2019 Fall

“Advanced Physical Metallurgy”

- Non-equilibrium Solidification -

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* Development strategy of completely new materials

a. Alloyed pleasures: Multi-metallic cocktails

b. Synthesize metastable phases

Equilibrium conditions → Non-equilibrium conditions

: non-equilibrium processing = “energize and quench” a material

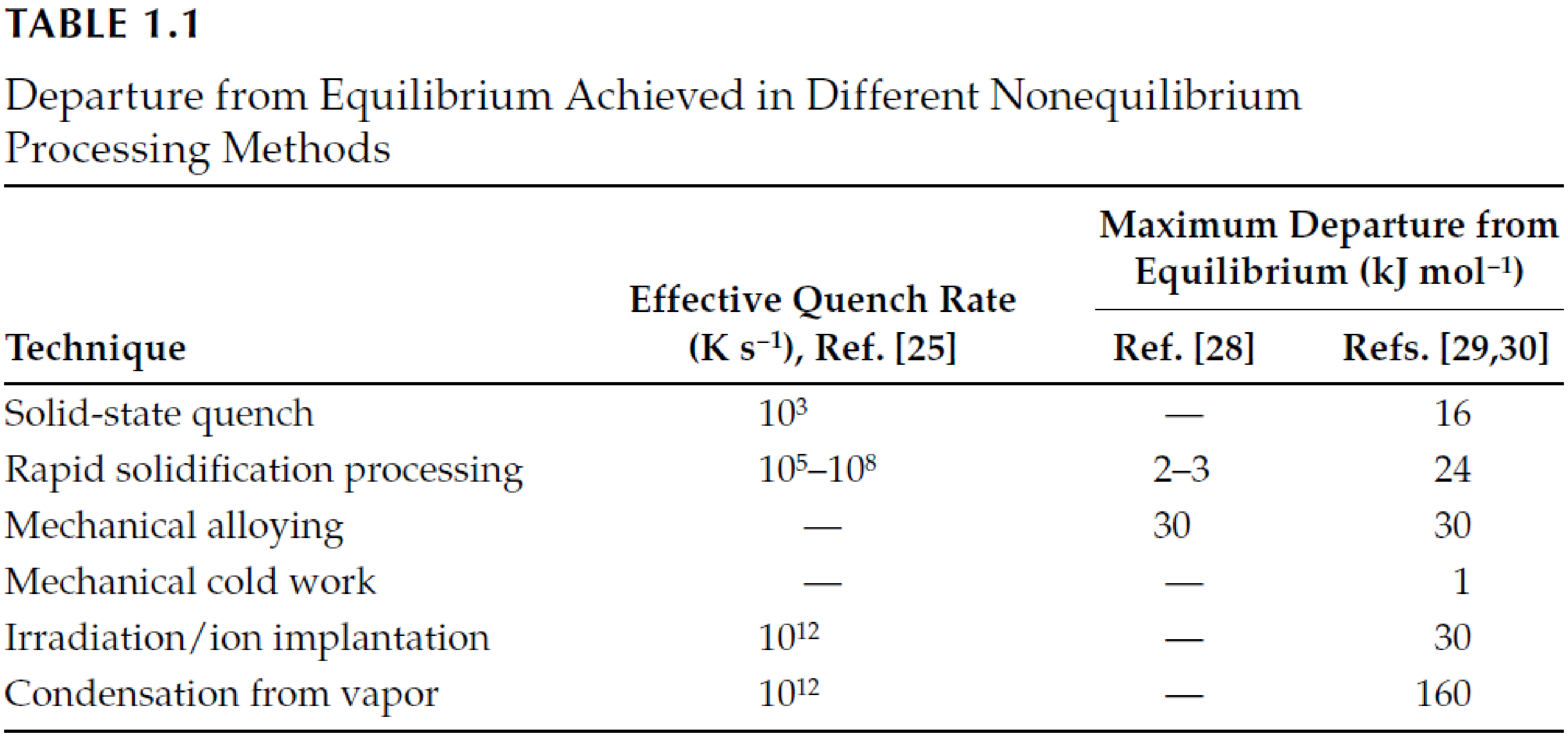


TABLE 1.1

Departure from Equilibrium Achieved in Different Nonequilibrium Processing Methods

Technique	Effective Quench Rate (K s^{-1}), Ref. [25]	Maximum Departure from Equilibrium (kJ mol^{-1}) Ref. [28]	Maximum Departure from Equilibrium (kJ mol^{-1}) Refs. [29,30]
Solid-state quench	10^3	—	16
Rapid solidification processing	10^5–10^8	2–3	24
Mechanical alloying	—	30	30
Mechanical cold work	—	—	1
Irradiation/ion implantation	10^{12}	—	30
Condensation from vapor	10^{12}	—	160

Classification of materials with structure

Perfect crystal → *disorder* (→ *quasicrystal*) → *amorphous*

: *unit cell*

: *underlying perfect crystalline lattice*

(a), (b), (c), (d)

Spin disorder

Vibrational disorder

ex) *icosahedral phase*

: *no topological ordering*

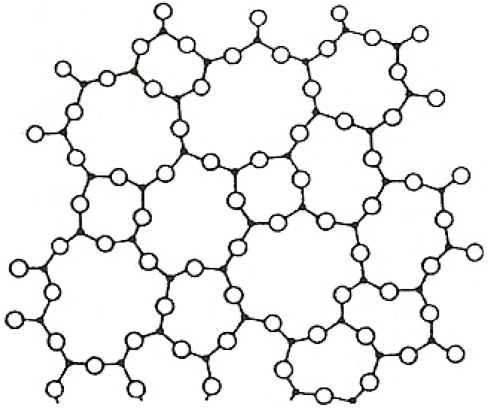
ex) *icosahedral glass*

(a) Topological disorder : various defects

(c) Substitutional disorder: Solid solution vs intermetallic compounds

➡ Hume-Rothery Empirical Rules for Alloys

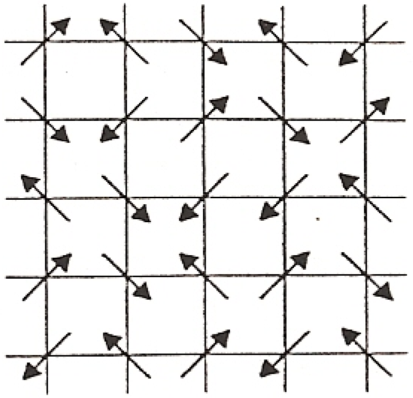
* Four types of disorder



a) Topological (or geometric) disorder

: no translational order at all

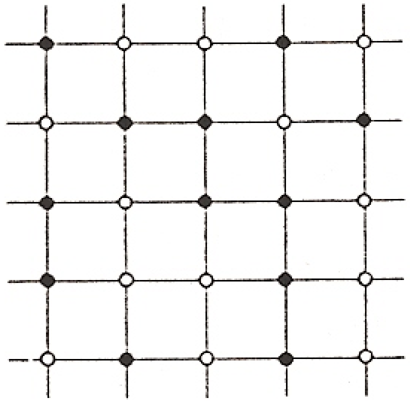
: but some degree of short range ordering



b) Spin disorder

: spin (or magnetic moment) exhibits random orientation.

: underlying perfect crystalline lattice

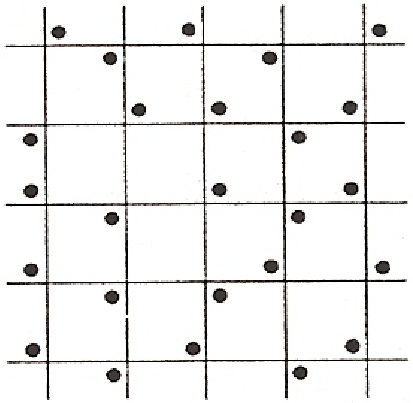


c) Substitutional disorder

: metallic alloy

: solid solution

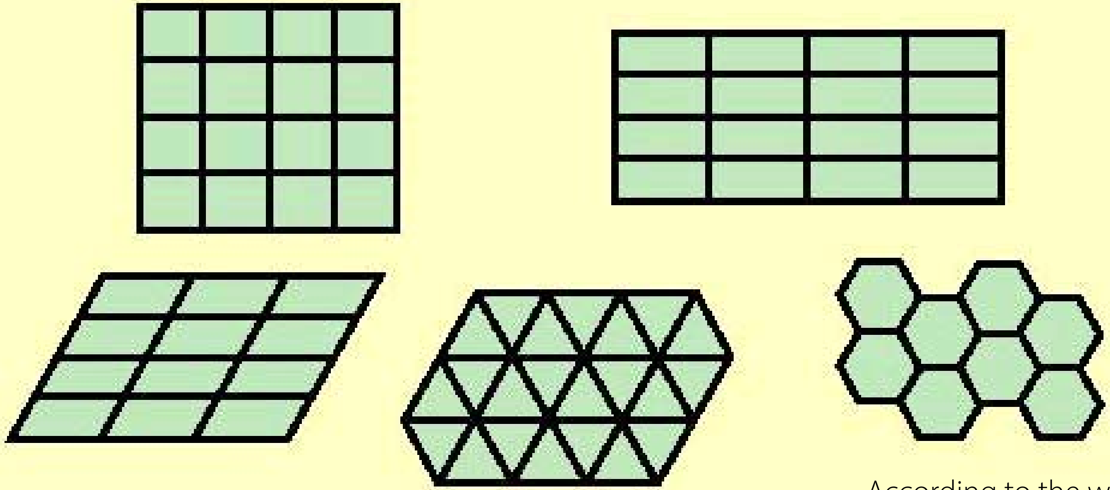
: underling perfect crystalline lattice



d) Vibrational disorder

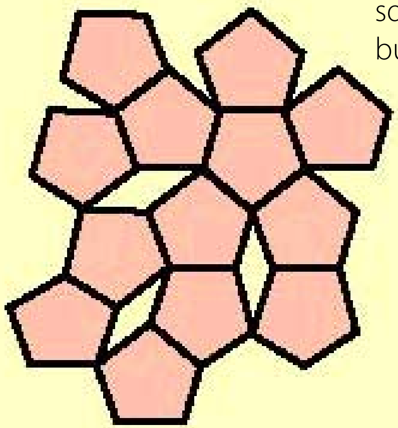
at any finite temperature the random motion of atoms about their equilibrium position destroys the perfect periodicity

QUASICRYSTALS VIOLATE
Theorems of Crystallography



Symmetry axes compatible
with periodicity

According to the well-known theorems of crystallography, only certain symmetries are allowed: the symmetry of a square, rectangle, parallelogram, triangle or hexagon, but not others, such as pentagons.



5-fold
Symmetry is
FORBIDDEN

QUASICRYSTALS

Similar to crystals, BUT…

- Orderly arrangement . . .
  But *QUASIPERIODIC* instead of *PERIODIC*

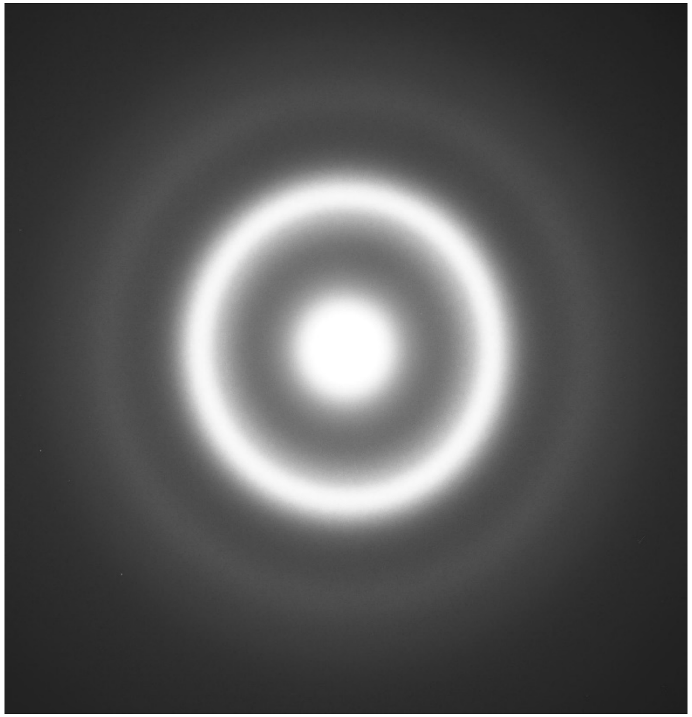
- Rotational Symmetry . . .
  But with *FORBIDDEN* symmetry

- Structure can be reduced to a finite number of repeating units

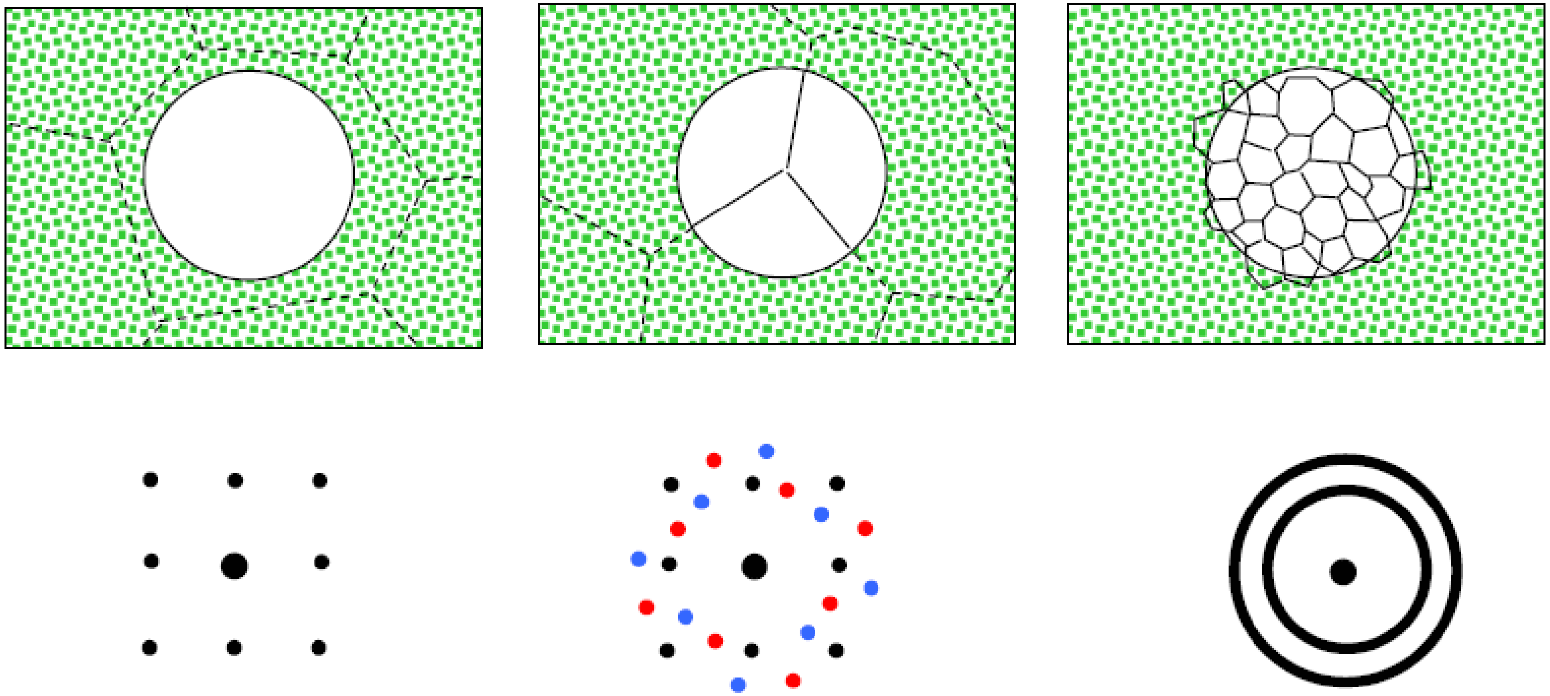
D. Levine and P.J. Steinhardt (1984)

Amorphous materials

- Diffused ring pattern
- Reflecting the short range ordered structure
- Often seen at contamination layer or on carbon support film

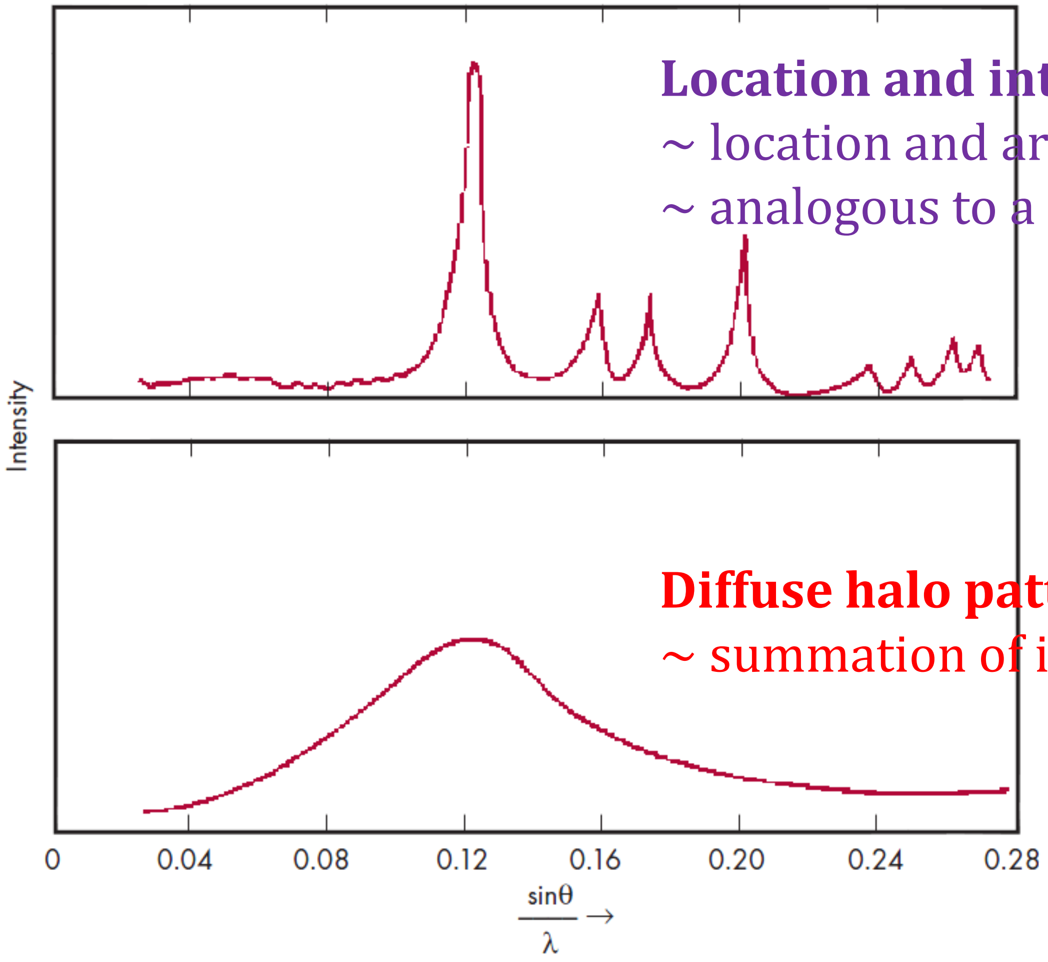


Electron Diffraction Pattern--Spot to Ring



(a) **(b)** **(c)**

X-ray or Neutron results



Location and intensity of peaks

~ location and arrangement of atoms

~ analogous to a fingerprint

Diffuse halo pattern

~ summation of interference

Figure 3. Characteristic Diffraction Patterns from Crystalline Material (Top) and Amorphous Material (Bottom).

Fundamentals of the Glass Transition

If liquid is cooled, two events can occur.

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

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

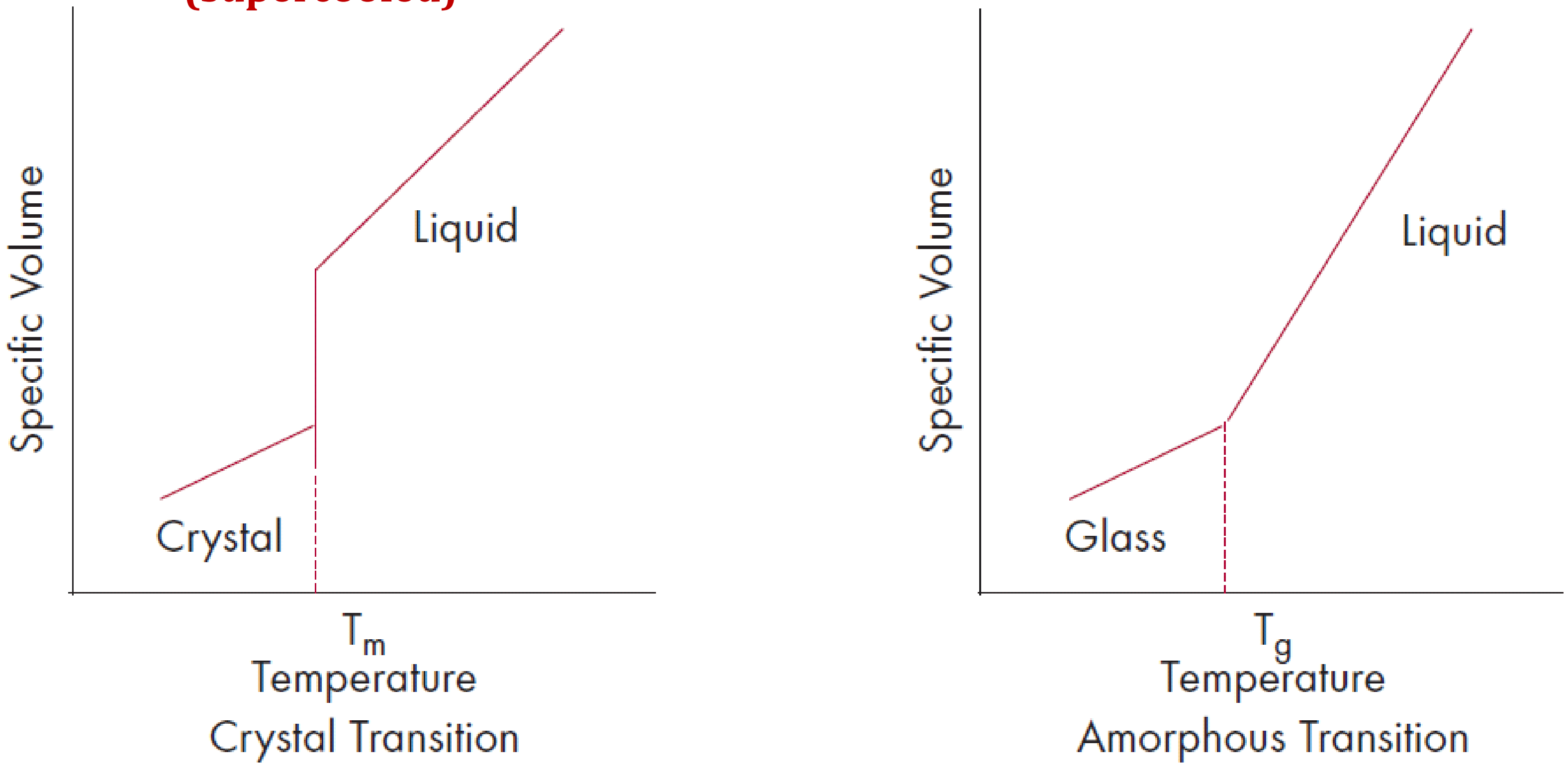


Figure 4. Liquid-Crystalline Solid Transition (Left) and Liquid-Glass Transition (Right).

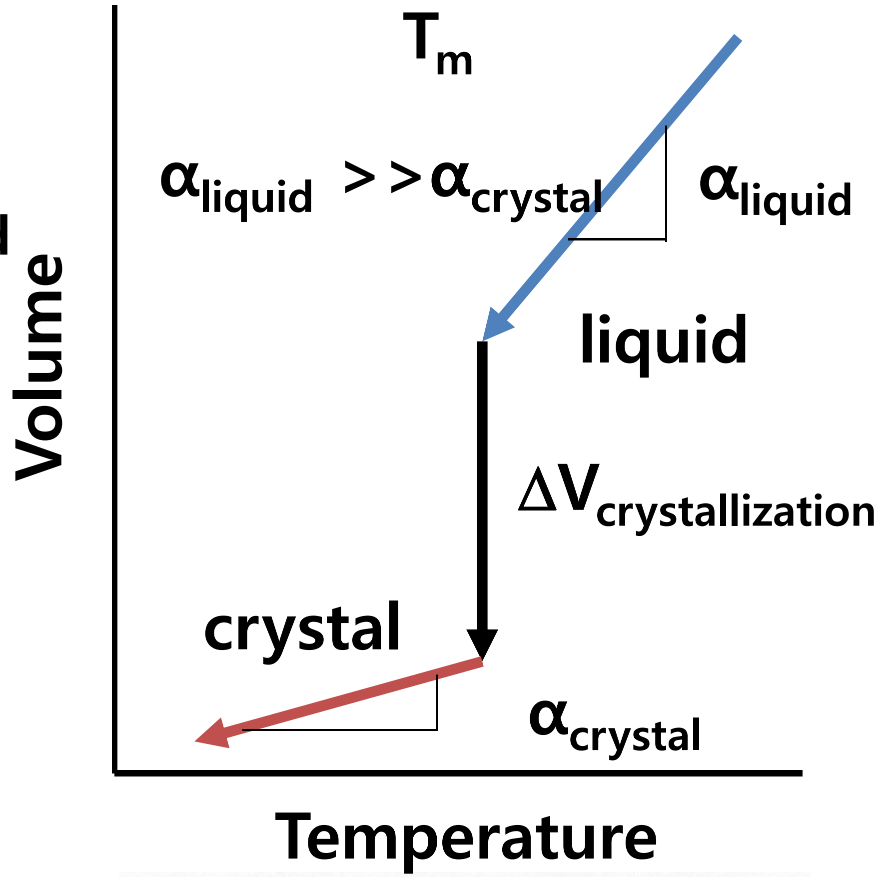
Fundamentals of the Glass Transition

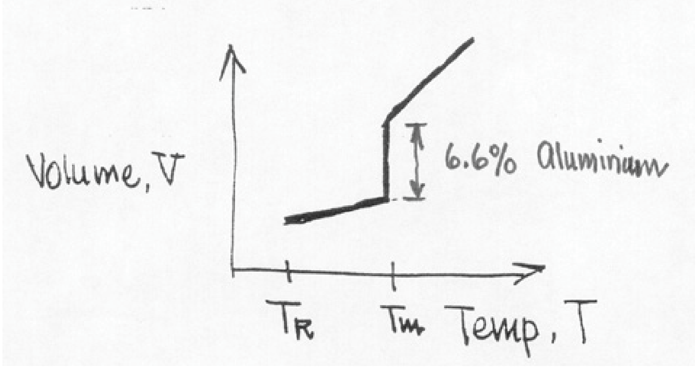
- **Melting and Crystallization are Thermodynamic Transitions**
  - Discontinuous changes in structure and properties at T_m
  - Structures are thermodynamically controlled and described by the Phase Diagram
  - $T_{melting}$ and $T_{liquidus}$ have fixed and specific values, 1710 ^oC for SiO_2, for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

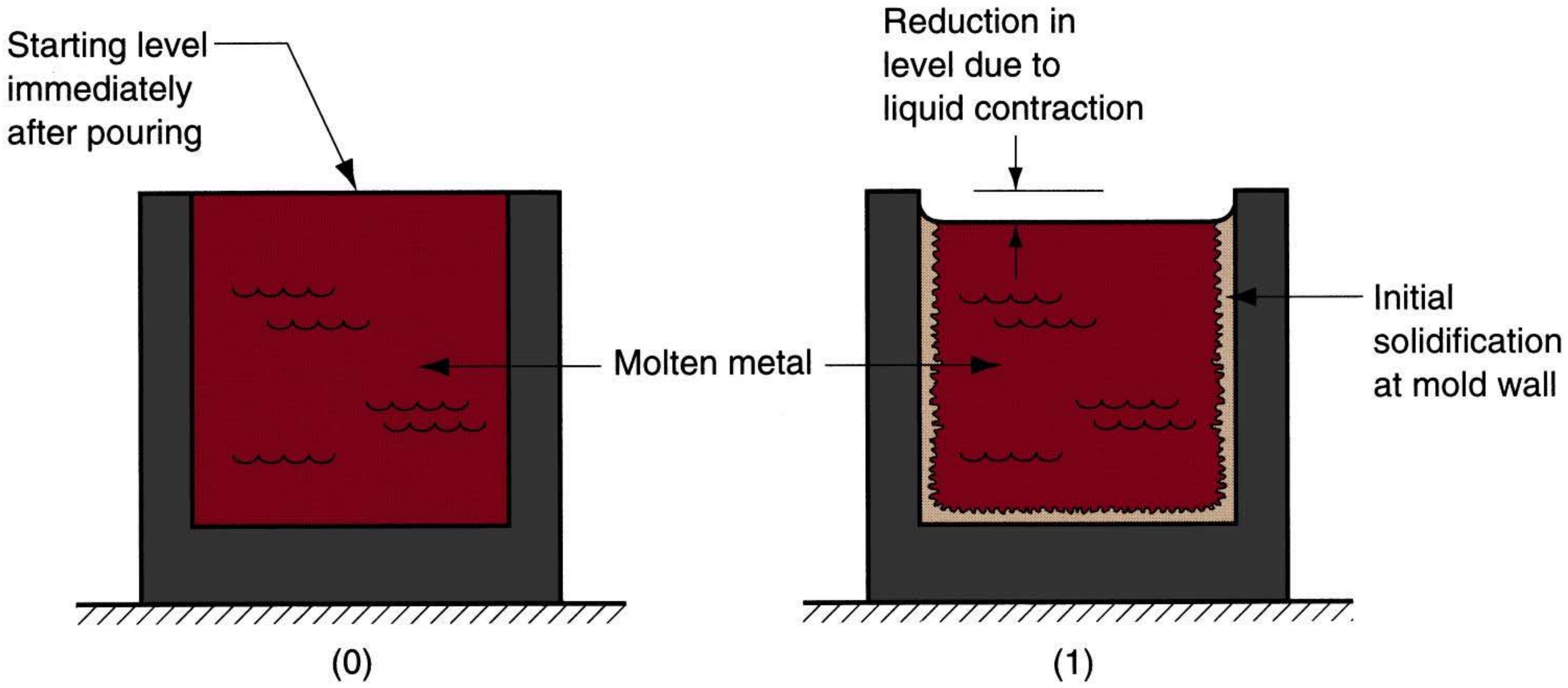
Crystallization is Controlled by Thermodynamics

- 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



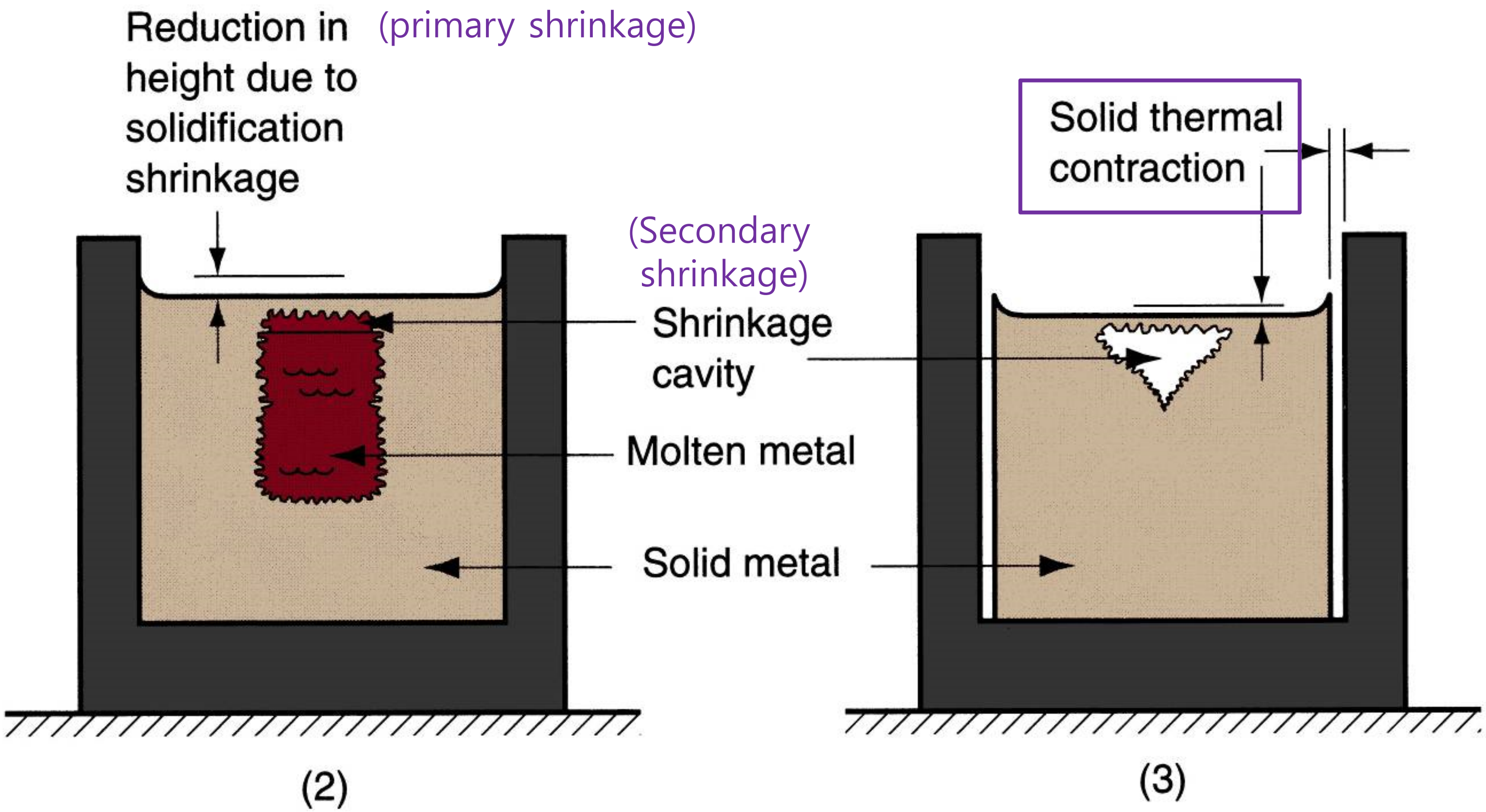


Shrinkage in Solidification and Cooling



* Shrinkage of a cylindrical casting during solidification and cooling: (0) starting level of molten metal immediately after pouring; (1) reduction in level caused by liquid contraction during cooling (dimensional reductions are exaggerated for clarity).

Shrinkage in Solidification and Cooling



* (2) reduction in height and formation of shrinkage cavity caused by solidification shrinkage; (3) further reduction in height and diameter due to thermal contraction during cooling of solid metal (dimensional reductions are exaggerated for clarity).

Shrinkage effect

* Formation of Voids during solidification

Central shrinkage:

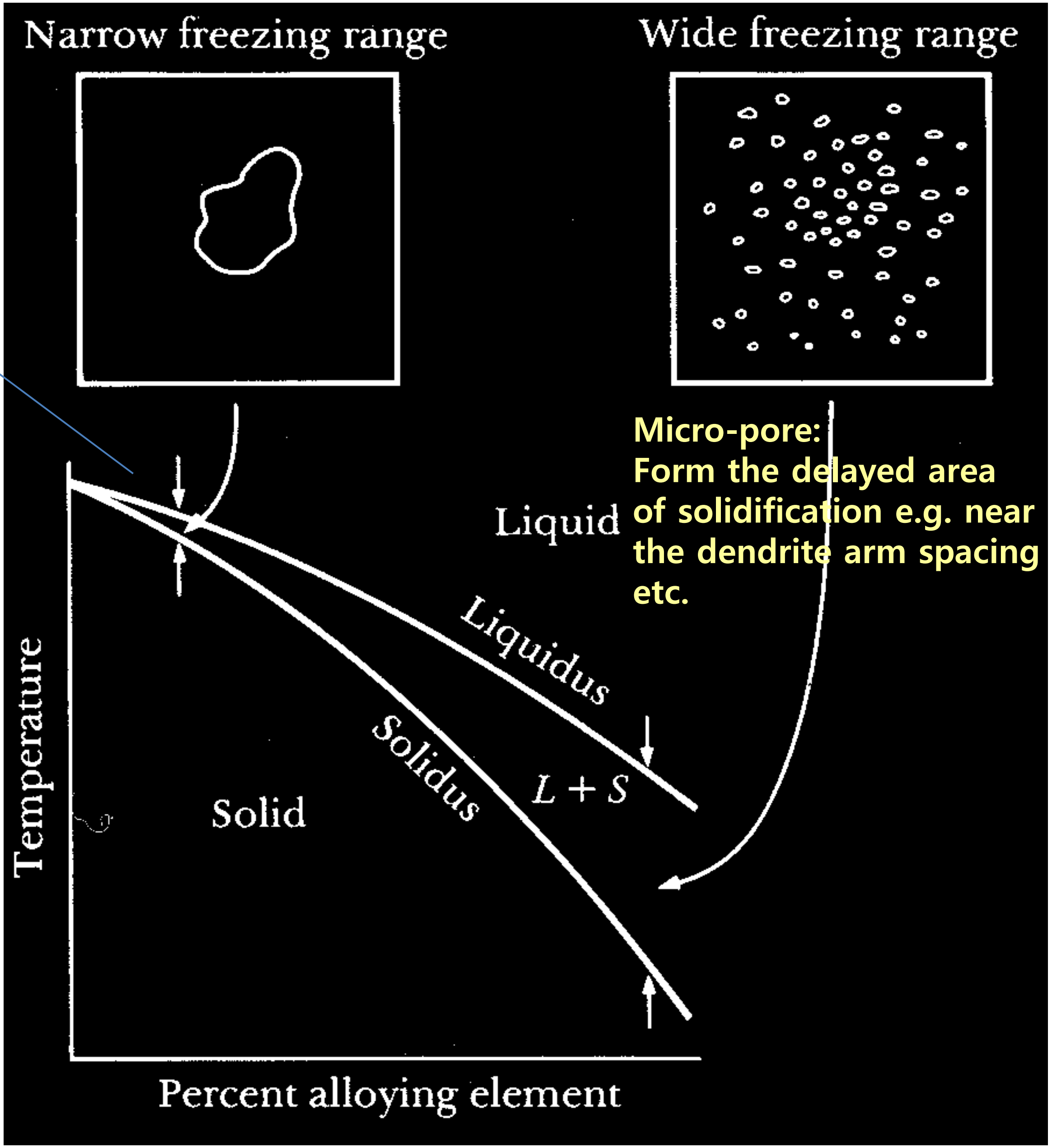
조성 변화가 크지 않은 주물의 응고 시 주로 응고수축, ΔV 에 의해 발생하는 주물 중심부에 발생

Dispersed Micro-Pore:

상당히 넓은 범위에 분산된 미소기공

외부수축 (몰드 주위) 및 1차수축공 (표면)을 제외하면, 이러한 수축공 결함은 주로 기포 결함임

기포 내에는 철합금에서는 CO, 질소, 산소, 수소 등이, 동합금에서는 수소, 산소, 알루미늄 합금에서는 수소 등의 가스가 존재



Micro-pore: Form the delayed area of solidification e.g. near the dendrite arm spacing etc.

Shrinkage in Solidification and Cooling

- Can amount to 5-10% by volume
- Gray cast iron expands upon solidification due to phase changes
- Need to design part and mold to take this amount into consideration

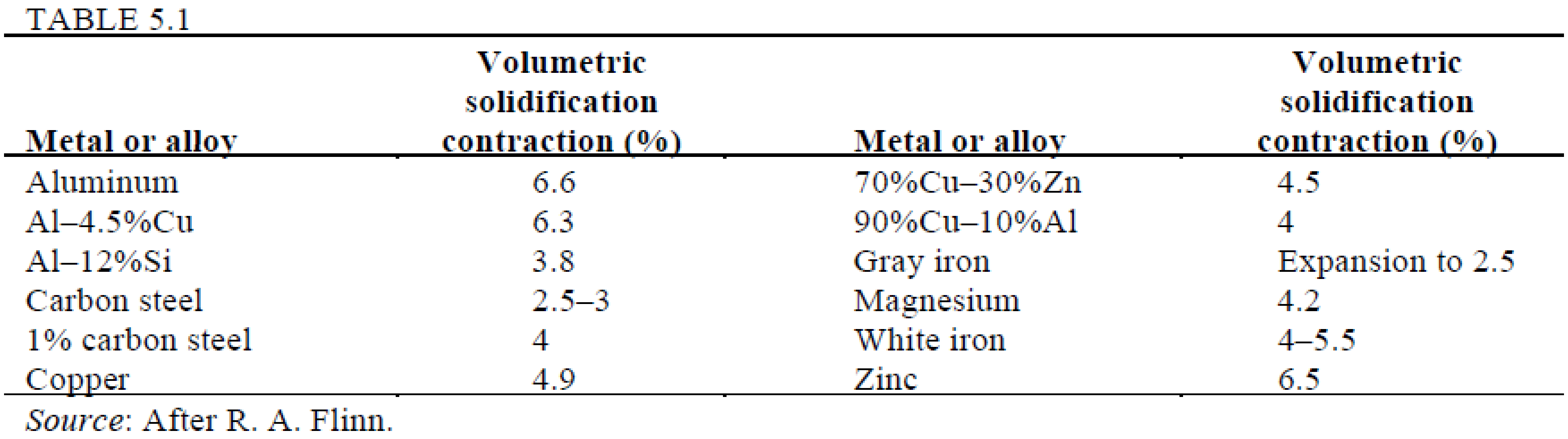


TABLE 5.1

Metal or alloy	Volumetric solidification contraction (%)	Metal or alloy	Volumetric solidification contraction (%)
Aluminum	6.6	70%Cu–30%Zn	4.5
Al–4.5%Cu	6.3	90%Cu–10%Al	4
Al–12%Si	3.8	Gray iron	Expansion to 2.5
Carbon steel	2.5–3	Magnesium	4.2
1% carbon steel	4	White iron	4–5.5
Copper	4.9	Zinc	6.5

Source: After R. A. Flinn.

*** Volumetric solidification expansion: H_2O (10%), Si (20%), Ge**

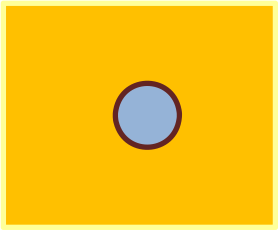
ex) Al-Si eutectic alloy (casting alloy)→ volumetric solidification contraction of Al substitutes volumetric solidification expansion of Si.

Cast Iron: Fe + Carbon (~ 4%) + Si (~2%)

→ precipitation of graphite during solidification reduces shrinkage.

Melting and Crystallization are Thermodynamic Transitions

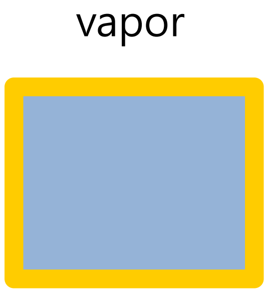
Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

No superheating required!



- Interfacial energy ⇨ No ΔT_N

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

Melting: Liquid ← Solid

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

Homogeneous Nucleation

Driving force for solidification

$G^L = H^L - TS^L$

$G^S = H^S - TS^S$

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

$L : \Delta H = H^L - H^S$

(Latent heat)

$T = T_m - \Delta T$

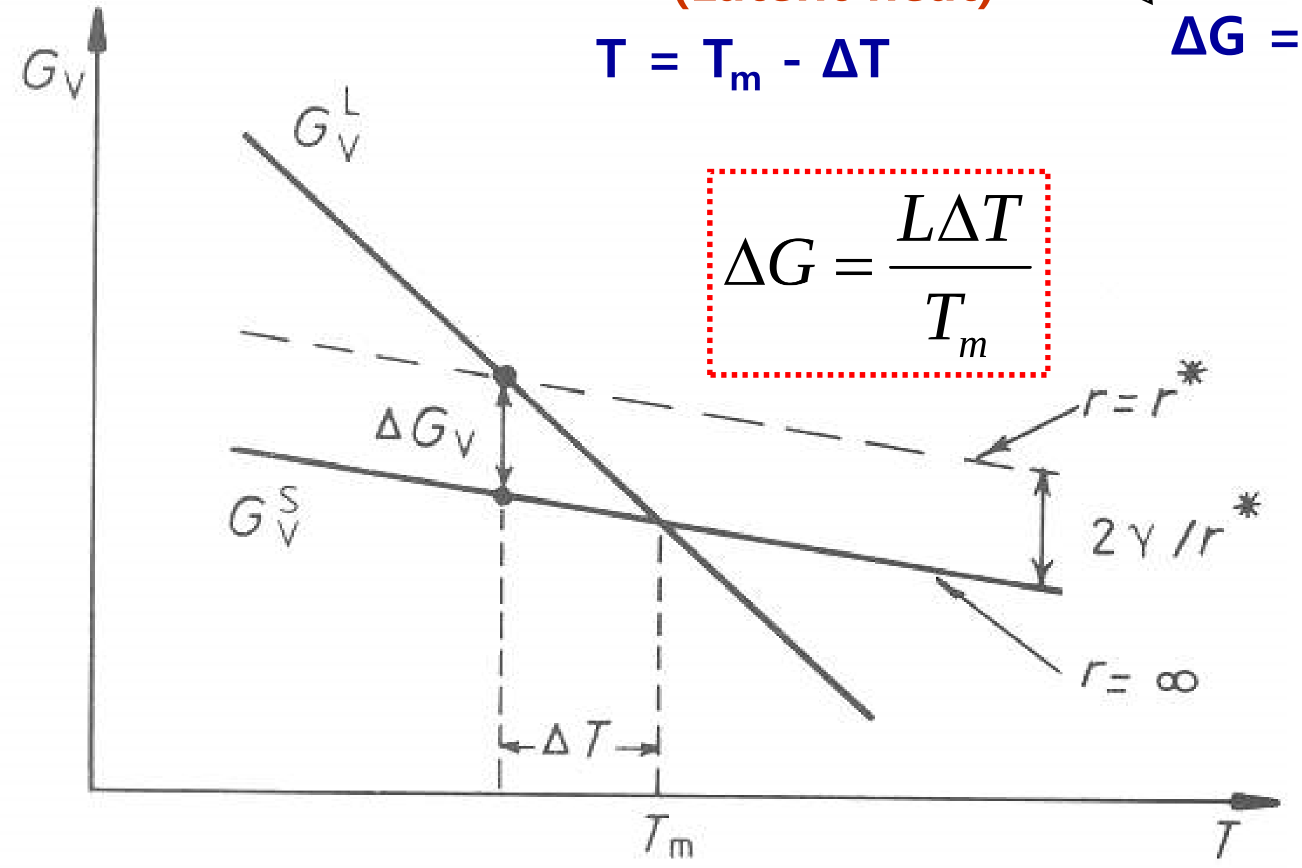
$\Delta G = 0 = \Delta H - T_m \Delta S$

$\Delta S = \Delta H / T_m = L / T_m$

$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$

$$\boxed{\Delta G = \frac{L\Delta T}{T_m}}$$

,



* Quasi-chemical approach

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

- 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 <u>one with 4 percent less E</u>,

although bond energy of liquid is changed by the positions.

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

4.1.4. Nucleation of melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

Why?

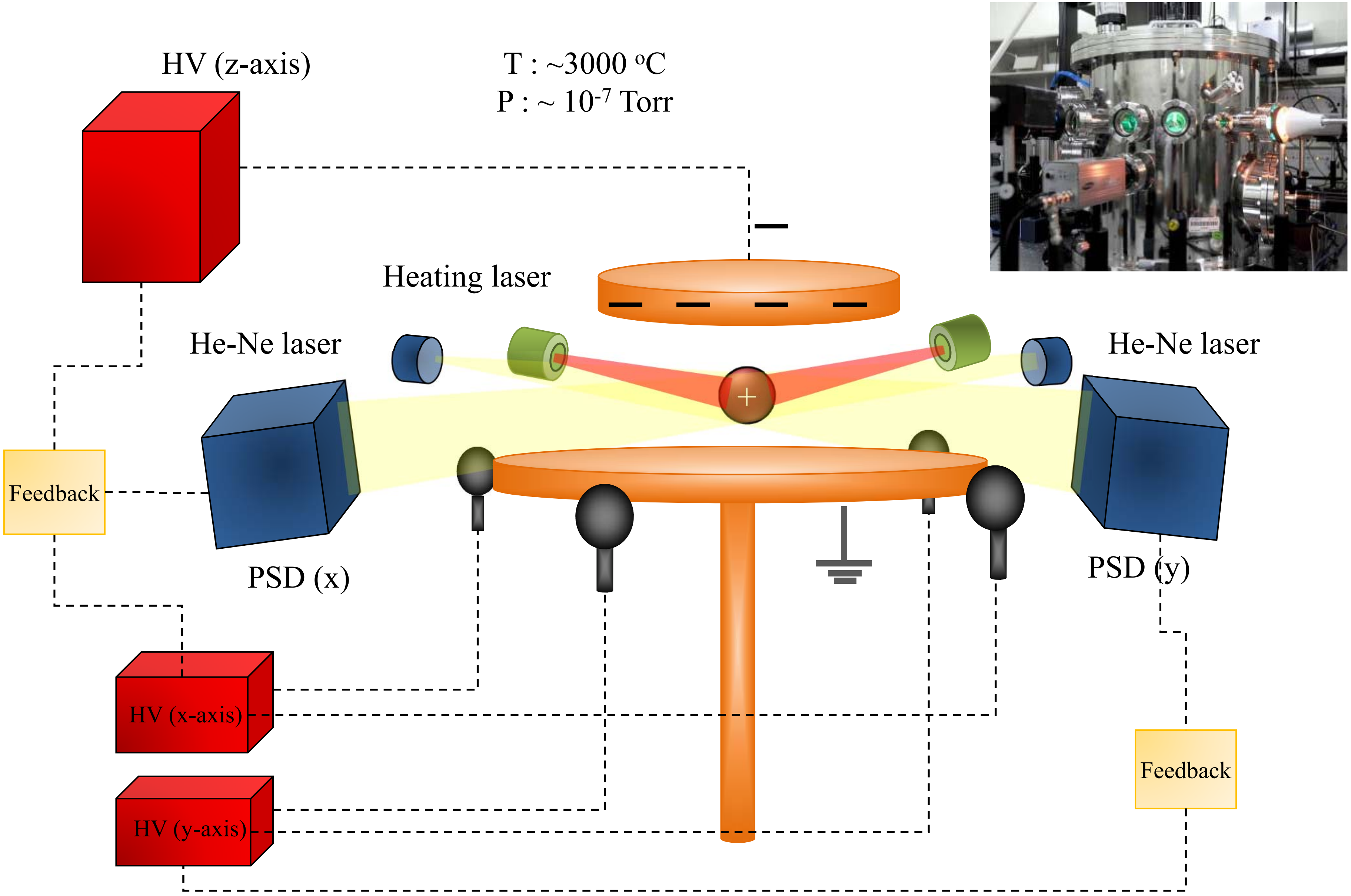
개념적으로 생각해보면

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$ (commonly)

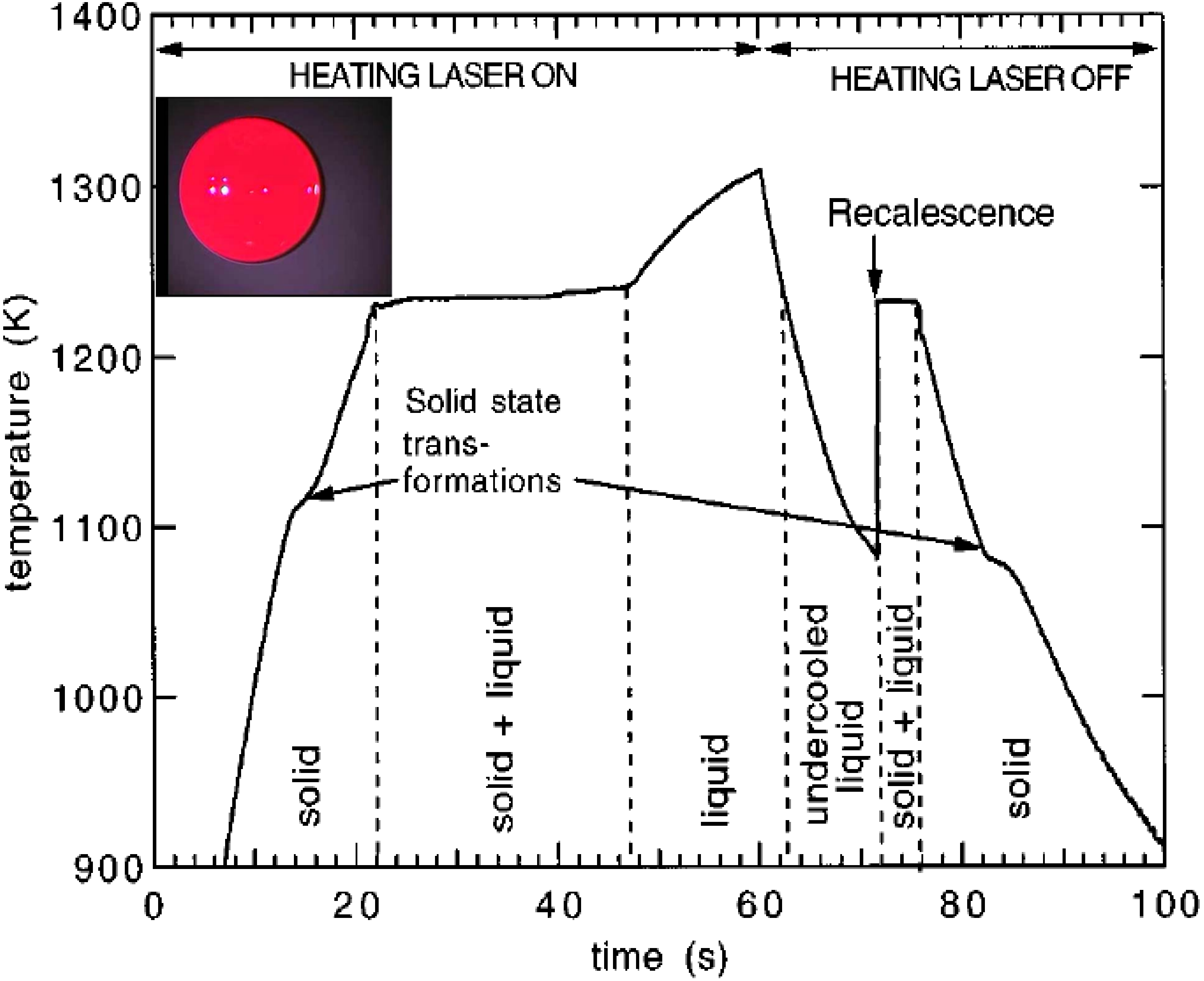
Solid -> liquid 로 원자 떼어내는 데 드는 힘 + Liquid-> Vapor 로 원자 떼어내는 데 드는 힘 < Solid-> Vapor 로 원자 떼어내는 데 드는 힘

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

Electrostatic levitation in KRISS



KRISS material : Dr. G.W.Lee


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

* Comparison between experiment and theory

Most metal ΔT_N < several K

but Turnbull and his coworker $\Delta T_N \rightarrow$ larger (~several hundreds K)

by formation of large number of very small drops

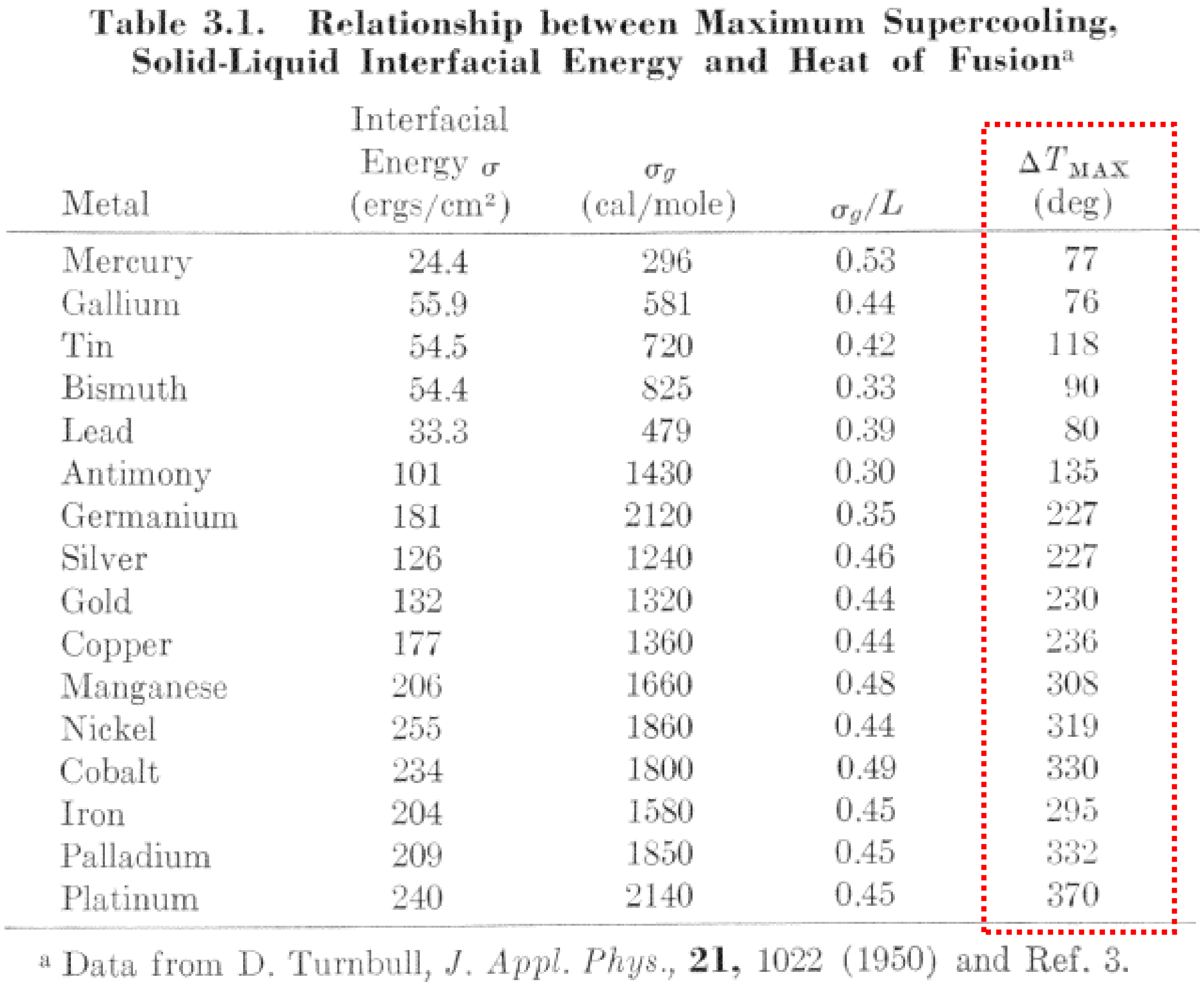


Table 3.1. Relationship between Maximum Supercooling, Solid-Liquid Interfacial Energy and Heat of Fusion[a]

Metal	Interfacial Energy σ (ergs/cm^2)	σ_g (cal/mole)	σ_g/L	ΔT_{MAX} (deg)
Mercury	24.4	296	0.53	77
Gallium	55.9	581	0.44	76
Tin	54.5	720	0.42	118
Bismuth	54.4	825	0.33	90
Lead	33.3	479	0.39	80
Antimony	101	1430	0.30	135
Germanium	181	2120	0.35	227
Silver	126	1240	0.46	227
Gold	132	1320	0.44	230
Copper	177	1360	0.44	236
Manganese	206	1660	0.48	308
Nickel	255	1860	0.44	319
Cobalt	234	1800	0.49	330
Iron	204	1580	0.45	295
Palladium	209	1850	0.45	332
Platinum	240	2140	0.45	370

[a] Data from D. Turnbull, *J. Appl. Phys.*, **21**, 1022 (1950) and Ref. 3.

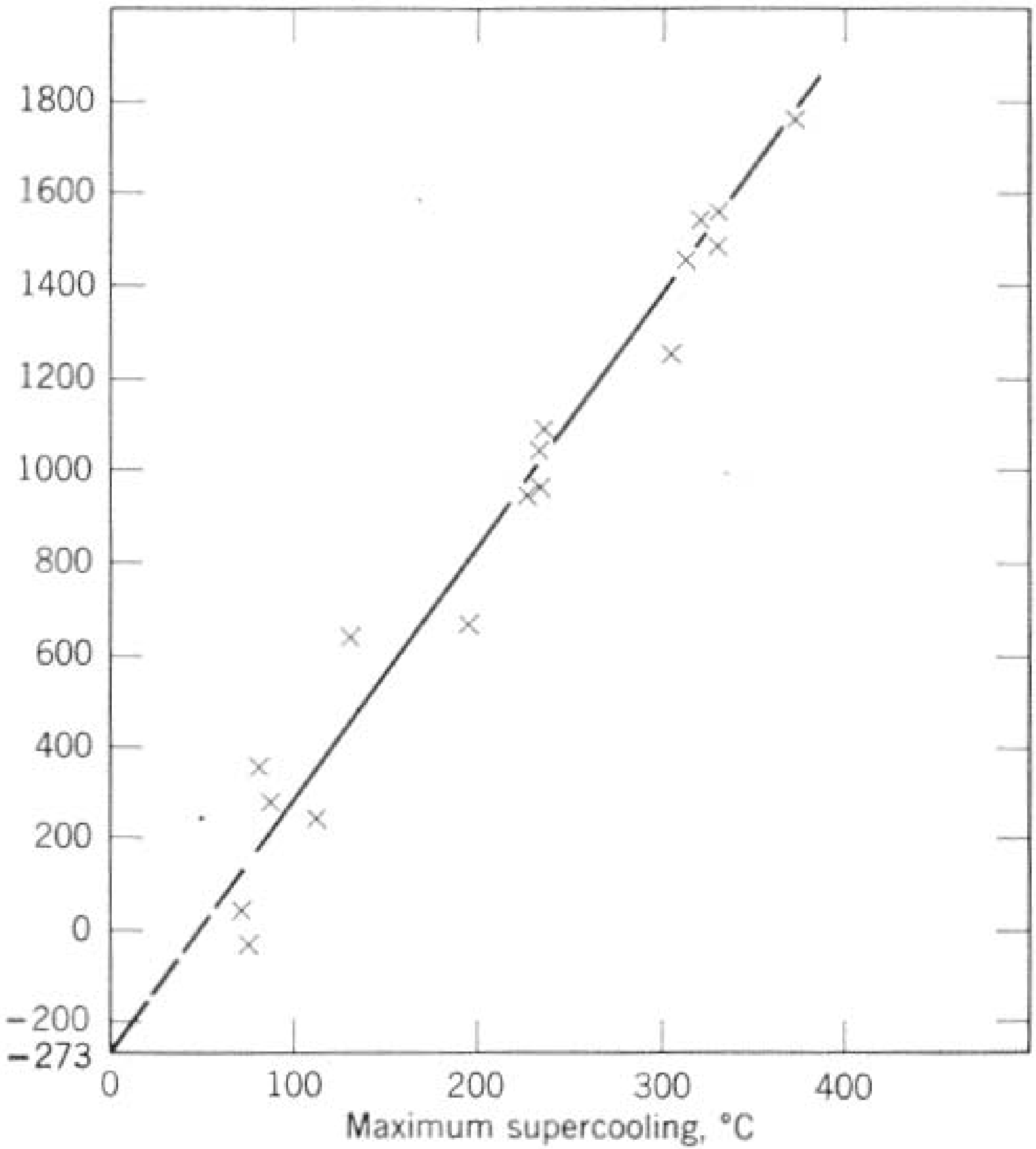
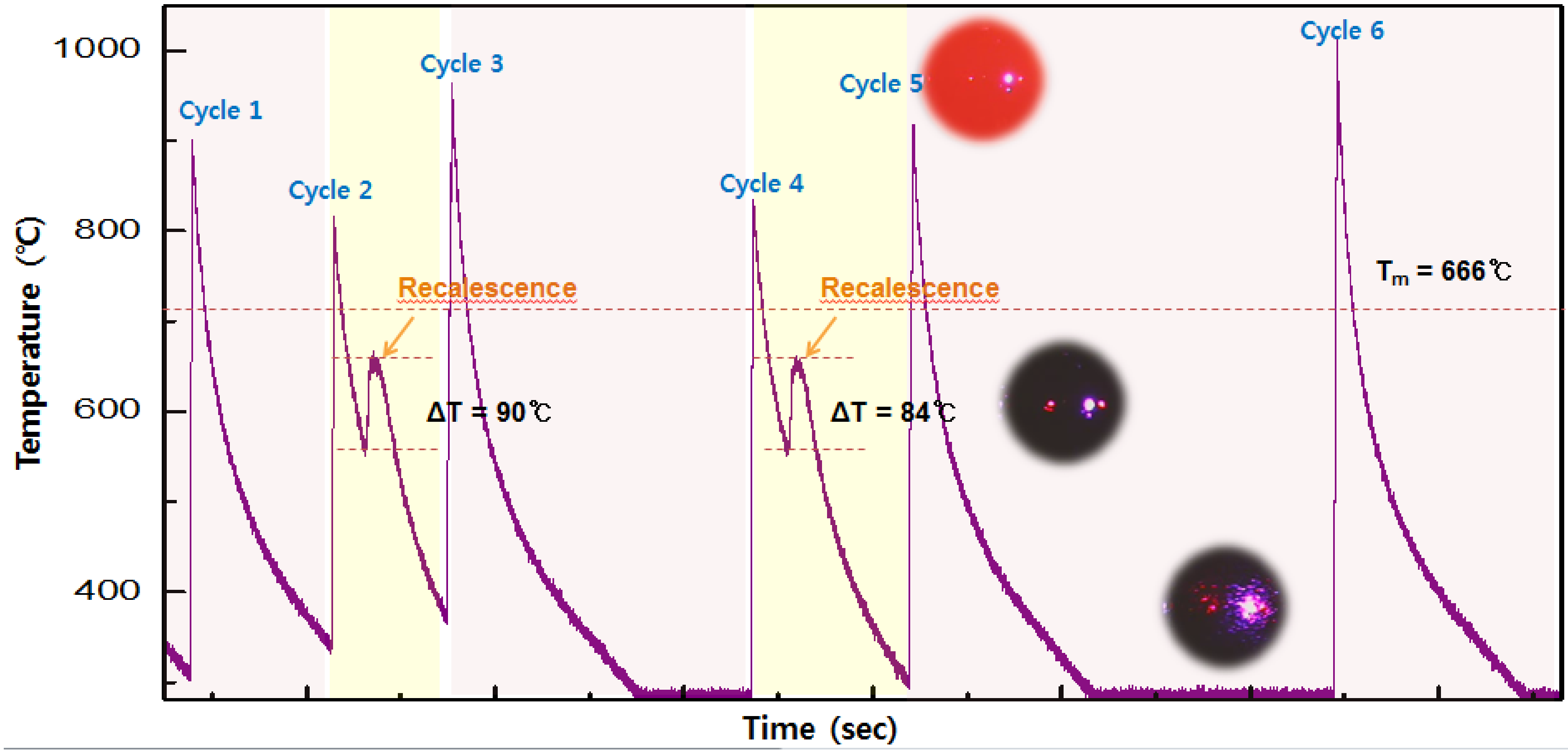


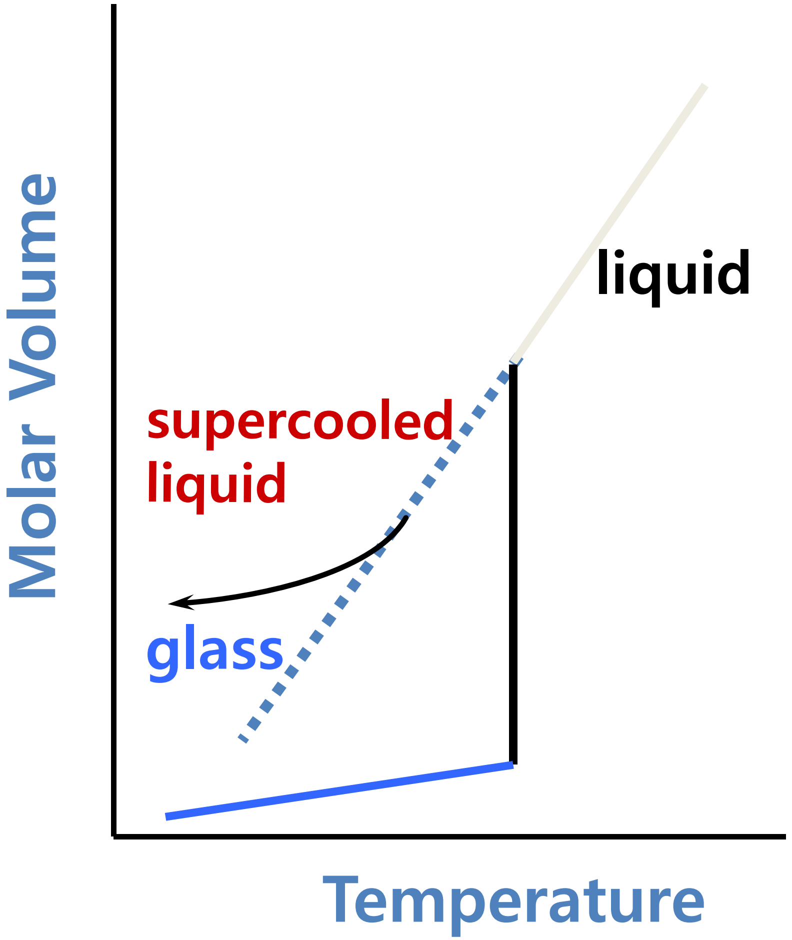
Fig. 3.7. Maximum supercooling as a function of melting point. (From *Thermodynamics in Physical Metallurgy*, American Society for Metals, Cleveland, 1911, p. 11.)

Cyclic cooling curves in ESL



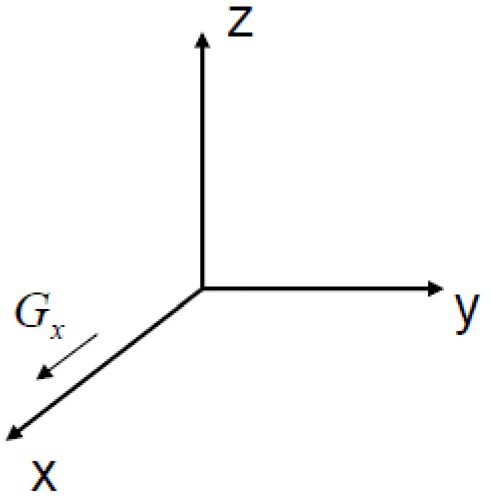
Glass Formation is Controlled by Kinetics

- 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: 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.**

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:

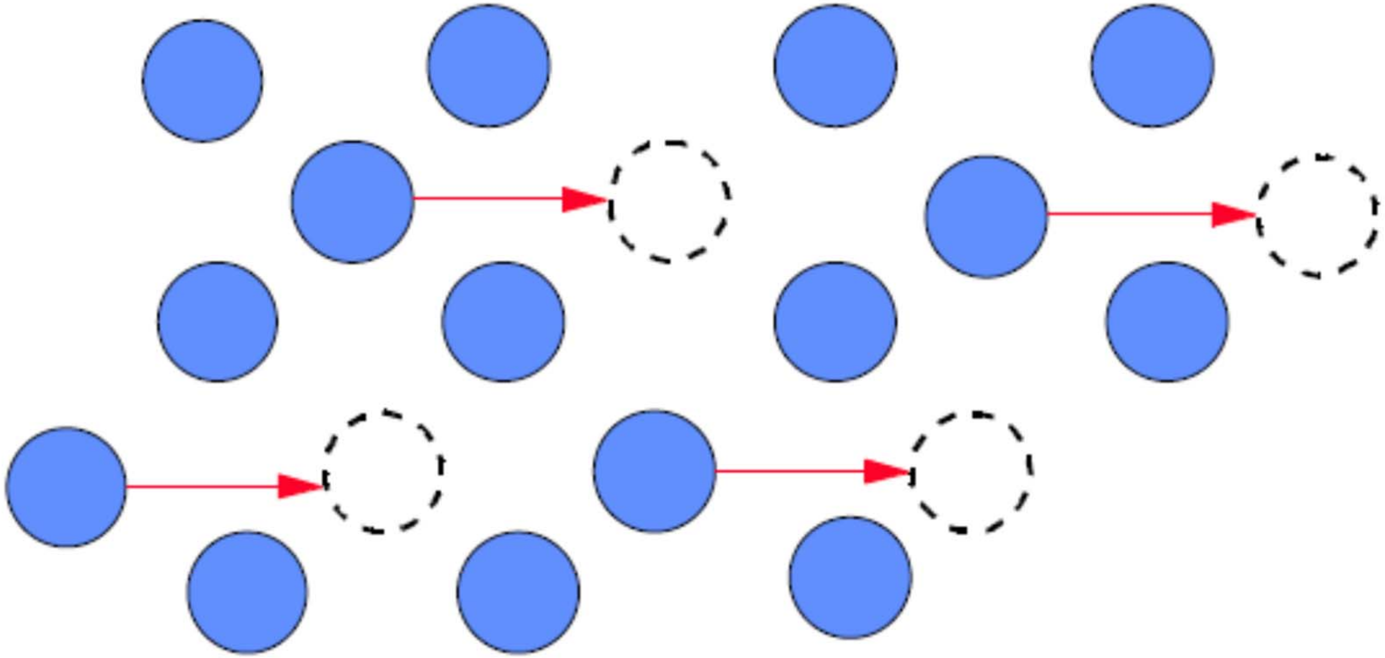
$$1\ \text{P} = 0.1\ \text{Pa s} \tag{2.1}$$

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:

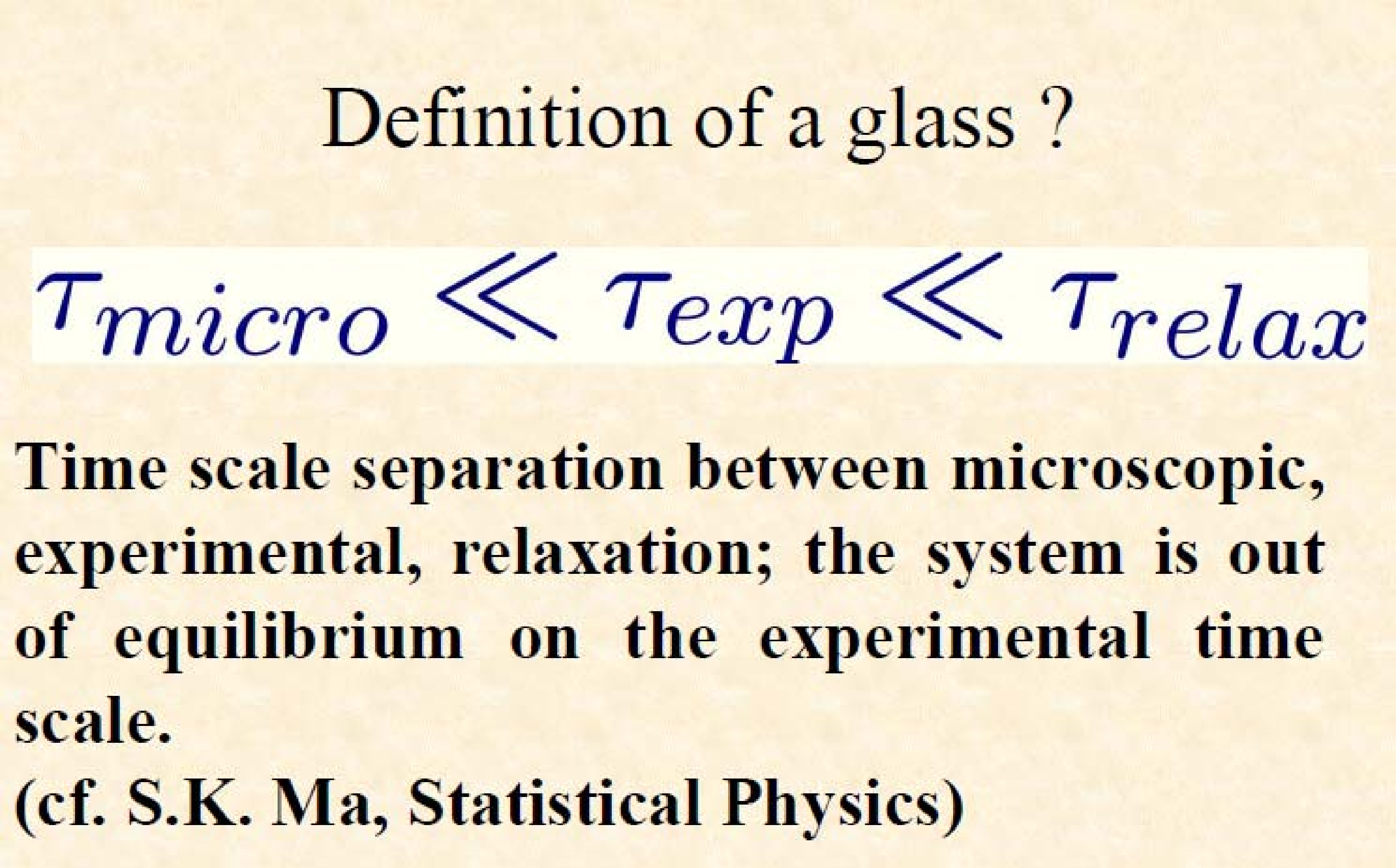
Water at 20°C	1.002 cP (1.002×10^{-3} Pa s)
Mercury at 20°C	1.554 cP (1.554×10^{-3} Pa s)
Pancake syrup at 20°C	2,500 cP (2.5 Pa s)
Peanut butter at 20°C	250,000 cP (250 Pa s)
Soda glass at 575°C	1×10^{15} cP (1×10^{12} Pa s)

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.

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 oneanother, the lower the resistance to flow.



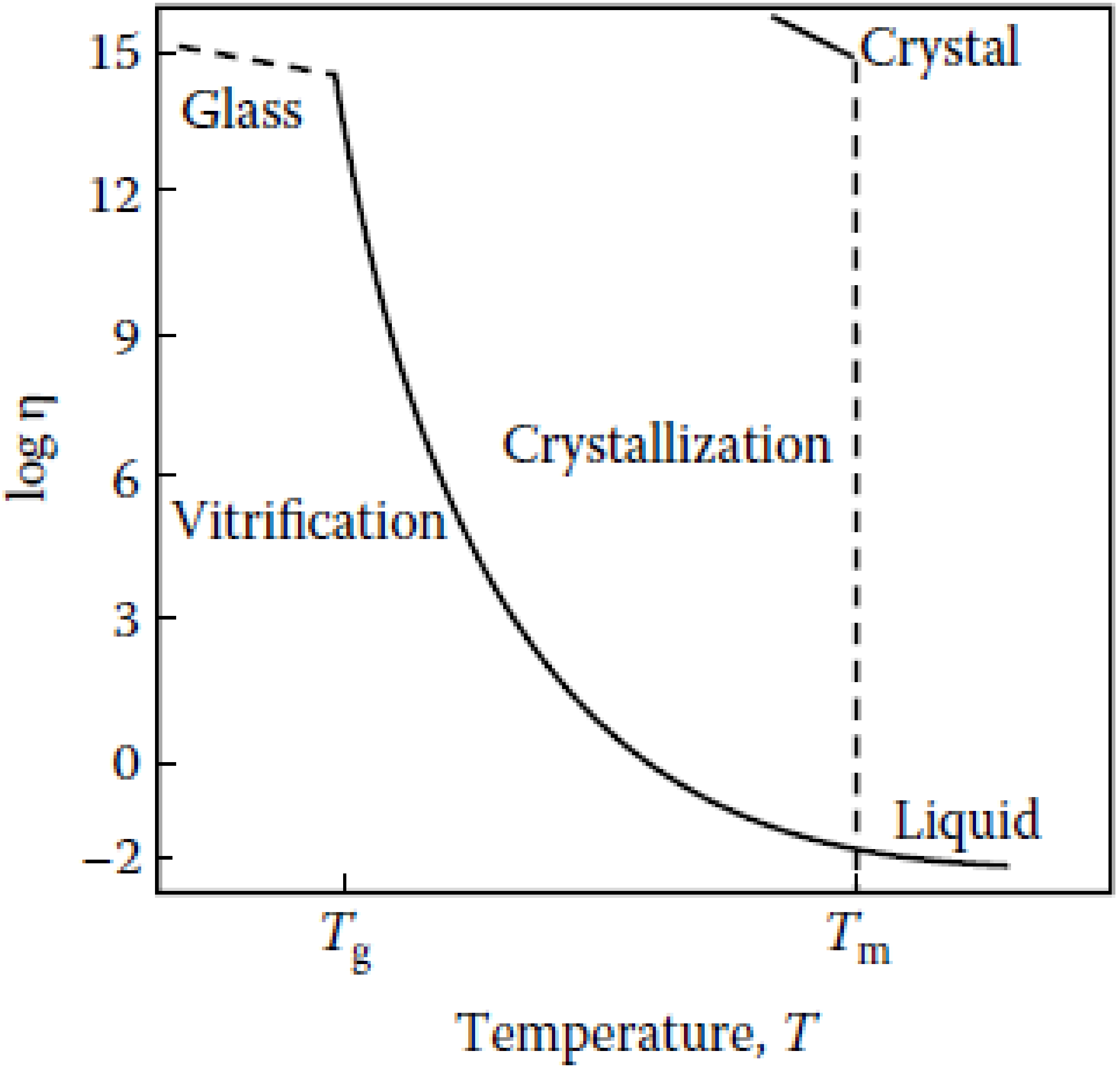
Definition of a glass ?

$$\tau_{micro} \ll \tau_{exp} \ll \tau_{relax}$$

Time scale separation between microscopic, experimental, relaxation; the system is out of equilibrium on the experimental time scale.
(cf. S.K. Ma, Statistical Physics)

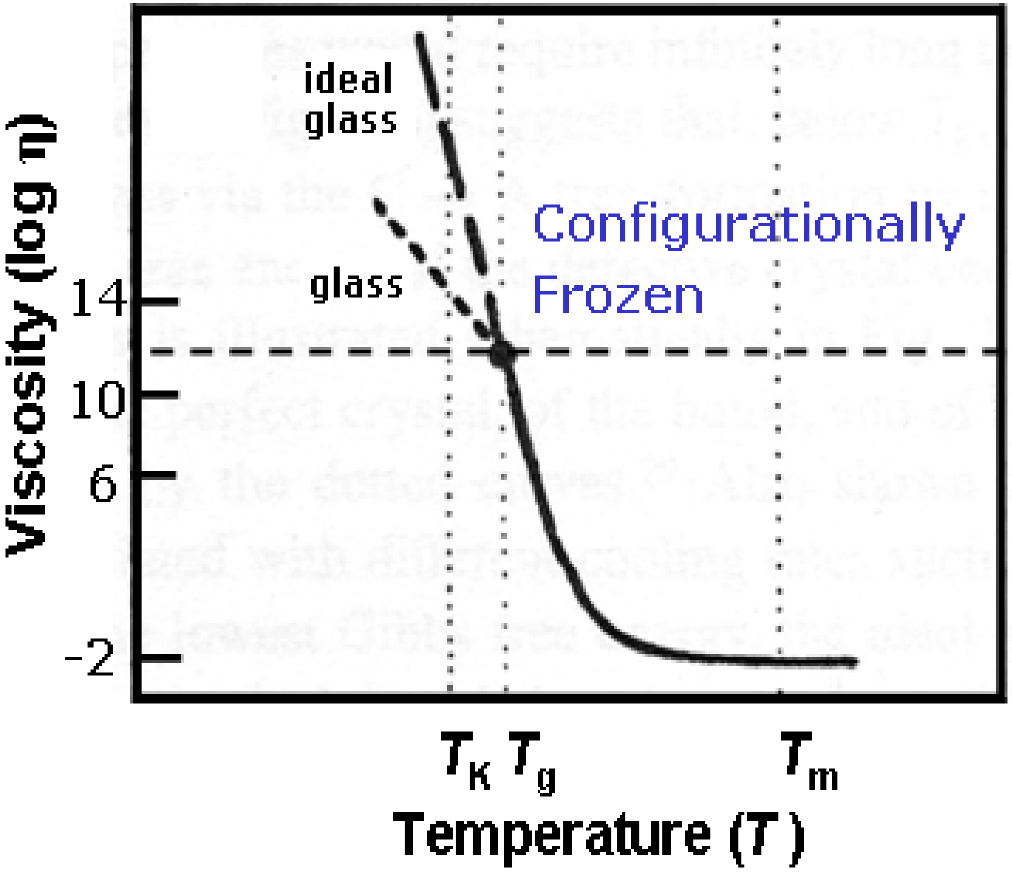
Microscopic time: time for events at sub-atomic distance and duration

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.

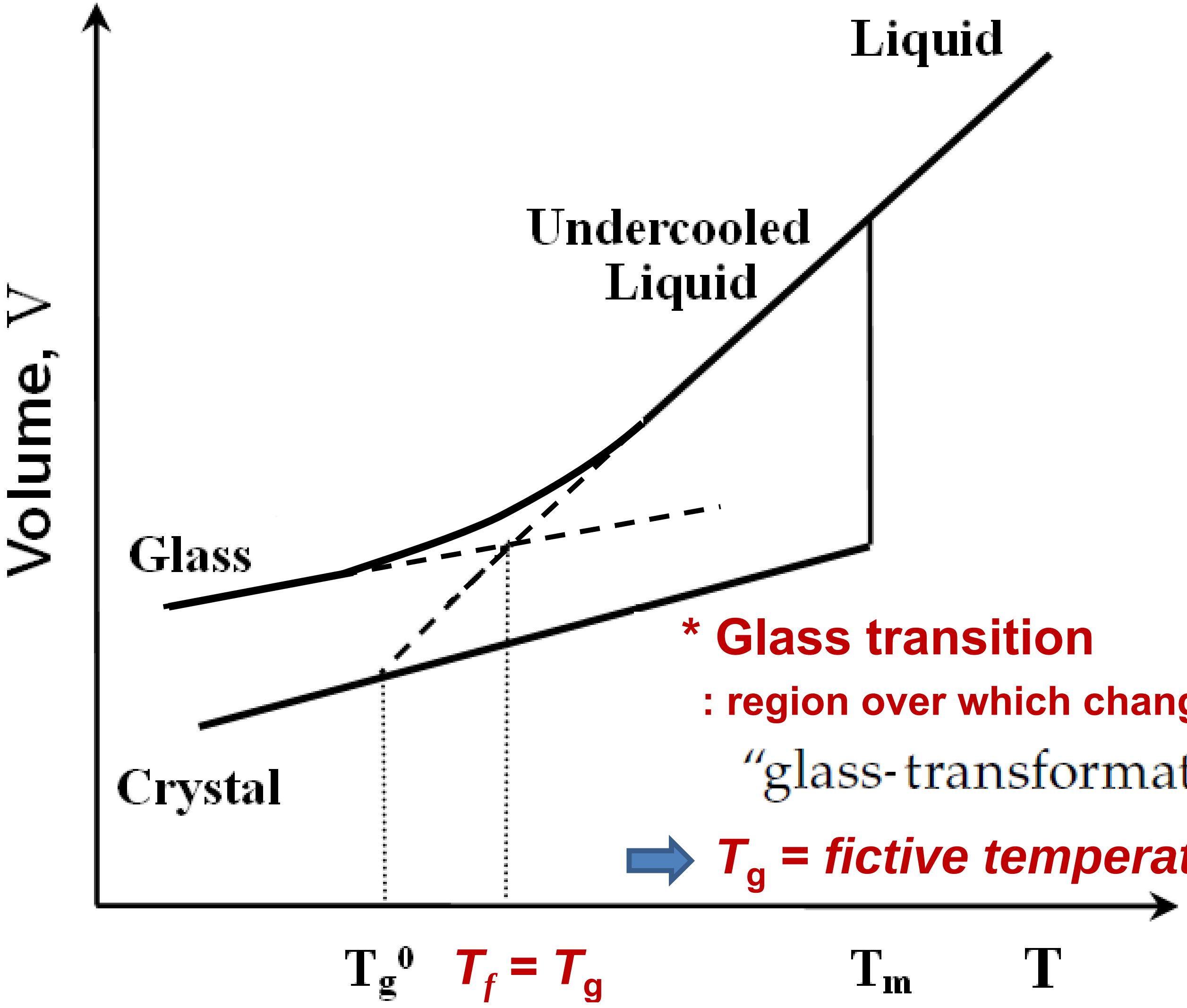


A solid is a materials whose viscosity exceeds $10^{14.6}$ centiPoise (10^{12} Pa s)

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. Eventually, homogeneously frozen at T_g.



*** Glass transition**

: region over which change of slope occurs

“glass-transformation interval.”

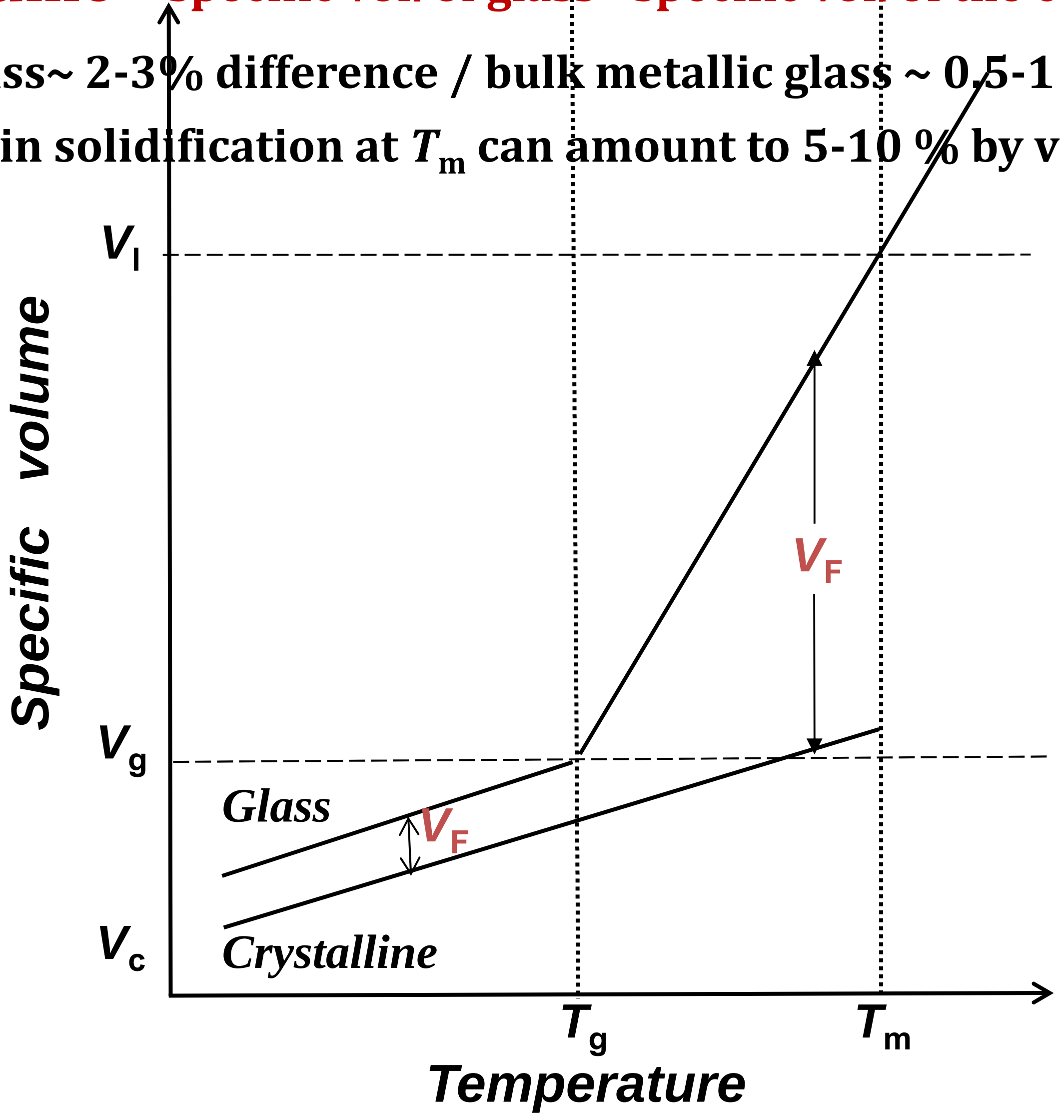
⇨ *T_g = fictive temperature, T_f*

thermodynamic property ?

thermodynamic property

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

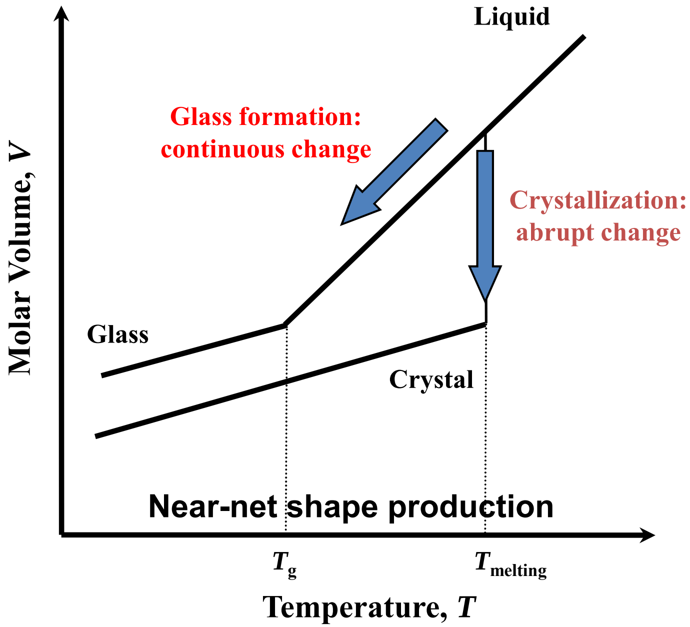
- **normal glass~ 2-3% difference / bulk metallic glass ~ 0.5-1 % difference**
- **Shrinkage in solidification at T_m can amount to 5-10 % by volume.**



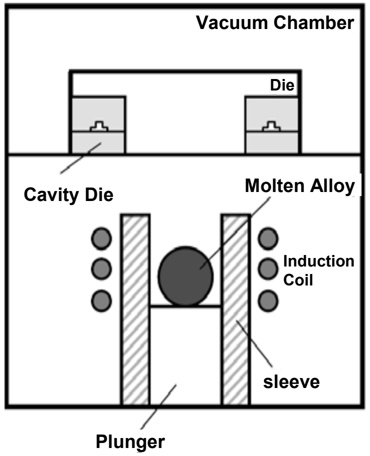
At the glass transition temperature, T_g, the free volume increases leading to atomic mobility and liquid-like behavior.

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

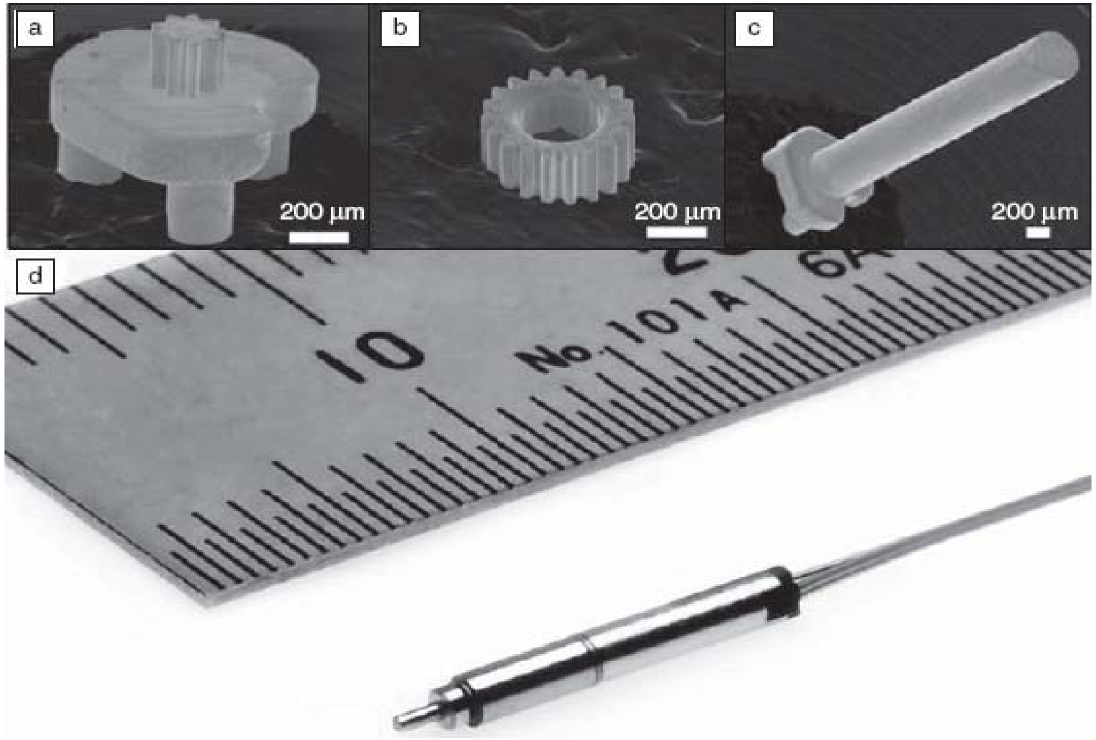
* Micro/Nano casting



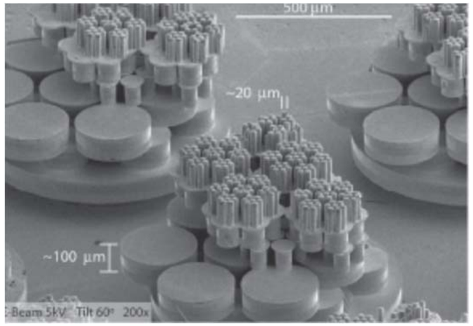
Near-net shape production



Precision die casting



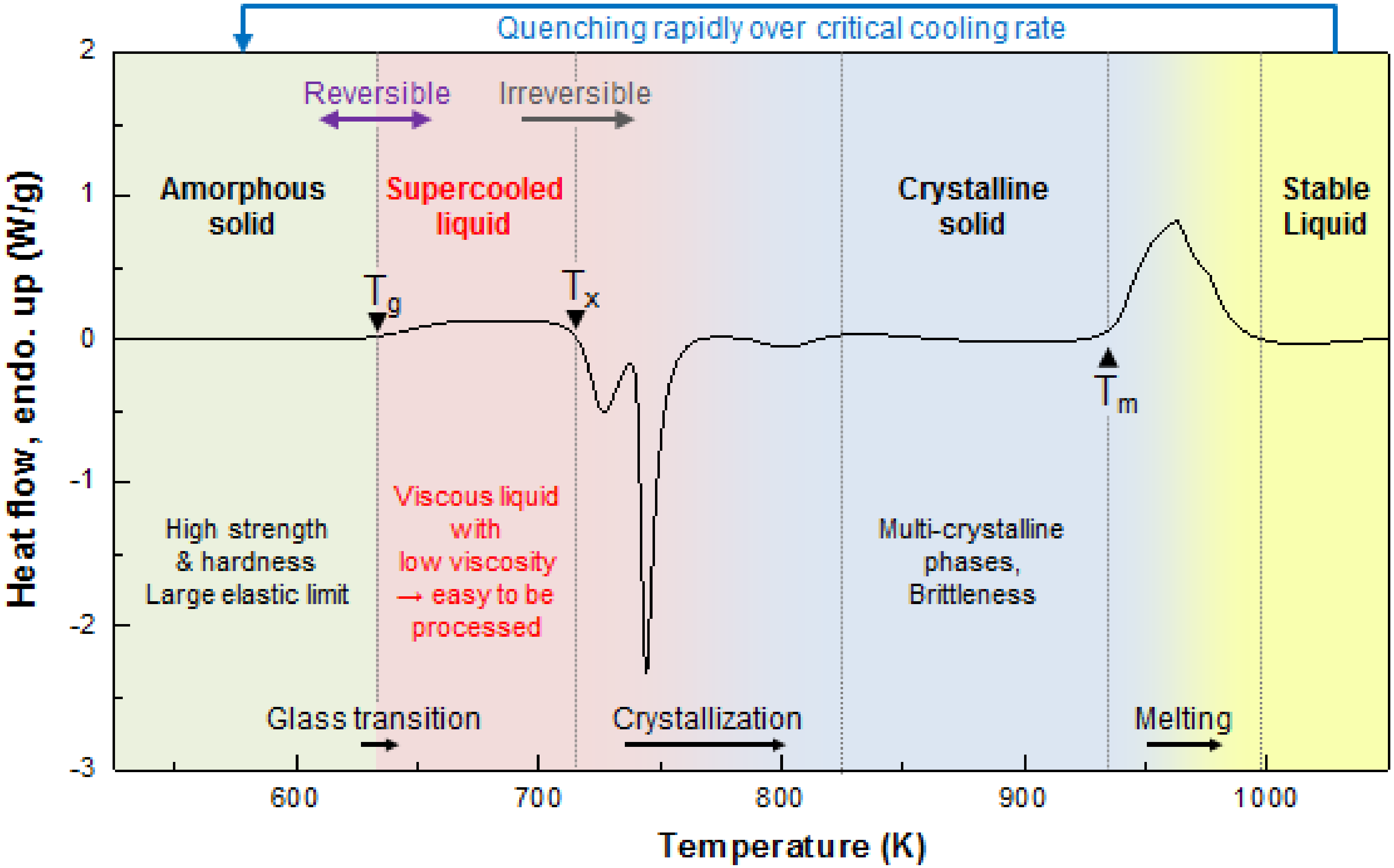
Precision Gears for Micro-motors



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

DSC trace of Vitreloy 1

: the temperature regions sectioned according to phase transformations

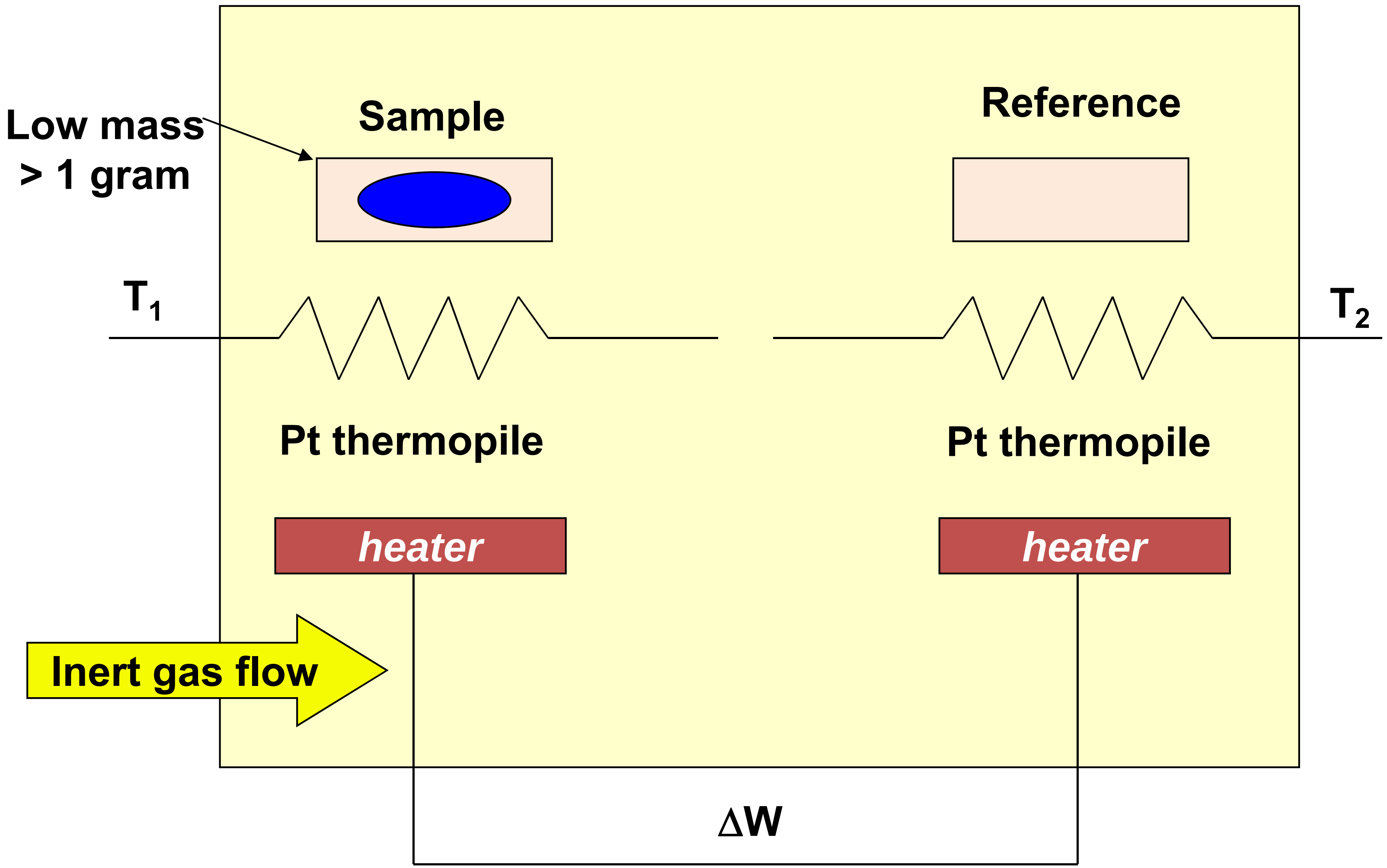


ΔT_x : indication of thermal stability of the glass produced

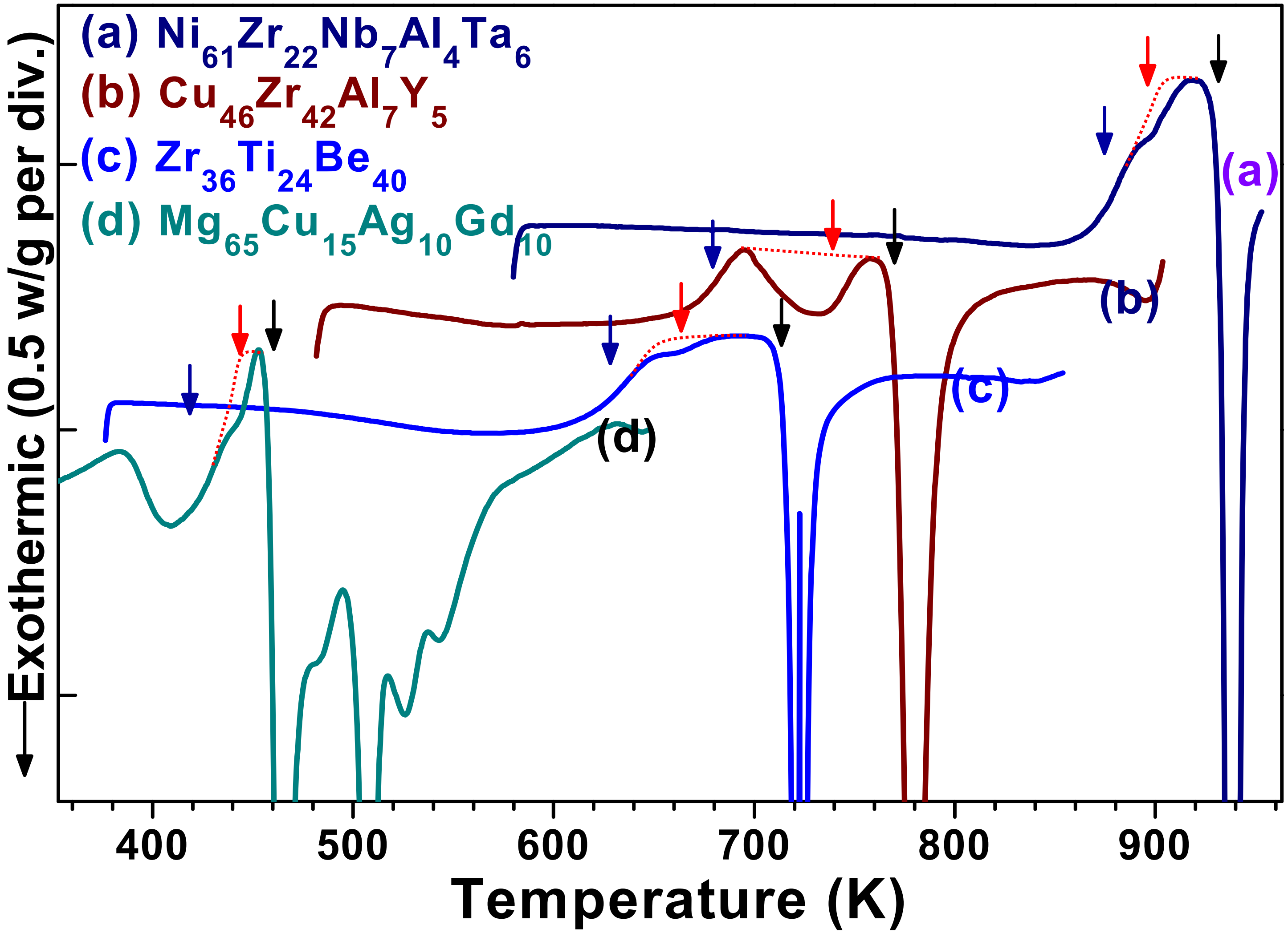
Thermal analysis: DSC

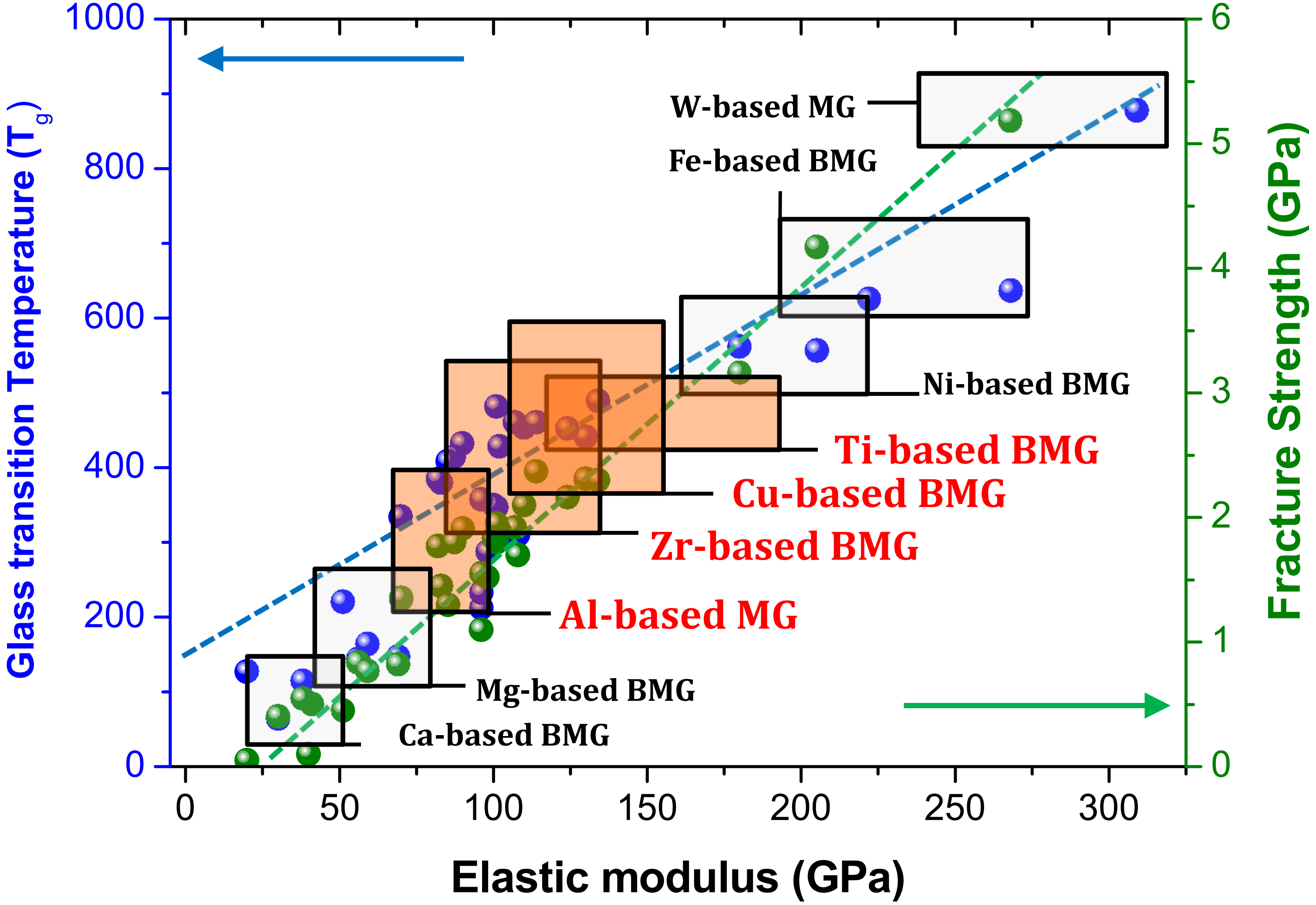
- **A *calorimeter* measures the heat into or out of a sample.**
- **A *differential calorimeter* measures the heat of a sample relative to a reference.**
- **A *differential scanning calorimeter* does all of the above and heats the sample with a linear temperature ramp.**
- **Differential Scanning Calorimetry (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





1000
800
600
400
200
0
Glass transition Temperature (T_g)
6
5
4
3
2
1
0
Fracture Strength (GPa)
0
50
100
150
200
250
300
Elastic modulus (GPa)
W-based MG
Fe-based BMG
Ni-based BMG
Ti-based BMG
Cu-based BMG
Zr-based BMG
Al-based MG
Mg-based BMG
Ca-based BMG

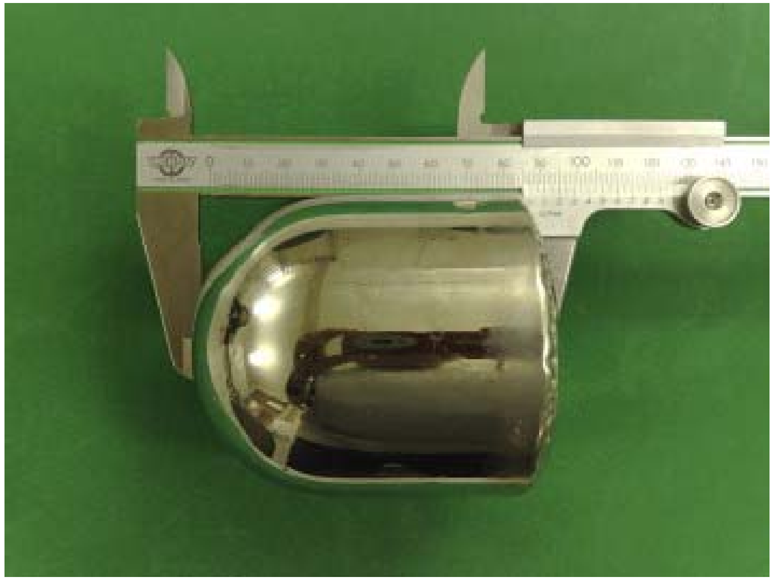
At a temperature T_x, which is higher than T_g, the supercooled liquid transforms into the crystalline phase(s). As mentioned earlier, the temperature interval between T_x and T_g is referred to as the width of the supercooled liquid region (SLR), that is, $\Delta T_x = T_x - T_g$. The value of ΔT_x 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.

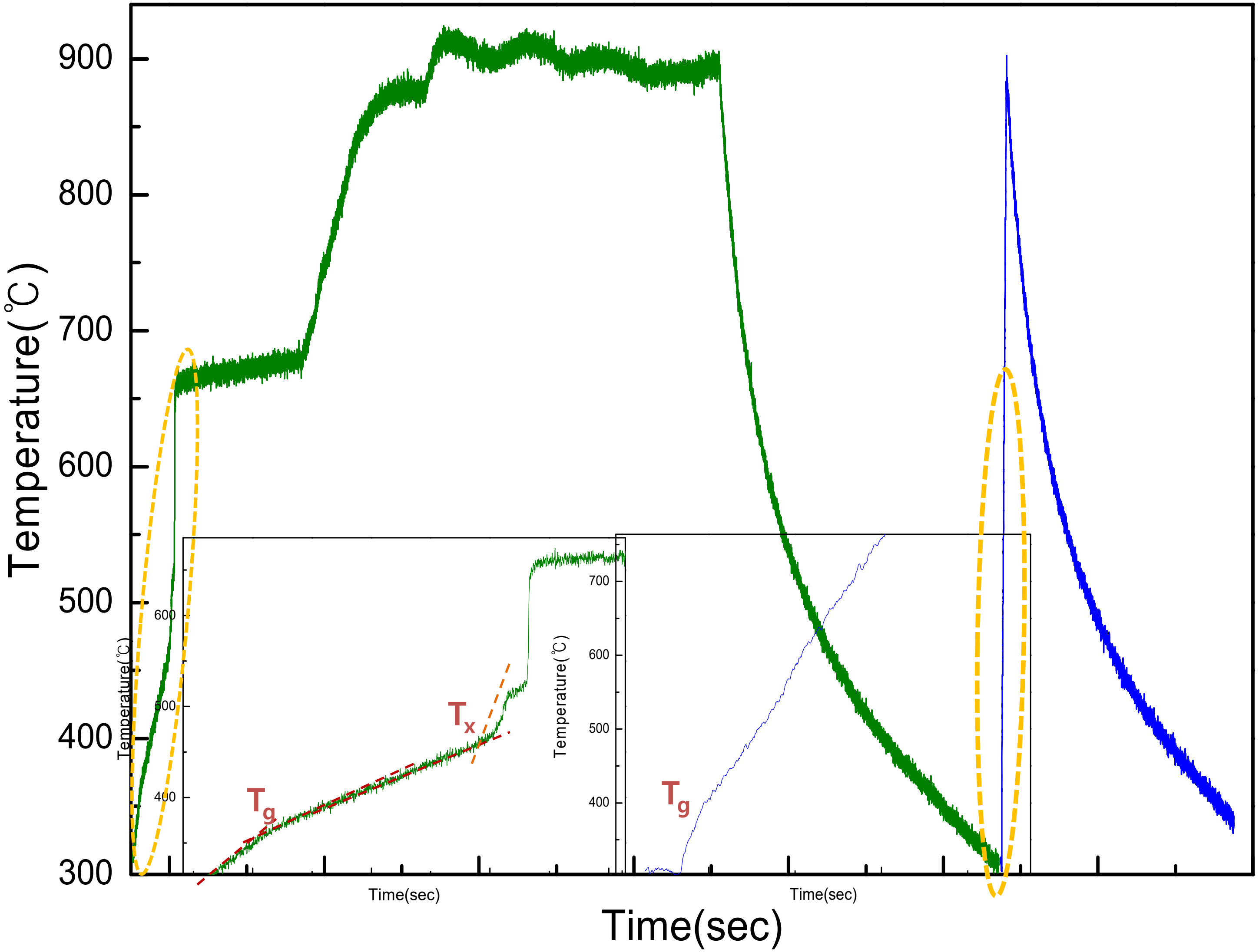
$Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$

2012

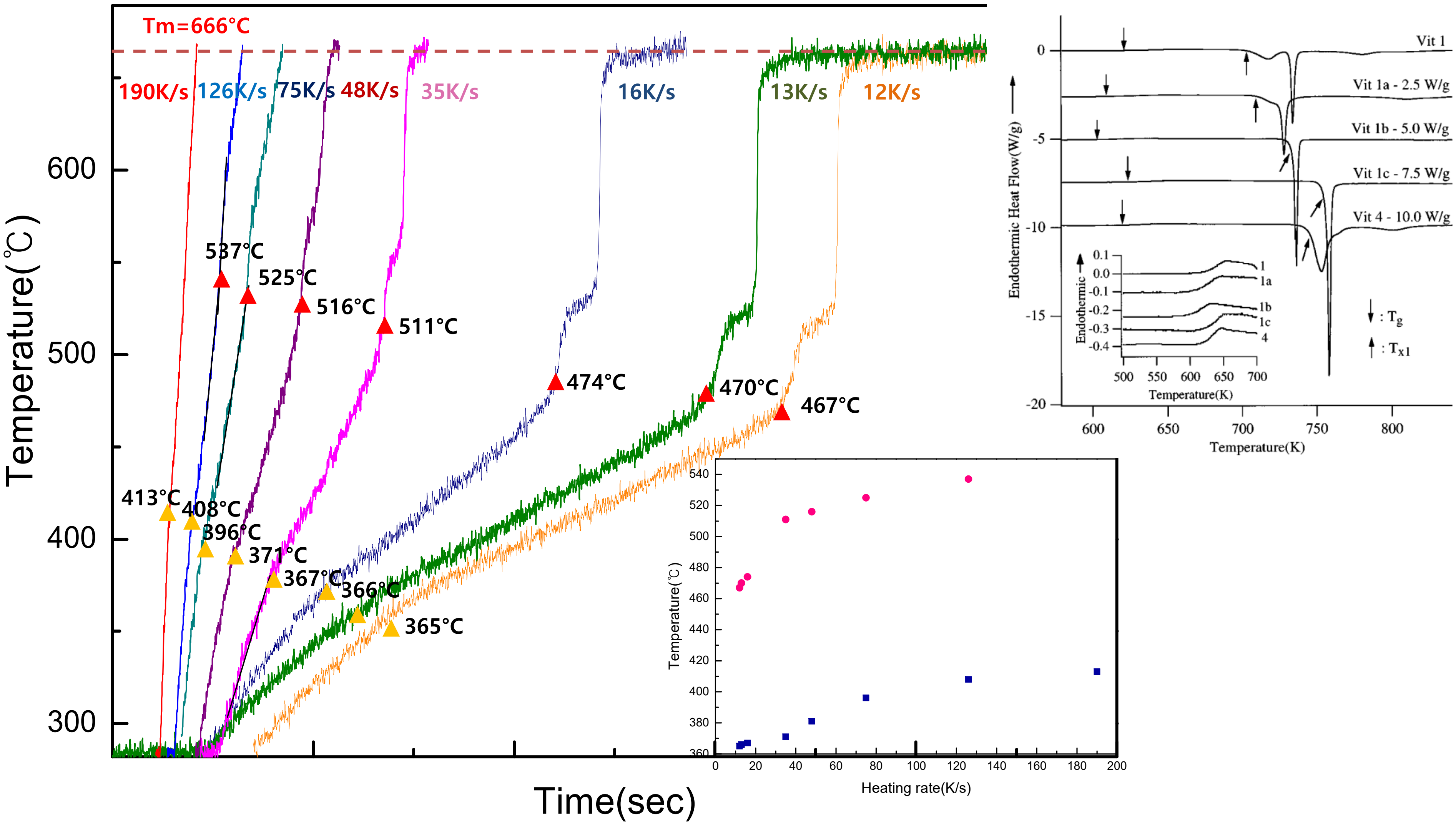
D_{max} 80mm

Intermetallics, Vol30, Nov2012, P 19–24




900
800
700
600
500
400
300
Temperature(℃)
Time(sec)
600
500
400
Temperature(℃)
Time(sec)
T_g
T_x
700
600
500
400
Temperature(℃)
Time(sec)
T_g

VIT 1

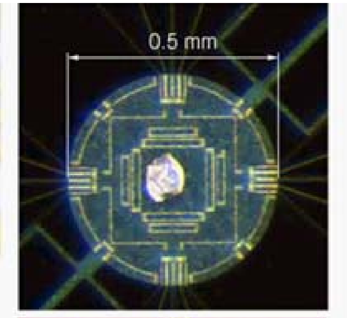


Tm=666°C
190K/s
126K/s
75K/s
48K/s
35K/s
16K/s
13K/s
12K/s
537°C
525°C
516°C
511°C
474°C
470°C
467°C
413°C
408°C
396°C
371°C
367°C
366°C
365°C
600
500
400
300
Temperature(℃)
Time(sec)
540
520
500
480
460
440
420
400
380
360
0
20
40
60
80
100
120
140
160
180
200
Temperature(℃)
Heating rate(K/s)
Vit 1
Vit 1a - 2.5 W/g
Vit 1b - 5.0 W/g
Vit 1c - 7.5 W/g
Vit 4 - 10.0 W/g
0
-5
-10
-15
-20
Endothermic Heat Flow(W/g)
600
650
700
750
800
Temperature(K)
↓ : Tg
↑ : Tx1
0.1
0.0
-0.1
-0.2
-0.3
-0.4
Endothermic
1
1a
1b
1c
4
500
550
600
650
700
Temperature(K)

Flash DSC 2+ (Mettler Toledo)

Firmware Ver. 3.04

- ***Heating rate***
  : $4*10^4$ K/s
- ***Cooling rate***
  : $4*10^3$ K/s
- ***Temperature range:***
  -90℃ - 1000℃

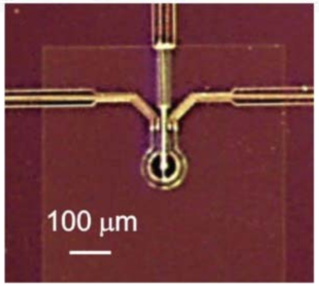


UFS

-90 – 450 ℃

Limited heating rate ~ $3*10^4$ K/s

Stable data regardless of sample weight

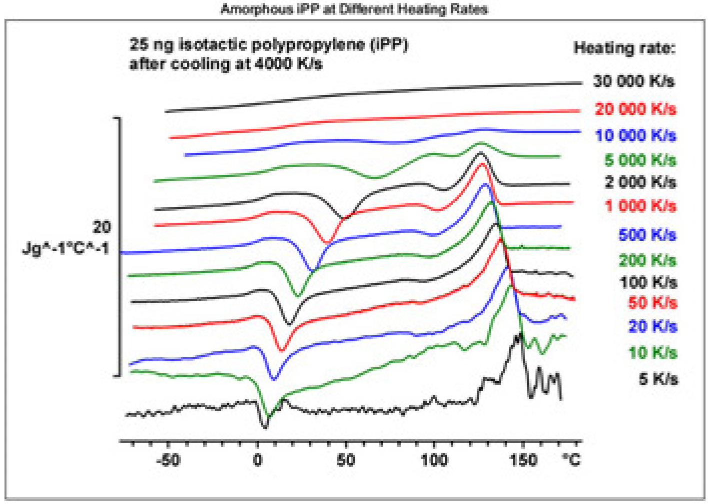


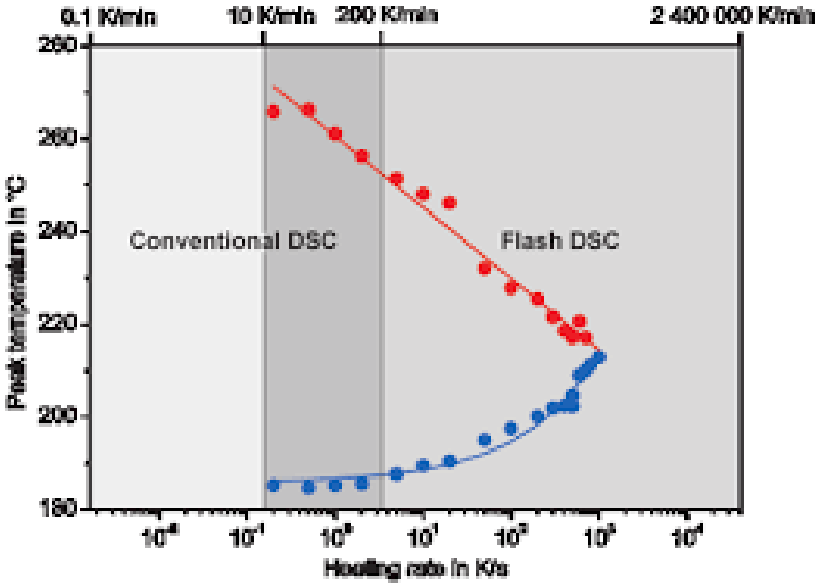
UFH

-90 – 1000 ℃

Sample weight less than 100ng is recommended

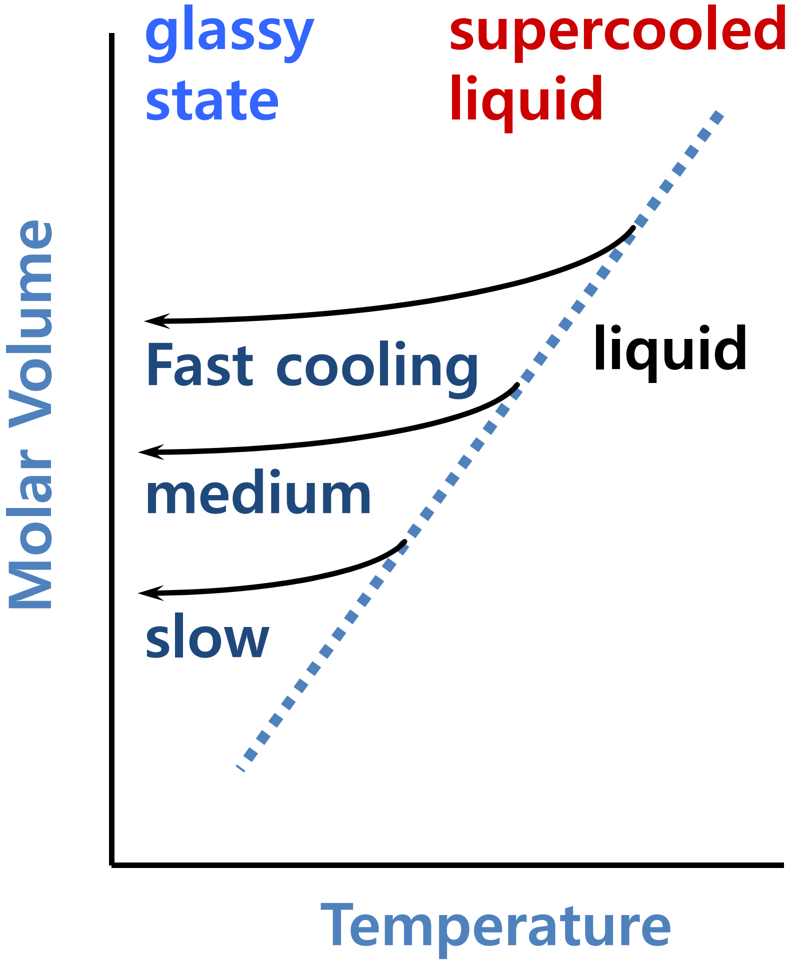
Extreme experimental condition → hidden kinetics of materials



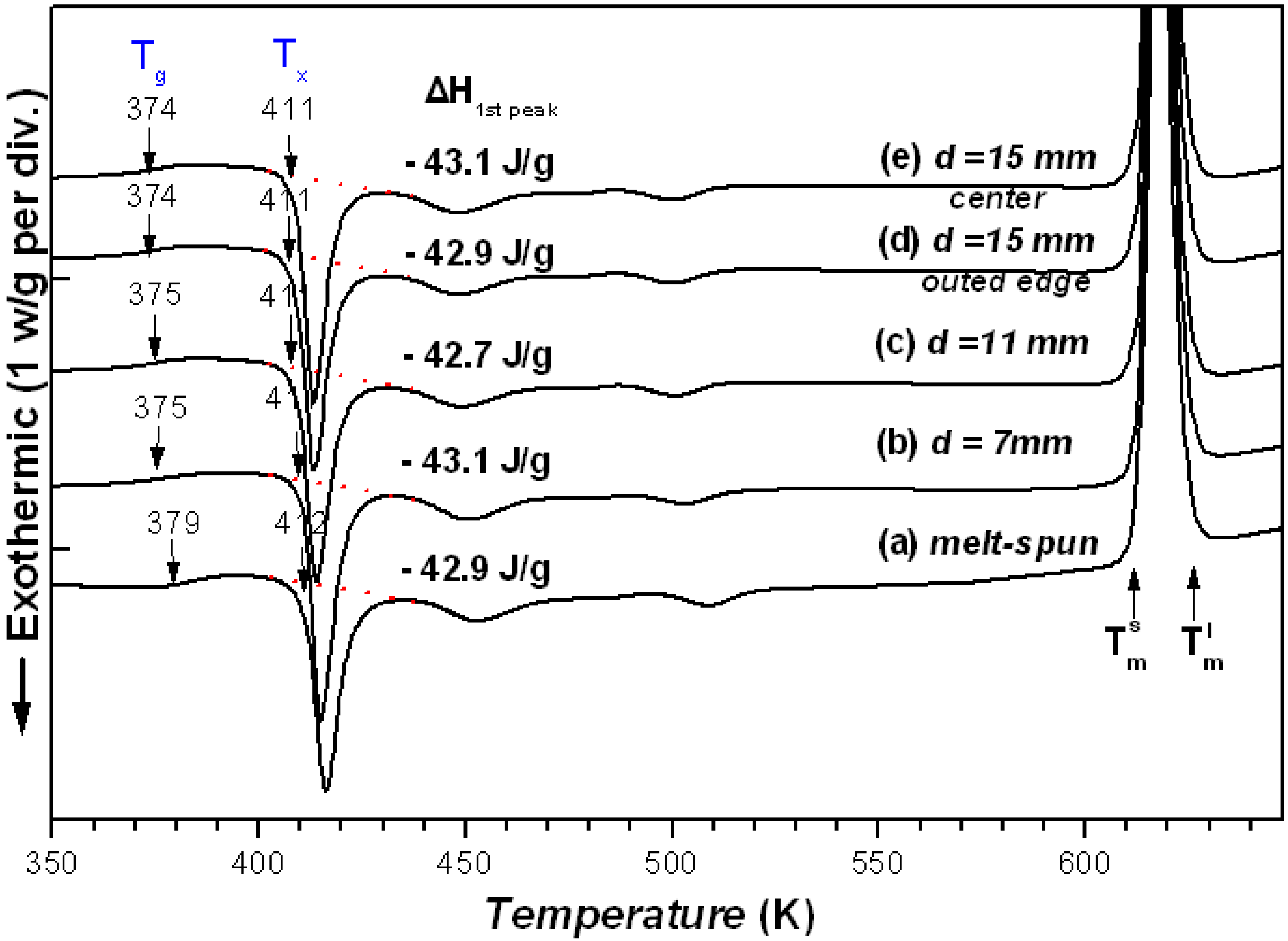


The Cooling Rate Affects the Properties of Glass

- 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

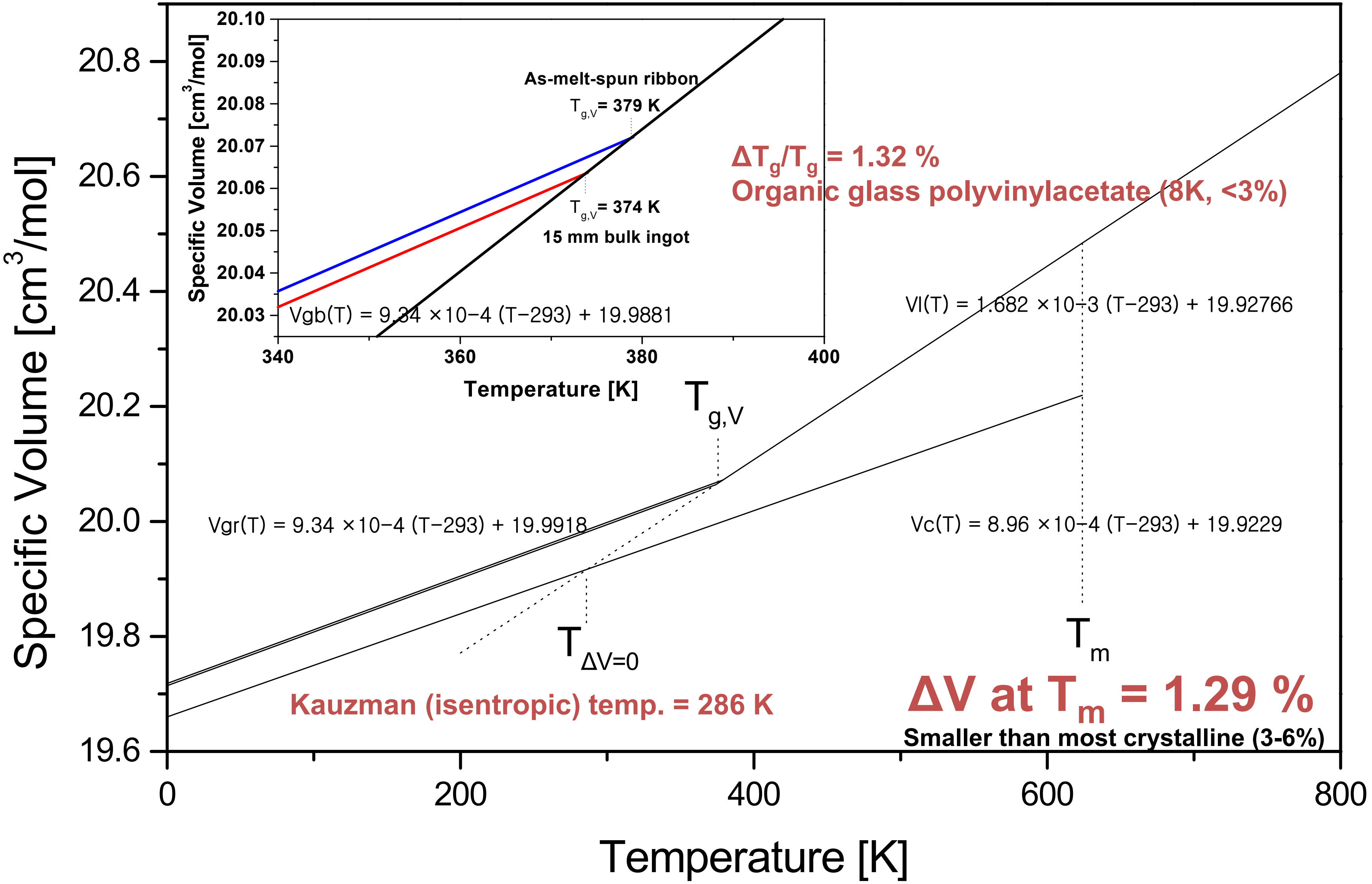


❖ Typically T_g is ~ 50-60% of the melting point. ($0.6T_m$)



* J Mater Res, 19 (2004) 685.

T_g depends on thermal history even in same alloy composition.



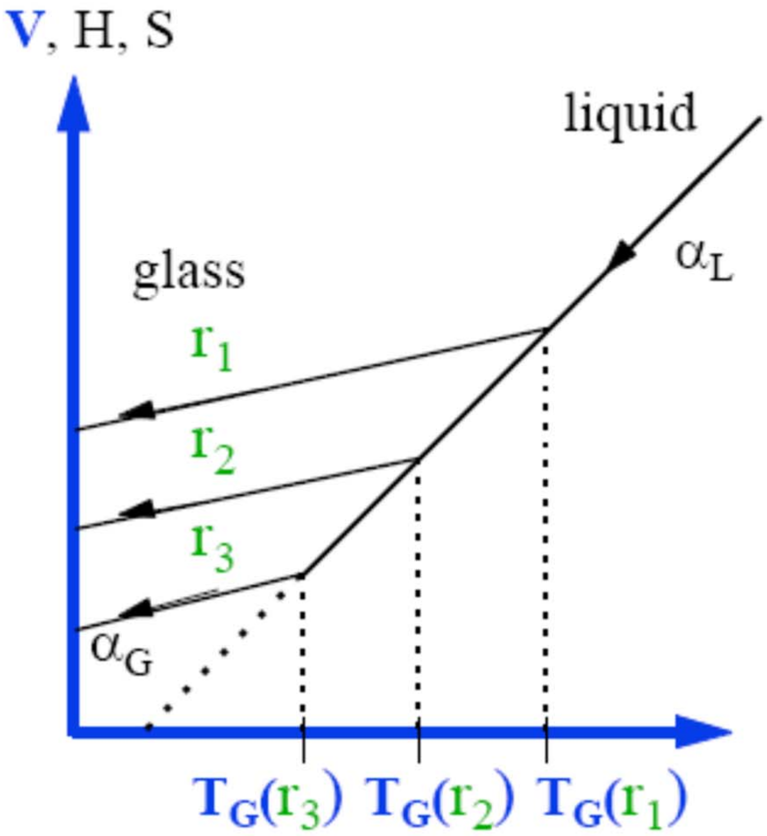
$\Delta T_g/T_g$ = 1.32 %
Organic glass polyvinylacetate (8K, <3%)

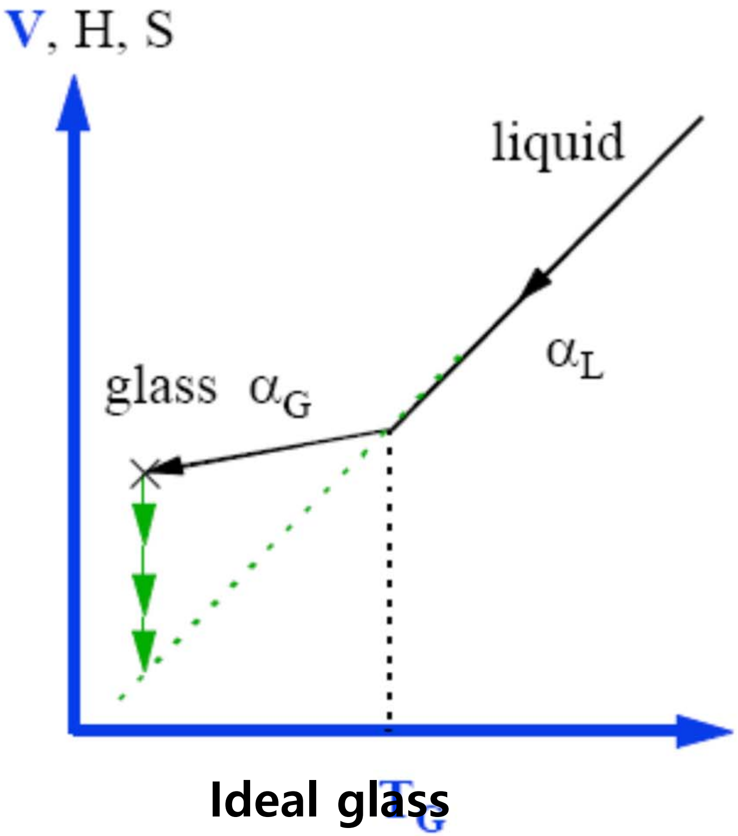
Kauzman (isentropic) temp. = 286 K

ΔV at T_m = 1.29 %
Smaller than most crystalline (3-6%)

*** APL, 92 (2008) 091915.**

* Kinetic Nature of the Glass Transition





Ideal glass

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**