

# MATERIAL SCIENCE

## ASSIGNMENT

### **TOPIC:-PRINCIPLES OF SOLIDIFICATION:NEUCLEATI ON AND GROWTH,HOMOGENEOUS AND HETEROGENEOUS NEUCLEATION**

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# INTRODUCTION TO SOLIDIFICATION

The processes of freezing and melting were present at the beginning of the Earth and continue to affect the natural and industrial worlds. These processes created the Earth's crust and affect the dynamics of magmas and ice floes, which in turn affect the circulation of the oceans and the patterns of climate and weather. A huge majority of commercial solid materials were “born” as liquids and frozen into useful configurations. The systems in which solidification is important range in scale from nanometers to kilometers and couple with a vast spectrum of other physics.

The solidification of a liquid or the melting of a solid involves a complex-interplay of many physical effects. The solid–liquid interface is an active free boundary from which latent heat is liberated during phase transformation. This heat is conducted away from the interface through the solid and liquid, resulting in the presence of thermal boundary layers near the interface. Across the interface, the density changes, say, from  $\rho_l$  to  $\rho_s$ . Thus, if  $\rho_s > \rho_l$ , so that the material shrinks upon solidification,

a flow is induced toward the interface from “infinity.”

If the liquid is not pure but contains solute, preferential rejection or incorporation of solute occurs at the interface. For example, if a single solute is present and its solubility is smaller in the (crystalline) solid than it is in the liquid, the solute will be rejected at the interface.

So Basically Solidification means

1. To make solid; make into a hard or compact mass; change from a liquid or gaseous to a solid form.
2. to unite firmly or consolidate.
3. to form into crystals; make crystallize
4. to become solid.
5. to form into crystals; become crystallized.

## USES OF SOLIDIFICATION

Solidification processing is of considerable industrial importance. It is extensively used for metals, and also for polymers and semiconductors. In most cases, the rate at which solidification occurs is controlled by the heat flow. However, there are also important solute

redistribution phenomena, particularly in metallic alloys and semiconductors, and there is often a complex interplay between heat flow, microstructure (including dendrite structure) and defect production (such as porosity and hot cracking). An understanding of the science of solidification is therefore essential for optimisation of these processes.

## TYPES OF SOLIDIFICATION

Directional solidification and progressive solidification are types of solidification within castings. Directional solidification is solidification that occurs from farthest end of the casting and works its way towards the sprue. Progressive solidification also known as parallel solidification, is solidification that starts at the walls of the casting and progress perpendicular from that surface.

**SPRUE:** A **sprue** is the vertical passage through which liquid material is introduced into a mold and it is a large diameter channel through which the material enters the mold. It connects pouring basin to the runner. In many cases it controls the flow of material into the mold.

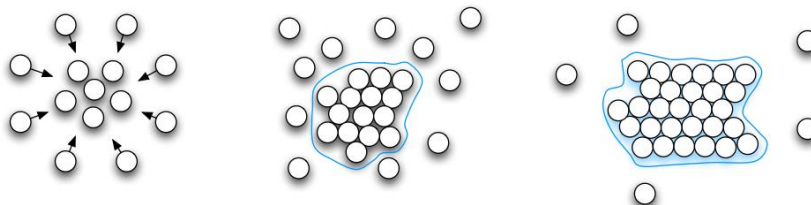
During casting or molding, the material in the sprue will solidify and need to be removed from the finished part. It

is usually tapered downwards to minimize turbulence and formation of air bubbles



## NUCLEATION AND GROWTH

Nucleation is the initial process that occurs in the formation of crystal from a solution, a liquid or a vapour, in which a small number of ions, atoms, or molecules become arranged in a pattern characteristic of a crystalline solid, forming a site upon which additional particles are deposited as crystal grows.



## DIFFERENCE BETWEEN NUCLEATION AND PARTICAL GROWTH

Nucleation is the formation of a new structure where as particle growth is the process of increasing the pre-existing structure. A distinction between the nucleation and the growth stages of a transformation becomes necessary for the following reason. When a  $\beta$  particle is formed, a new interface is created between the particle and the liquid. Like all surfaces, this interface has a positive energy, which must be supplied during the transformation process. A tiny particle has a large surface area to volume ratio and can therefore be unstable. For a spherical particle of radius  $r$ ,

$$\text{Surface area/volume} = \frac{(4\pi r^2)}{\frac{4\pi r^3}{3}} = \frac{3}{r}$$

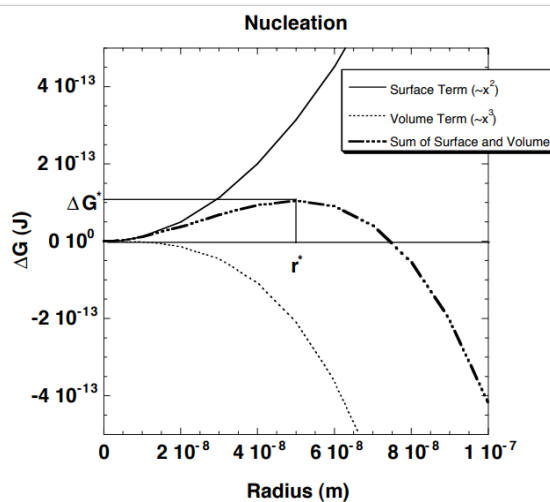
As  $r \rightarrow 0$ , this ratio can become very large and the energy of the surface can effectively prevent the initial formation of a tiny particle. A particle is said to have nucleated, when it becomes stable and will not disappear due to thermal fluctuations. Once the particle has attained this stage, it can grow further with a continuous decrease in energy. The surface energy is no longer a dominant factor in the growth process.

## **TEMPERATURE DEPENDENCE OF**

# NEUCLEATION

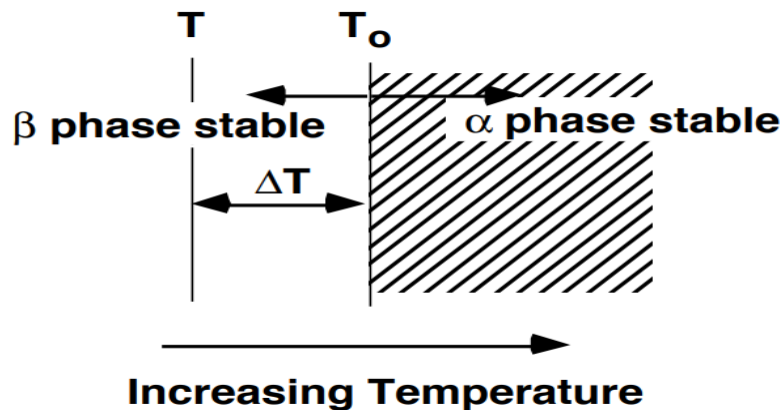
It has been found that the nucleation centres decrease drastically as the temperature increases .

- Consider the nucleation of a new phase at a temperature  $T$ . The transition temperature ( $T$ ) is below that predicted by thermodynamics when surface or volume are not considered
- We can estimate the free energy change as a function of the radius of the nuclei from the volume and surface terms
- When  $r$  is small, surface dominates



- When  $r$  is large, volume dominates
- $r^*$  is the inflection point

$$\Delta T = T_0 - T$$



$r^*$  is the critical size nucleus and inflection point on the curve

$$\text{At } r^*: \frac{\partial \Delta G_r}{\partial r} = 0$$

- We can use this to calculate  $r^*$  and  $\Delta G_r^*$

$$s^* = -\frac{2\gamma}{\Delta m_v} \quad \Delta G_r^* = 16\pi\gamma^3 / 3(\Delta G_v)^2$$

## FREE ENERGY CHANGE VS RADIUS OF NUCLEUS

$$\Delta G_t = \frac{4\pi r^3}{3} \Delta\mu + 4\pi r^2 \gamma$$

$\Delta G_t$  – total free-energy change

$r$  – radius of embryo or nucleus

$\Delta\mu$  – volume free energy

$\gamma$  - specific surface free energy

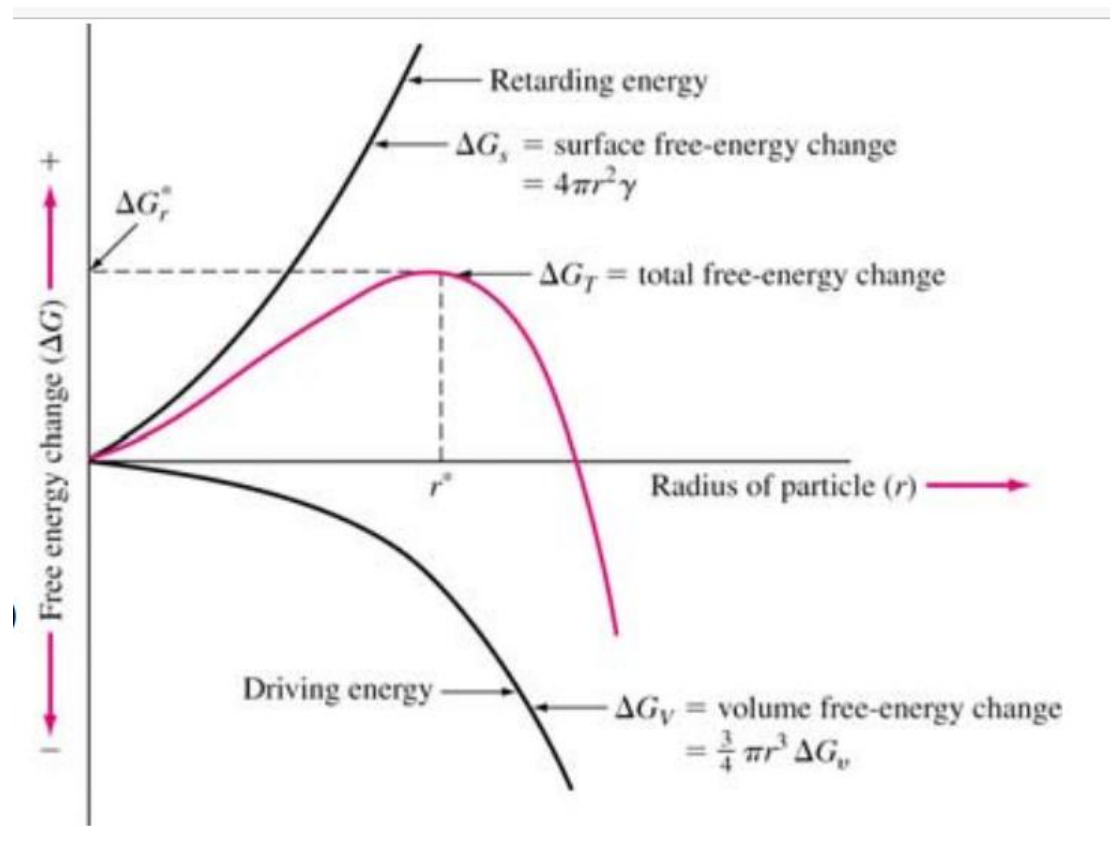


Two components: (i) volume free energy change ( $\Delta G_v$  or  $\Delta\mu$ ) and (ii) surface free-energy change  $\Delta G_s$

$$\Delta\mu = \mu_S - \mu_L < 0$$

$$\mu_S < \mu_L$$

(i) is negative, (ii)  $\Delta G_v$  is positive

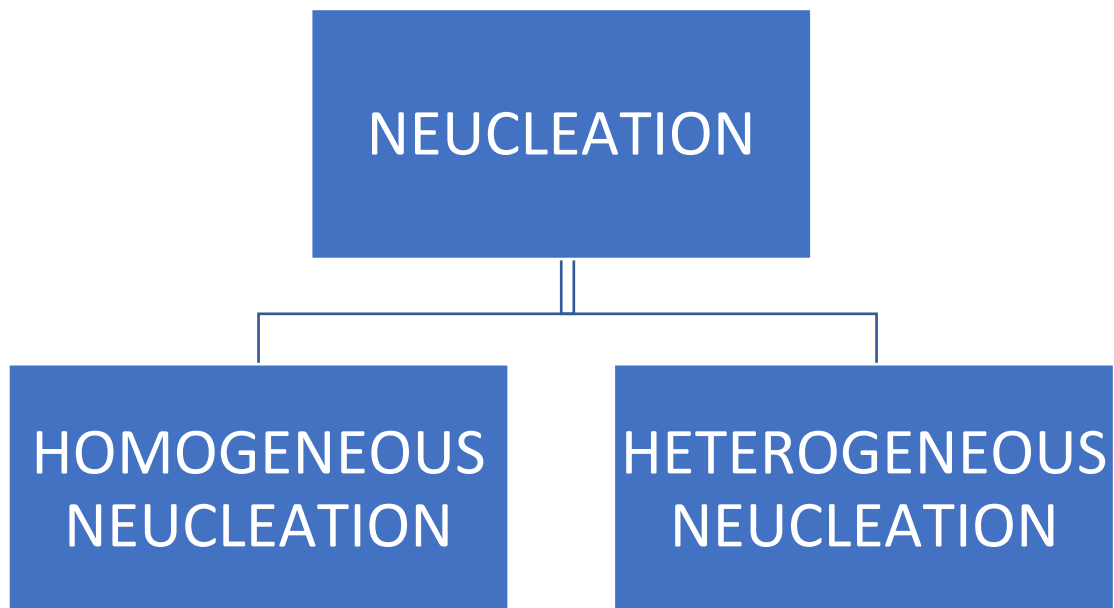


$r^*$  - critical radius

-if  $r < r^*$ , droplet can shrink or dissolve

-if  $r > r^*$ , droplet grows

## TYPES OF NEUCLEATION



## **HOMOGENEOUS NUCLEATION**

Homogeneous nucleation is the process of nucleation that takes place away from the surface of the system. In homogeneous nucleation, the probability of nucleation occurring at any given site is identical to that at any other site within the volume of the parent phase. We will consider this type of nucleation first. If  $f$  is the free energy change accompanying the formation of a spherical new phase particle, we can write

$$\Delta f = \frac{4}{3} \pi r^3 \Delta g + 4\pi r^2 \gamma$$

$r$  is the radius of the particle,  $g$  is the Gibbs free energy change where per unit volume and  $\gamma$  is the surface energy per unit area of the interface separating the parent and the product phases. The surface energy term is always positive. If  $g$  is negative, the function  $f$  passes through a maximum. Initially as the new phase particle starts to form, the energy of the system increases, as the surface energy term is dominant. At the maximum, the variations with  $r$  of the surface energy and the volume (Gibbs) free energy exactly balance each other.

Thereafter, the variation in the volume term becomes dominant and, as this term is negative, there is a continuous decrease in the energy of the system

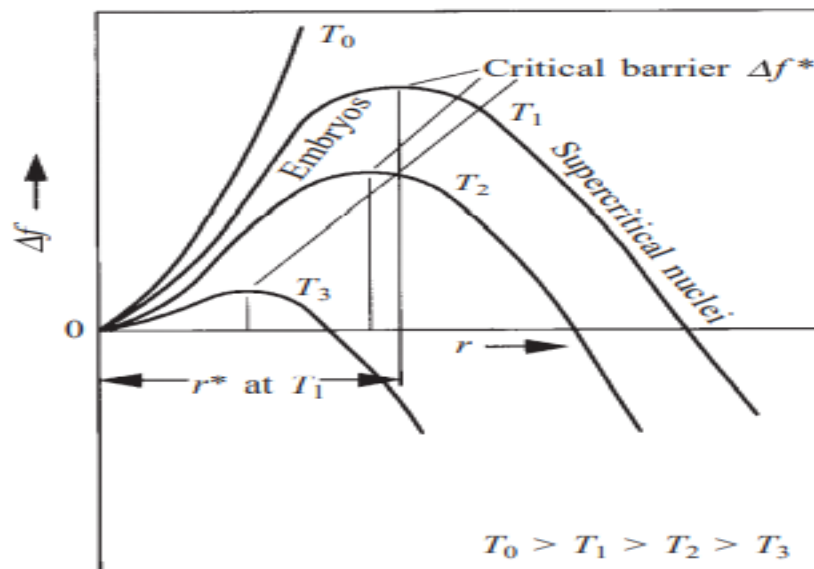
. By setting  $(df/dr) = 0$ , the values corresponding to the maximum, called the critical values and denoted by the superscript \*, are obtained

$$r^* = -\frac{2\gamma}{\Delta g}$$

$$\Delta f^* = \frac{16}{3} \pi \gamma^3 / (\Delta g)^2$$

$f$  is plotted as a function of  $r$  for different temperatures . The critical values of the free energy of nucleation  $f^*$  and of the particle radius  $r$  are indicated in the figure. Particles which are smaller than the critical size are called embryos. Those which are larger than the critical

size are called nuclei (not to be confused with atomic nuclei). The critical sized particle is a critical nucleus. As  $\Delta f$  becomes more negative with a lowering of the temperature, the critical condition occurs at smaller values of  $\Delta f$  and  $r$

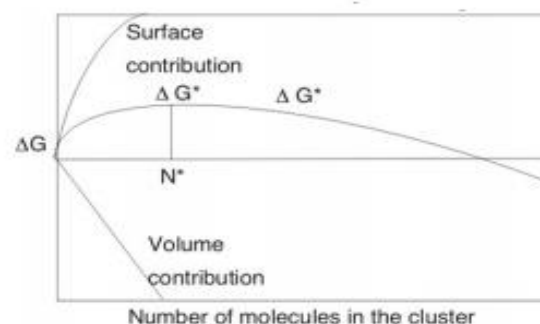
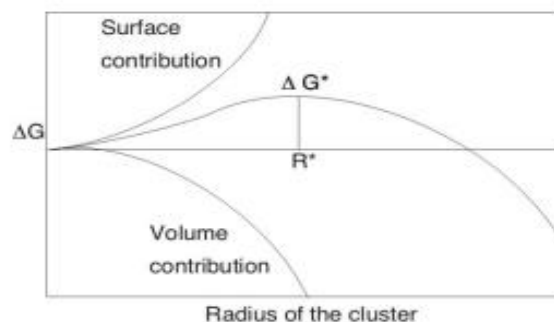


T3 Fig. 9.3 The free energy change  $\Delta f$  during nucleation, as a function of the particle radius  $r$  at different temperature.

The classical binary homogenous nucleation theory describes the gibbs free energy change during the formation of a spherical nucleus of radius  $r$  containing  $n_1$  and  $n_2$  number of molecules of two different compounds under constant temperature  $T$  and pressure conditions as

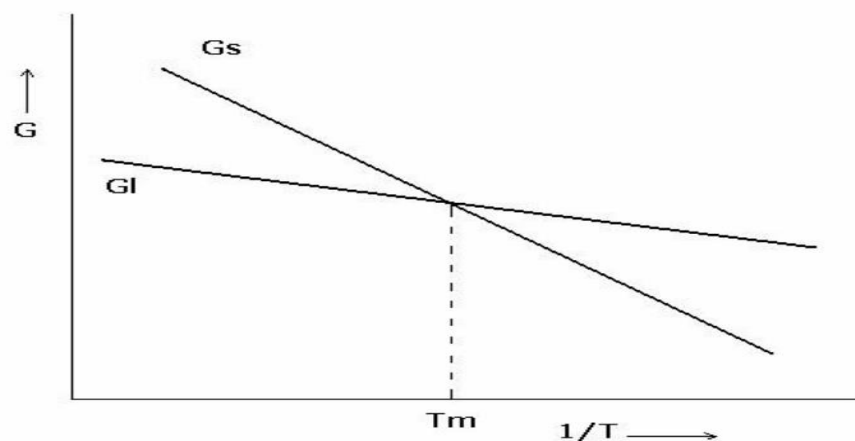
$$\Delta G_{\text{hom}} = -k_B T \sum_{i=1}^2 n_i \ln \left( \frac{P_i}{P_{s,i}} \right) + 4\pi\sigma r^2,$$

Where  $P_i$  is the ambient partial pressure of free molecules of species  $i$ ,  $P_{s,i}$  is the equilibrium vapour pressure of species  $s_i$  above a flat solution surface, and  $\sigma$  is the surface tension of a flat liquid-vapour interface with the same composition as the nucleus. The fraction  $S_i = \frac{P_i}{P_{s,i}}$  is known as the saturation ratio. If we were to plot the free energy of formation as a function of the number of molecules, we would obtain a surface (not a curve as in one-component case), since  $n_1$  and  $n_2$  are treated separately



Nucleation free energy  $\Delta G$  as a function of the radius and the number of molecules in the cluster. The classical nucleation theory describes the free energy as the sum of the surface and volume contributions

When a pure metals cools down in the liquid state, it will transform to the solid state at some state at some temperature there is only one temperature at which a pure solid metal can co-exists with pure liquid metal. At this temperature, corresponding to the equilibrium lower than  $T_m$ , the free energies of liquid and solid are equal. At temperature lower than  $T_m$  the solid has a lower free energy and will be the stable state.  $T_m$  is also the temperature of melting of the solid on heating. A metal will tend to solidify when its temperature is below the melting point because there is decrease in free energy of undercooling the larger the driving force to transform from liquid to solid



Variation of free energy for a pure liquid ( $G_L$ ) and a pure solid ( $G_S$ ) as a function of  $1/T$ ;  $T_m$  is the equilibrium melting temperature

Some facts about homogenous nucleation

- (1) it is also known as **self nucleation**
- (2) in this the formation of nuclei starts in the interior of a uniform substance such as pure liquid metal
- (3) it is a slower process
- (4) it occurs with much more difficulty.
- (5) in this we need to provide supercooling or superheating to occur nucleation.
- (6) the surface area that contributes to the growth of nucleus is high.
- (7) the whole mixture is in the same phase.

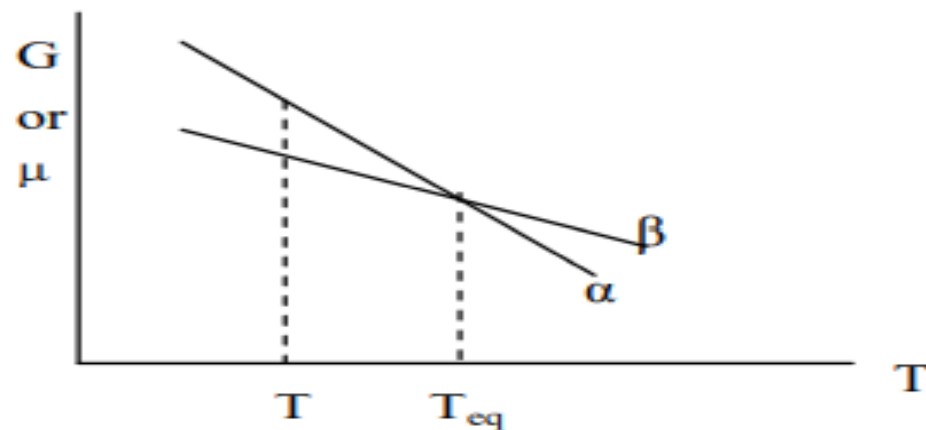
A special case: homogeneous nucleation in solid-solid phase transformation

In a solid-solid transformation, a small change in specific volume that occur must be accommodated elastically, leading to strain energy effect. Such a strain energy change must be included, together with the volume free

energy and interfacial energy changes, into the free energy change of a solid-solid transformation

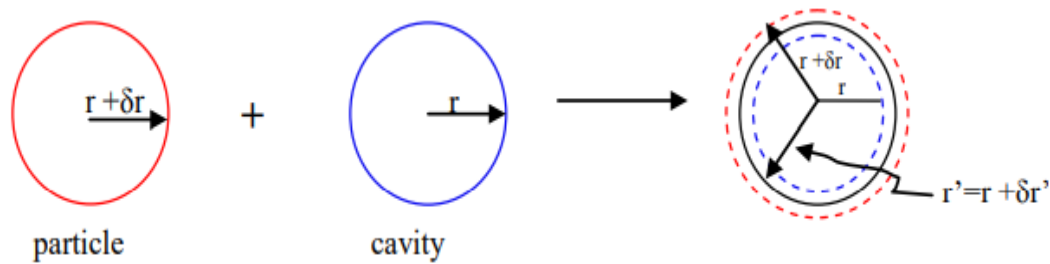
$$\Delta G(r) = \frac{4\pi}{3} r^3 \Delta G_v + 4\pi r^2 \gamma + \text{strain energy}$$

Now let's derive the strain energy consider  $\alpha \rightarrow \beta$  below  
Solid-solid transformation depicted below



Assuming  $V_M^\beta > V_M^\alpha$ , when a beta particle of radius  $r$  forms in a matrix, both particle and matrix must deform elastically to accommodate the phase transformation. The formation of such a coherent interface raises the free energy of the system on account of the elastic strain fields that arise. Somehow we can consider such a misfit as fitting a beta particle of radius  $r + \delta r$  into a cavity of radius  $r$  in  $\alpha$  as depicted below





With the mutual deformation of the two phases the net radial strain as

$$\mathbf{E} = \frac{\delta r}{r'} \cong \frac{\delta r}{r}$$

## Summary of homogeneous nucleation in solids

- (1) Typically for solid state nucleation elastic energy contribution dominates at small particles sizes and the interfacial energy can be reduced significantly by adopting a coherent structure.
- (2) In supersaturated crystalline solutions the particles of the new phase initially formed are generally coherent with the matrix due to the lowest interfacial energy compared to the semi-coherent or incoherent sources
- (3) When the nucleation phase has a different volume or shape then the matrix it replaces elastic energy must be considered as part of the volumetric contribution to nucleation as described in the equation

$$\Delta G(r) = \frac{4\pi}{3}r^3\Delta G_V + 4\pi r^2\gamma + \frac{4\pi}{3}r^3C'E^2 = \frac{4\pi}{3}r^3(\Delta G_V + \Delta G_S) + 4\pi r^2\gamma.$$

## **HETEROGENEOUS NUCLEATION**

Heterogeneous nucleation occurs much more often than homogeneous nucleation. It requires less energy than homogeneous nucleation. Heterogeneous nucleation applies to the phase transformation between any two phase of gas, liquid, or solid, typically for example, condensation of gas/vapor, solidification from liquid, bubble formation from liquid, etc.

**Heterogeneous nucleation forms at preferential sites such as phase boundaries, surfaces (of container, bottles, etc.) or impurities like dust. At such preferential sites, the effective surface energy is lower, thus diminishes the free energy barrier and facilitating nucleation.**

Many important industrial processes rely on heterogeneous catalysis, in which the catalyst is in a different phase. Usually the catalyst is a solid and the reactants are gases, and so the rate-limiting step occurs at the solid surface. Thus heterogeneous catalysis is also referred to as surface catalysis.

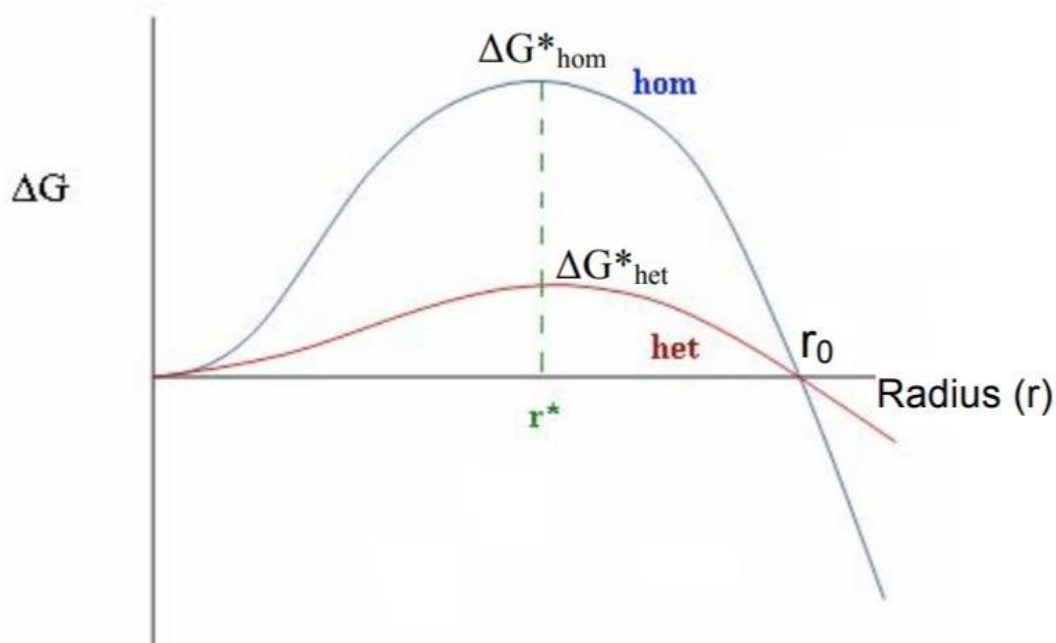
Surfaces promote nucleation because of wetting – contact angles greater than zero between phases facilitate particles to nucleate. The free energy needed for heterogeneous nucleation is equal to the product of homogeneous nucleation and a function of the contact angle ( $\theta$ ):

$$\Delta G_{\text{heterogeneous}} = \Delta G_{\text{homogeneous}} * f(\theta)$$

where

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

The barrier energy needed for heterogeneous nucleation is reduced (see the plot below). The wetting angle determines the ease of nucleation by reducing the energy needed.



Some examples of heterogeneous nucleation include:

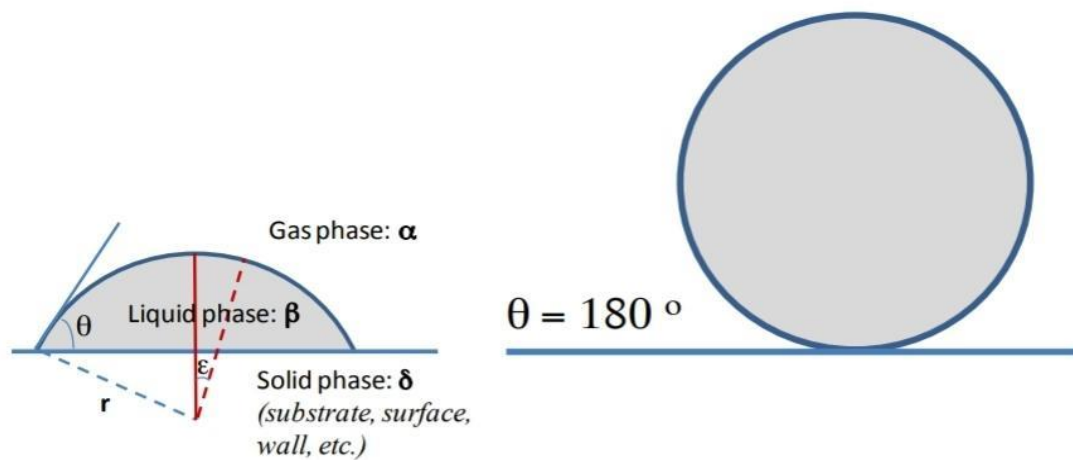
1) Bubbles of carbon dioxide nucleate shortly on the inner surface of a container after it is gently opened (as the pressure is released). Since the surface is smooth and flat (specific surface area is small), bubble formation on such surface is usually slow as you often see in life.

2) Putting a finger into the carbonated water usually facilitates the bubble formation as you see from the picture below, because finger surface (more rough compared to the glass or plastic substrate) provides much larger surface area.

3) Putting a chalk (with even larger surface area due to the porous structure) leads to much faster formation (nucleation) of bubbles from the carbonated water.

A droplet of liquid on a flat solid surface takes the shape of a truncated sphere. The surface must be spherical since a liquid does not support a shear stress --- and  $\gamma$

is isotropic.



There are three different surface energies of interest:

$$\gamma_{\alpha\beta} = (\text{gas - liquid}), \quad \gamma_{\alpha\delta} = (\text{gas - solid}), \quad \gamma_{\beta\delta} = (\text{liquid - solid})$$

Consider a droplet of liquid on a flat surface with fixed volume. The total surface energy of the system is a function of the shape of the droplet.

The diagram above shows two different shapes of the same volume, but of different surface area leading to different Surface energy:

$$G_s = \gamma_{\alpha\beta} A_{\alpha\beta} + \gamma_{\alpha\delta} A_{\alpha\delta} + \gamma_{\beta\delta} A_{\beta\delta}$$

where  $A_{\alpha\beta}$ ,  $A_{\alpha\delta}$  and  $A_{\beta\delta}$  are areas of  $\alpha\beta$ ,  $\alpha\delta$  and  $\beta\delta$  interfaces, respectively.

Assume  $r$  be the radius of curvature of the droplet, then:

At equilibrium,

$$dG_S = \left(\frac{\partial G_S}{\partial r}\right)_\theta dr + \left(\frac{\partial G_S}{\partial \theta}\right)_r d\theta = 0$$

then,

$dG_S =$

$$\{4 \pi r \gamma_{\alpha\beta} (1 - \cos\theta) + 2 \pi r (\gamma_{\beta\delta} - \gamma_{\alpha\delta}) \sin^2\theta\} dr + \{2 \pi r^2 \gamma_{\alpha\beta} \sin\theta + 2 \pi r^2 (\gamma_{\beta\delta} - \gamma_{\alpha\delta}) \sin\theta \cos\theta\} d\theta = 0$$

Volume of  $\beta$ ,  $V_\beta$ , can be obtained as,

$$V_\beta = \int_0^\theta (\pi r^2 \sin^2 \varepsilon)(r d\varepsilon \cdot \sin \varepsilon) = \pi r^3 \int_0^\theta \sin^3 \varepsilon d\varepsilon = \frac{\pi r^3}{3} [2 - 3 \cos\theta + \cos^3 \theta]$$

Since volume of  $\beta$  remains fixed,

$$dV_\beta = 0 = \left(\frac{\partial V_\beta}{\partial r}\right)_\theta dr + \left(\frac{\partial V_\beta}{\partial \theta}\right)_r d\theta$$

then, we have

$$dr = -\frac{r \sin\theta(1 + \cos\theta)}{(2 - \cos\theta - \cos^2\theta)} d\theta$$

replacing  $\rightarrow$ , then we have,

$$\cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}} \quad (3)$$

Now let's derive the heterogeneous nucleation energy and critical size:

Assume nucleus to be spherical with radius  $r$ , the free energy change for the nucleation is:

$$\begin{aligned}\Delta G(r) &= V_{\beta}\Delta G_V + \gamma_{\alpha\beta}A_{\alpha\beta} + (\gamma_{\beta\delta} - \gamma_{\alpha\delta})A_{\beta\delta} \quad (\text{two contributions: volumetric free energy} + \text{surface energy}) \\ &= \frac{\pi r^3}{3} [2 - 3\cos\theta + \cos^3\theta] \Delta G_V + \gamma_{\alpha\beta} 2\pi r^2 [1 - \cos\theta] + (\gamma_{\beta\delta} - \gamma_{\alpha\delta}) \pi r^2 \sin^2\theta\end{aligned}$$

From Eq. (3), we have  $(\gamma_{\beta\delta} - \gamma_{\alpha\delta}) = -\gamma_{\alpha\beta} \cos\theta$ , replacing this into above equation, then we have

$$\begin{aligned}\Delta G(r) &= \frac{\pi r^3}{3} \Delta G_V [2 - 3\cos\theta + \cos^3\theta] + \gamma_{\alpha\beta} 2\pi r^2 [1 - \cos\theta] - \gamma_{\alpha\beta} \pi r^2 \cos\theta \sin^2\theta \\ &= \left[ \frac{4\pi}{3} r^3 \Delta G_V + 4\pi r^2 \gamma_{\alpha\beta} \right] \cdot \left[ \frac{2 - 3\cos\theta + \cos^3\theta}{4} \right] \quad (\text{note: } \sin^2\theta = 1 - \cos^2\theta)\end{aligned}$$

*Note the first term in parenthesis is the  $\Delta G(r)$  for homogenous nucleation.*



Then we can re-write

$$\Delta G_{\text{het}}(r) = \Delta G_{\text{hom}}(r) \cdot f(\theta) \quad (4)$$

$$\text{where } f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

$$0 \leq f(\theta) \leq 1.0$$

for  $\theta=180^\circ$ ,  $f(\theta) = 1 \rightarrow$  no wetting of the surface, and thus no catalysis by the surface --- falling into the case of homogeneous nucleation.

for  $\theta=0^\circ$ ,  $f(\theta) = 0 \rightarrow$  full wetting, fully catalyzed, no barrier for nucleation at surface.

The  $\Delta G(r)$  must go through a maximum, where  $\frac{d\Delta G(r)}{dr} = 0$ , then,

$$\left. \frac{d\Delta G(r)}{dr} \right|_{r^*} = 0 = 4\pi r^2 \Delta G_V + 8\pi r \gamma$$

Then we have the critical radius,

$$r^* = -\frac{2\gamma_{\alpha\beta}}{\Delta G_V}$$

*It is important to note that the critical radius  $r^*$  remains unchanged for heterogeneous nucleation and homogeneous nucleation. However, the volume ( $V_\beta$ ) can be significantly less for heterogeneous nucleation due to the wetting angle affecting the shape of the nucleus.*

$$V_\beta (\text{het}) = \frac{\pi r^3}{3} [2 - 3 \cos \theta + \cos^3 \theta] = \frac{4\pi r^3}{3} \left[ \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right] = V_\beta (\text{hom}) \cdot f(\theta)$$

From Eq. (4), we also have

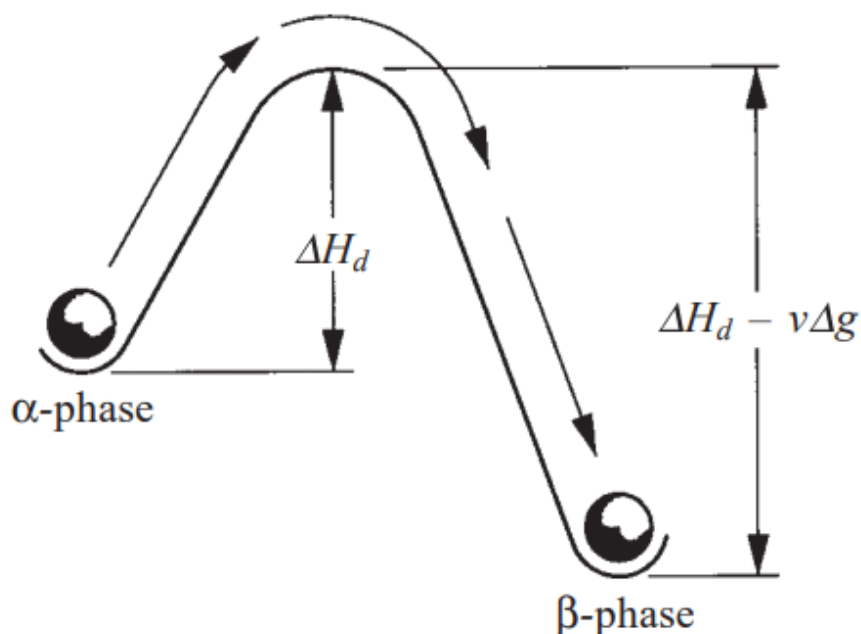
$$\begin{aligned} \Delta G_{\text{het}}^* &= \Delta G_{\text{het}}(r^*) = \Delta G_{\text{hom}}(r^*) \cdot f(\theta) = \Delta G_{\text{hom}}^* \cdot f(\theta) \\ &= \left[ -\frac{4\pi}{3} r^{*3} \Delta G_V + 4\pi r^{*2} \gamma_{\alpha\beta} \right] \cdot f(\theta) = \frac{16\pi \gamma_{\alpha\beta}^3}{3\Delta G_V^2} \cdot f(\theta) \end{aligned}$$

*--- nucleation barrier can be significantly lower for heterogeneous nucleation due to wetting angle affecting the shape of the nucleus.*

**Note:** *The above addressed nucleation is for gas-to-liquid nucleation. The similar theoretical treatment is also applied to the liquid-to-solid nucleation.*

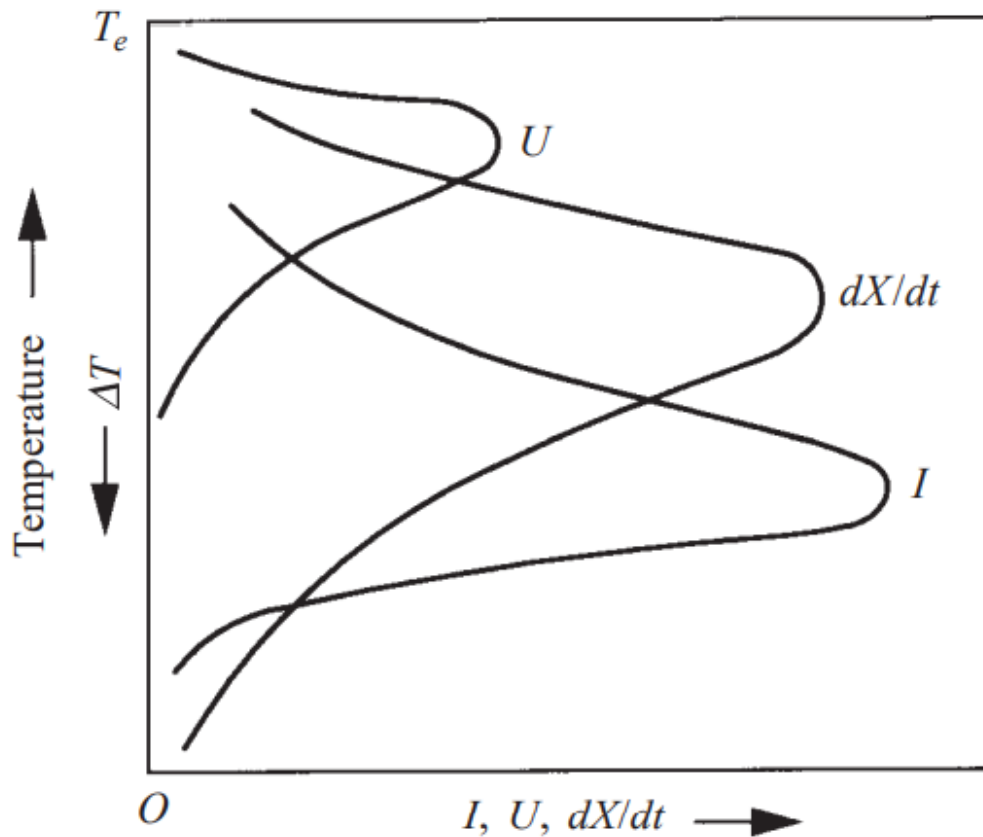
## GROWTH

Growth is the increase in size of the product particle after it has nucleated. Growth usually occurs by the thermally activated jump of atoms from the parent phase to the product phase. Consider the transformation  $\alpha \rightarrow \beta$ .



As a function of temperature, the growth rate first increases with increasing degree of supercooling, but eventually starts to decrease as the thermal energy  $RT$  falls. In Fig. the temperature dependence of the growth rate  $U$  is shown along with the temperature dependence of the nucleation rate  $I$ . The growth rate is also a maximum at some intermediate degree of supercooling. The maximum in the growth rate usually occurs at a

higher temperature than the maximum in the nucleation rate.



The overall transformation kinetics can be described as some function of the growth rate and the nucleation rate:

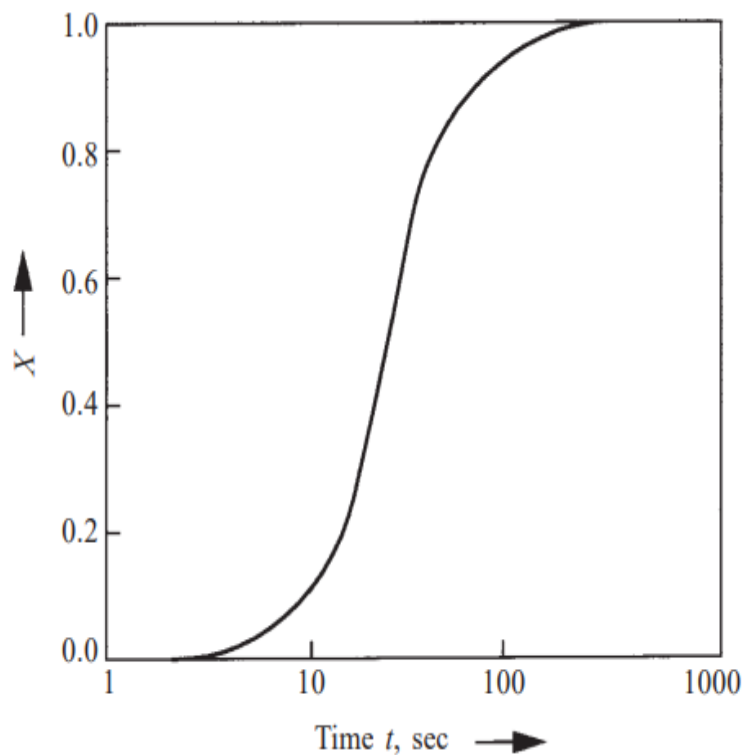
$$dX/dt = f(U, I)$$

where  $dX/dt$  is the rate at which the fraction  $X$  of the new phase increases with time  $t$ . Assuming that a constant rate of nucleation occurs randomly in the untransformed phase and that the product particles

grow at a constant rate as spheres, till impingement with neighbouring particles occurs, the fraction  $X$  can be derived as a function of  $t$ :

$$x = 1 - e^{-\frac{\pi}{3}IU^3t^4}$$

A plot of  $X$  versus  $t$ :



### summery:

- By considering the balance between the release of free energy by transformation and the cost of creating new interface, the critical free energy for nucleation and the critical size of the nucleus can be derived.

- The exponential dependence of nucleation rate on undercooling means that, in effect, no nucleation will be observed until a minimum undercooling is achieved.
- The undercooling required for nucleation is increased by volume changes on transformation, but decreased by the availability of heterogeneous nucleation sites.

**THANK YOU**