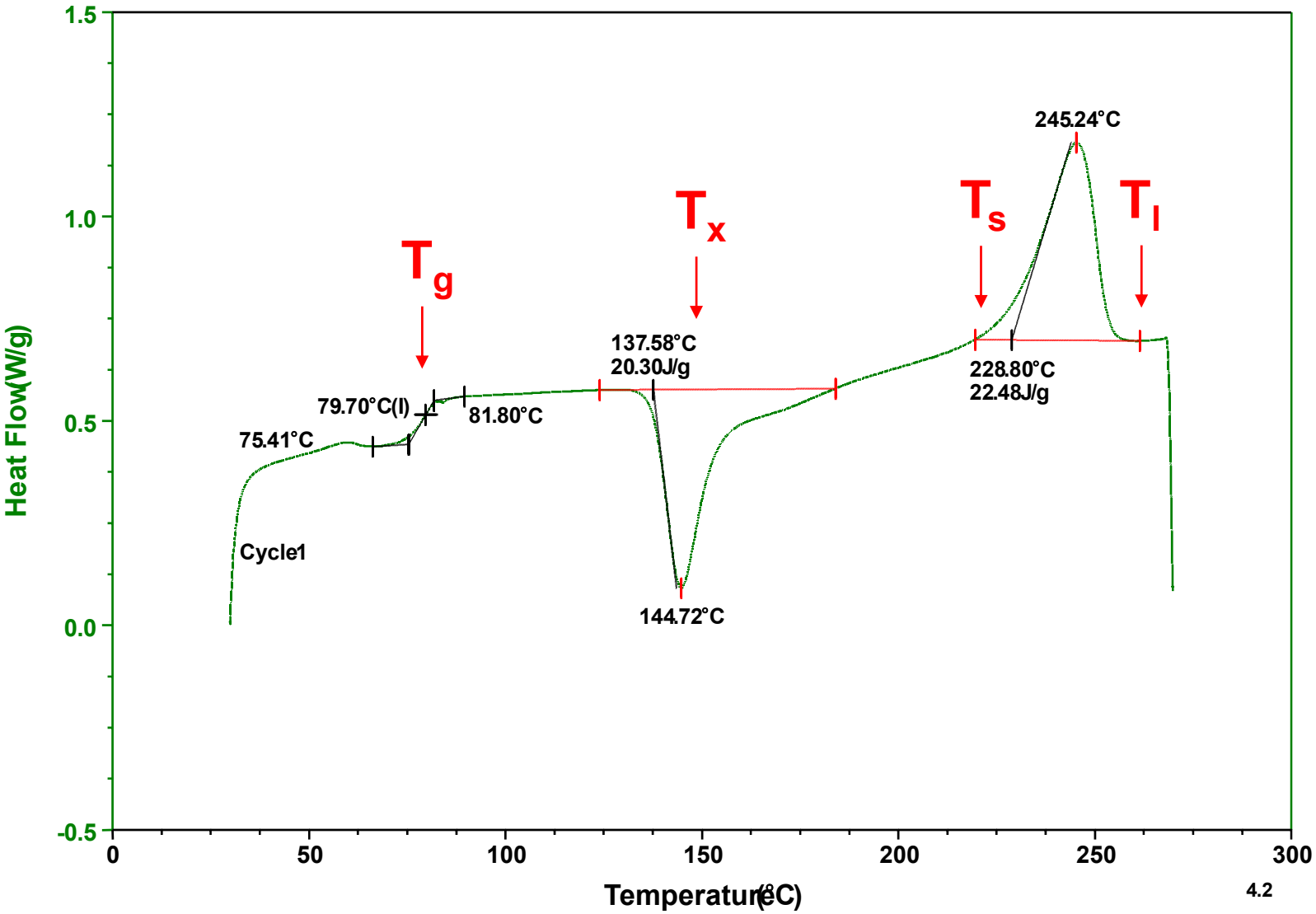
T_f = *fictive temperature*

This is the temperature at which the actual atomic scale structure of a quenched glass would be the *metastable equilibrium* structure (relative to the crystalline state) of the corresponding supercooled liquid (SCL). One always has:

$$T_f \geq T_g$$

T_f can also be defined as the temperature at which the strucuture of the SCL was *instantaneously frozen* into the glassy state, which has therefore kept the original structure of the SCL and it can be estimated by the intersection between the SCL line and the extrapolated glass line, in a specific volume vs temperature diagram of the type previously shown. For slow enough cooling rates, $T_f \rightarrow T_g$. For fast cooling, T_f may become considerably larger than the value of T_g measured at typical heating rate of ~10-20 K/s.

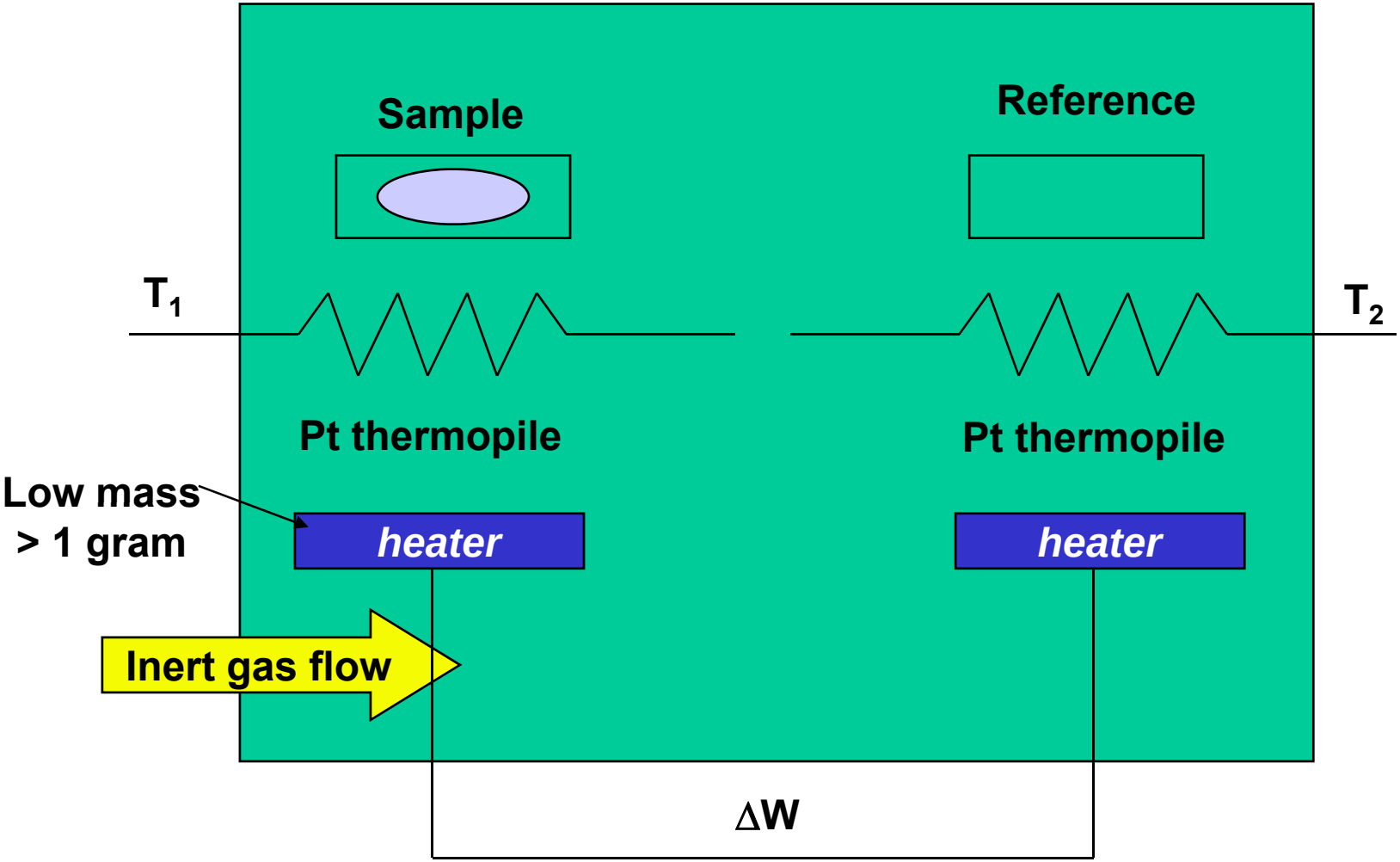
Example DSC – PET (polyethylene terephthalate)



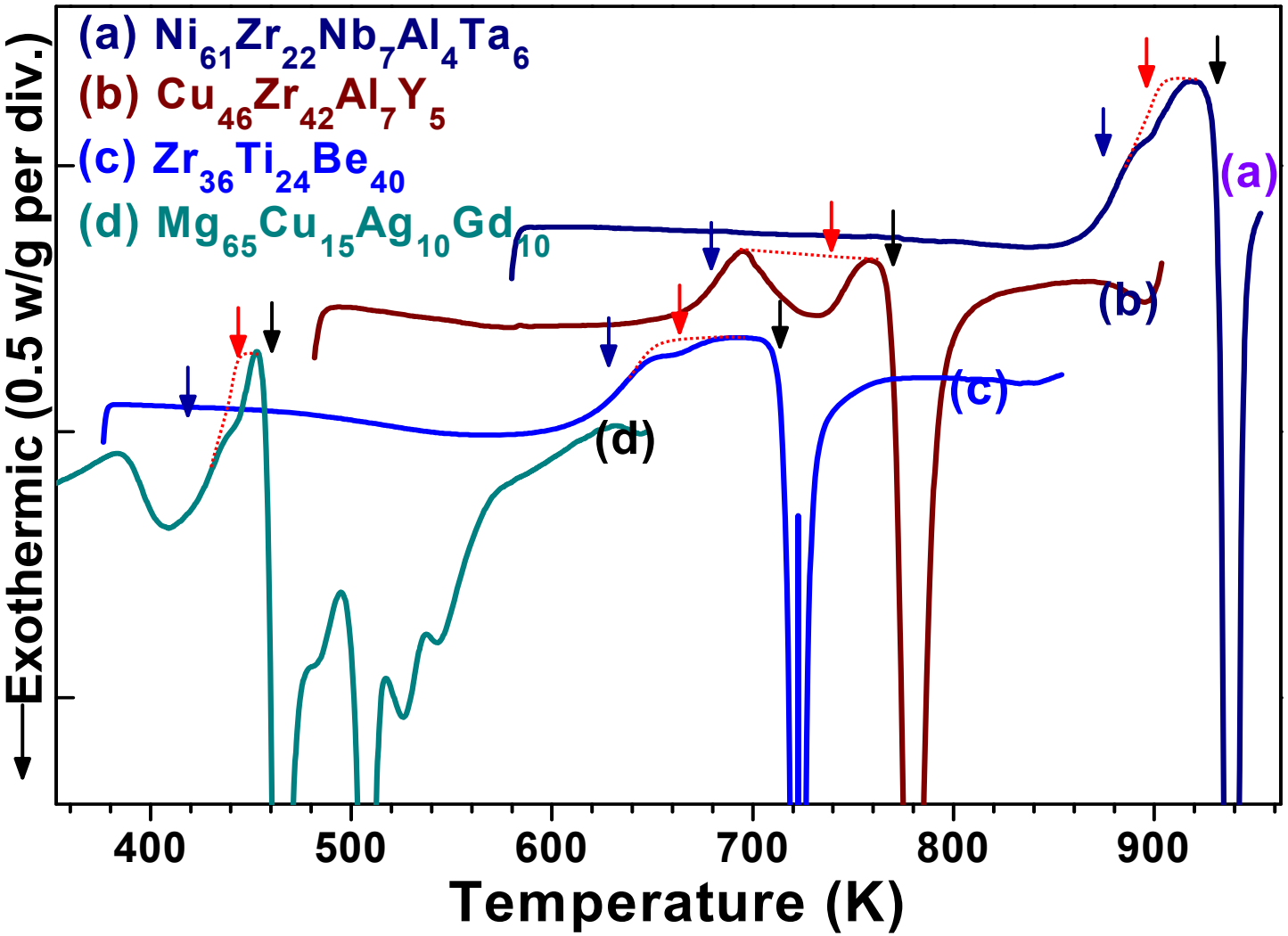
Thermal analysis: DSC

- A *calorimeter* measures the heat into or out of a sample.
- A *differential calorimeter* measures the heat of a sample relative to a reference.
- A *differential scanning calorimeter* does all of the above and heats the sample with a linear temperature ramp.
- Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere.

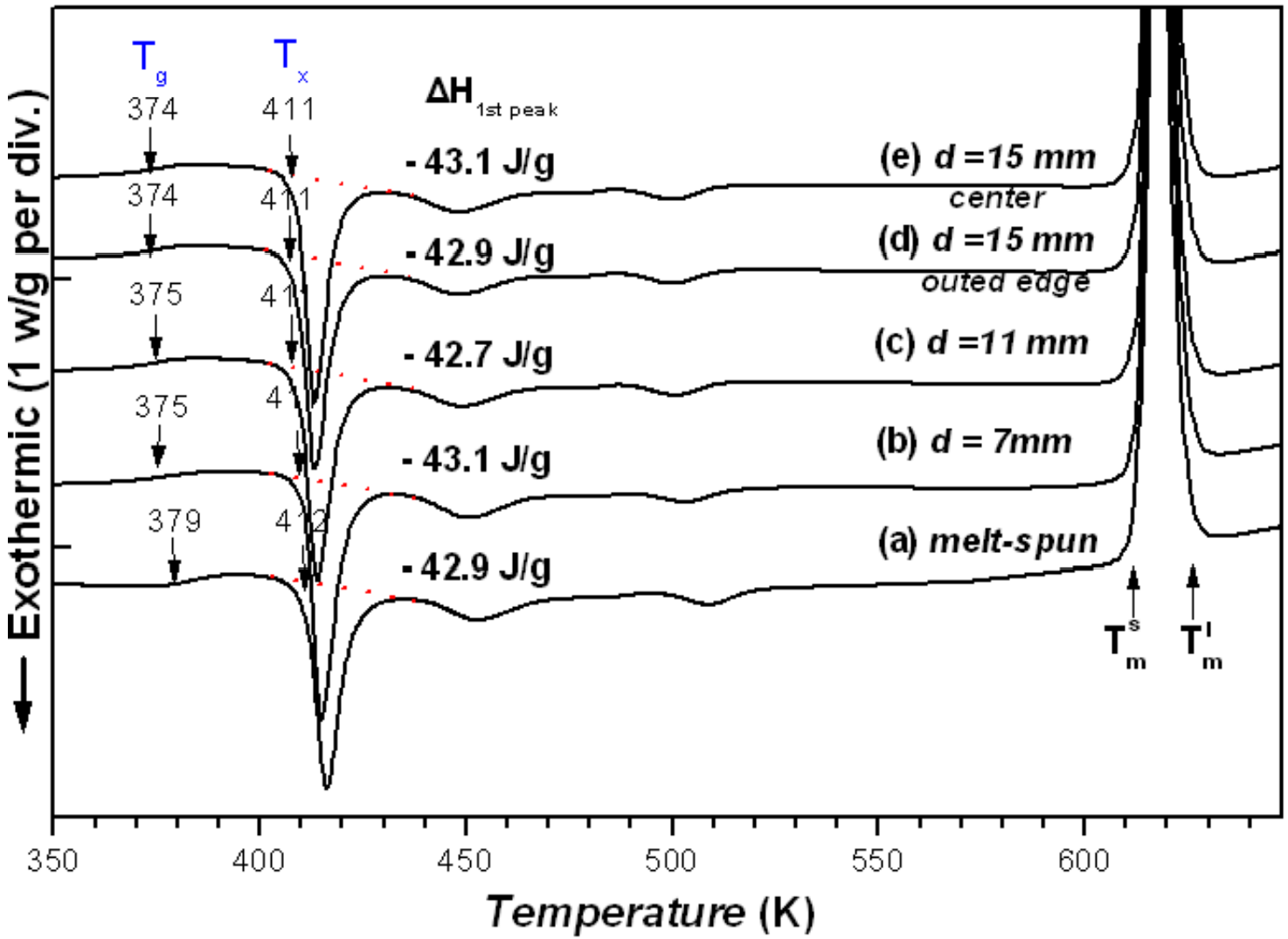
Schematic of DSC Instrument



Variation of T_g depending on alloy compositions

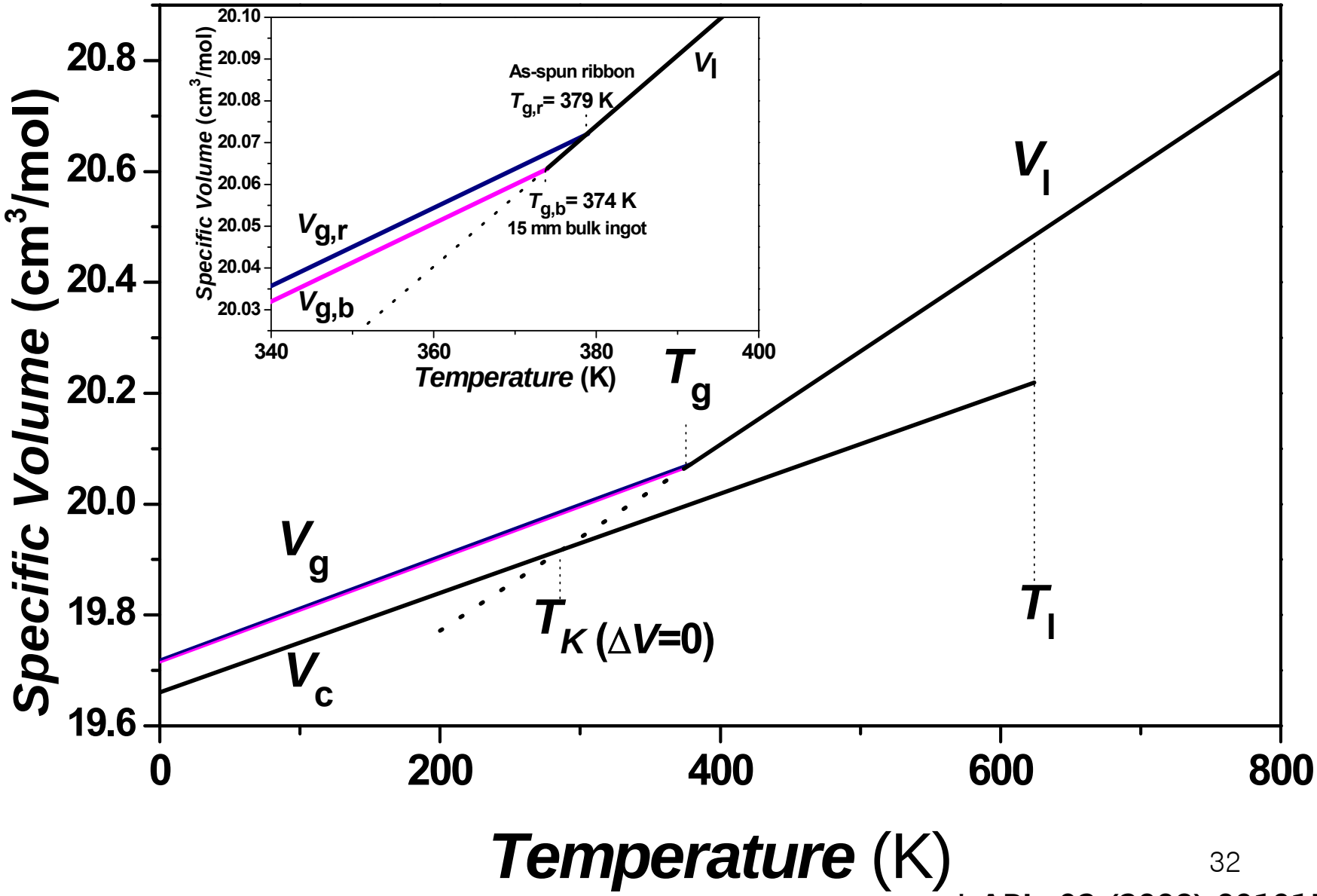


❖ **Typically Tg is ~ 50-60% of the melting point.**



* J Mater Res, 19 (2004) 685.

- ***T_g depends on thermal history even in same alloy composition.***



* APL, 92 (2008) 091915.