2014 Spring

"Advanced Physical Metallurgy"

- Bulk Metallic Glasses -

03.18.2014

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by appointment

Chapter 2. Metallic Glass

Glass is any noncrystalline solid obtained by continuous cooling from the liquid state, and *amorphous solid* is any noncrystalline material obtained by any other method, except by continuous cooling from the liquid state.

Fundamentals of the Glass Transition

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

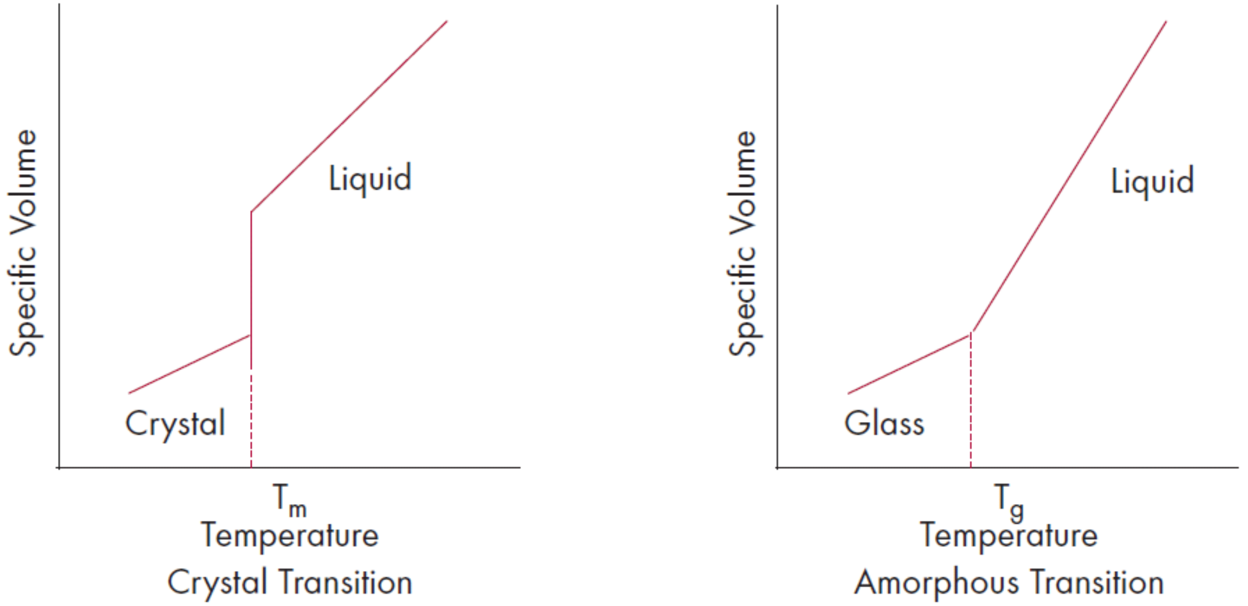


Figure 4. Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).

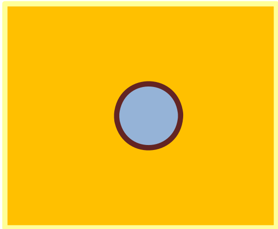
Fundamentals of the Glass Transition

- **Melting and Crystallization are Thermodynamic Transitions**
  - Discontinuous changes in structure and properties at 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 near T_g
  - Structure and properties are continuous with temperature
  - Structures and properties can be changed continuously by changing the kinetics of the cooled or reheated liquid

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid | T_m | Undercooled Liquid | Solid

No superheating required!

vapor

- Interfacial energy ⇨ No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

Melting: Liquid ← Solid

In general, wetting angle = 0 ⇨ No superheating required!

* Quasi-chemical approach

* Solid: force between pairs of atoms
  → vaporize: break all "pairwise" bonds

For, example: Copper (Cu)

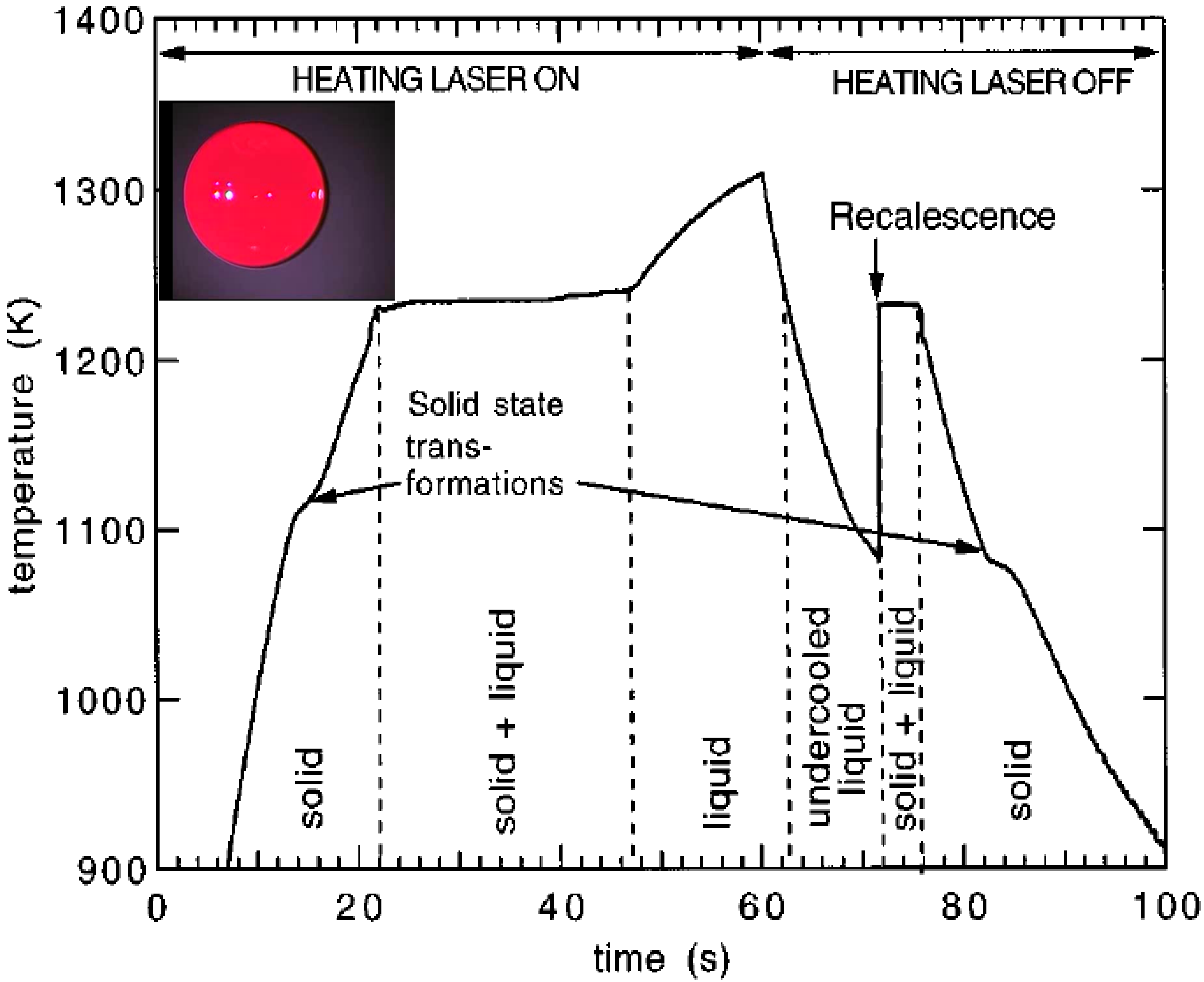
Vaporization | Melting
Heat of vaporization 80 Kcal/mole vs Heat of fusion 3.1 Kcal/mole

↔ 25 times → 1/25 broken

Melting: each bond is replaced by one with 4 percent less E,

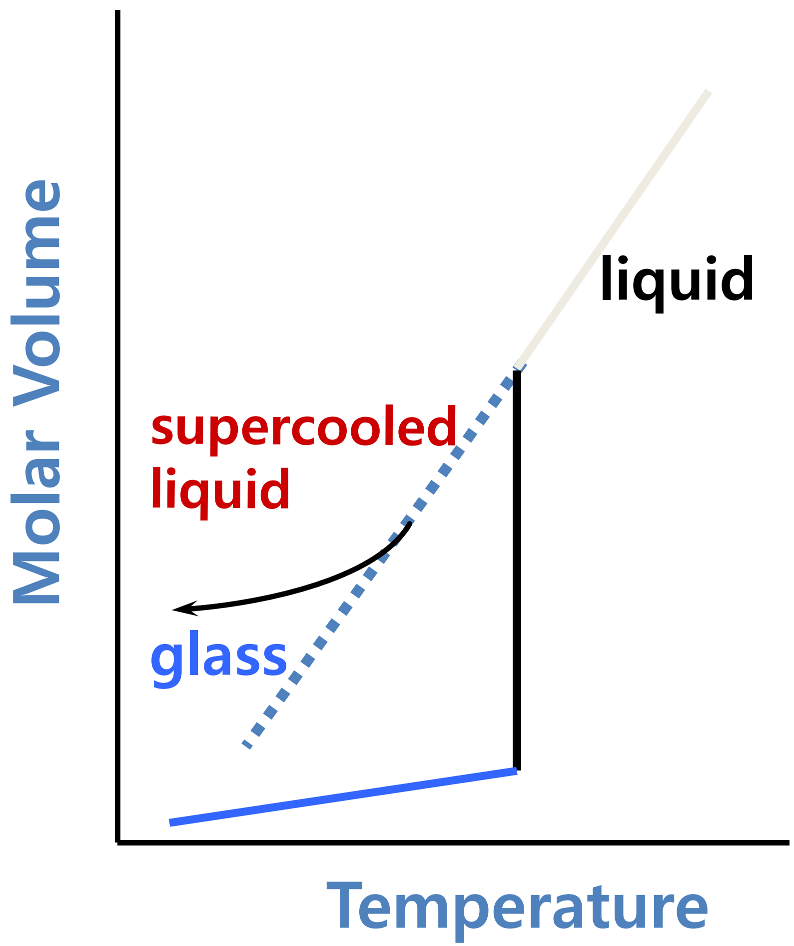
although bond energy of liquid is changed by the positions.

→ Heat of fusion during melting: need to generate weaker liquid bonds


HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state trans-formations
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid
temperature (K)
time (s)
1400
1300
1200
1100
1000
900
0
20
40
60
80
100

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 <u>makes it difficult for atoms of the liquid to diffuse (rearrange) into the crystalline structure</u>
- 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



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

Viscosity indicates the resistance to flow of a system and is a measure of its internal friction. The International System unit of viscosity is Pa s = kg m^{-1} s^{-1}. An older unit is Poise, P with the relationship:

$$1 \text{ P} = 0.1 \text{ Pa s} \tag{2.1}$$

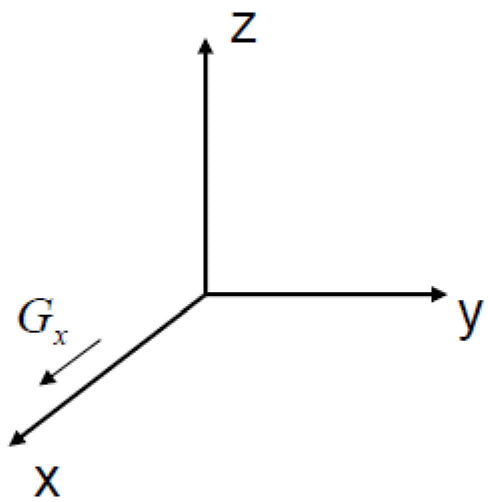
As a reference point, water at 20°C has a viscosity of 1 centiPoise, cP (10^{-2} Poise). The viscosities of some substances of common use are:

Water at 20°C	1.002 cP (1.002×10^{-3} Pa s)
Mercury at 20°C	1.554 cP (1.554×10^{-3} Pa s)
Pancake syrup at 20°C	2,500 cP (2.5 Pa s)
Peanut butter at 20°C	250,000 cP (250 Pa s)
Soda glass at 575°C	1×10^{15} cP (1×10^{12} Pa s)

As defined above, the glass transition temperature, T_g, is the temperature at which the supercooled liquid becomes solid glass. To be more accurate, this should be called the thermal or calorimetric glass transition. It is also important to realize that this "transition" is not a true thermodynamic phase transition, but its origin is strictly kinetic, since the value of T_g depends on the cooling rate and, more generally, on the way the glass is prepared.

* 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

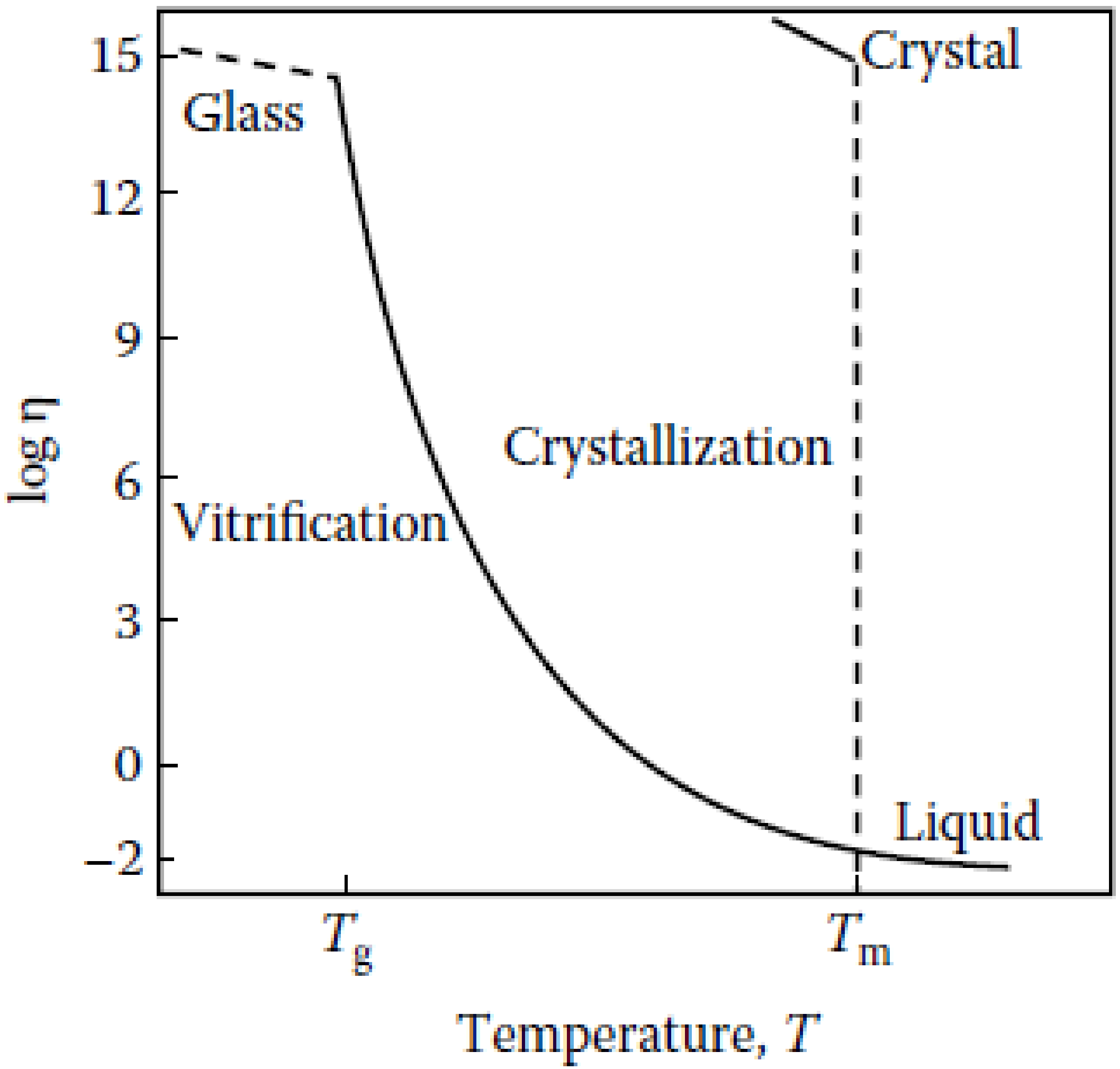
ex) *100 N applies for one day to 1 cm³ of material having viscosity of $10^{14.6}$ poise*

→ *yield deformation of 0.02 mm*

just measurable

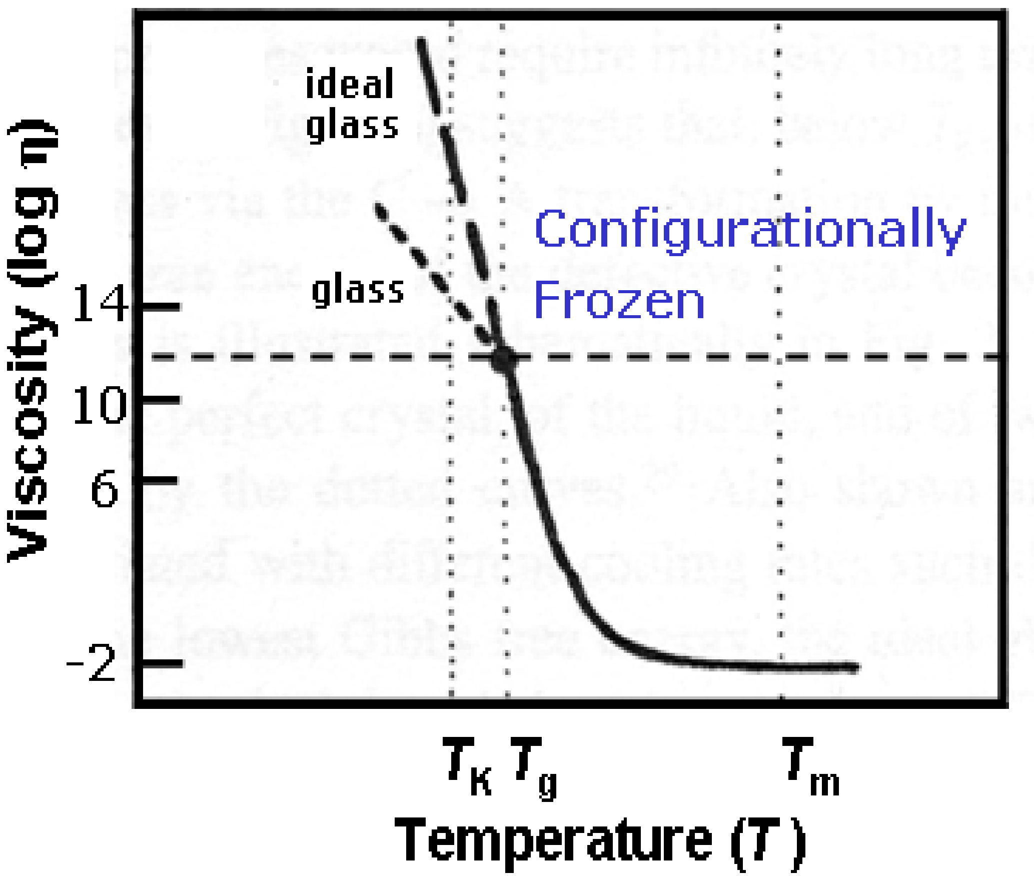
→ ***Solid*** **: application of small force for one day produces no permanent change.**

Variation of viscosity with temperature for crystal and glass formation



Glass : undercooled liquid with high viscosity

The higher the structural relaxation, the closer it moves toward a "true" glass.

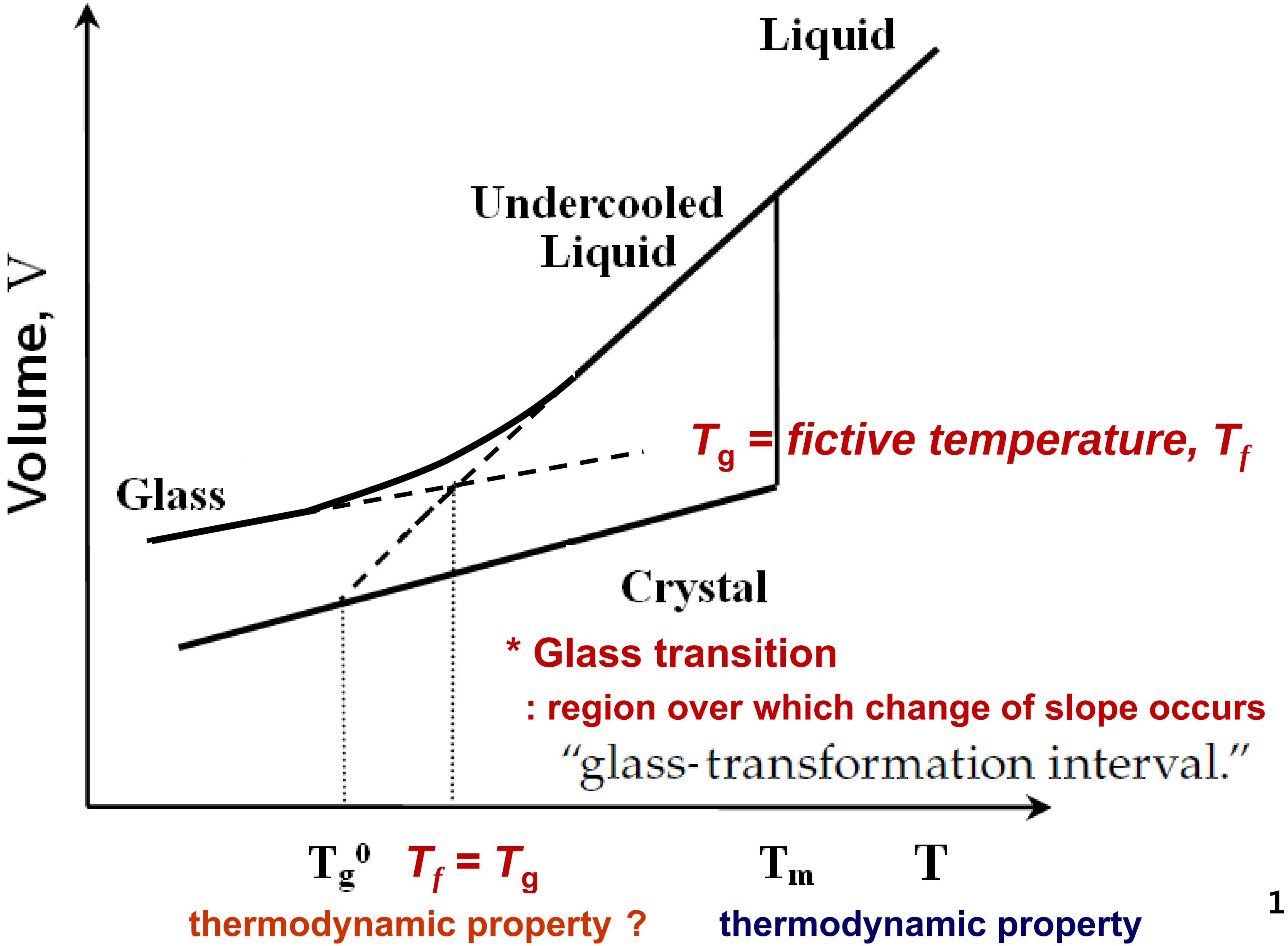


A solid is a materials whose viscosity exceeds $10^{14.6}$ poise

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

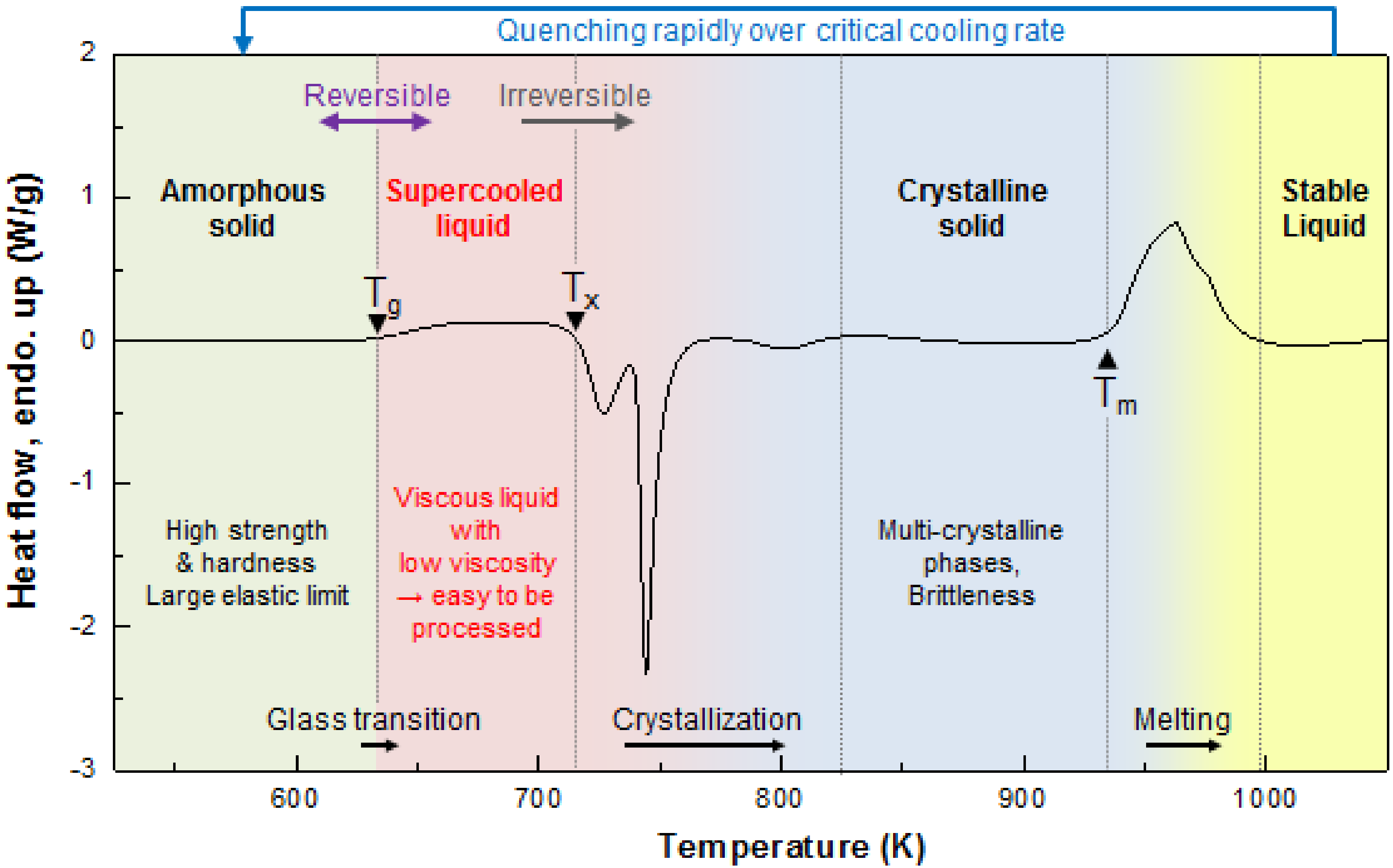
* Glass transition

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. <u>Eventually, homogeneously frozen at T_g.</u>



DSC trace of Vitreloy 1

: the temperature regions sectioned according to phase transformations

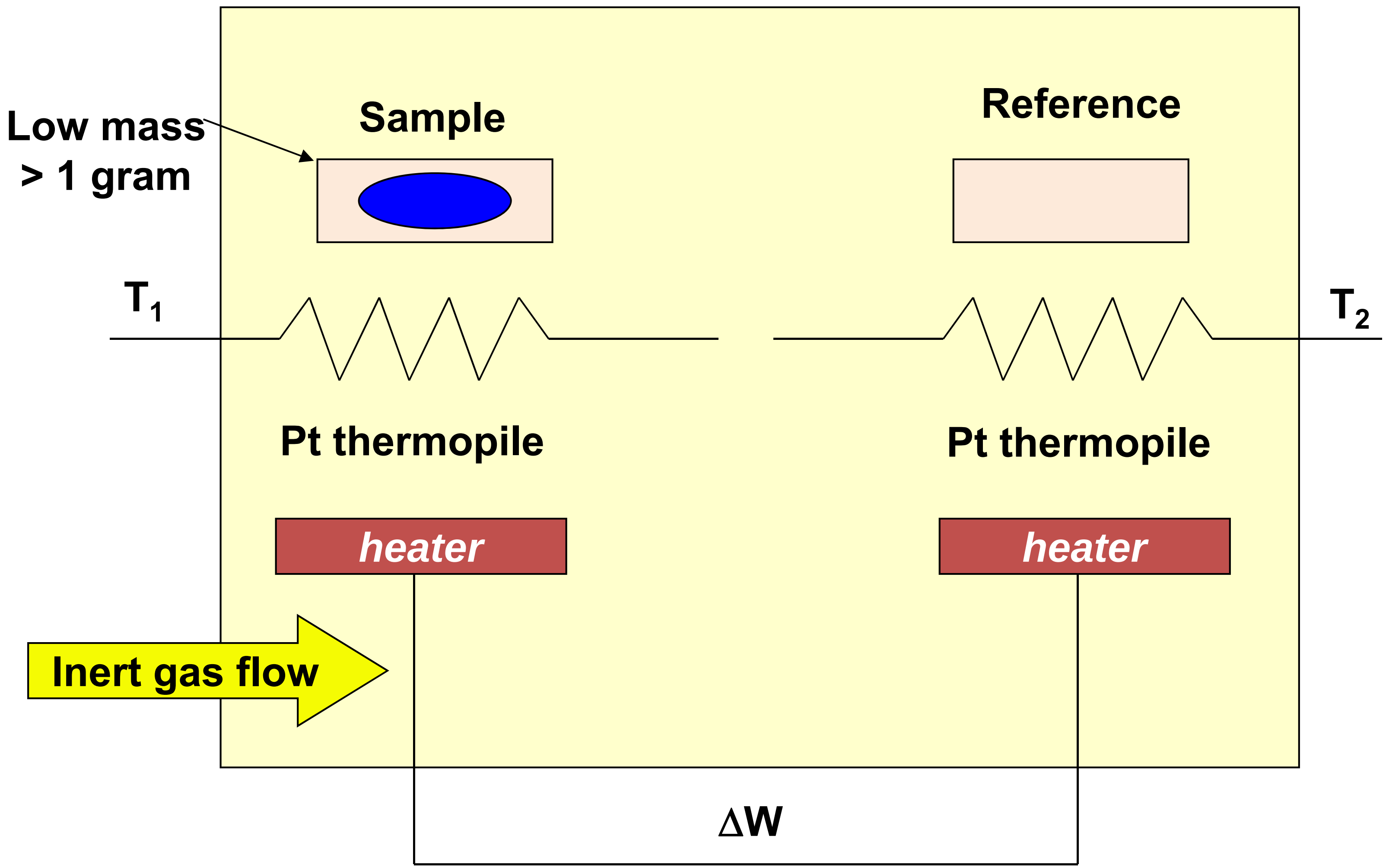


ΔT_x : indication of thermal stability of the glass produced

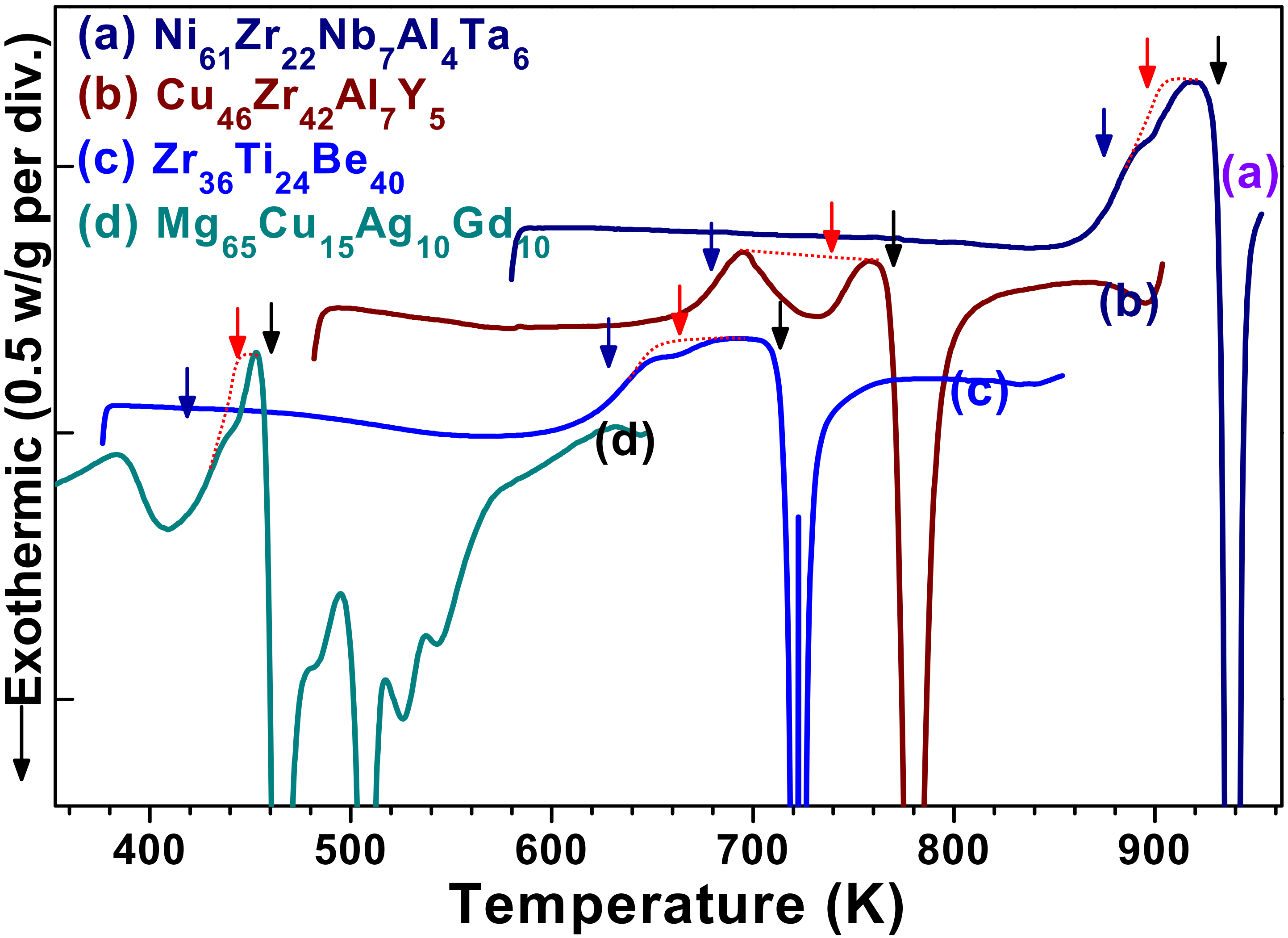
Thermal analysis: DSC

- **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



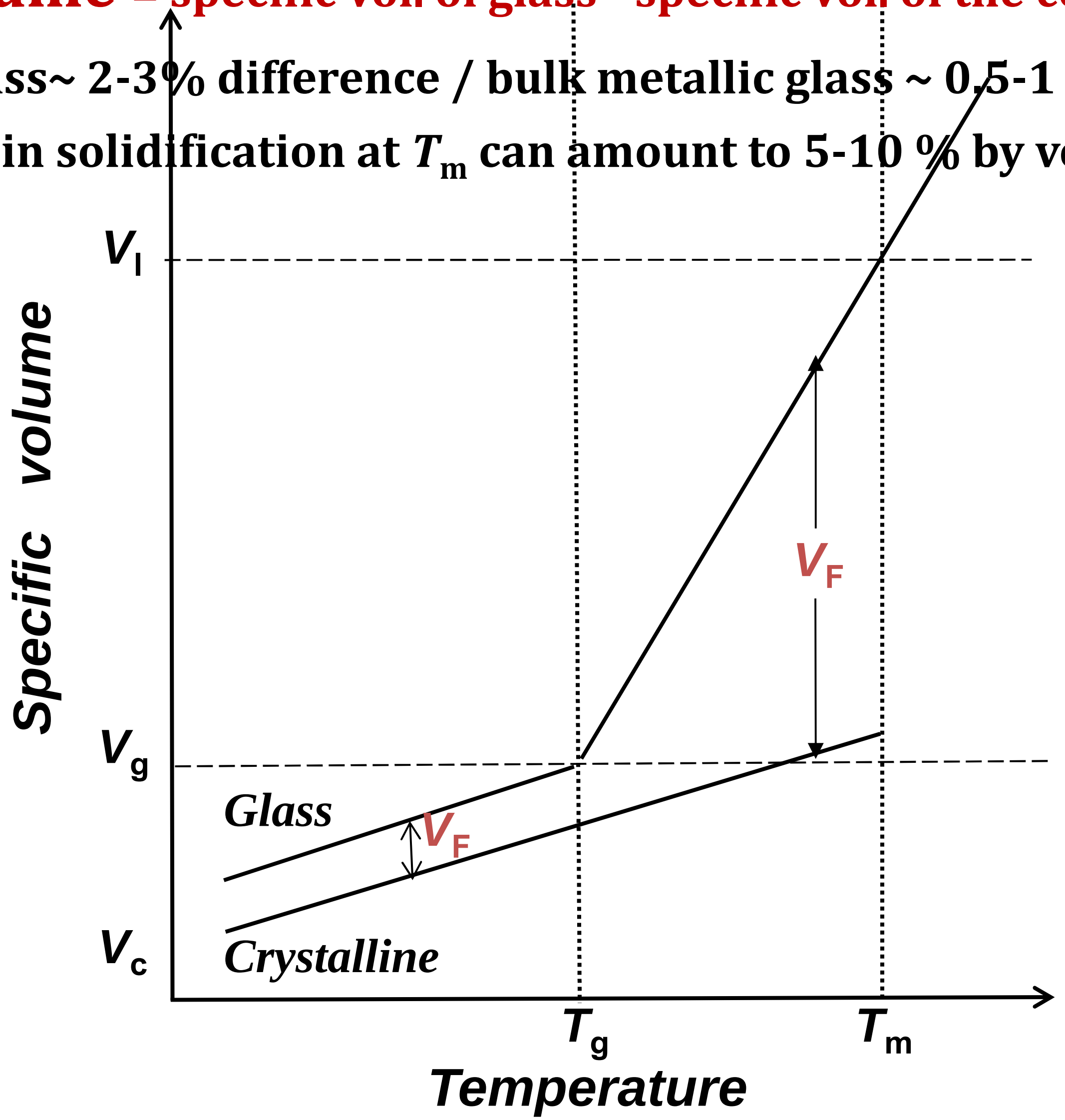
Variation of T_g depending on alloy compositions → Broken Bonds



At a temperature T_x, which is higher than T_g, the supercooled liquid transforms into the crystalline phase(s). As mentioned earlier, the temperature interval between T_x and T_g is referred to as the width of the supercooled liquid region (SLR), that is, $\Delta T_x = T_x - T_g$. The value of ΔT_x is different for different glasses, and is usually taken as an indication of the thermal stability of the glass produced. In the case of BMGs, this temperature interval is usually quite large and values of over 120 K have been reported; the highest reported to date is 131 K in a $Pd_{43}Cu_{27}Ni_{10}P_{20}$ BMG alloy [17]. In the case of rapidly solidified thin ribbon glasses, and marginal glass-formers, the value of ΔT_x is very small, if observed at all.

* Free volume = specific vol. of glass - specific vol. of the corresponding crystal

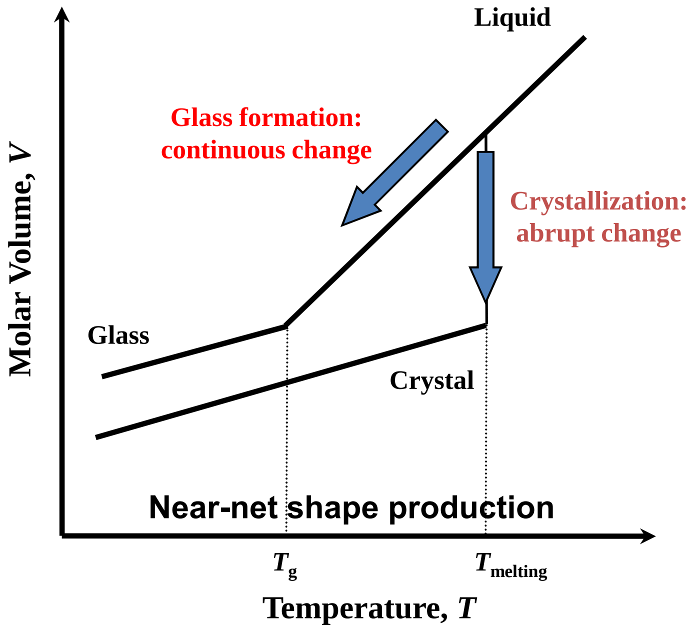
- normal glass~ 2-3% difference / bulk metallic glass ~ 0.5-1 % difference
- Shrinkage in solidification at T_m can amount to 5-10 % by volume.

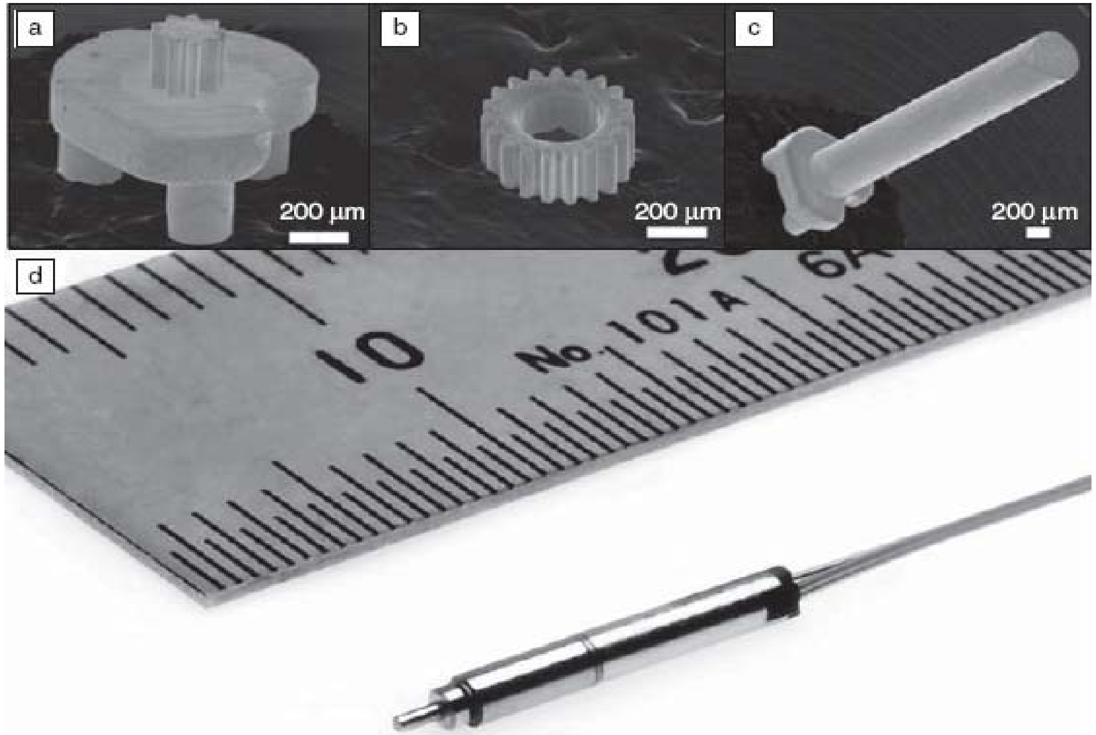


At the glass transition temperature, T_g, the free volume increases leading to atomic mobility and liquid-like behavior.

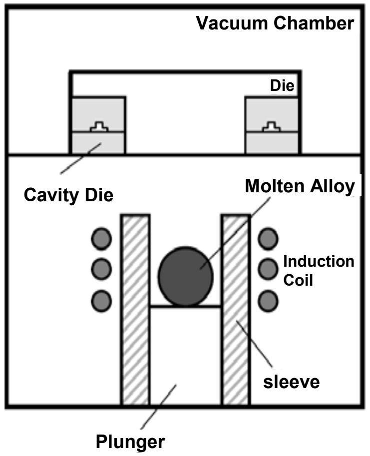
Below the glass transition temperature, atoms (ions) are not mobile and the material behaves like solid

* Micro/Nano casting

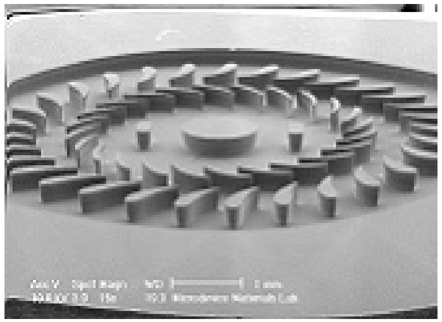


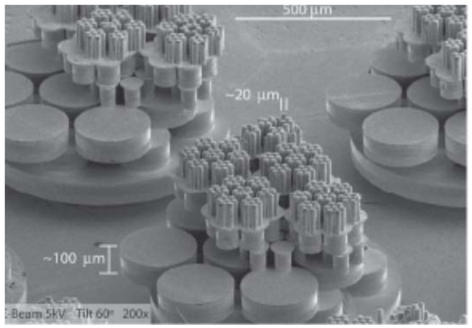


Precision Gears for Micro-motors



Precision die casting

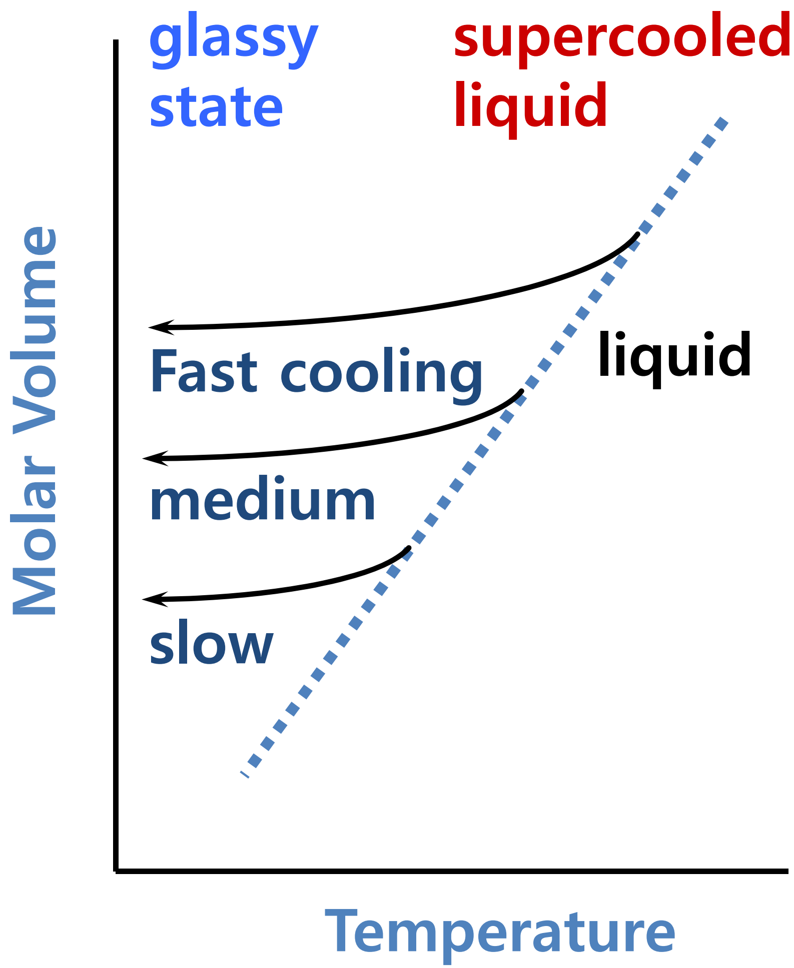




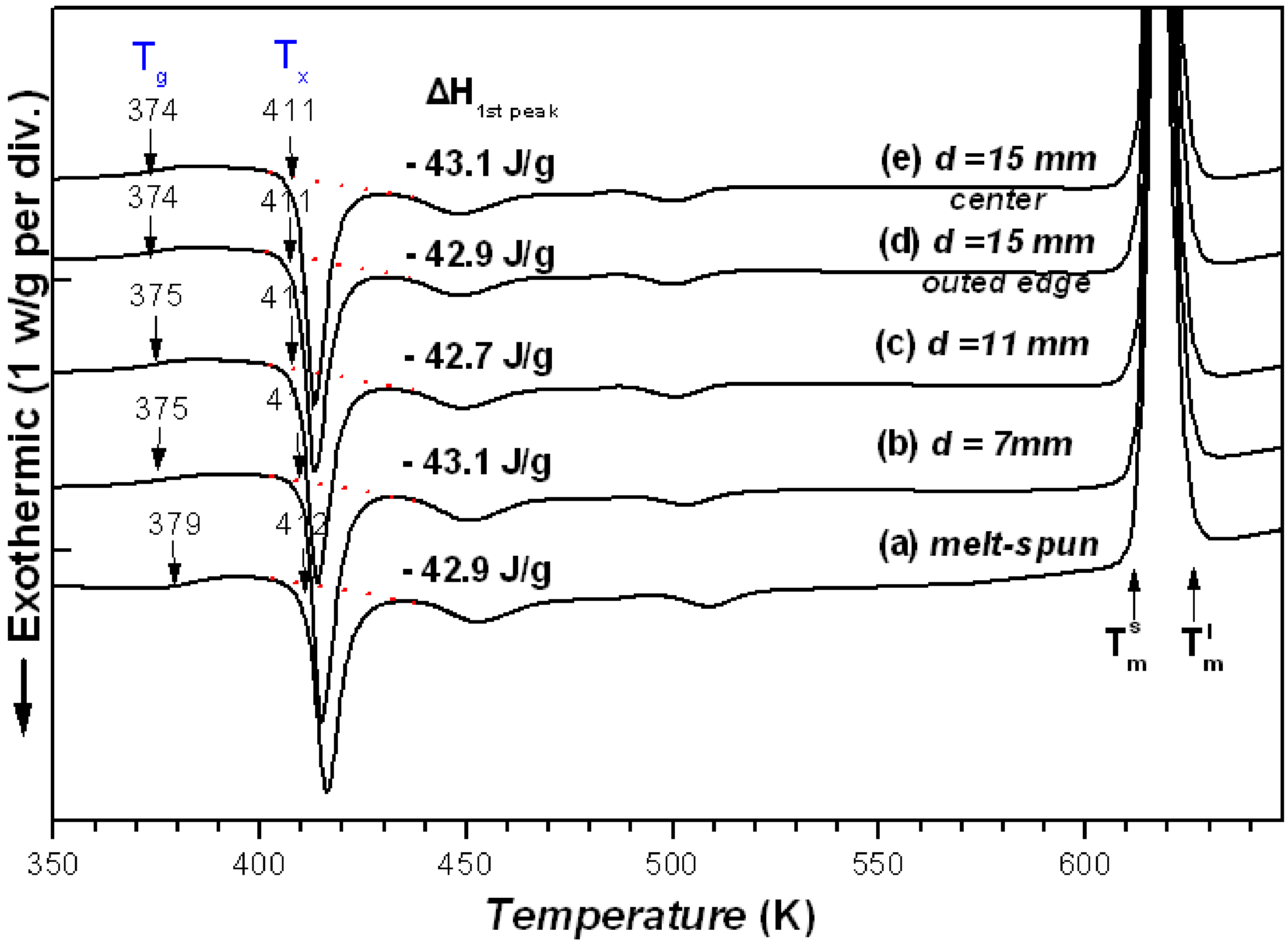
MRS BULLETIN ***32*** *(2007)654.*

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

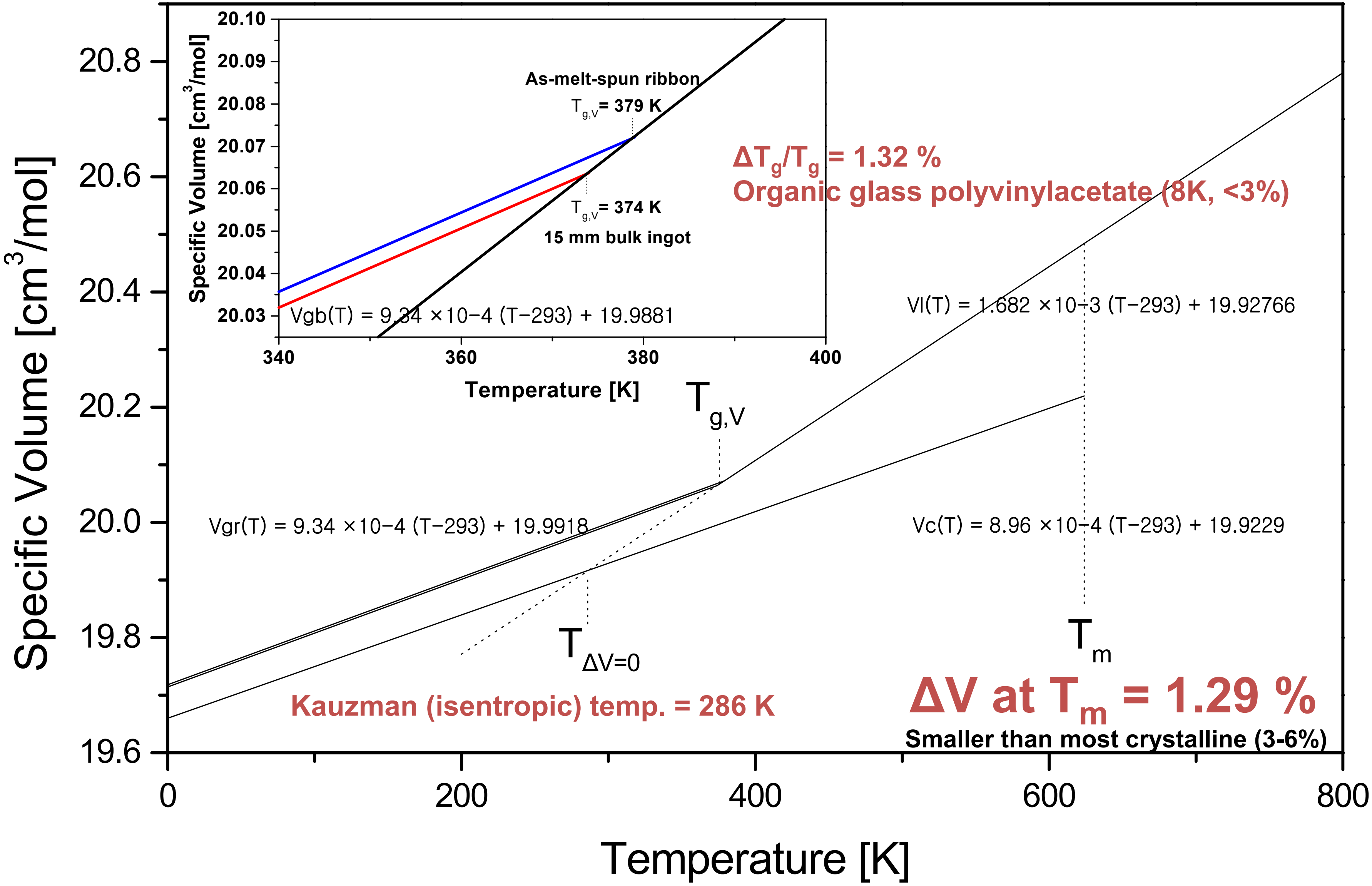


❖ Typically T_g is ~ 50-60% of the melting point. ($0.6T_m$)



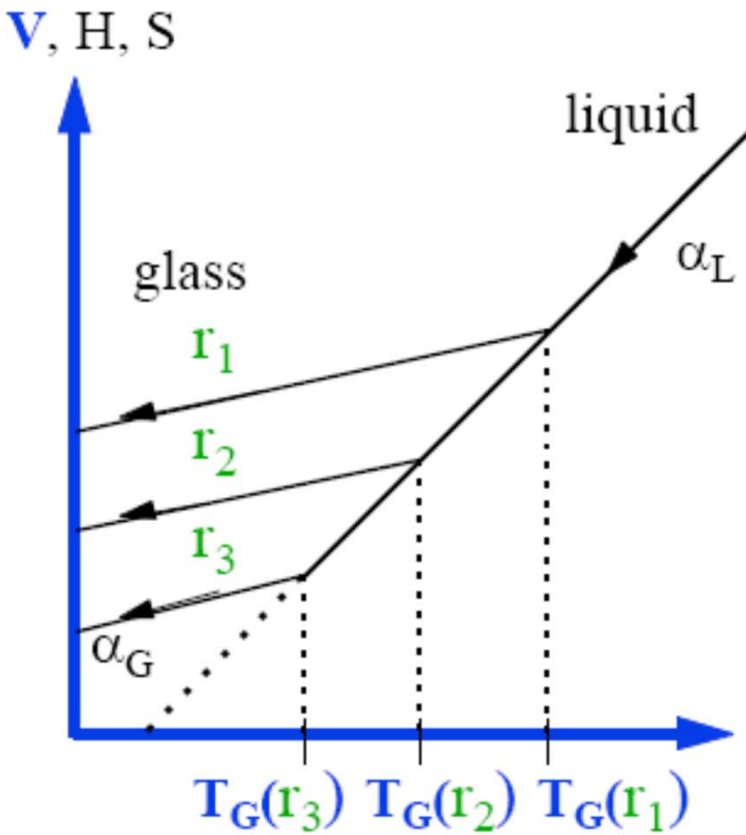
* J Mater Res, 19 (2004) 685.

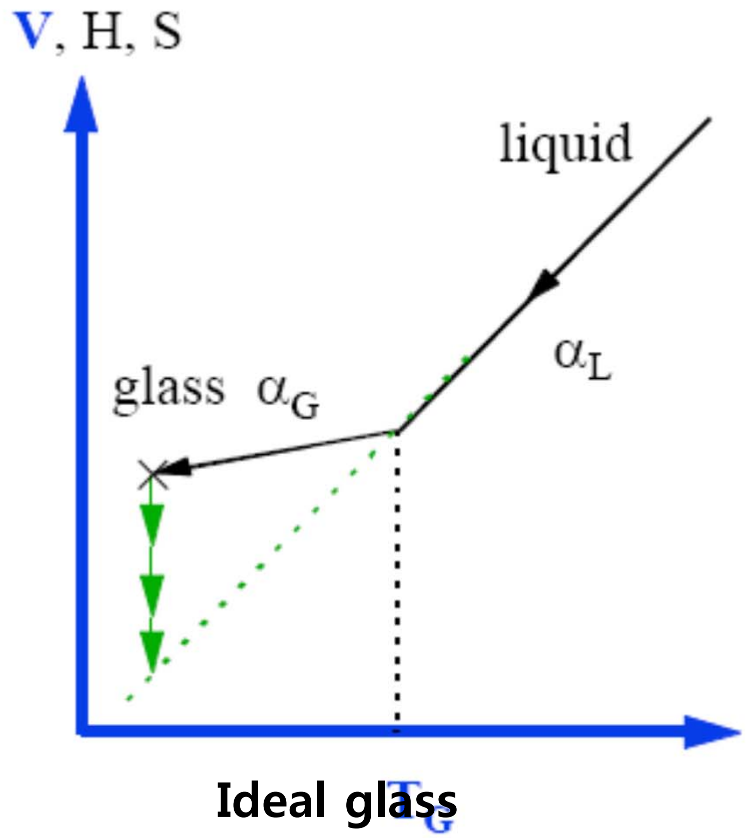
* T_g depends on thermal history even in same alloy composition.



* APL, 92 (2008) 091915.

* 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 $T < T_g$

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