

## Part II : Interfaces

### Module 3 : Nucleation of precipitates from a supersaturated matrix

#### 3.1 Motivation

A solid contains many defects: vacancies, dislocations, stacking faults, grain and interphase boundaries, and free surfaces. During nucleation, hence, in a solid, there are much more of heterogeneous sites that are available as compared to a pure metal that solidifies from its melt. What are the relative importance of these sites with reference to nucleation?

#### 3.2 Homogeneous nucleation

In the previous module, we discussed the homogeneous and heterogeneous nucleation of a solid from its (undercooled) pure melt. In this module, we discuss homogeneous and heterogeneous nucleation in solids. More specifically, we consider a binary alloy whose phase diagram is as shown in Fig. 15. Let us consider an alloy of composition  $c_0$  cooled from  $T_1$  to  $T_2$  as shown. Since at  $T_2$ , two phases  $\alpha$  and  $\beta$  are in equilibrium, and the composition of  $\alpha$  is leaner in  $B$  atoms, from this supersaturated  $\alpha$  phase,  $\beta$  phase precipitates out by the nucleation and growth mechanism.

As in the case of homogeneous nucleation of a solid from its undercooled melt, in this case also, we are interested in calculating the critical size of the nucleus for homogeneous nucleation and the associated free energy changes.

In the case of a solid-solid phase transformation, in addition to the changes in bulk free energy and interfacial energy, typically, there is also a strain energy contribution which needs to be accounted for; this is because, typically, the volumes of the original  $\alpha$  and the resultant  $\beta$  are not the same, and unlike fluids, solids can support shear stresses. This strain energy (known as misfit energy because this is related to the imperfect fitting of the transformed phase into the original volume) can be shown to be proportional to the volume of the transformed phase. It is in this respect that the homogeneous nucleation of precipitation differs from that of the solid from its pure melt.



In other words, during solid-solid transformation,

$$\delta G = V_\beta \Delta G + \gamma_{\alpha\beta} A_{\alpha\beta} + V_\beta \Delta G_{misfit} \quad (40)$$

where  $\delta G$  is the total change in free energy,  $\Delta G = G_\beta - G_\alpha$ , the driving force for the transformation,  $\gamma_{\alpha\beta}$  is the free energy per unit area of the  $\alpha - \beta$  interface (of area  $A_{\alpha\beta}$ ), and  $\Delta G_{misfit}$  is the misfit or strain energy per unit volume of the  $\beta$  phase; further, also note that since in a solid different interfaces have different energies in general,  $\gamma_{\alpha\beta} A_{\alpha\beta} = \sum_i \gamma_i A_i$  where  $i$  is the index of planes that enclose the precipitate (with the interfacial energy being  $\gamma_i$  and area being  $A_i$  for the  $i$ -th plane).

If we assume that the interfacial energy is isotropic, then, as in the earlier case, we can obtain the critical radius of the nuclei (by assuming a spherical shape for the nuclei) as follows:

$$r_c = -\frac{2\gamma_{\alpha\beta}}{\Delta G - \Delta G_{misfit}} \quad (41)$$

That is, in the case of a solid-solid phase transformation, the gain in free energy has to compensate both for the increase in interfacial energy and the misfit energy (see Fig. 16).

Using arguments similar to those used in the earlier module, we can obtain the homogeneous nucleation rate. However, in the case of solid-solid transformations, the temperature dependence of the frequency factor in terms of the atomic migration has to be explicitly accounted for (see tutorial section).

Apart from the inclusion of strain energy, the nucleation of precipitates also differs from that of a solid in its pure melt in another important aspect, namely, that the driving force for the first precipitate to nucleate is different from the total free energy change when precipitation is complete. This is related to the fact that the  $\Delta G$  term should be calculated keeping in mind the changes in composition associated with the nucleation, as shown in the following subsection.

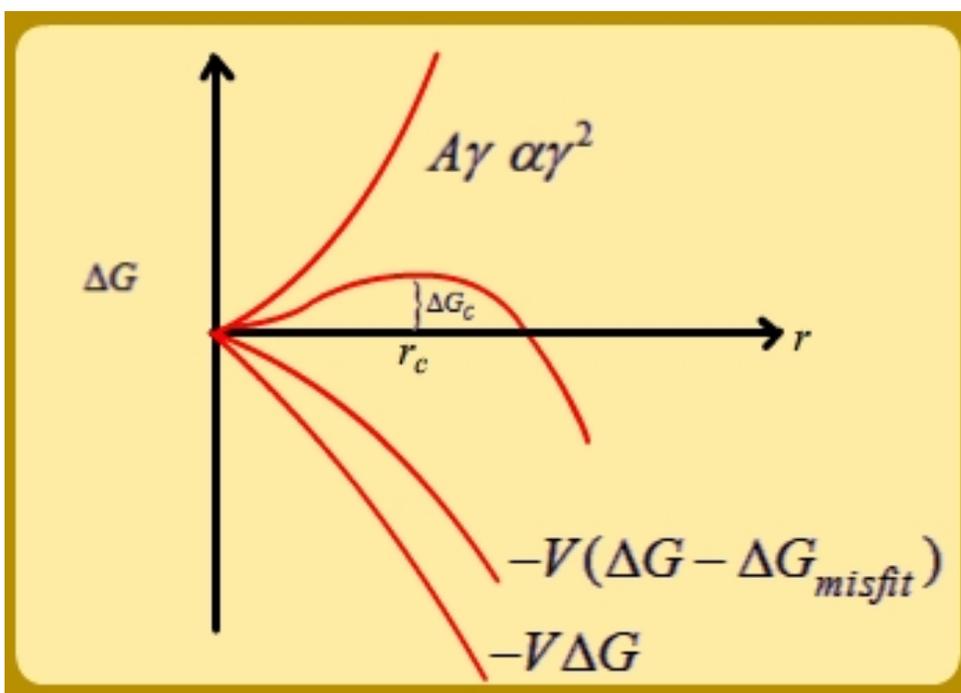


Figure 16: Nucleation energetics during solid-solid transformations.

### 3.3 Driving force for nucleation

Consider the phase diagram and the free energy versus composition diagram shown in Fig. 17. From the figure, it is clear that the undercooling in a solid is dependent on the overall alloy composition (which decides on the temperature at which phase separation takes place) and the temperature of quench. As the undercooling increases, the supersaturation associated with the  $\alpha$  phase also increases, thus, increasing the driving force for precipitation.

For simplicity's sake, we have assumed that the  $\beta$  phase is a line compound – that is, the composition of the  $\beta$  phase in equilibrium with  $\alpha$  of any composition is the same.

From the free energy versus composition diagram, it is clear that the overall driving force for the precipitation transformation is  $\Delta G_0$  as shown. However, the free energy change associated with the formation of the first precipitate is given by the line PQ in the figure:  $\Delta G_n$ . This is because, when the first precipitate forms, the overall composition of the  $\alpha$  phase is the overall alloy composition  $c_0$  itself and not  $c_\alpha^e$ . In such a case, the free energy change is calculated as follows:

The decrease in free energy (per mole) when a small amount of material is removed from the  $\alpha$  phase to form a nucleus of  $\beta$  with composition  $c_\beta^e$  is  $\Delta G_1$  and is given by

$$\Delta G_1 = \mu_A^\alpha c_A^\beta + \mu_B^\alpha c_B^\beta \quad (42)$$

$\Delta G_1$  is represented by the point P as shown in the Fig. 17.

When this removed material is transformed into the  $\beta$  phase, the total free energy will increase by an amount  $\Delta G_2$  and is given by

$$\Delta G_2 = \mu_A^\beta c_A^\beta + \mu_B^\beta c_B^\beta \quad (43)$$

$\Delta G_2$  is represented by the point Q as shown in the Fig. 17.

Thus, per mole of  $\beta$ , the net free energy change is  $\Delta G_n = \Delta G_2 - \Delta G_1$ , which is nothing but PQ as claimed earlier. By dividing this quantity by the

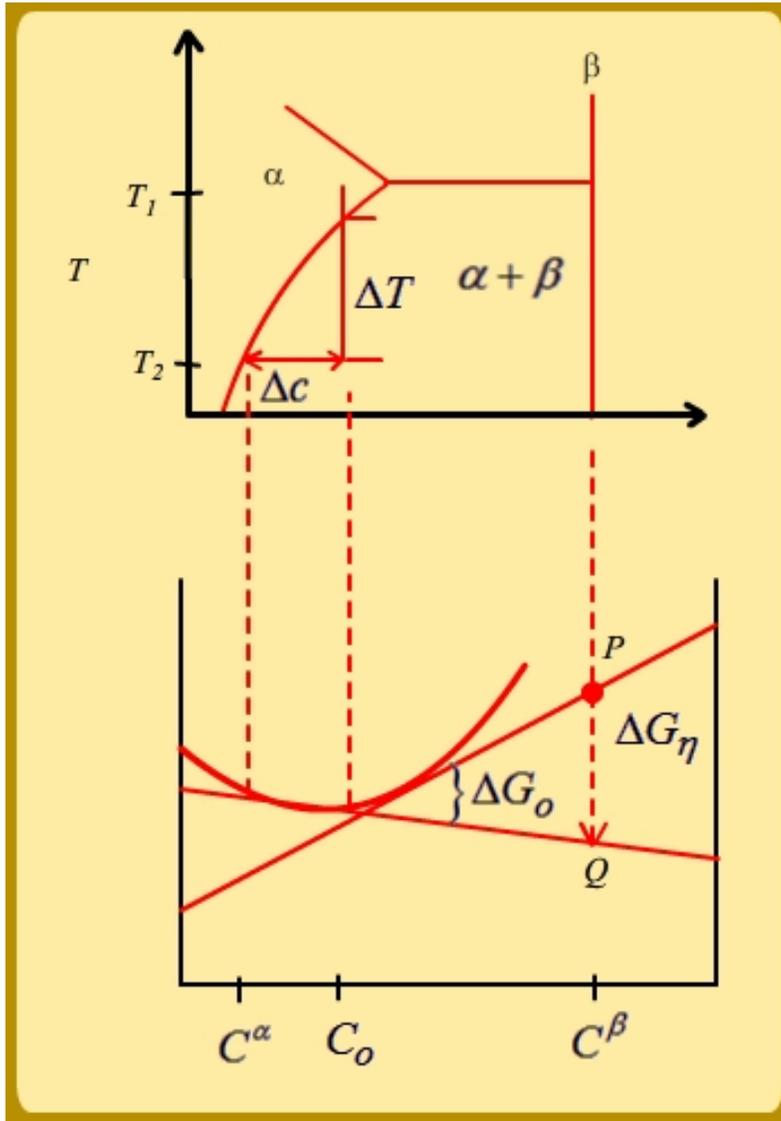


Figure 17: Driving force for the start of nucleation is different from that of the overall transformation.

molar volume  $V_m$  of the  $\beta$  phase, one obtains the volume free energy change associated with the formation of the first precipitate  $\Delta G_{volume}$ .

It can be shown, that for dilute solutions,  $\Delta G_{volume} \propto \Delta c = c_0 - c_e^\alpha$ . Thus, with increasing undercooling, the driving force for precipitation increases as claimed at the beginning of this subsection.

### 3.4 Variation of homogeneous nucleation rate with undercooling

Consider the homogeneous nucleation rate

$$N_{hom} = \omega C_0 \exp \left[ \frac{\Delta G_m}{k_B T} \right] \exp \left[ \frac{[\Delta G]_c}{k_B T} \right] \quad (44)$$

where  $\omega$  is the vibration frequency of atoms and  $\Delta G_m$  is the activation energy per atom for atomic migration (see the tutorial problem).

For an alloy, we would like to calculate  $N_{hom}$  as a function of the temperature given  $c_0$ . For this, then, we need to know the variation of the two exponential terms. In Fig. 18 we show the variation of these two exponential terms as a function of undercooling. Note that in these figures, we also show the variation of  $\Delta G_{volume}$  and  $\Delta G_{misfit}$ , the effect of  $\Delta G_{misfit}$  being to reducing the effective equilibrium temperature. From the figure, it is clear that the nucleation rate is a maximum at the intermediate temperatures. This is because, at smaller undercoolings, the driving force for the transformation is low, while at very large undercoolings the temperature dependent atomic mobility term becomes very small making the kinetic term the rate controlling one.

### 3.5 Heterogeneous nucleation

As with the nucleation of a solid from its pure melt, during solid-solid transformations also the heterogeneous nucleation dominates. Unlike the solidification scenario, where heterogeneous nucleation takes place in the mold walls external to the system, in the case of solids, the internal defects such

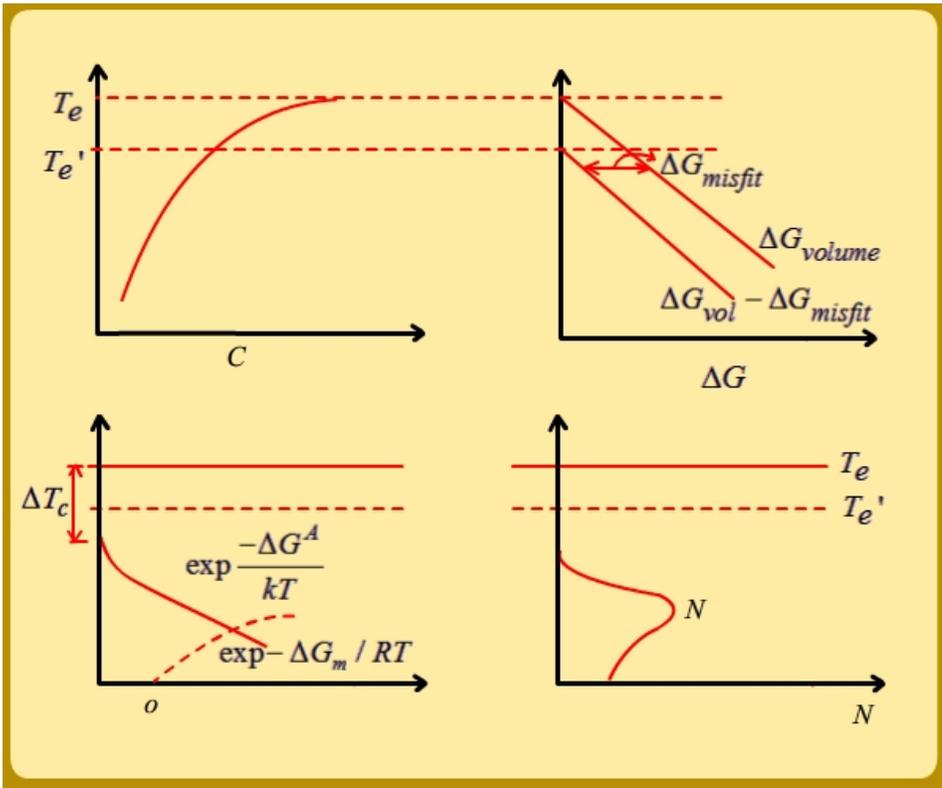


Figure 18: Variation of number of nuclei as a function of undercooling.

as vacancies, dislocations, stacking faults, grain boundaries, inclusions and free surfaces act as heterogeneous nucleation sites.

For heterogeneous nucleation, the net reduction in energy is given by

$$\{\delta G\}_{het} = V(\Delta G - \Delta G_{misfit}) + A\gamma - \Delta G_d \quad (45)$$

where  $\Delta G_d$  is the free energy gain due to the removal of a defect (which was replaced by the nuclei).

### 3.6 Rate of heterogeneous nucleation

Consider the various heterogeneous nucleation sites. In terms of increasing defect energies  $\Delta G_d$ , these sites can be ordered as follows:

1. Free surfaces;
2. Grain and interphaseboundaries;
3. Stacking faults;
4. Dislocations; and,
5. Vacancies.

In other words, this is the order in which the heterogenous nucleation will preferentially take place. However, the relative ease of occurrence of these defects should also be considered. Hence, if  $C_1$  is the concentration of heterogeneous nucleation sites per unit volume, and if the critical energy for nucleation at this site is  $[\Delta G]_c^{het}$ , then,

$$\frac{N_{het}}{N_{hom}} = \frac{C_1}{C_0} \exp\left(\frac{[\Delta G]_c^{hom} - [\Delta G]_c^{het}}{k_B T}\right) \quad (46)$$

Thus, while the exponential term tells about the relative ease from the energetic point of view, the pre-exponential term accounts for the relative availability of these easy nucleation sites.

### 3.7 Tutorial problems and questions

1. Derive the expression for homogeneous nucleation rate for precipitation, namely,

$$N_{hom} = \omega C_0 \exp \left[ \frac{\Delta G_m}{k_B T} \right] \exp \left[ \frac{[\Delta G]_c}{k_B T} \right] \quad (47)$$

2. Comment on the assumptions made in deriving the homogeneous precipitate nucleation rate and their implications.
3. Comment on heterogeneous nucleation during continuous cooling as opposed to the same during isothermal treatment.

### 3.8 Solutions to the tutorial

1. The number of clusters (per unit volume) that have reached a critical size  $C^*$  in a solid that contains  $C_0$  atoms per unit volume as

$$C^* = C_0 \exp \left\{ \frac{\Delta G_{hom}}{k_B T} \right\} \quad (48)$$

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

$$N_{hom} = f_0 C_0 \exp \left\{ \frac{\Delta G_{hom}}{k_B T} \right\} \quad (49)$$

It is possible to write  $f_0$  as  $\omega \exp -\Delta G_m/kT$  where  $\omega$  contains the dependence on vibration frequency and surface area of the critical nucleus while  $\Delta G_m$  is the activation energy per atom for diffusion. Hence,

$$N_{hom} = \omega C_0 \exp \left[ \frac{\Delta G_m}{k_B T} \right] \exp \left[ \frac{[\Delta G]_c}{k_B T} \right] \quad (50)$$

2. Typically the nucleation rate is assumed to be a constant. However, as time goes by, when the nuclei start growing, the rate for further nucleation drops since the supersaturation in the matrix is reduced.

The nuclei are assumed in our treatment to be spherical; they are also assumed to be of the composition and structure of equilibrium  $\beta$ . However, in the initial stages where interfacial energy is the key parameter, it is possible that the equilibrium phase is not the one that nucleates but a phase with as small an interfacial energy as possible. The formation of GP zones discussed later is an example of the formation of such metastable phases.

3. As discussed in the heterogeneous nucleation section, during heterogeneous nucleation, there are two factors that are to be accounted for: one is the smaller barrier for nucleation; the other is the availability of sites with such small barriers. Thus, during isothermal transformations for example, with increasing driving force for nucleation, the nucleation sites change from grain corners, to grain edges to grain boundaries and so on. However, during continuous cooling, the driving force for nucleation keeps increasing with time; hence, the availability of sufficient number of sites is essential for any heterogeneous site to contribute to nucleation.

### 3.9 Supplementary information

The elastic stress effects, both in the case of coherent precipitates and incoherent precipitates, favours equilibrium shapes for precipitates that are non-spherical; for example, in Fig. 19 we show (schematically) the variation of misfit strain energy for an ellipsoidal shape, which clearly indicates that as far as the elastic strain energy is considered sphere is not the minimum energy shape.

A more detailed discussion of heterogeneous nucleation on grain boundaries, dislocations and excess vacancies can be found in Porter, Easterling and Sherif [1] and Raghavan [2].

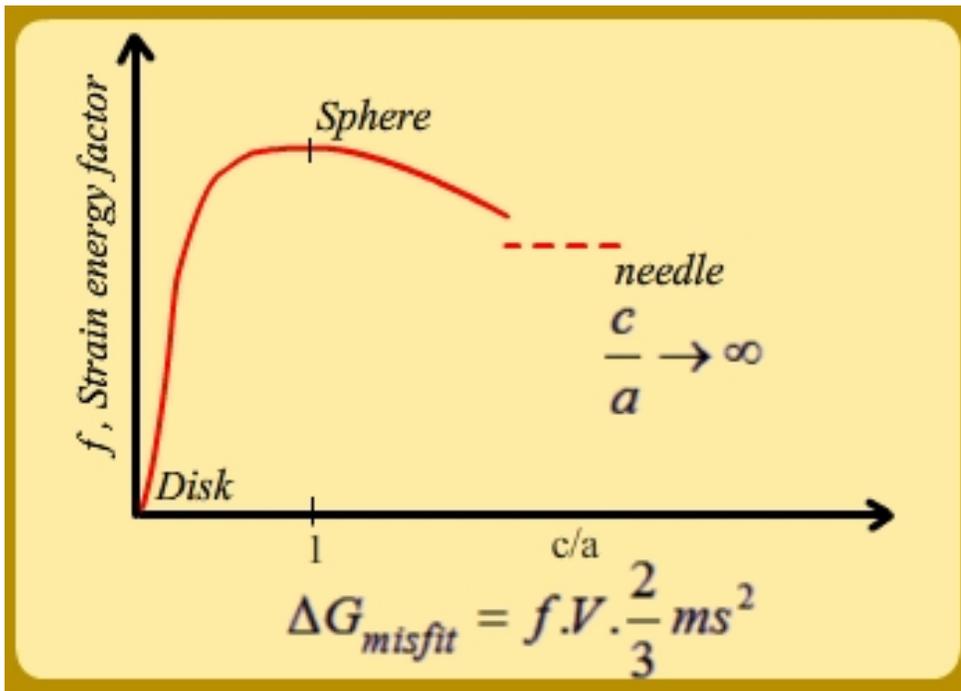


Figure 19: Change in the strain energy of an ellipsoidal precipitate with shape. Note that the preferred shape is not a sphere. In the energy expression,  $f$  is a geometric factor.  $\delta$  is the misfit strain.  $\mu$  is the shear modulus.  $V$  is the volume of the precipitate.