

## Part II : Interfaces

### Module 2 : Nucleation of solids from their melt

## 2. Nucleation of solids from their melt

### 2.1 Motivation

If a pure material is kept at its freezing point, there will be no solidification. It needs some undercooling for the liquid to solid transformation to take place. More importantly, there is a critical undercooling above which there is almost no nuclei that form and below which there is an explosion in the number of nuclei that form. Why?

### 2.2 Homogeneous nucleation

Consider a pure melt which is cooled below its melting temperature. Such a liquid is known as undercooled. Let a small volume  $V_s$  of the liquid turn into solid. If  $G_s$  is the free energy per unit volume of the solid, and  $G_l$  that of the liquid, if  $A_{ls}$  is the solid-liquid interfacial area, and if  $\gamma_{sl}$  is the interfacial free energy, then, the total free energy of the system is given by

$$G_f = V_s G_s + V_l G_l + \gamma_{ls} A_{ls} \quad (11)$$

Before the small volume of solid formed, the free energy of the system is given by

$$G_i = (V_s + V_l) G_l \quad (12)$$

Thus, the total free energy change associated with the transformation of a small volume of liquid  $V_s$  into solid is given by

$$\delta G = G_f - G_i = V_s (G_s - G_l) + \gamma_{ls} A_{ls} \quad (13)$$

If  $\Delta G = G_s - G_l$ ,

$$\delta G = V_s \Delta G + \gamma_{ls} A_{ls} \quad (14)$$

Note that the interfacial energy is always positive. Hence the contribution from the second term is always positive. However, depending on whether the liquid is above or below the melting temperature,  $\Delta G$  is positive or negative. Hence, in an undercooled liquid, where  $\Delta G$  is negative, the system will try to minimize the shape in such a way that the overall interfacial energy is reduced so that the maximum reduction in free energy can be achieved.

If we assume interfacial energy to be isotropic, then the volume transformed is a sphere of radius  $r$  (since the maximum volume is enclosed for the minimal surface area for a sphere), we get

$$\delta G = \frac{4}{3}\pi r^3 \Delta G + 4\pi r^2 \gamma_{ls} \quad (15)$$

In Fig. 9, we show the variation of the volume free energy, interfacial energy and the overall free energy change as a function of  $r$ . Since the interfacial contribution goes as  $r^2$  and that of bulk free energy as  $r^3$ , at smaller  $r$ , interfacial energy always dominates, and being a positive energy, it actually suppresses the formation of solid. Unless the size of the solid is above some size wherein the (negative) bulk free energy change can more than compensate for the (positive) interfacial energy, the solid will not be stable (even if it forms). Thus, one can identify the critical radius of the solid that is stable when formed in the undercooled liquid by minimizing  $\delta G$  with respect to  $r$ :

$$\left[ \frac{d\delta G}{dr} \right]_{r=r_c} = 0 = 4\pi r_c^2 \Delta G + 8\pi r_c \gamma_{ls} \quad (16)$$

This implies,

$$r_c = -\frac{2\gamma_{ls}}{\Delta G} \quad (17)$$

Note that since  $\Delta G$  is negative in sign and  $\gamma_{ls}$  positive in sign, as expected, the  $r_c$  is a positive quantity.

In other words, there is a critical radius for which the overall free energy change is zero; any particle above this size will reduce the overall free energy and any particle below this size will increase the overall free energy. In the nucleation literature, particles which are smaller in size than the critical radius are known as embryos.

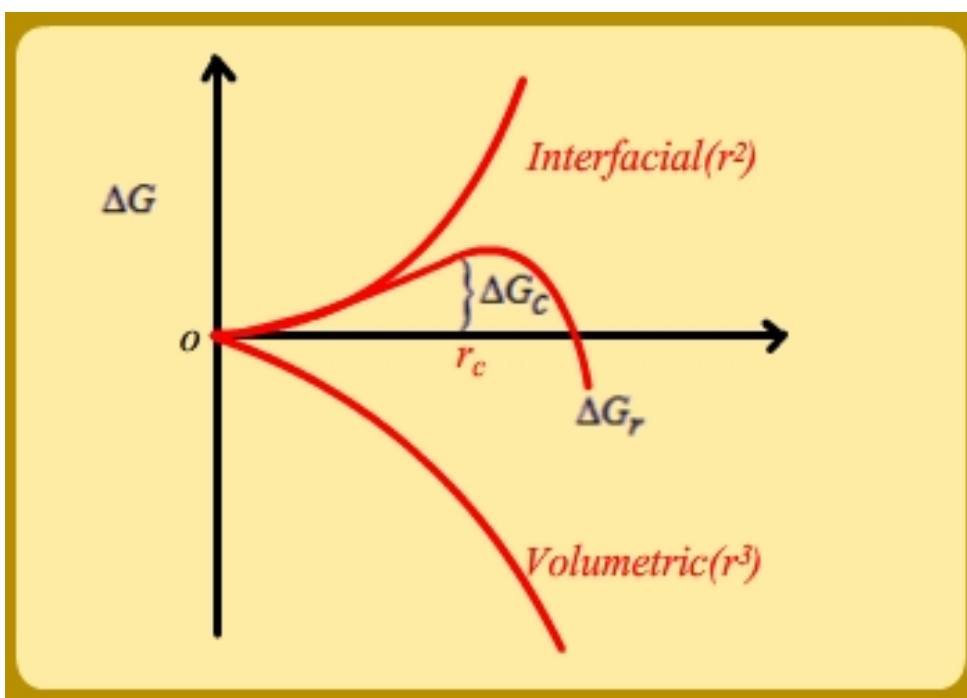


Figure 9: Energetics of homogeneous nucleation of a solid from its melt.

One can calculate the  $\delta G$  at  $r_c$  as follows:

$$[\delta G]_c = \frac{4}{3}\pi r_c^3 \Delta G + 4\pi r_c^2 \gamma_{ls} = -\frac{32}{3}\pi \frac{\gamma_{ls}^3}{(\Delta G)^2} + 16\pi \frac{\gamma_{ls}^3}{(\Delta G)^2} \quad (18)$$

$$[\delta G]_c = \frac{16\pi \gamma_{ls}^3}{3(\Delta G)^2} \quad (19)$$

It is possible to relate the undercooling of the melt to the radius of the critical nucleus and the free energy change associated with the critical nucleus; see the tutorial.

### 2.2.1 Critical undercooling

Consider any liquid. Inside the liquid, due to thermal fluctuations, clusters of various sizes keep forming. The probability of finding a cluster of given radius  $r$  is given by the Boltzmann distribution:

$$n = n_0 \exp\left(\frac{\delta G}{k_B T}\right) \quad (20)$$

where  $n_0$  is the total number of atoms,  $k_B$  is the Boltzmann constant, and  $\delta G$  is the free energy change associated with the formation of a solid of size  $r$  (and is given by Eq. 15).

Above the melting temperature of the solid, any such cluster that forms also breaks down immediately. However, below melting point, that is, in an undercooled melt, if the radius of the cluster formed is greater than  $r_c$ , then, that cluster becomes part of a solid and the given equation is no longer valid.

Using the above equation for thermal fluctuations, it is also possible to calculate the size of the biggest cluster (of radius, say,  $r_{max}$ ) that has a reasonable probability of occurrence. In Fig. 10, we show the variation of this cluster size as a function of undercooling  $\Delta T$ . In the same plot, we have also shown the variation of  $r_c$  with undercooling. From this plot, it is clear that there is a critical undercooling at which these two curves intersect; in other words, due to thermal fluctuations, there is a reasonable probability to form a cluster of size equal to the critical nucleus size. Thus, when this undercooling is reached, one expects that homogeneous nucleation will take place in the undercooled melt.

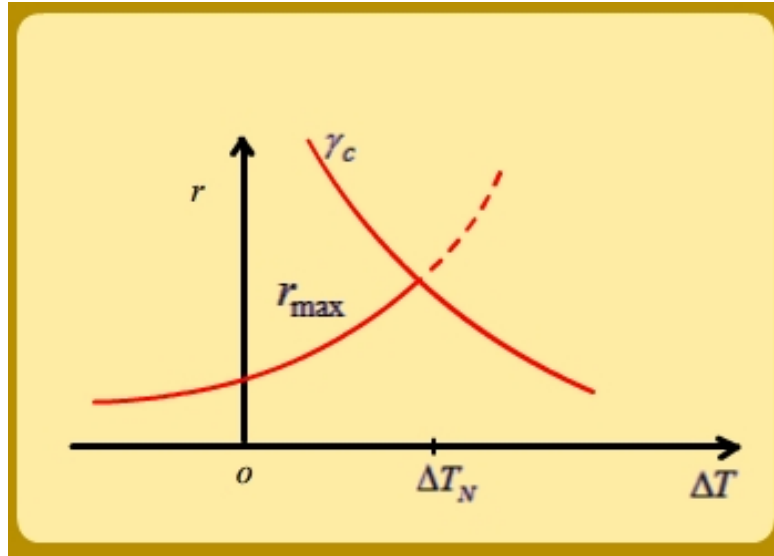


Figure 10: Thermal fluctuation versus critical nucleus size: need for critical undercooling.

### 2.2.2 Homogeneous nucleation rate

Consider an undercooled pure melt. Using the Boltzmann statistical expression for fluctuations, one can derive the number of clusters (per unit volume) that have reached a critical size  $C^*$  in a liquid that contains  $C_0$  atoms per unit volume as

$$C^* = C_0 \exp \left\{ \frac{\Delta G_{hom}}{k_B T} \right\} \quad (21)$$

An addition of a single atom to these clusters will transform them from embryos to stable nuclei. Let  $f_0$  be the frequency of attachment of an atom to such a cluster; it is a complex function of vibration frequency of atoms, diffusivity of atoms in the undercooled melt, and the surface area of the critical nuclei. Using  $f_0$ , one obtains the homogeneous nucleation rate (in units of nuclei per unit volume per second) as

$$N_{hom} = f_0 C_0 \exp \left\{ \frac{\Delta G_{hom}}{k_B T} \right\} \quad (22)$$

Accounting for the negative sign of the  $\Delta G_{hom}$  using  $-|\Delta G_{hom}|$ , and using the inverse relationship between  $\Delta G$  and  $(\Delta T)^2$ , one can show (see tutorial section):

$$N_{hom} = f_0 C_0 \exp \left[ -\frac{A}{(\Delta T)^2} \right] \quad (23)$$

where  $A$  is a constant that can be assumed to be independent of temperature. In Fig. 11 we show the  $N_{hom}$  as a function of  $\Delta T$ ; this plot clearly indicates the explosive formation of nuclei at a critical undercooling.

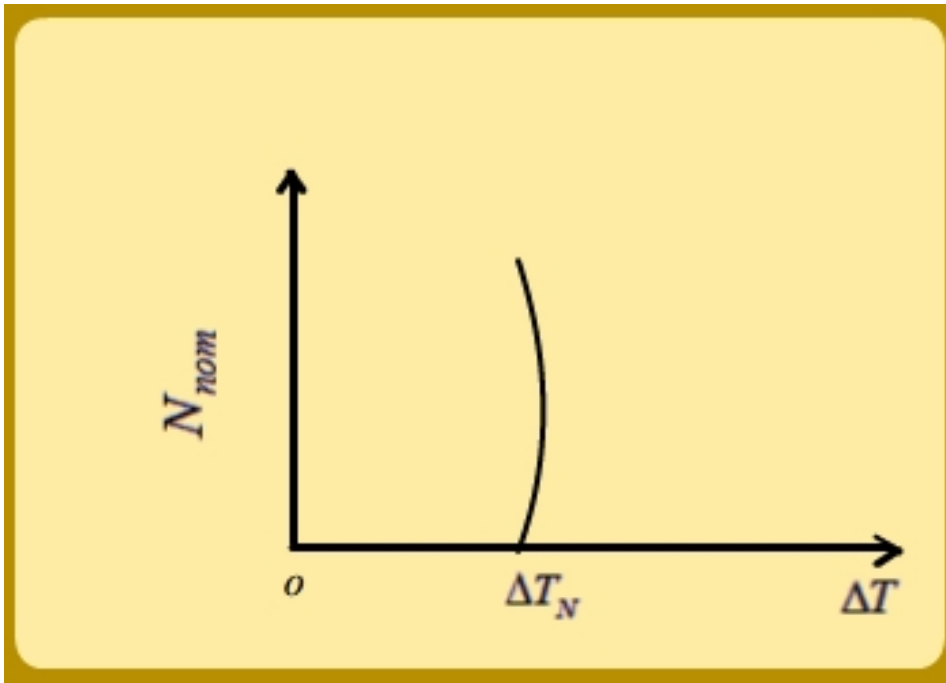


Figure 11: The critical undercooling for homogeneous nucleation.

## 2.3 Heterogeneous nucleation

During solidification, unless special care is taken (for example, by keeping the liquid in air using electromagnetic levitation), the nucleation is always heterogeneous; that is, the liquid nucleates on another solid (mold walls, for example) and grows into the undercooled liquid.

We can understand the ubiquity of heterogeneous nucleation by considering the heterogeneous nucleation of a spherical cap on a flat mold wall as shown in Fig. 12. In such a case, the excess free energy associated with the formation of a solid in the undercooled liquid is given by

$$\Delta G_{het} = V_s \Delta G + \gamma_{ls} A_{ls} + \gamma_{ms} A_{ms} - \gamma_{lm} A_{ms} \quad (24)$$

where  $V_s$  is the volume of the spherical cap,  $A_{ms}$  and  $A_{ls}$  are the areas of the mold wall/solid and liquid-solid interfaces, and the  $\gamma_{ls}$ ,  $\gamma_{ms}$  and  $\gamma_{lm}$ , are, respectively, the interfacial energies of the liquid-solid, mold-solid and liquid-mold interfaces, respectively.

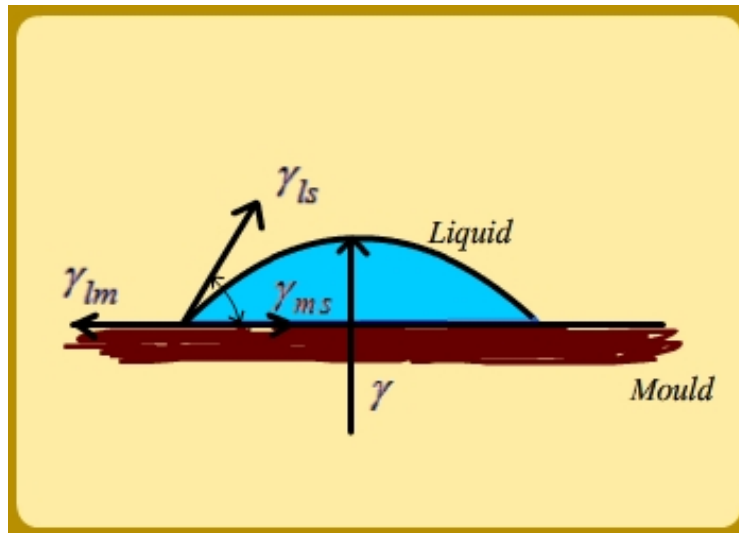


Figure 12: Heterogeneous nucleation on mould walls.

In terms of the wetting angle (see tutorial section), it can be shown that

$$\Delta G_{het} = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \left[ \frac{1}{3} \pi r^3 \Delta G + 4 \pi r^2 \gamma_{ls} \right] \quad (25)$$

In other words, except for the  $S(\theta) = 0.25(2 + \cos \theta)(1 - \cos \theta)^2$  term, the expression is identical to that obtained in the homogeneous solidification case above.

Hence, one obtains the following relationships:

$$r_c^{het} = -\frac{2\gamma_{ls}}{\Delta G} \quad (26)$$

$$[\delta G]_c^{het} = [\Delta G]_c^{hom} S(\theta) \quad (27)$$

In other words, while the critical nucleus size for heterogeneous nucleation is only dependent on the undercooling, the activation energy barrier is smaller than that of homogeneous nucleation by a factor of  $S(\theta)$ ; hence, one can expect the critical undercooling also to be smaller as shown in Fig. 13.

## 2.4 Tutorial problems and questions

1. Derive the relationship between the undercooling ( $\Delta T$ ) and the change in free energy  $\Delta G$ . Indicate any assumptions that are made.
2. Derive the critical nucleus size using Gibbs-Thomson equation.
3. What are the assumptions made in the cluster size calculation by thermal fluctuations? Comment their correctness.
4. Derive the relationship between  $N_{hom}$  and  $\Delta T$ .
5. While it is possible to undercool a melt below melting temperature without freezing, it is not possible to heat a solid above melting temperature without melting setting in. Why?



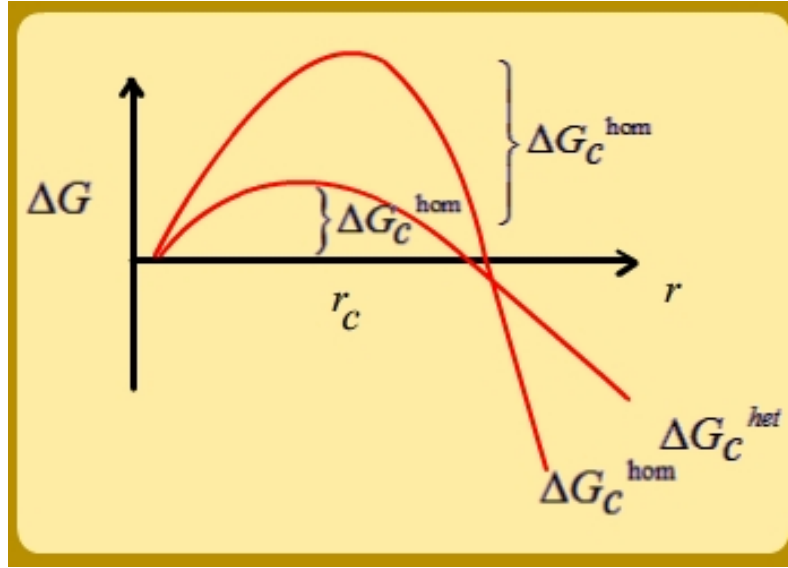


Figure 13: Critical free energy barrier: homogeneous versus heterogeneous nucleation.

6. Calculate the wetting angle  $\theta$  for the heterogeneous nucleation of a spherical cap on a flat mould wall.
7. Let  $\theta$  be the wetting angle. Then, show that

$$\Delta G_{het} = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \left[ \frac{1}{3} \pi r^3 \Delta G + 4 \pi r^2 \gamma_{ls} \right] \quad (28)$$

## 2.5 Solutions to the tutorial

1. Consider the Gibbs free energy,  $G = H - TS$ . Hence, the change in free energy associated with phase transformation  $\Delta G$  at the transformation temperature  $T_m$  is  $\Delta G = \Delta H - T_m \Delta S = 0$ . See Fig. 1. Since the change in enthalpy at the transformation temperature is the latent heat  $L$ , one obtains  $\Delta S = \frac{L}{T_m}$  which is known as the entropy of transformation.

At very small undercoolings, we can assume that the difference in the specific heats of the solid and liquid can be ignored and hence, both  $\Delta H$  and  $\Delta S$  can be assumed to be independent of temperature. Hence, for small  $\Delta T$ ,  $\Delta G \approx L - T \frac{L}{T_m} = \frac{L \Delta T}{T_m}$

2. One can obtain the critical nucleus size from the Gibbs-Thomson equation. At the transformation temperature, the solidified sphere and the liquid should be in equilibrium; that is, their free energies should be equal. However, a sphere of radius  $r$  will have an excess free energy per unit volume of  $\frac{2\gamma}{r}$ . From Fig. 14, one can see that this leads to  $r_c = \frac{2\gamma_{ls}}{\Delta G}$ .

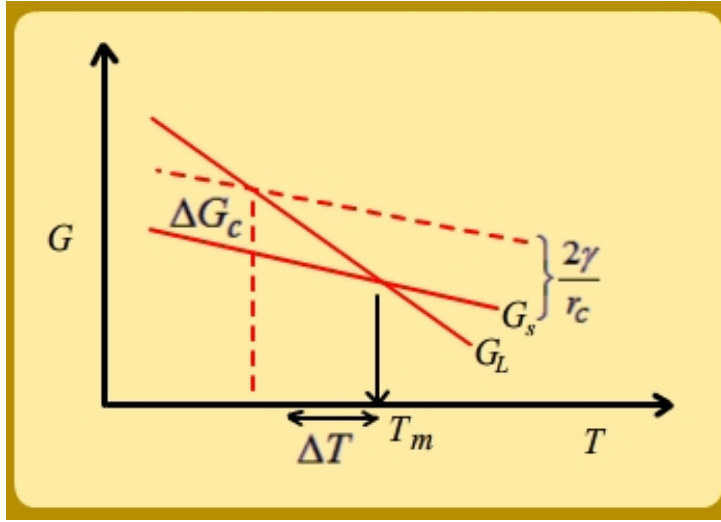


Figure 14: Critical nucleus size from Gibbs-Thomson effect.

3. We assume that the small clusters (with few tens of atoms) are (a) spherical and (b) that their interfacial energy is the same as that of large clusters. Both these assumptions need not be true.
4. Consider the Eq. 22:

$$N_{hom} = f_0 C_0 \exp \left\{ \frac{\Delta G_{hom}}{k_B T} \right\} \quad (29)$$

Also, from Eq. 19 we have

$$\Delta G_{hom} = \frac{16\pi\gamma_{ls}^3}{3(\Delta G)^2} \quad (30)$$

In the above expression, using the result from the first problem in this tutorial, one can substitute for  $\Delta G$  the term  $L\Delta T/T_m$ : hence,

$$\Delta G_{hom} = \frac{16\pi\gamma_{ls}^3 T_m^2}{3L^2(\Delta T)^2} \quad (31)$$

Hence,

$$N_{hom} = f_0 C_0 \exp \left\{ -\frac{A}{(\Delta T)^2} \right\} \quad (32)$$

where

$$A = \frac{16\pi\gamma_{ls}^3 T_m^2}{3L^2 kT} \quad (33)$$

5. It is generally found that the vapour-solid, liquid-solid, and vapour-liquid free energies are such that  $\gamma_{ls} + \gamma_{vl} < \gamma_{vs}$ . Hence, the wetting angle  $\theta$  is zero, and there is no need for superheating for the nucleation of liquid to take place. Hence, melting starts at the melting temperature when a solid is heated.
6. Consider the Fig. 12. From the figure, it is clear that the interfacial tensions  $\gamma_{lm}$ ,  $\gamma_{ms}$ , and  $\gamma_{ls}$  balance on the mould wall if  $\gamma_{lm} = \gamma_{ms} + \gamma_{ls} \cos \theta$ . Or,

$$\theta = \cos^{-1} \left( \frac{\gamma_{lm} - \gamma_{ms}}{\gamma_{ls}} \right) \quad (34)$$

7. Consider

$$\Delta G_{het} = V_s \Delta G + \gamma_{ls} A_{ls} + \gamma_{ms} A_{ms} - \gamma_{lm} A_{ms} \quad (35)$$

From Fig. 12, one can show the following:

$$A_{ls} = 2\pi r^2 (1 - \cos \theta) \quad (36)$$

$$A_{ms} = \pi r^2 \sin^2 \theta \quad (37)$$

$$V_s = \pi r^2(1 - \cos \theta)^2(2 + \cos \theta)/3 \quad (38)$$

Hence, it follows that

$$\Delta G_{het} = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \left[ \frac{1}{3} \pi r^3 \Delta G + 4 \pi r^2 \gamma_{ls} \right] \quad (39)$$

## 2.6 Supplementary information

In this module, we did not talk microstructures during pure material solidification and alloy solidification. Solidification is an important phase transformation associated with processing of materials such as casting and welding. However, since we restrict ourselves only to solid-solid transformations, we refer the interested reader to [1].