

Part III. Nucleation and growth

Module 1 : Effect of interfaces

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In this part, we discuss the effect of interfaces on equilibrium and growth, the nucleation of a solid from its pure melt, the nucleation of a precipitate from the matrix, growth of precipitates, and the kinetics of nucleation and growth. Our discussion is primarily based on Porter, Easterling and Sherif [1]; we also refer the reader to a concise text book by Raghavan [2] for further reading on some of the aspects that we discuss here.

1. Effect of interfaces

1.1 Motivation

Very small particles of gold melt at a temperature lower than the melting point of bulk gold. Why?

1.2 Effect of interfaces on equilibrium

Interfaces have a very strong effect on equilibrium. For example, consider the equilibrium between two phases; as we noted earlier, at equilibrium, the Gibbs free energies of the two phases are equal – see Fig. 1; the temperature at which the two free energies becomes equal is known as the transformation temperature.

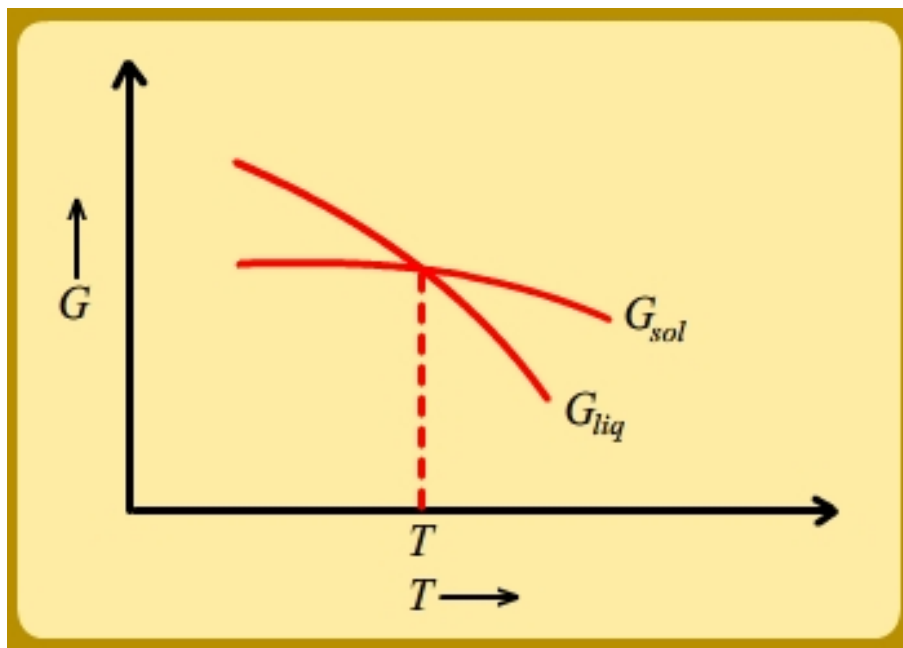


Figure 1: Equilibrium transformation temperature.

In Fig. 1, we have only considered the bulk free energies of the two phases as a function of temperature. However, as we noted in the earlier part, the interface between the two phases has an excess free energy associated with it. This interfacial excess free energy is an energy per unit area and hence, depending on the area of the interface between the two phases, it will also contribute to the Gibbs free energies and hence will shift the equilibrium transformation temperature.

Let us consider the β phase in equilibrium with α phase as shown in Fig. 2. The β phase is a sphere of radius r and if γ is the interfacial energy, by analogy with soap bubbles, the excess pressure inside the β phase due to γ will be $\frac{2\gamma}{r}$. This is also known as Laplace pressure. If V_m is the molar volume of the β phase then, the β phase has a higher free energy of $\frac{2\gamma V_m}{r}$ as shown, and hence, as indicated in Fig. 3, there is a shift in the equilibrium transformation temperature.

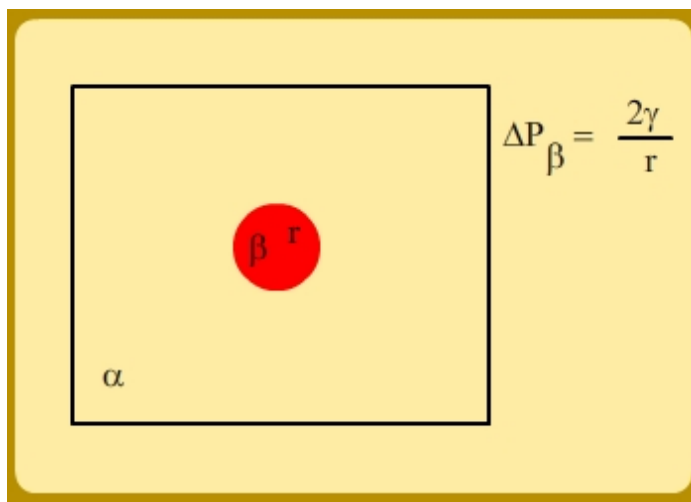


Figure 2: Equilibrium of a β phase with α across a curved interface.

In the case of pure nanomaterials, such shifts in equilibrium transformation temperatures are well known. For example, in the case of gold, while the

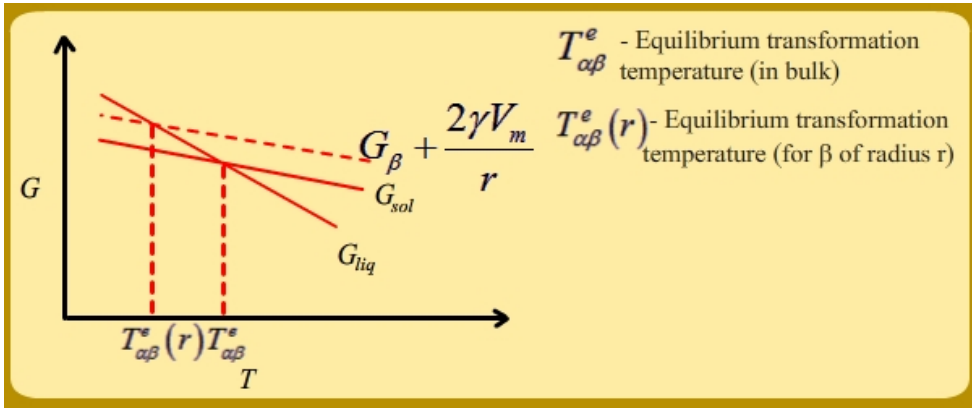


Figure 3: Shift in equilibrium due to interface curvature.

equilibrium melting temperature for bulk gold is 1064°C, gold nanoparticles of size 3 nm and 2 nm, melt at about 750°C and 300°C, respectively.

It is also possible to understand the melting point depression in gold nanoparticles using a bond-breaking model. To melt a gold particle, all the bonds are to be broken, and the supplied thermal energy is used in breaking these bonds. In a bulk gold particle, there are very few surface atoms – atoms for which some of the bonds are already broken. However, as the size of the particle becomes smaller, the ratio of the atoms on surface to that in the bulk becomes larger and larger and hence the thermal energy required to break the bonds become smaller and smaller leading to a depression in melting point.

As we show in the tutorial section below, the interfacial energy also changes the equilibrium composition of the coexisting phases in binary alloys when the particle sizes are very small. Thus, at early stages of phase transformation where the particle sizes are indeed very small, this effect becomes very important.

The effect of interfacial energy on equilibrium properties (transformation temperature, coexistence composition etc) is known by the generic name of Gibbs-Thomson effect.

1.3 Effect of interfaces on growth

Interfaces can also have a strong effect on growth. For example, consider the growth of an hcp phase into a fcc phase across a coherent interface. As indicated in Fig. 4, if this growth of hcp phase occurs by individual atomic jumps (known as continuous growth), it results in very high energy and unstable configuration (two atoms at two B sites, one directly above another). In such cases, the mobility of the interface is very low. Hence, the system typically prefers what is known as ‘ledge’ growth instead of the continuous growth mechanism. In the ledge mechanism, as shown in Fig. 5, the growth of the interface takes place by the transverse migration of ledges.

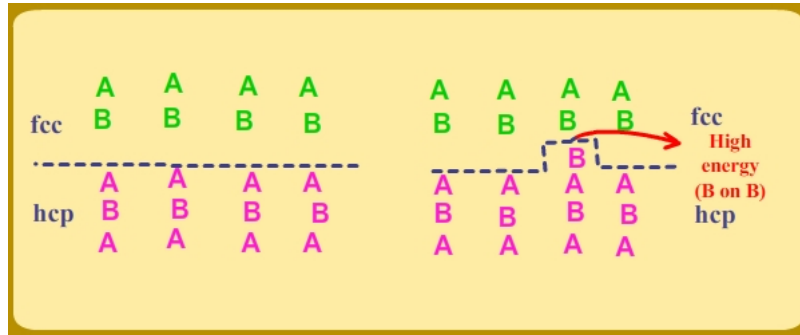


Figure 4: Difficulty with continuous growth across a coherent interface.

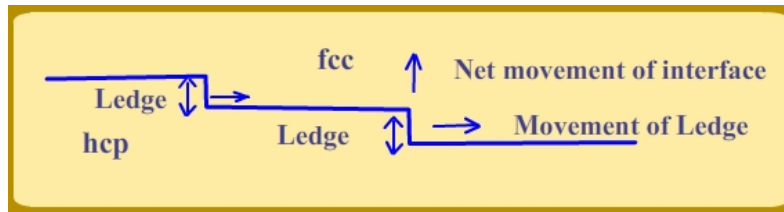


Figure 5: The schematic of ledge grown mechanism; the precipitate thickens by the later movement of ledge

As we show in the tutorial section below, interface migration, in general, is classified into two types, namely, diffusion controlled and interface controlled.

1.4 Tutorial problems and questions

1. Derive an expression for the solubility of a phase β (assuming it to be almost pure B) in a solid solution of α (assuming it to be a regular solution). Derive the expressions both for planar and curved α - β interfaces.
2. Consider a β precipitate of almost pure B growing behind a planar interface into A -rich α . Show that the interface mobility affects the chemical driving force required to move the interface.

1.5 Solutions to the tutorial

- Given β is pure B and α is a solid solution (assumed to be regular), the phase diagram and the free energy versus composition diagrams at the temperature T_1 are as shown in Fig. 6. As we notice, since A has almost no solubility in β , the free energy curve for β raises sharply with concentration and the maximum concentration of B soluble in A is given by the common tangent condition,

$$\mu_B^\alpha = \mu_B^\beta \approx G_B^\beta \quad (1)$$

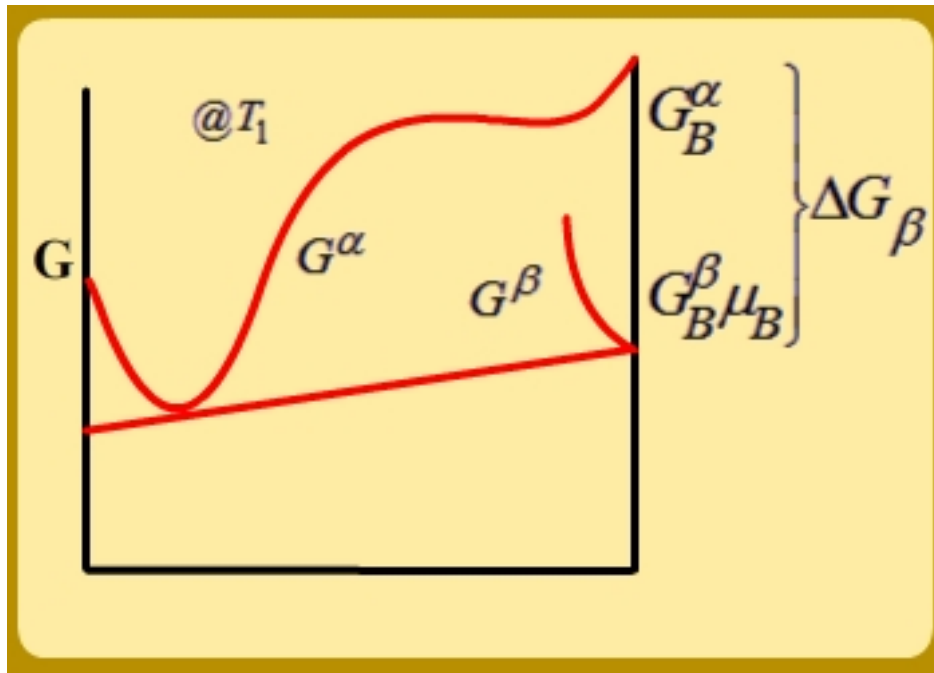


Figure 6: Free energy versus composition diagram.

For regular solution,

$$\mu_B^\alpha = G_B^\alpha + \Omega(1 - X_B)^2 + RT \ln X_B = \mu_B^\beta \approx G_B^\beta \quad (2)$$

Also, from Fig. 6, since $\Delta G_B = G_B^\alpha - \mu_B^\alpha$, we get

$$\Delta G_B = -RT \ln X_B^e - \Omega(1 - X_B^e)^2 \quad (3)$$

For low solubility, $X_B^e \ll 1$,

$$X_B^e = \exp \left[-\frac{\Delta G_B + \Omega}{RT} \right] \quad (4)$$

As shown in Fig. 7, due to the the Gibbs-Thomson effect, the free energy of the β phase raises by $\frac{2\gamma V_m}{r}$; hence,

$$X_r = \exp \left[-\frac{\Delta G_B + \Omega - 2\gamma V_m/r}{RT} \right] \quad (5)$$

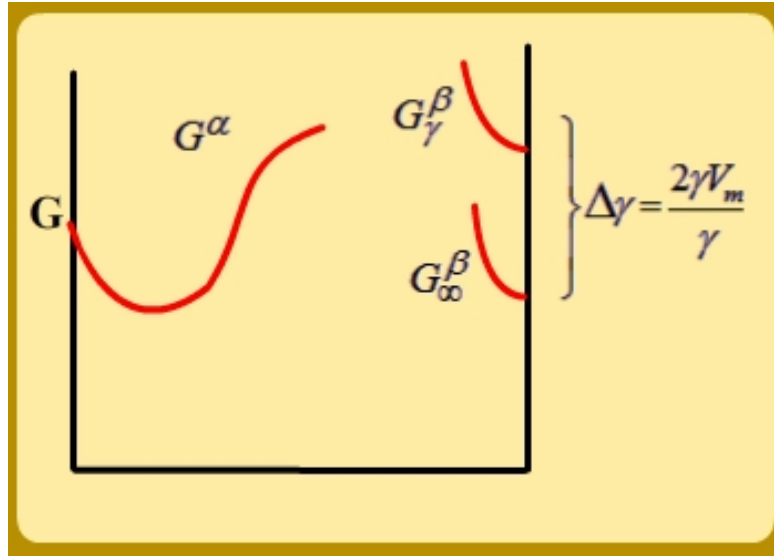


Figure 7: Capillary (Gibbs-Thomson) effect induced increase in free energy shown on a free energy versus composition plot.

That is, if X_∞ is the equilibrium concentration for a planar interface between the α and β phases,

$$X_r = X_\infty \exp \left[\frac{2\gamma V_m}{RT r} \right] \quad (6)$$

For small values of the exponent, this can further be simplified as

$$X_r = X_\infty \left(1 + \frac{2\gamma V_m}{RT r} \right) \quad (7)$$

2. Consider the growth of a β precipitate of almost pure B growing behind a planar interface into A -rich α ; the initial composition of α is X_0 . The composition profile across the interface, the driving forces in terms of chemical potentials and the schematic free energy versus composition diagrams are shown in Fig. 8. At the α - β interface, the net flux of B atoms from α to β makes the interface grow with a velocity v which is given by

$$v = \frac{M \Delta \mu_B^i}{V_m} \quad (8)$$

where M is the interface mobility, V_m is the molar volume of the β phase, and $\Delta \mu_B^i$ is the driving force for B atoms to move from the α to β phase. Hence, the flux of B atoms (moles per m^2 per s) is given by

$$J_B^i = -\frac{M \Delta \mu_B^i}{V_m^2} \quad (9)$$

In α phase the diffusional flux of B atoms due to the concentration gradients is given by

$$J_B^\alpha = -D \left(\frac{\partial C_B}{\partial x} \right)_{interface} \quad (10)$$

At steady state, the fluxes balance: $J_B^i = J_B^\alpha$.

From these expressions, it is clear that the value of M has a say on $\Delta \mu_B^i$ and hence on X_i . If M is large, then $\Delta \mu_B^i$ can be very small; in other words, in such circumstances $X_i \approx X_e$. Such cases are known as diffusion controlled growth; in these cases the diffusional flux of atoms from the α phase to the interface is what controls the rate of the growth

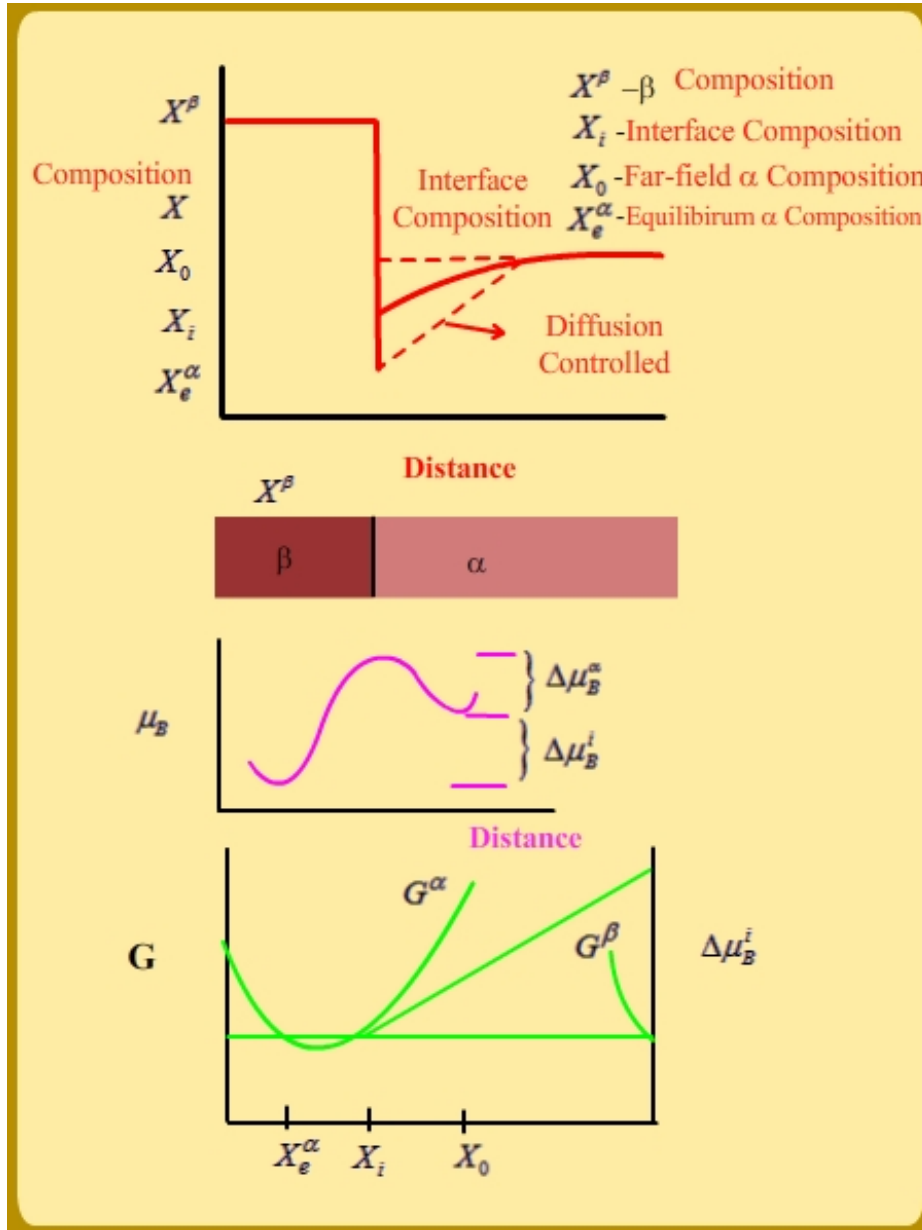


Figure 8: Interface and diffusion control: composition profiles, free energy changes and free energy versus composition diagrams.

of the β phase. On the other hand, if M is very small, larger $\Delta\mu_B^i$ are required to drive the reaction; this means, the interface composition X_i is not the equilibrium composition X_e but is different; it could even be X_0 . Such cases are said to be interface controlled growth; in these cases, it is not the diffusion in the α phase but the reaction at the interface that controls the rate of growth of the β phase.

1.6 Supplementary information

Gibbs-Thomson effect also plays a key role in coarsening or Ostwald ripening by giving the required driving force for small particles to shrink and bigger ones to grow at the cost of smaller ones. This will be discussed in one of the later sections of this course notes.