

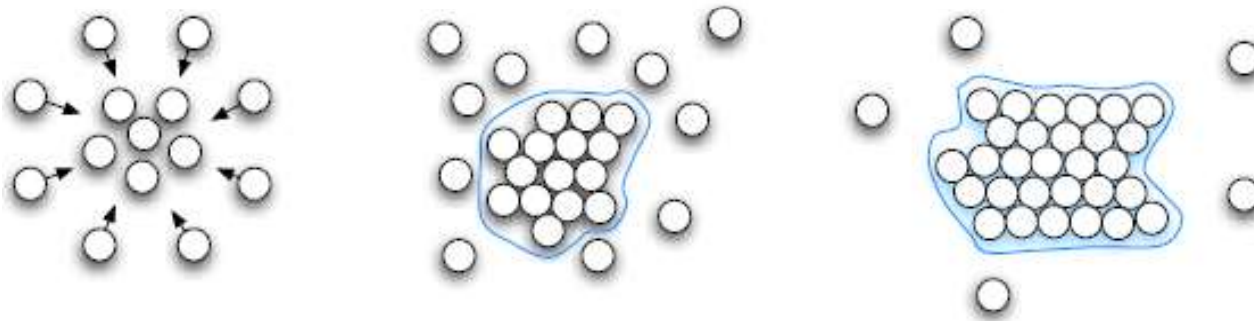
Unit II - Solidification

Solidification

- Nucleation in pure metals
- Growth of a pure Solid
- Alloy Solidification
- Solidification during Quenching from Melt.

Solidification

- During Solidification the atomic arrangement changes from a **random** or **short-range order** to a **long range order** or crystal structure.
- Nucleation occurs when a small **nucleus** begins to form in the liquid, the nuclei then **grows** as atoms from the liquid are attached to it.



- The crucial point is to understand it as a balance between the free energy available from the driving force, and the energy consumed in forming new interface. Once the rate of change of free energy becomes negative, then an embryo can grow.

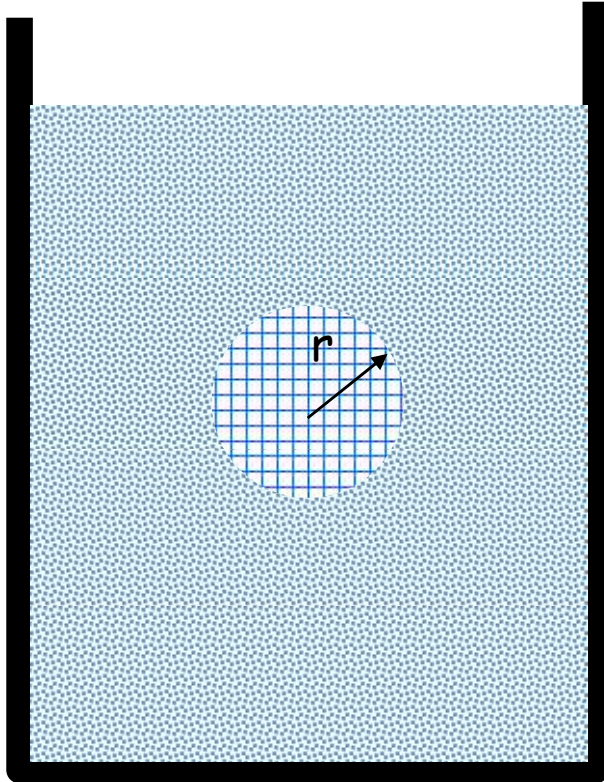
Solidification

- Nucleation
- Growth

Driving Force:

When $T < T_L$, so the driving force for solidification increases. This driving force is often called *undercooling or Supercooling*

Homogeneous nucleation



Spherical ball of solid of radius R in the middle of the liquid at a temperature below T_m

Homogeneous nucleation

G_L = free energy of liquid per unit volume

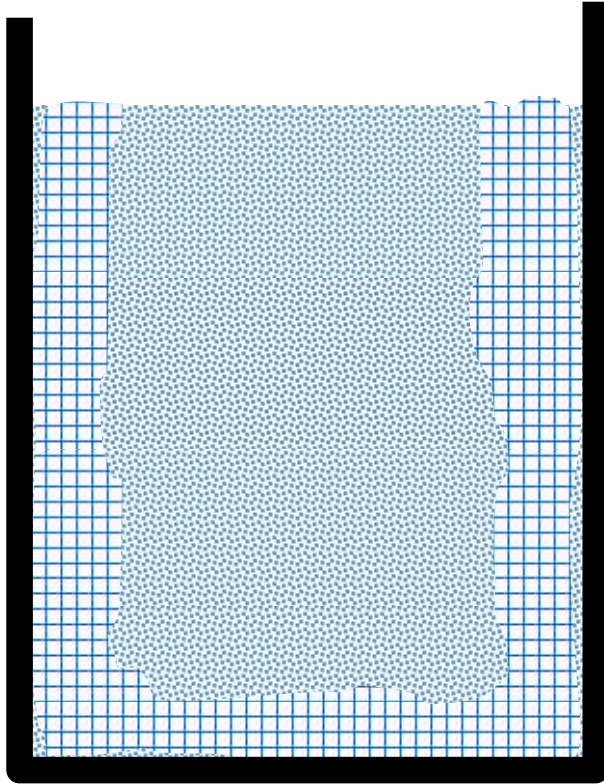
G_S = free energy of solid per unit volume

$$\Delta G = G_S - G_L$$

Nucleation without preferential nucleation sites is homogeneous Nucleation. Driving force is *undercooling or Supercooling*

Heterogeneous nucleation

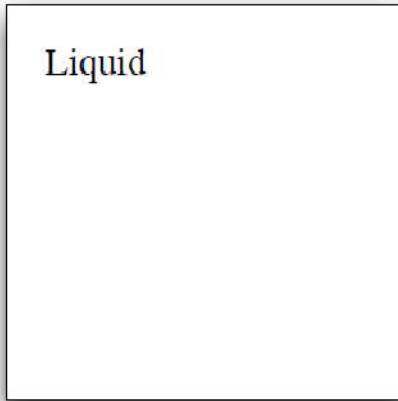
How does solidification begins?



Usually at the walls of the container

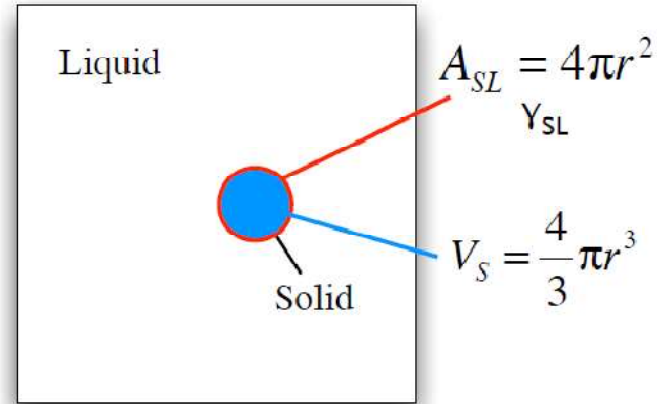
nucleation sites on surfaces

Homogeneous Nucleation



$$G_1$$

$$G_1 = (V_S + V_L)G_V^L$$



$$G_2 = G_1 + \Delta G$$

$$G_2 = V_S G_V^S + V_L G_V^L + A_{SL} \gamma_{SL}$$

$$\Delta G = G_2 - G_1$$

$$= V_S (G_V^S - G_V^L) + A_{SL} \gamma_{SL}$$

$$= -V_S \Delta G_V + A_{SL} \gamma_{SL}$$

$$\Delta G_V = \frac{L_V \Delta T}{T_m}$$

$$\Delta G = \underbrace{-\frac{4}{3} \pi r^3 \Delta G_V}_{-ve} + \underbrace{4 \pi r^2 \gamma_{SL}}_{+ve}$$

When $r < r^*$, $\Delta G \rightarrow$ unstable

When $r > r^*$, $\Delta G \rightarrow$ stable

Driving Force for Solidification

Gibbs energy of L and S at temp. T is given by,

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

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

At temperature T,

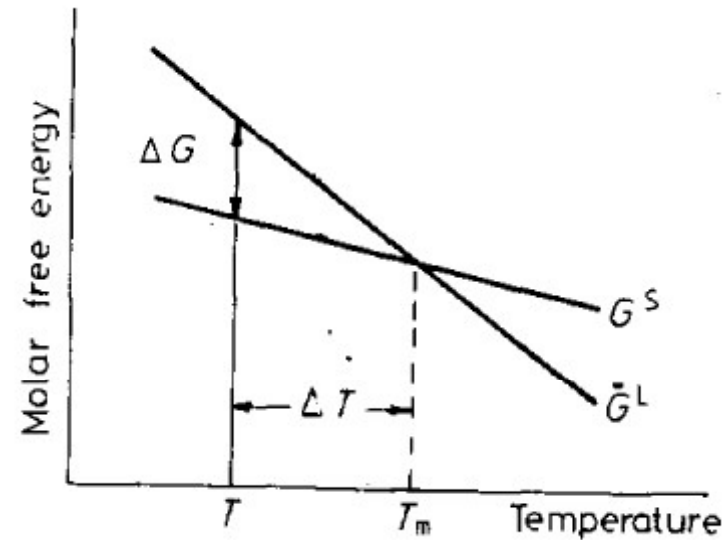
$$\Delta G = \Delta H - T\Delta S$$

At T_m , $\Delta G=0$

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

$$\Delta S = \frac{\Delta H}{T_m} = \frac{L}{T_m}$$

Entropy of fusion



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

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

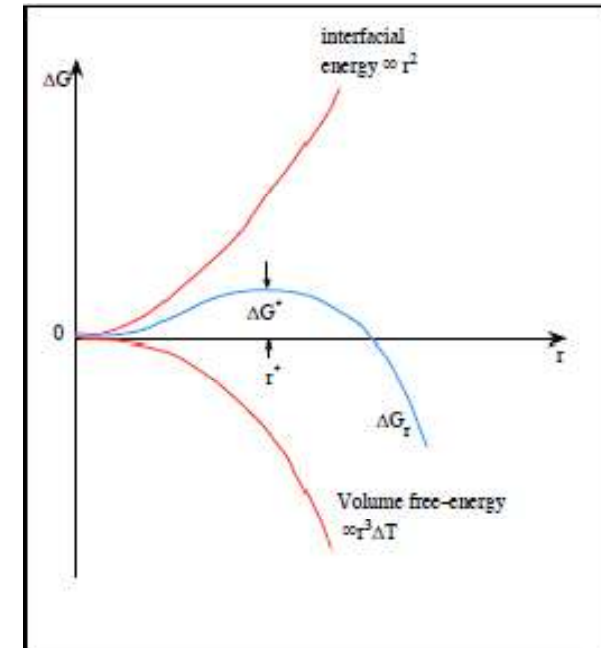
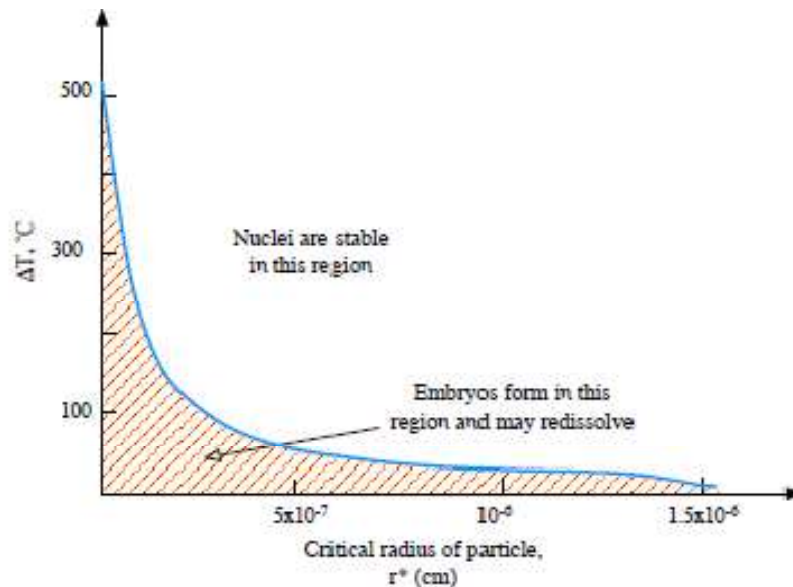
Differentiate to find the stationary point,

$$\frac{d(\Delta G)}{dr} = 0$$

$$-4\pi(r^*)^2 \Delta G_v + 8\pi r^* = 0$$

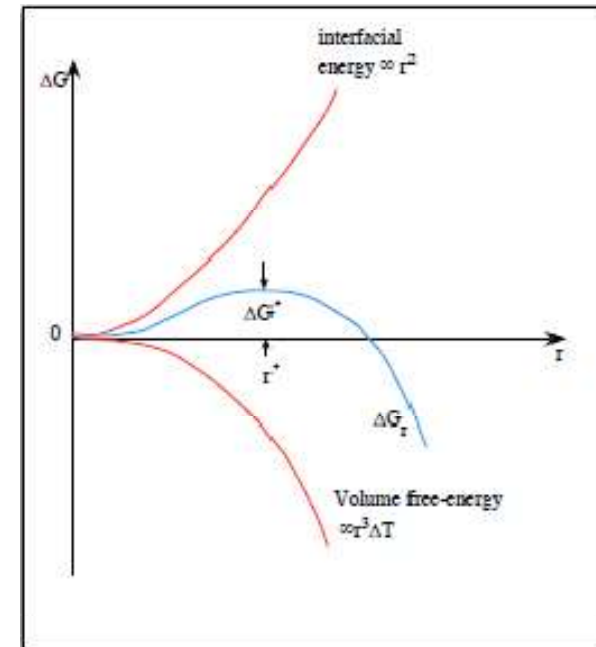
$$r^* = \frac{2\gamma_{SL}}{\Delta G_v} = \left(\frac{2\gamma_{SL} T_m}{L_v} \right) \frac{1}{\Delta T}$$

$$\Delta G_v^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2} \right) \frac{1}{(\Delta T)^2}$$



$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi^2 \gamma_{SL}$$

- if $r < r^*$ the system can lower its free energy by dissolution of the solid
- Unstable solid particles with $r < r^*$ are known as **clusters** or **embryos**
- if $r > r^*$ the free energy of the system decreases if the solid grows
- Stable solid particles with $r > r^*$ are referred to as **nuclei**
- Since $\Delta G = 0$ when $r = r^*$ the critical nuclei is effectively in (unstable) equilibrium with the surrounding liquid



At r^* , the solid phase is equilibrium with its Surrounding, then

$$\Delta G_v = \frac{2\gamma_{SL}}{r^*}$$

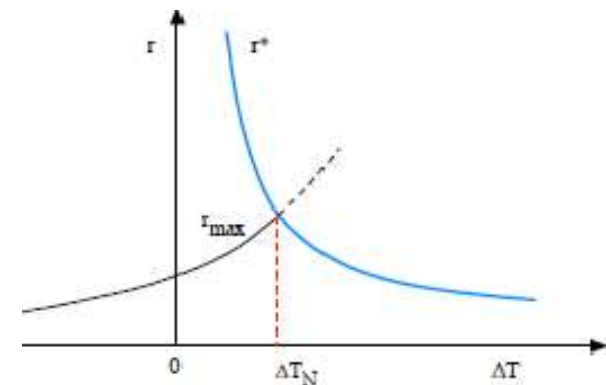
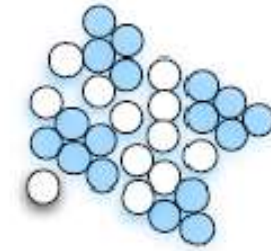
Variation of r^* and r_{\max} with ΔT

- Although we now know the critical values for an embryo to become a nucleus, we do not know **the rate** at which nuclei will appear in a real system.
- To estimate the **nucleation rate** we need to know the population density of embryos of the critical size and the rate at which such embryos are formed.
- The population (concentration) of critical embryos is given by

$$n_r = n_o \exp\left(-\frac{\Delta G_r}{kT}\right)$$

k is the Boltzmann factor, n_o is the total number of atoms in the system

ΔG_r is the excess of free energy associated with the cluster



Homogeneous Nucleation Rate

- $\Delta G = \Delta G^*$, then the concentration of clusters to reach the critical size can be written as:

$$C^* = C_o \exp\left(-\frac{\Delta G_{hom}^*}{kT}\right) \text{ clusters/m}^3$$

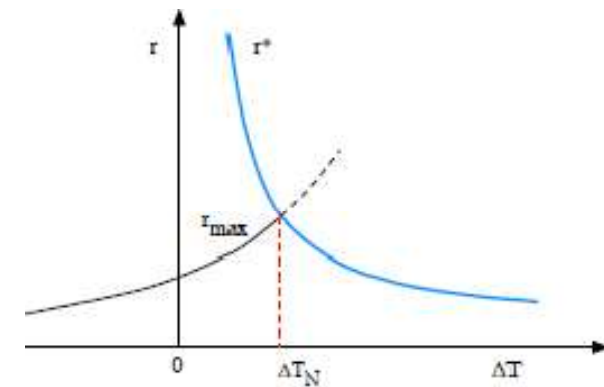
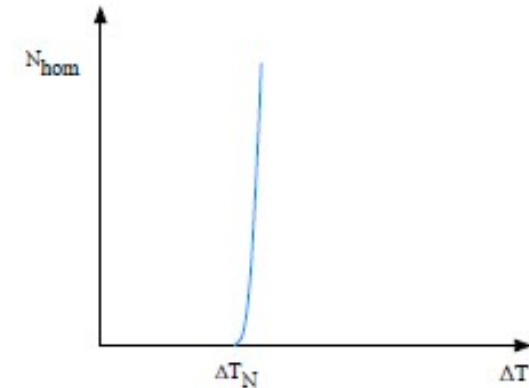
The addition of one more atom to each of these clusters would convert them into stable nuclei. If this happens with a frequency f_o ,

$$N_{hom} = f_o C_o e^{-\frac{\Delta G_{hom}^*}{kT}} \text{ nuclei/m}^3$$

$$N_{hom} = f_o C_o e^{-\frac{T}{(\Delta T)^2}} \text{ nuclei/m}^3$$

$$A = \frac{16\gamma_{SL}^3 T_m^2}{3L_v^2 kT}$$

- The effect of undercooling on the nucleation rate is drastic, because of the non-linear relation between the two quantities as is shown in the plot



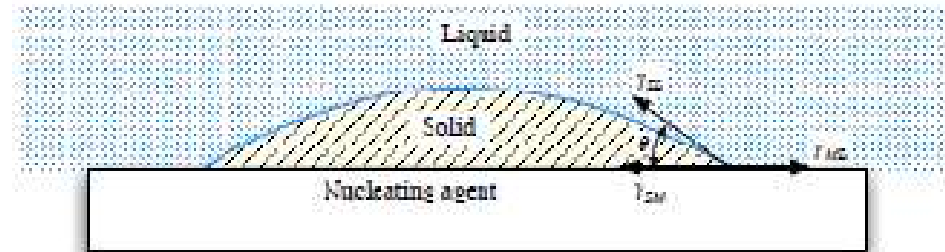
Heterogeneous Nucleation

$$\Delta G_v^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2} \right) \frac{1}{(\Delta T)^2}$$

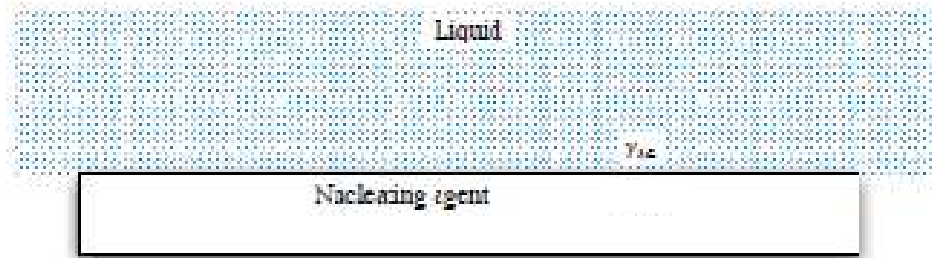
it is clear that for nucleation to be facilitated the interfacial energy term should be reduced

$$\gamma_{ML} = \gamma_{SM} + \gamma_{SL} \cos\theta$$

$$\cos\theta = \frac{(\gamma_{ML} - \gamma_{SM})}{\gamma_{SL}}$$



$$G_1 = (V_S + V_L)G_V^L + (A'_{ML} + A_{ML})\gamma_{ML}$$



$$G_2 = V_S G_V^S + V_L G_V^L + A'_{ML} \gamma_{ML} + A_{SL} \gamma_{SL} + A_{SM} \gamma_{SM}$$



$$\Delta G = G_2 - G_1 = -V_S \Delta G_V + A_{SL} \gamma_{SL} + A_{SM} \gamma_{SM} - A_{ML} \gamma_{ML}$$

$$\Delta G_{het} = \left\{ -\frac{4}{3} \pi r^3 \Delta G_v + 4\pi^2 \gamma_{SL} \right\} S(\theta)$$

$$S(\theta) = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} < 1$$

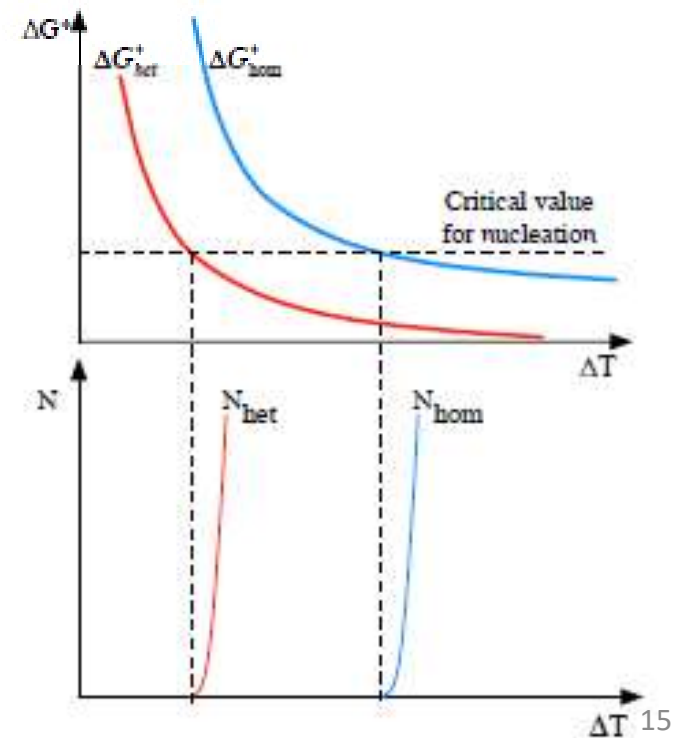
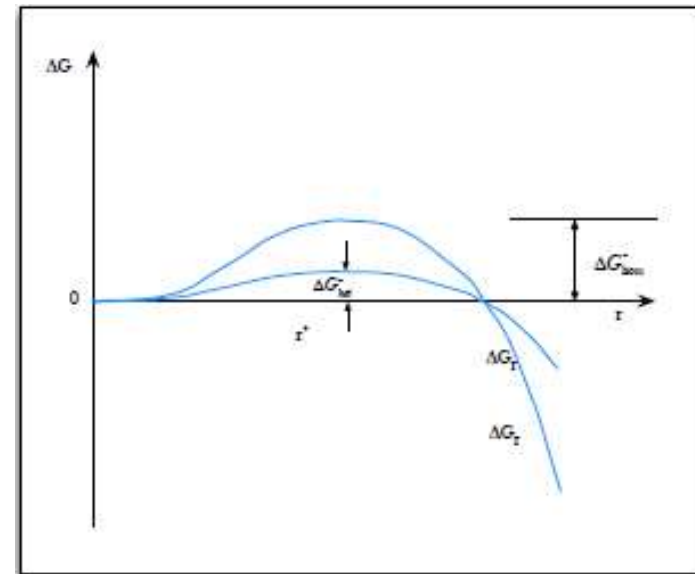
$$r^* = \frac{2\gamma_{SL}}{\Delta G_v}$$

$$\Delta G_{hetro}^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2} S(\theta)$$

$$\Theta = 10^\circ \rightarrow S(\theta) = 10^{-4}$$

$$\Theta = 30^\circ \rightarrow S(\theta) = 0.02$$

Model does not work for $\Theta = 0^\circ$



Nucleation of Melting

- Nucleation during solidification requires some undercooling. But, melting invariably occurs at the equilibrium temperature even at relatively high rates of heating.
- It is mainly due the relative Gibbs energies of the S/V, S/L and L/V interfaces.

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

The wetting angle $\theta=0$ and no superheating is required for nucleation of the liquid

- A copper-aluminium diffusion couple develops a certain concentration profile after an isothermal treatment at 600°C for 10 hours. The time required to achieve the same concentration profile at 500°C is _____ (in hours *to 1 decimal place*)
- **Given:** The interdiffusion coefficient for copper in aluminium at 500°C and 600°C are $4 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ and $8 \times 10^{-13} \text{ m}^2\text{s}^{-1}$.

Growth of a Pure Solid

Types of S/L interface:

- Atomically rough or diffuse interface (metals)
 - Atom migrate by a continuous growth process – diffusion controlled process
 - In pure metals, growth occurs at rate controlled by heat conduction (diffusion)
 - In alloy solidification, growth is controlled by solute diffusion.
- Atomically flat or sharply defined interface (non-metals)
 - Lateral growth process involving ledges.

Growth of a Pure Solid

- Pure solid solidification is controlled by the rate at which the latent heat of solidification can be conducted away from the S/L interface

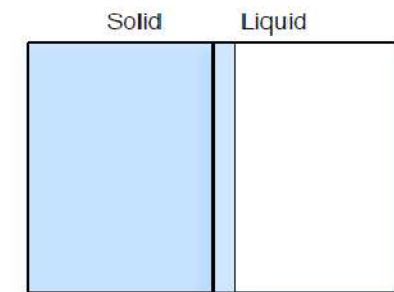
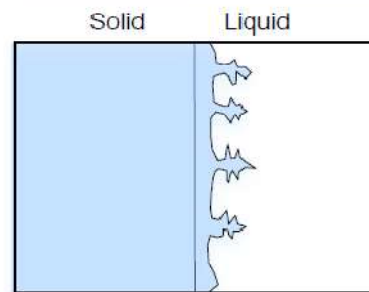
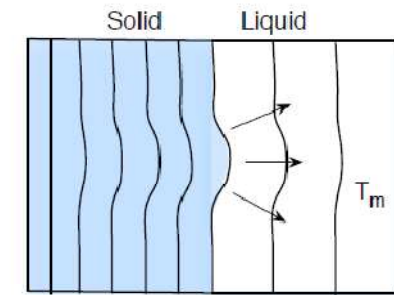
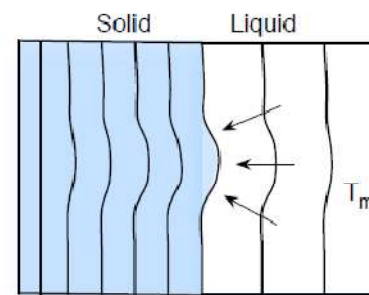
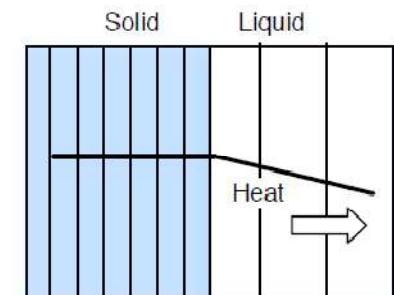
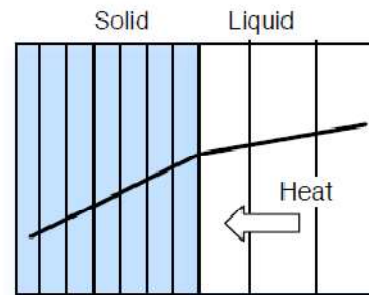
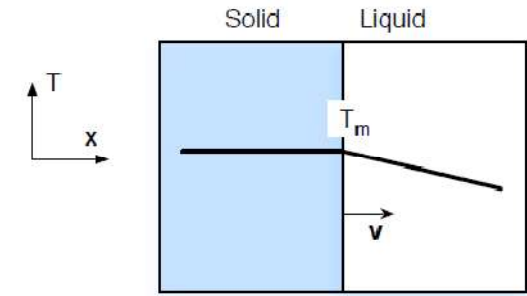
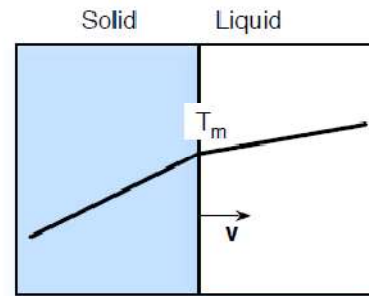
$$k_s \frac{dT_s}{dx} = k_L \frac{dT_L}{dx} + vL_v$$

k_s and k_L – Thermal conductivity of solid(S) and liquid (L)

T_s and T_L – Temperature of Solid and liquid.

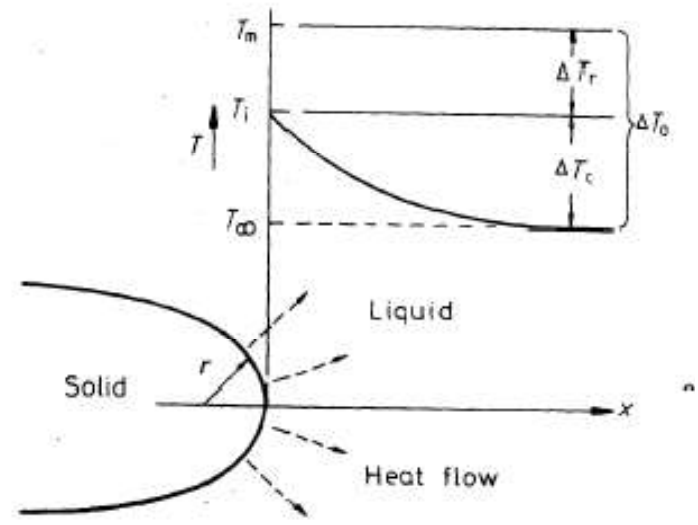
L_v – latent heat

v - Velocity of solid growth



Heat conduction through solid

Heat conduction through liquid



Temperature distribution at the tip of a growing thermal dendrite.

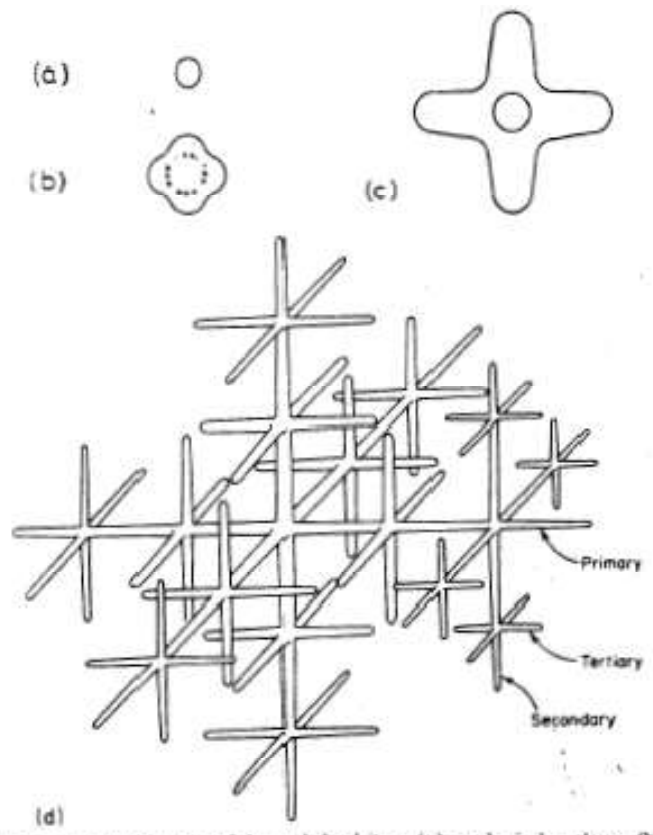


Fig. 4.17 The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions (100 in cubic crystals); (d) secondary and tertiary arms develop (after R.E. Reed-Hill, *Physical Metallurgy Principles*, 2nd. edn., Van Nostrand, New York, 1973).

Alloy Solidification

The partition coefficient k is

$$k = \frac{X_S}{X_L}$$

X_S and X_L are the mole fraction of solute in solid and liquid in equilibrium at a given temperature.

Alloy solidification depends on complex way of

- temp. gradient
- Cooling rates
- Growth rates

Infinitely slow (Equilibrium solidification)

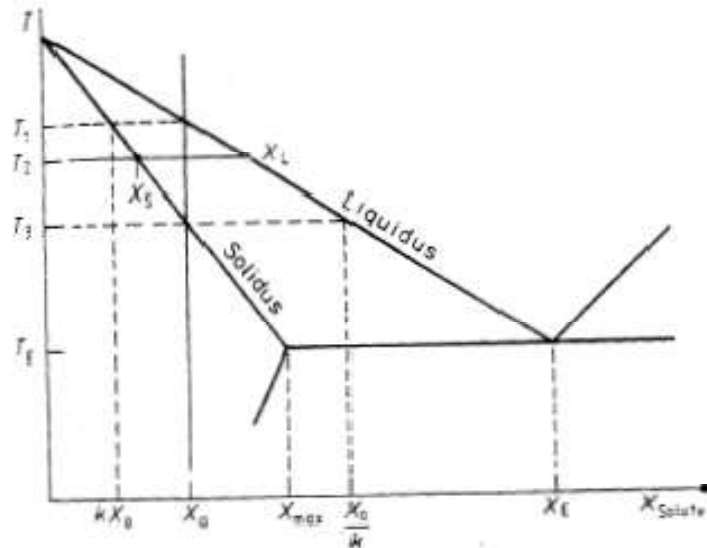


Fig. 4.19 A hypothetical phase diagram. $k = X_s/X_L$ is constant.

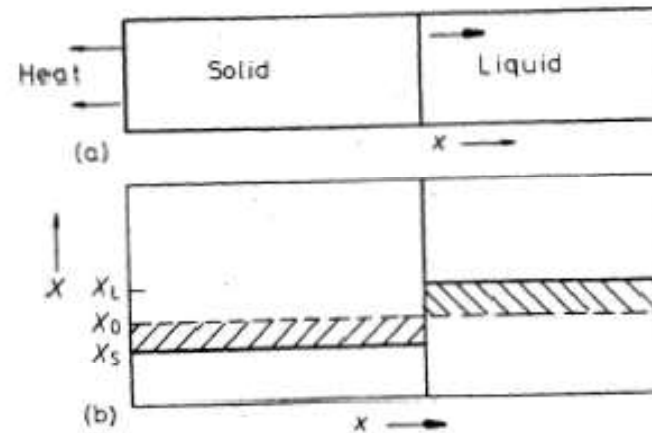


Fig. 4.20 Unidirectional solidification of alloy X_0 in Fig. 4.19. (a) A planar S/L interface and axial heat flow. (b) Corresponding composition profile at T_2 assuming complete equilibrium. Conservation of solute requires the two shaded areas to be equal.

No diffusion in solid and perfect mixing in liquid

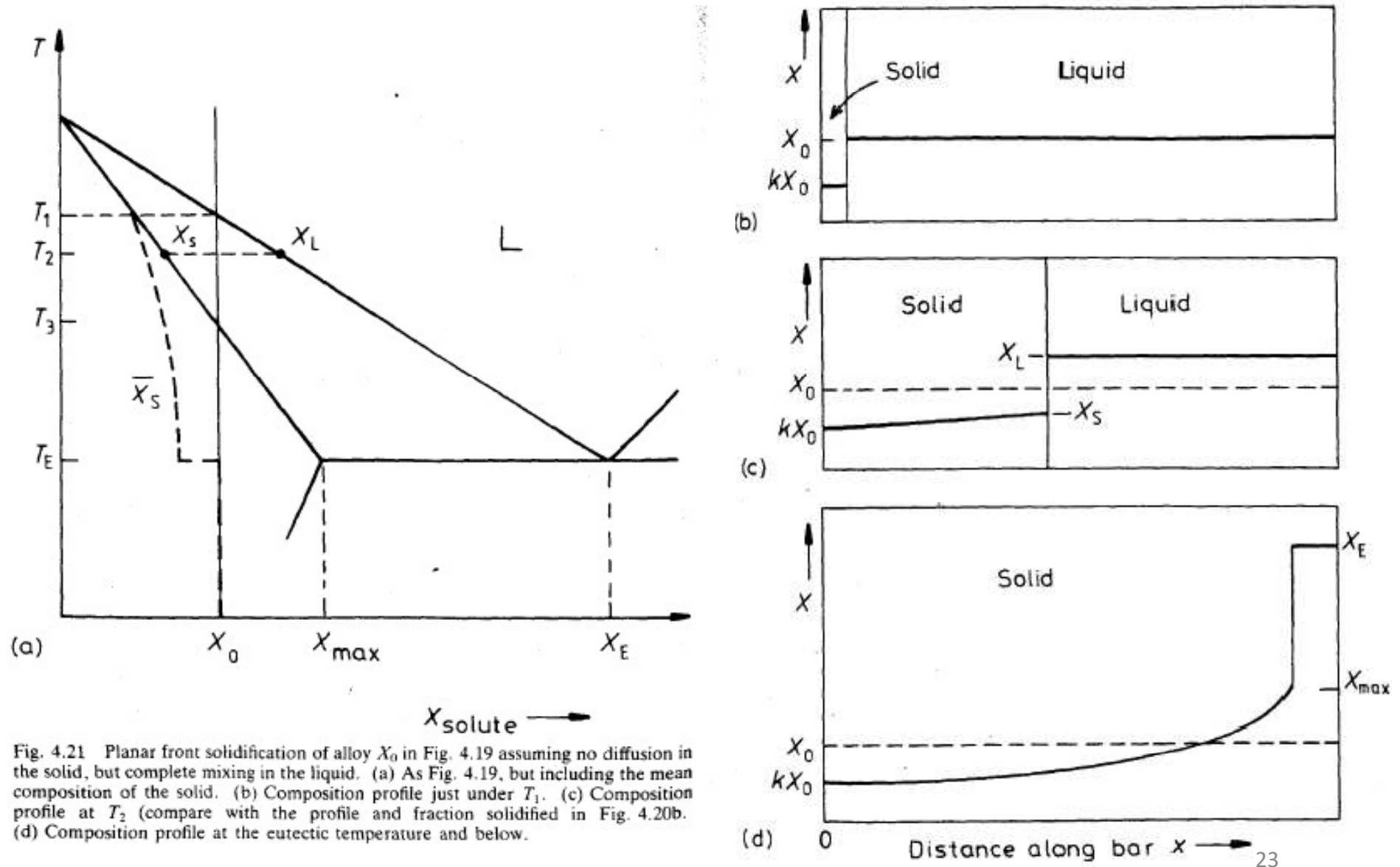


Fig. 4.21 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in the solid, but complete mixing in the liquid. (a) As Fig. 4.19, but including the mean composition of the solid. (b) Composition profile just under T_1 . (c) Composition profile at T_2 (compare with the profile and fraction solidified in Fig. 4.20b. (d) Composition profile at the eutectic temperature and below.

No diffusion
in solid,
diffusional
mixing in
liquid

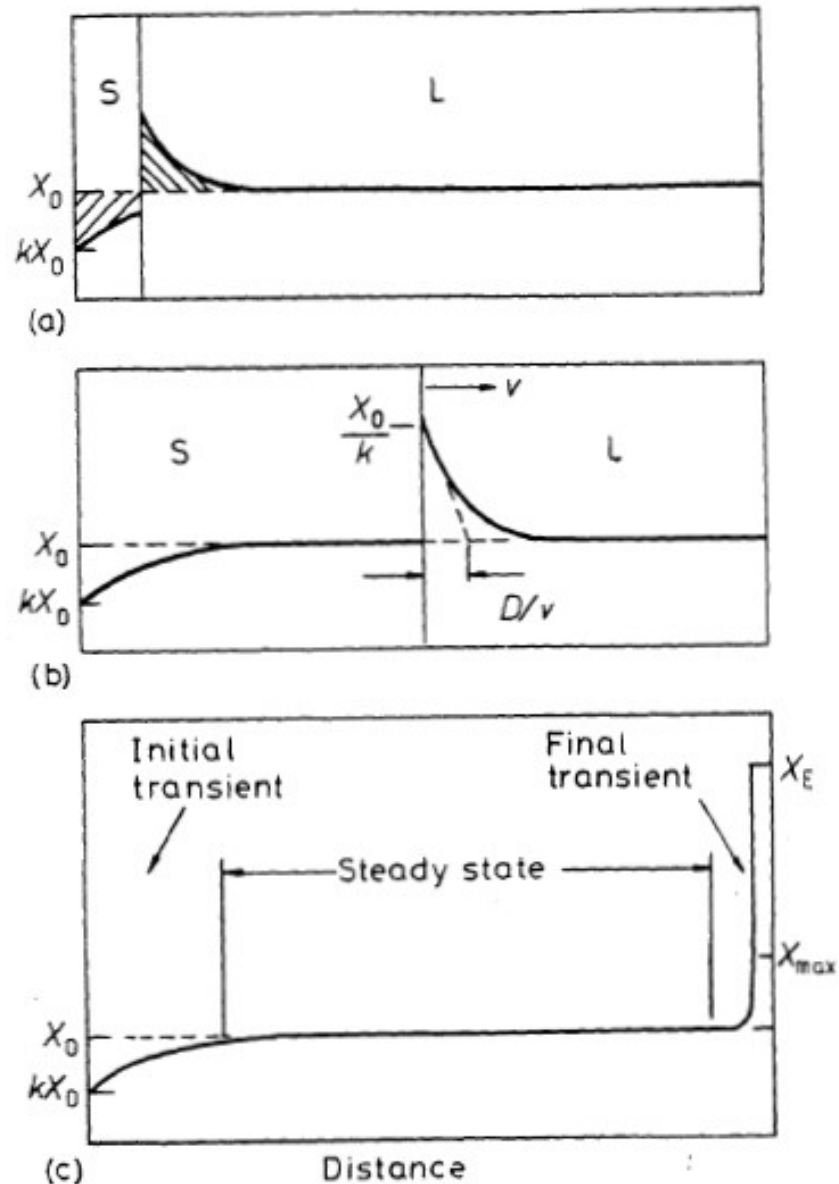


Fig. 4.22 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in the solid and no stirring in the liquid. (a) Composition profile when S/L interface temperature is between T_2 and T_3 in Fig. 4.19. (b) Steady-state solidification at T_3 . The composition solidifying equals the composition of the liquid far ahead of the solid (X_0). (c) Composition profile at T_E and below, showing the final transient.

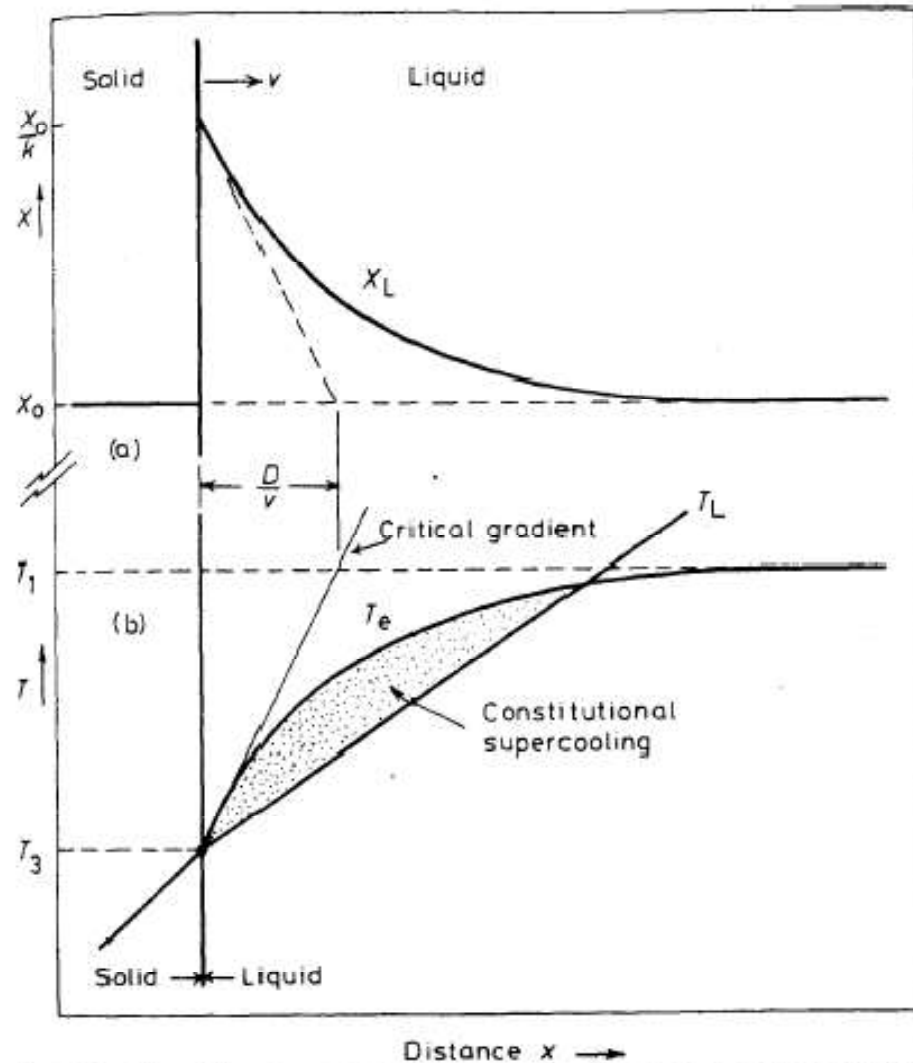
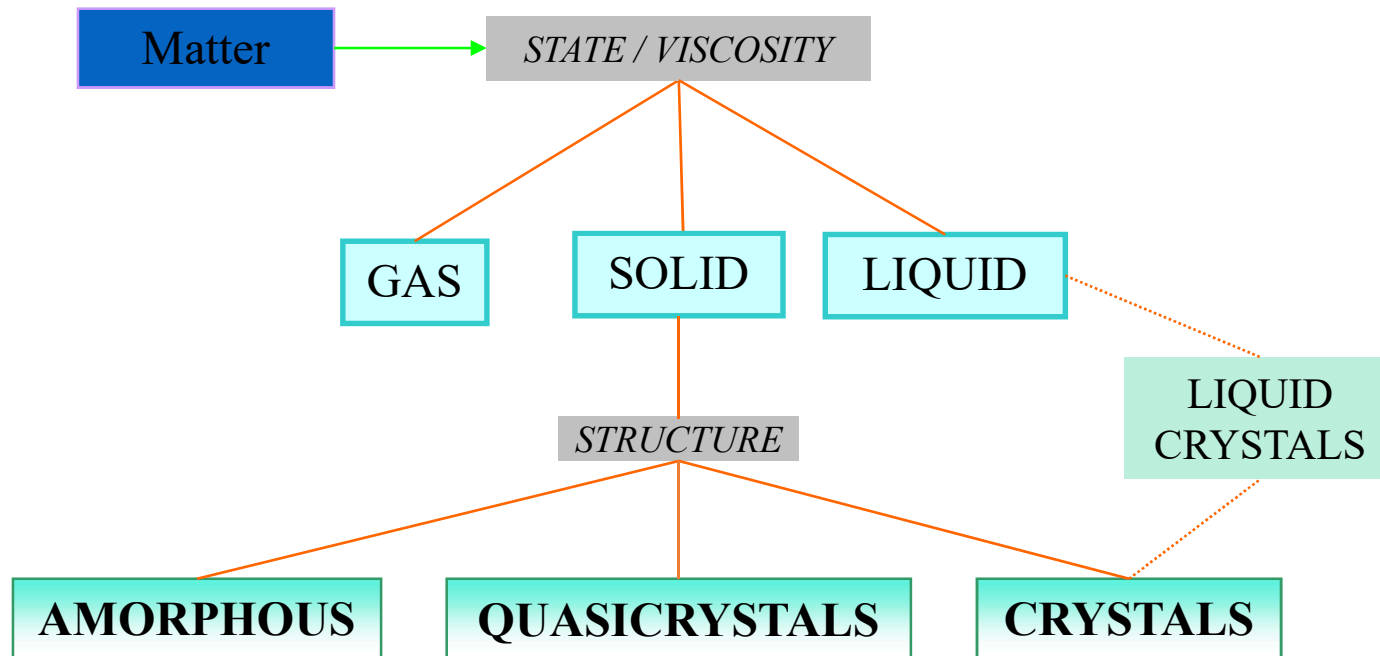
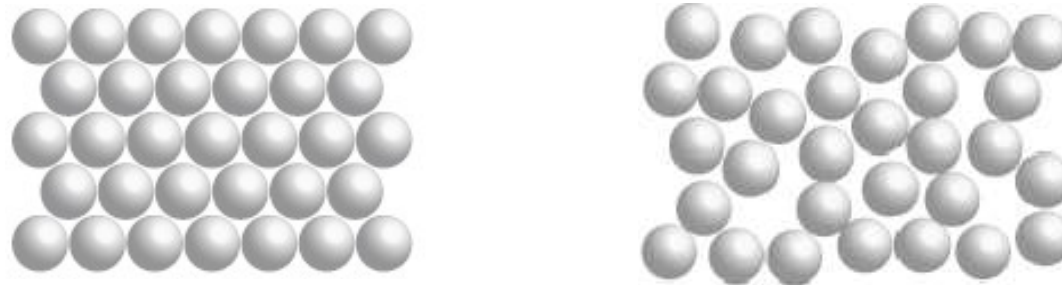


Fig. 4.23 The origin of constitutional supercooling ahead of a planar solidification front. (a) Composition profile across the solid/liquid interface during steady-state solidification. The dashed line shows dX_L/dx at the S/L interface. (b) The temperature of the liquid ahead of the solidification front follows line T_L . The equilibrium liquidus temperature for the liquid adjacent to the interface varies as T_e . Constitutional supercooling arises when T_L lies under the critical gradient.

Solidification during Quenching from Melt





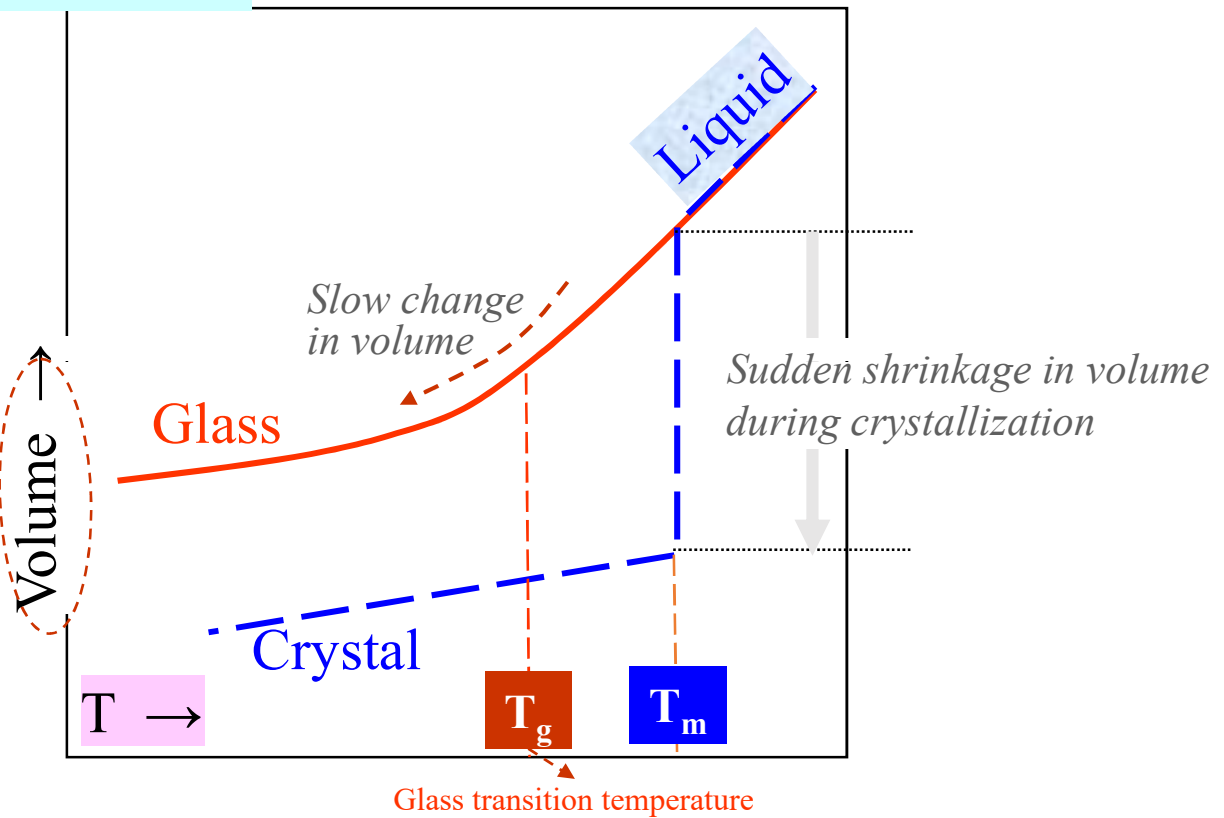
Atomic arrangement in: (a) conventional crystalline material, (b) in amorphous material

Materials in which such a disordered structure is produced directly from the liquid state during cooling are called "**glasses**", and so amorphous metals are commonly referred to as "**metallic glasses**" or "**glassy metals**".

Glass Transition

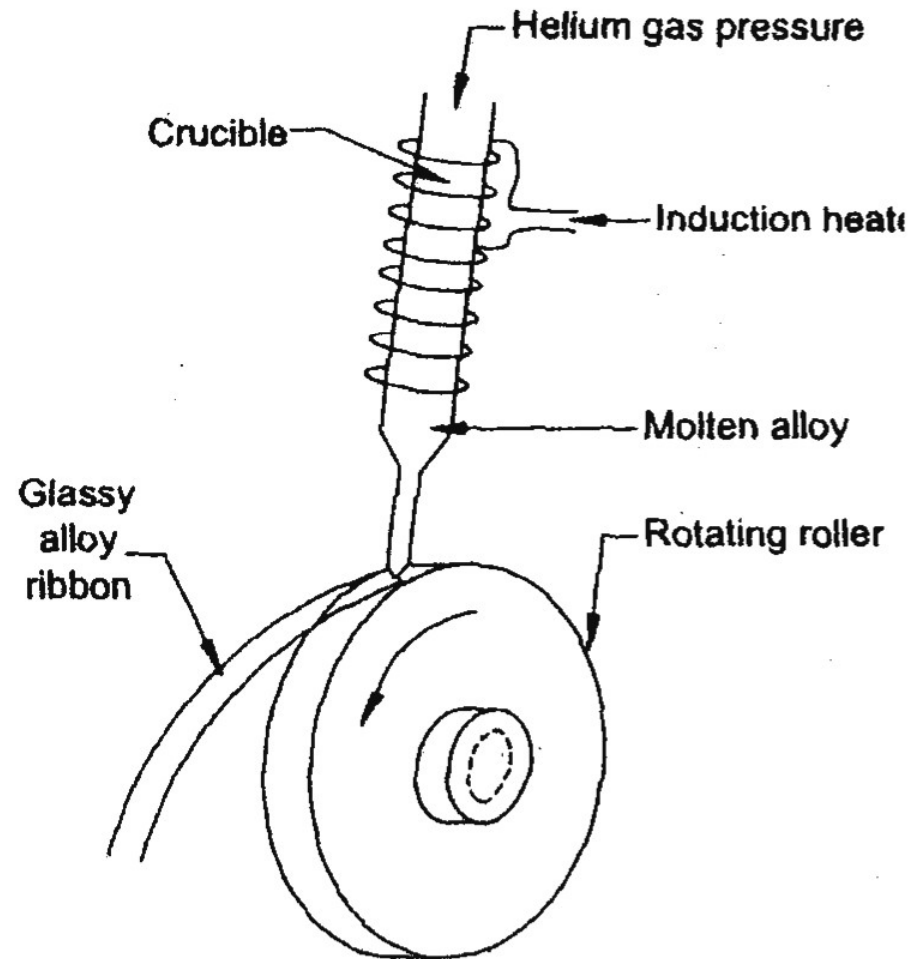
“All materials would amorphize on cooling *unless* crystallization intervenes”

Instead of V we can plot other **extensive** thermodynamic quantities (*i.e. they all show same behaviour*) \rightarrow **S, H, E**



Amorphous metals can be produced, including:

- physical vapor deposition
- solid-state reaction,
- melt spinning
- mechanical alloying



- like other kinds of glasses they experience a glass transition into a supercooled liquid state upon heating.
- the amorphous atomic structure means that metallic glasses do not have the crystalline defects called dislocations
 - The combination of high strength and low stiffness gives metallic glass very high resilience,



Liquid metal Technologies produced the golfing putter shown here:

<https://www.youtube.com/watch?v=Evji4-VUmo>

- Glasses are **metastable**.
- On heating glasses they tend to crystallize. This process occurs by **nucleation** and **growth** of crystallites in the amorphous matrix.
- Many different kinds of materials can be obtained in the amorphous state. These include: polymers, inorganic materials, organic materials, metals and alloys, semiconductors, etc.
- As expected, polymeric glasses will have poor tolerance to heat, while inorganic glasses may withstand high temperatures.

Glass formation

- Certain materials are easy glass formers (e.g. silicates, long chain polymers, etc.), while others are difficult to amorphize (e.g. pure metals, simple alloys, etc.).
- Glasses can be synthesized in many ways. Three typical ways are listed below.
 - 1) **From the vapour state**
 - By condensing the vapour of the material onto a cold substrate.
 - 2) **From the liquid state**
 - Quenching from the melt (usually fast cooling from the molten state). The rate of quenching required depends on the material. To amorphize certain alloys cooling rates of the order of 10^6 K/s need to be employed, while certain special alloys and silicate materials can be slowly cooled to get glass (even ~ 1 K/s).
 - 3) **In the solid state**
 - By severely deforming the crystals (say a polycrystal) an amorphous state can be obtained. Ball milling has been one of the popular examples for this method (for alloys).

Glass Forming Ability & Resistance to Crystallization

- ❑ The tendency for a material to form a glass while quenched is called **glass forming ability**
- ❑ **Glass Formation Ability (GFA)** should be differentiated with **Resistance to Crystallization (RTC)**. Many parameters have been developed to characterize materials with respect to GFA and RTC.
- ❑ Most important parameter for for GFA are:
 - **Critical Cooling Rate (q_{cr})** and
 - **Critical Diameter (d_{cr})**.
- ❑ These two parameters are related to one another

Heating of Glass

- ❑ A glass will tend to crystallize on heating.
- ❑ If crystallization does not intervene, then glasses will slowly soften (i.e. the viscosity will decrease) and will begin to flow.
- ❑ This implies that glasses do not have a well defined melting point like crystals.

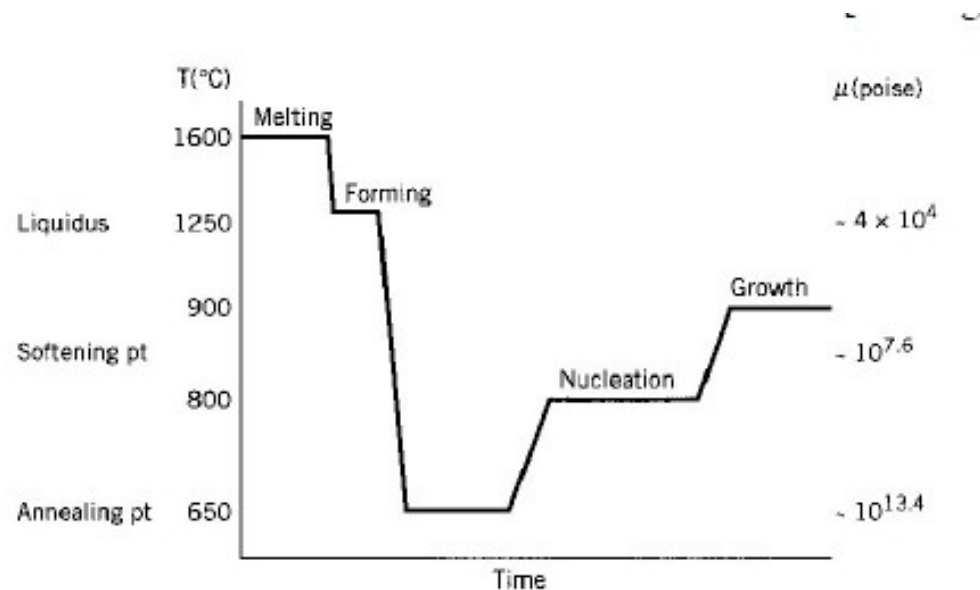


Fig. 5.75 Typical processing cycle for $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass ceramics.

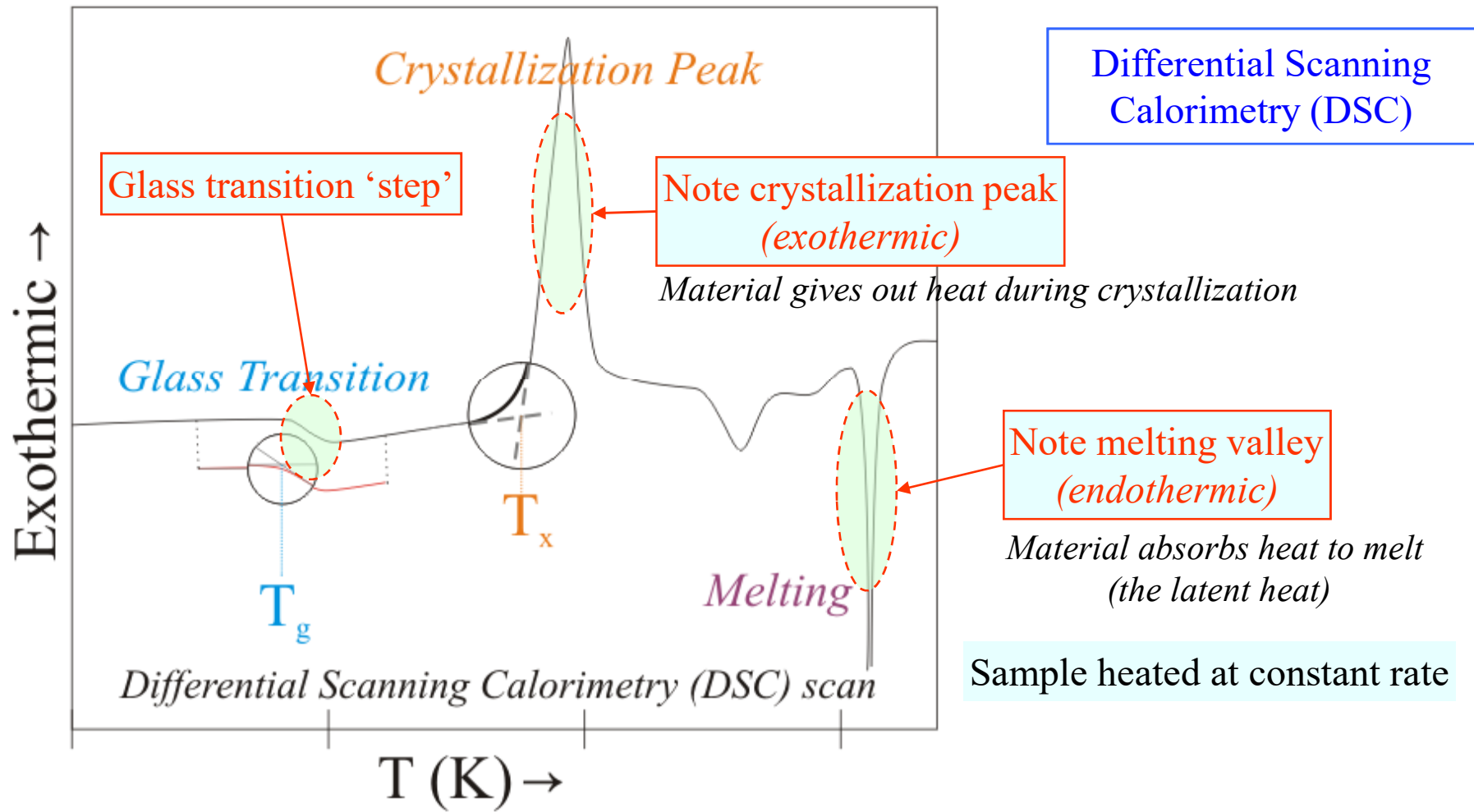
□ The crystallization of glass can be studied by using Differential Scanning Calorimetry (DSC)

□ In a DSC

(i) glass transition appears as a step,

(ii) crystallization(s) as exothermic peak(s) and melting as an endothermic valley.

More than one crystallization peaks may be observed if more than one type of crystal forms during the heating.

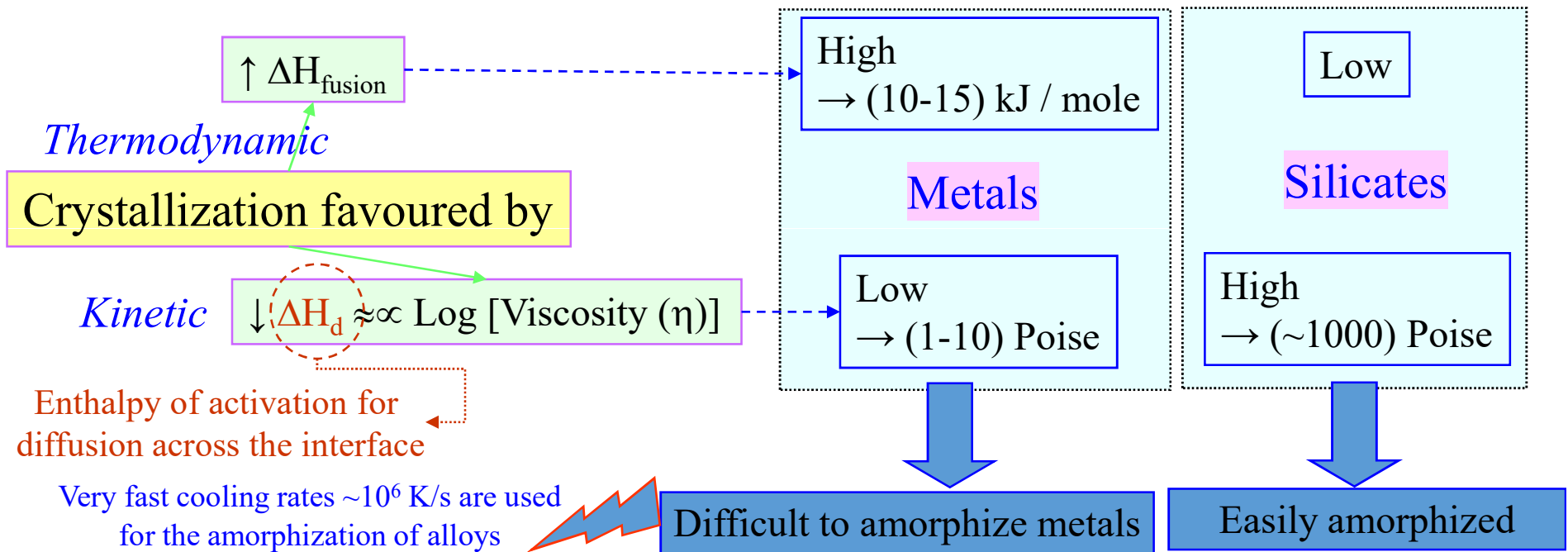


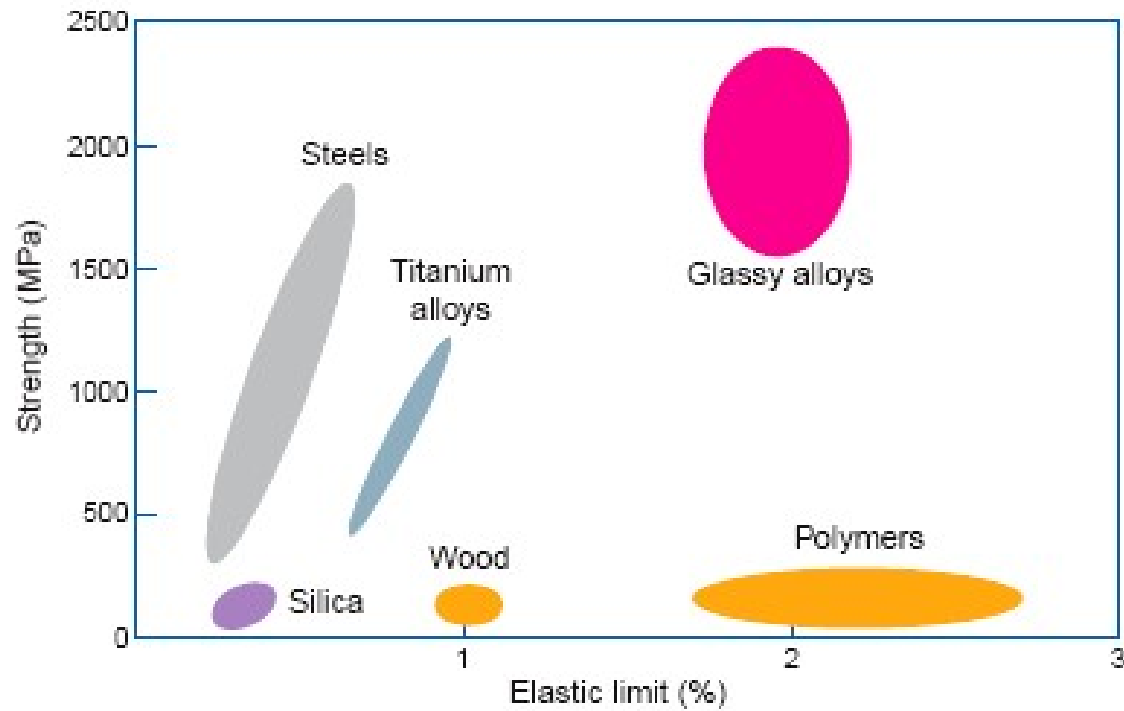
❑ Crystallization is favoured by high enthalpy of fusion (ΔH_{fusion}) and a low viscosity (η).

- The critical Gibbs free energy for the nucleation of a crystal is related to the enthalpy of fusion as in the equation below. Large ΔH_{fusion} implies a lower $\Delta G^*_{\text{crystallization}}$, which further implies ease of crystallization.

$$\Delta G^* \propto \frac{1}{\Delta H_{\text{fusion}}^2}$$

- An embryo becomes a nucleus by jump of atom across the interface from liquid to crystal. This requires a activation enthalpy (ΔH_d). The activation enthalpy is related to the log of viscosity. This implies that a lower viscosity allows for easier atomic jumps, which in turn favours crystallization.





Amorphous metallic alloys combine higher strength than crystalline metal alloys with the elasticity of polymers.