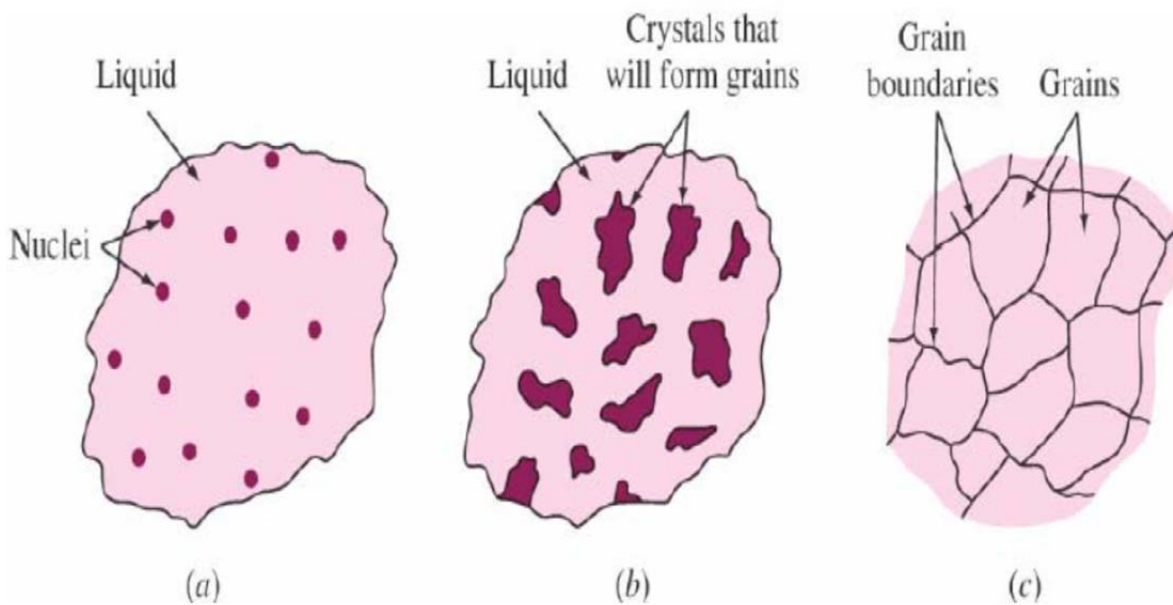


### Chapter 3: Solidification

Solidification is basically phase transformation from liquid phase to solid phase. The progress of a phase transformation takes place in two stages: nucleation and growth. Nucleation involves the appearance of very small particles, or nuclei of the new phase (often consisting of only a few hundred atoms), which are capable of growing. During the growth stage these nuclei increase in size, which results in the disappearance of some (or all) of the parent phase.



#### Driving Force

Solidification is undoubtedly the most important processing route for metals and alloys. Consider a pure metal (Fig. 1). At the fusion temperature  $T_f$ ,  $\Delta G = 0$  so that

$$\Delta G_f = \Delta H_f - T_f \Delta S_f = 0 \text{ or } \Delta H_f = T_f \Delta S_f$$

where  $\Delta H_f$  is the latent heat of fusion,  $\Delta G_f$  is the Gibb's and  $\Delta S_f$  is the entropy, i.e. positive for melting. For any  $T$ ,

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

$$\text{Or } \Delta G \cong \Delta H_f - T \Delta S_f$$

$$= \Delta S_f (T_f - T) = \Delta S_f \Delta T$$

Where  $\Delta T$  is undercooling.

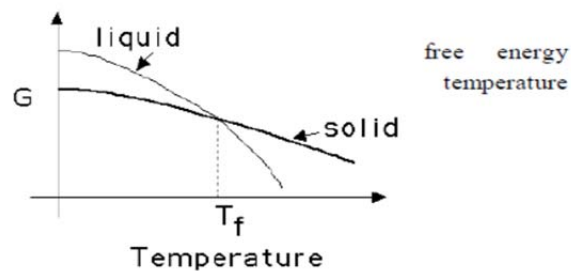


Fig.1 Driving Force for nucleation.

The driving force is therefore proportional to the undercooling provided that the latent heat and the entropy of fusion do not vary much with temperature.

**Nucleation** There are two types of nucleation: *homogeneous and heterogeneous*. The distinction between them is made according to the site at which nucleating events occur. For the homogeneous type, nuclei of the new phase form uniformly throughout the parent phase, whereas for the heterogeneous type, nuclei form preferentially at structural in homogeneities, such as container surfaces, insoluble impurities, grain boundaries, dislocations, and so on.

**Homogeneous Nucleation** Nucleation without preferential nucleation sites is homogeneous nucleation. Homogeneous nucleation occurs spontaneously and randomly, but it requires Superheating or supercooling of the medium. Let us first consider the solidification of a pure material, assuming that nuclei of the solid phase form in the interior of the liquid as atoms cluster together so as to form a packing arrangement similar to that found in the solid phase. Furthermore, it will be assumed that each nucleus is spherical in geometry and has a radius  $r$ .

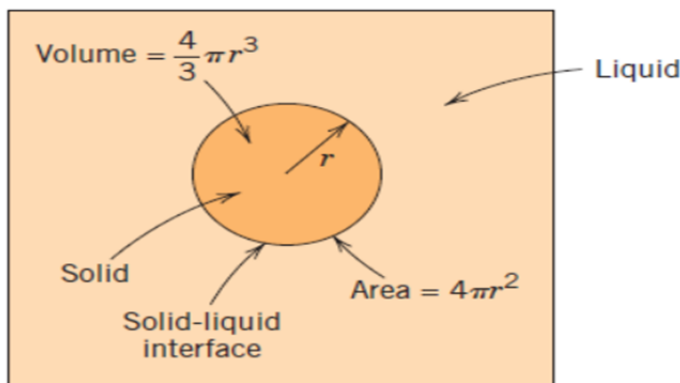
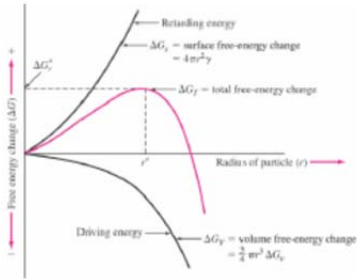


Fig.2 Schematic diagram showing the

There are two contributions to the total free energy change that accompany a solidification transformation.

- (i) The first is the free energy difference between the solid and liquid phases, or the volume free energy, i.e  $\frac{4}{3} \pi r^3 \Delta G_V$ . where  $\Delta G_V$  is the volume free energy change .
- (ii) The second is the surface energy, results from the formation of the nucleation of a spherical solid particle in a liquid, i.e  $4 \pi r^2 \gamma$ .

Finally, the total free energy change ( $\Delta G$ ) is equal to the sum of these two contributions—that is



$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma \dots (1)$$

### Critical Radius( $r^*$ )-

Differentiate the equation (Equation 1) with respect to  $r$ , set the resulting expression equal to zero, and then solve for critical radius ( $r^*$ ). That is and activation free energy ( $\Delta G^*$ )

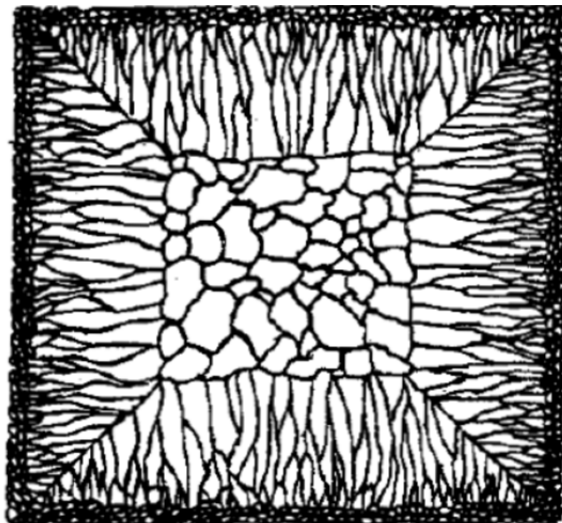
$$r^* = \frac{-2\gamma}{\Delta G_v} = \frac{-2\gamma T_f}{\Delta H_f \Delta T}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v} = \frac{16\pi\gamma^3 T_f^2}{3\Delta H_f^2 \Delta T}$$

When radius ( $r$ ) is less than critical radius ( $r^*$ ), termed as an embryo. and when radius ( $r$ ) is greater than critical radius ( $r^*$ ), termed as an nuclei.

### Geometry of Solidification

The chill zone contains fine crystals nucleated at the mould surface. There is then selective growth into the liquid as heat is extracted from the mould. If the liquid in the centre of the mould is undercooled sufficiently there may also be equiaxed grains forming.



## Phase diagram

- Map that gives relationship between phases in equilibrium in a system as a function of T, P and composition. Map demarcating regions of stability of various phases Variables/Axis of phase diagrams
- The axes can be:
  - o Thermodynamic (T, P, V)
  - o Kinetic (t) or Composition variables (C, %X)
- In single component systems (unary systems) the usual variables are T & P
- In phase diagrams used in materials science the usual variable are T & %X
- In the study of phase transformation kinetics TTT diagrams or CCT diagrams are also used where the axis are T & t

System Components Phase diagrams and the systems they describe are often classified and named for the number (in Latin) of components in the system:

Number of components	Name of system or diagram
<i>One</i>	Unary
<i>Two</i>	Binary
<i>Three</i>	Ternary
<i>Four</i>	Quaternary
<i>Five</i>	Quinary
<i>Six</i>	Sexinary
<i>Seven</i>	Septenary
<i>Eight</i>	Octanary
<i>Nine</i>	Nonary
<i>Ten</i>	Decinary

## Experimental Methods

**Thermal Analysis:** A plot is made of temperature vs. time, at constant composition, the resulting cooling curve will show a change in slope when a phase change occurs because of the evolution of heat by the phase change. This method seems to be best for determining the initial and final temperature of solidification. Phase changes occurring solely in the solid state generally involve only small heat changes, and other methods give more accurate results.

**Metallographic Methods:** This method consists in heating samples of an alloy to different temperatures, waiting for equilibrium to be established, and then quickly cooling to retain their high temperature structure. The samples are then examined microscopically. This method is difficult to apply to metals at high temperatures because the rapidly cooled samples do not always retain their high temperature structure, and considerable skill is then required to interpret the observed microstructure correctly.

**X-ray diffraction:** Since this method measures lattice dimensions, it will indicate the appearance of a new phase either by the change in lattice dimension or by the appearance of a new crystal structure. This method is simple, precise, and very useful in determining the changes in solid solubility with temperature.

### Gibbs Phase Rule

- The phase rule connects the Degrees of Freedom, the number of components in a system and the number of phases present in a system via a simple equation.
- To understand the phase rule one must understand the variables in the system along with the degrees of freedom.
- We start with a general definition of the phrase “degrees of freedom”.

**Degrees of Freedom:** The degree of freedom,  $F$ , are those externally controllable conditions of temperature, pressure, and composition, which are independently variable and which must be specified in order to completely define the equilibrium state of the system.

For a system in equilibrium

$$F = C - P + 2$$

or

$$F - C + P = 2$$

$F$ – Degrees of Freedom
$C$ – Number of Components
$P$ – Number of Phases

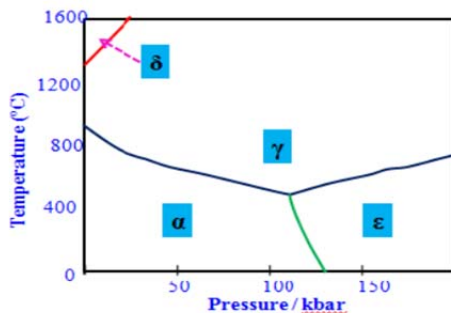
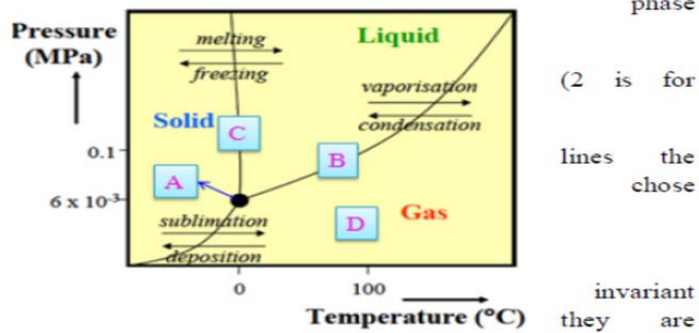
The degrees of freedom cannot be less than zero so that we have an upper limit to the number of phases that can exist in equilibrium for a given system. Variables in a phase diagram

- $C$  – No. of components

- P – No. of phases
- F – No. of degrees of freedom
- Variables in the system = Composition variables + Thermodynamic variables
- Composition of a phase specified by (C – 1) variables (If the composition is expressed in %ages then the total is 100% → there is one equation connecting the composition variables and we need to specify only (C - 1) composition variables)
- No. of variables required to specify the composition of all phases: P(C – 1) (as there are P phases and each phase needs the specification of (C – 1) variables).

### Unary Phase Diagram

- Let us start with the simplest system possible: the unary system wherein there is just one component.
- Though there are many possibilities even in unary phase diagram (in terms of the axis and phases), we shall only consider a T-P unary phase diagram.
- Let us consider the water (H<sub>2</sub>O) unary diagram
- The Gibbs phase rule here is:  $F=C-P+2$  T&P) (no composition variables here)
- Along the 2 phase co-existence (at B & C) degree of freedom (F) is 1→ i.e. we can either T or P and the other will be automatically fixed.
- The 3 phase co-existence points (at A) are points with  $F=0$ . (Invariant point implies fixed for a given system).
- The single phase region at point D, T and P can both be varied while still being in the single phase region with  $F = 2$ .



- The above figure represents the phase diagram for pure iron. The triple point temperature and pressure are 490°C and 110 kbars, respectively.  $\alpha$ ,  $\gamma$  and  $\epsilon$  refer to ferrite, austenite and  $\epsilon$ -iron, respectively.  $\delta$  is simply the higher temperature designation of  $\alpha$ .