

Part V. Solid-solid transformations II

Module 1 : Spinodal decomposition

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In this part, we discuss two transformations namely spinodal decomposition and ordering. Spinodal decomposition takes place through a mechanism known as spinodal which is different from nucleation and growth. Ordering is a second order transformation unlike the transformations discussed in the previous part. 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.

Spinodal decomposition

1.1 Motivation

Consider an atomistic picture of diffusion in a binary alloy as shown in Fig. 1. Assuming random jumps for the atoms (and that the jump frequency is independent of composition), as can be seen from the schematic, purely because of the difference in the number of atoms of a particular type, there is a net flux. And this flux is opposite to the concentration gradient. Thus, Fick's first law, which states that the flux of atoms is proportional to concentration gradient and is in such a way as to reduce concentration gradients **to a very reasonable one**:

$$J = -D\nabla c \quad (1)$$

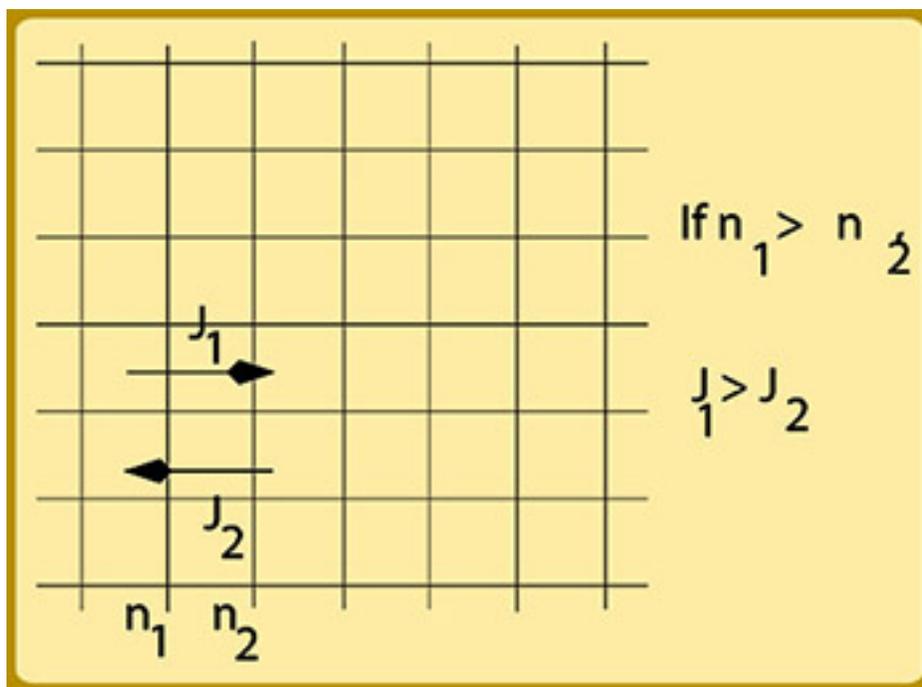


Figure 1: An atomistic picture in which if we assume random jumps for atoms and that the jump frequency is independent of composition, the atomic flux is proportional to composition gradient.

As noted in Part I of these course notes, the proportionality constant D is known as diffusivity and is positive. Again as noted in Part I, coupling this constitutive law with the conservation law for mass, one obtains the classical diffusion equation, namely

$$\frac{\partial c}{\partial t} = D \nabla^2 c \quad (2)$$

Even though the classical diffusion equation is based on a reasonable constitutive law and a conservation law it is known to fail in certain cases. Such failure occurs in what is known as phase separating systems. Why? And, how does one fix this failure?

1.2 Spinodal mechanism

In phase separating systems, at low temperatures, the Gibbs free energy consists of regions of concave curvature (as shown in Fig. 2) and in such regions the binary alloy separates into a mechanical mixture of A and B-rich regions instead of remaining a solid solution. This is because such a phase separation into mechanical mixture reduces the free energy of the system.

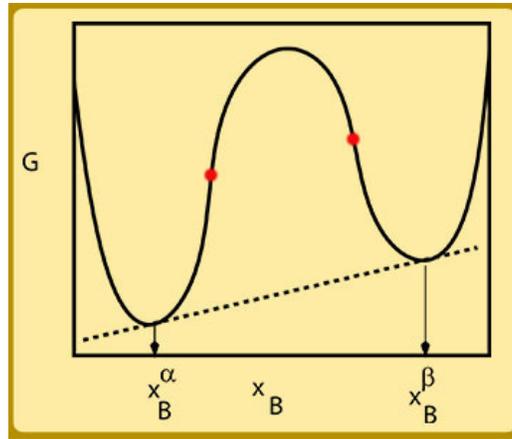


Figure 2: The free energy of a system with concave curvature. In the concave curvature region, the system becomes a mechanical mixture of A rich α and B rich β phases with the given compositions marked in this figure.

Further, in such systems with concavity of free energy, for certain compositions, the mechanism of phase separation changes from the classical nucleation and growth to spinodal decomposition. The change in the mechanism is related to the curvature of the free energy curve as shown in Fig. 3. In Fig. 4 we show the phase separation region along with the points at every temperature at which the curvature of the free energy versus composition plot changes its sign; the locus of these points is as shown and is known as chemical spinodal.

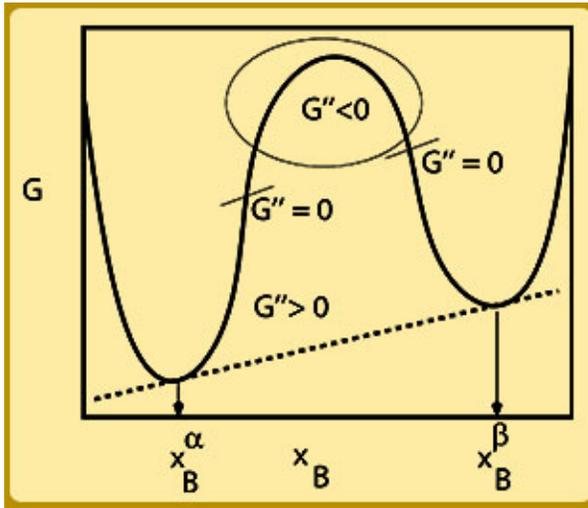


Figure 3: Positive curvature (nucleation) and negative curvature (spinodal) regions of the free energy versus composition diagram; phase separation mechanism changes from nucleation to spinodal at the point of zero curvature.

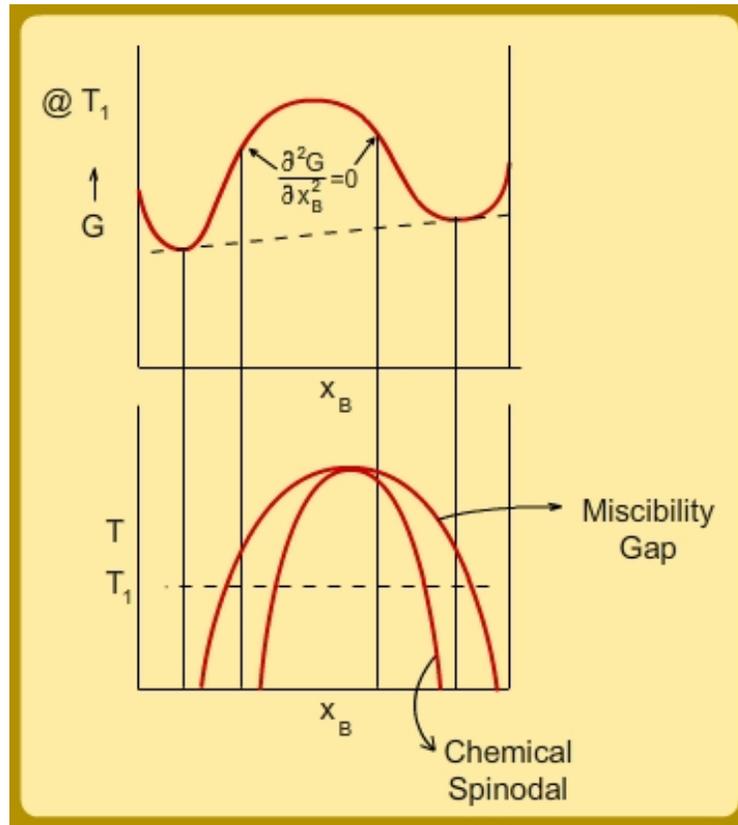


Figure 4: Phase diagram and chemical spinodal using free energy versus composition diagrams

In the case of spinodal phase separation, any small composition fluctuation grows leading to A-rich regions becoming richer in A and B-rich regions becoming richer in B. This is because such a process leads to a decrease in free energy as shown in Fig. 5.

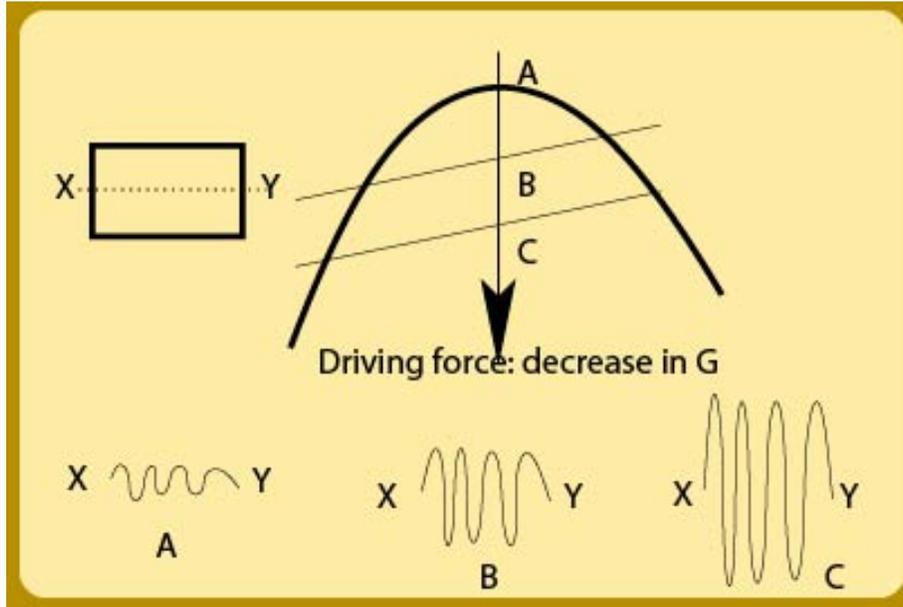


Figure 5: In regions of negative curvature, A-rich (and B-rich) regions spontaneously become richer in A (and B), because, the free energy decreases in such a process.

Thus, the process of spinodal decomposition is in contrast to the classical diffusion equation scenario which predicts that regions with positive curvature for composition profile grow in time while those with negative curvature decay leading to homogenisation. This difference is shown in Fig. 6.

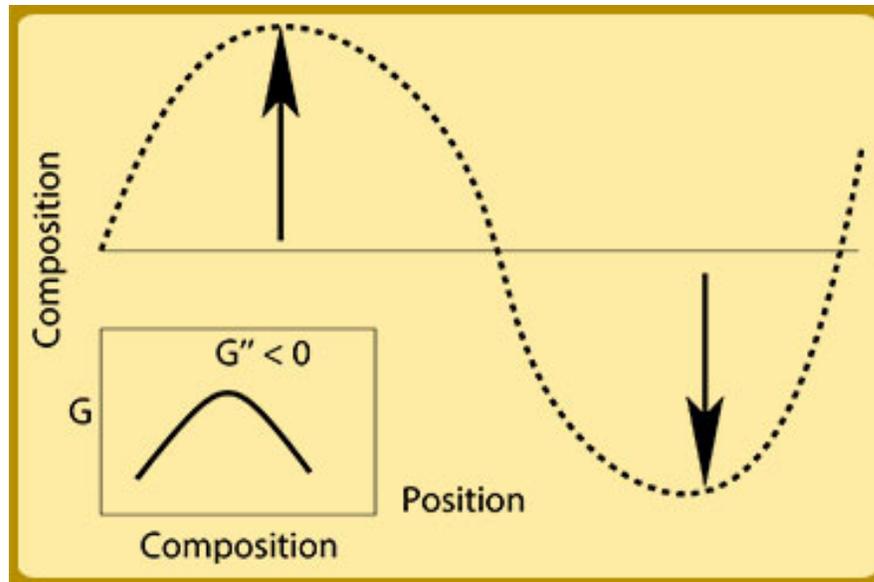


Figure 6: Evolution of composition during homogenisation and phase separation. While homogenisation obviously follows from the classical diffusion equation (Fick's second law), phase separation implies $D < 0$.

The reason why classical diffusion equation fails to describe the spinodal decomposition process can also be understood by looking at the free energy reduction. The driving force for any process is the free energy reduction; in the case of mass flow, this driving force manifests itself as equalising chemical potential. As energy flows till temperature becomes equal, and volumes change till pressures become equal, the mass flow takes place till chemical potentials become equal. Even though in the classical cases such free energy reduction is also accompanied by decay of compositional heterogeneities, in the case of spinodal it is not so. Hence, the Fick's first law should be given in terms of chemical potentials and not composition. The chemical potential driving force is shown pictorially in Fig. 7

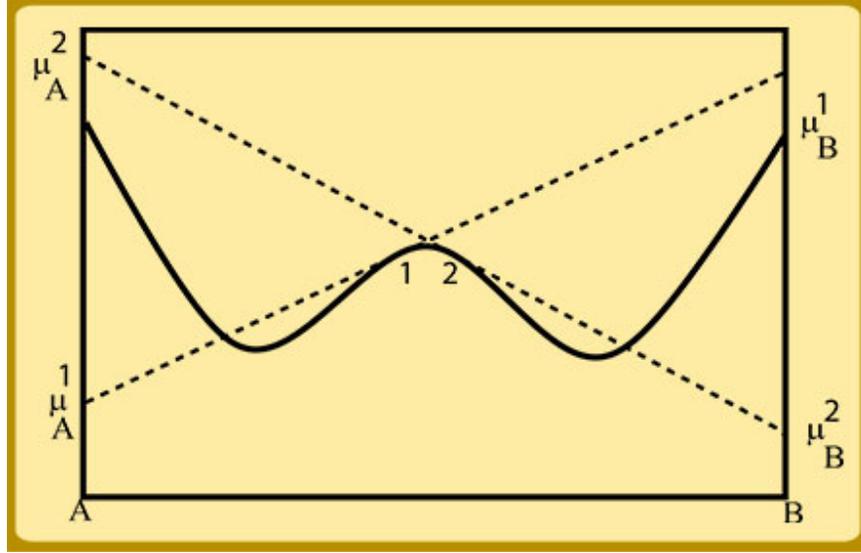


Figure 7: Flux in a compositionally heterogeneous system is always driven to even out chemical potential differences. In some cases this also results in the evening out of compositions. But in the case of spinodal shown here, the homogenisation of chemical potential leads to heterogeneities in composition.

If we modify the Fick's first law as

$$J = -N_V M \nabla \mu \quad (3)$$

where N_V is the Avogadro number, M is the mobility and μ is the chemical potential difference given by $\mu = \frac{\partial G}{\partial N_B}$ where N_B is the number of B atoms and G is the free energy, then, one can show that the diffusion equation becomes

$$\frac{\partial x_B}{\partial t} = \left(\frac{M}{N_V} \right) \left[\frac{\partial^2 G}{\partial x_B^2} \right] \nabla^2 x_B \quad (4)$$

In other words, in addition to the curvature of the composition profile one should also consider the curvature of the free energy with respect to composition. Once both the curvatures are considered, the spinodal behaviour is easy to understand. This is shown schematically in Fig. 8.

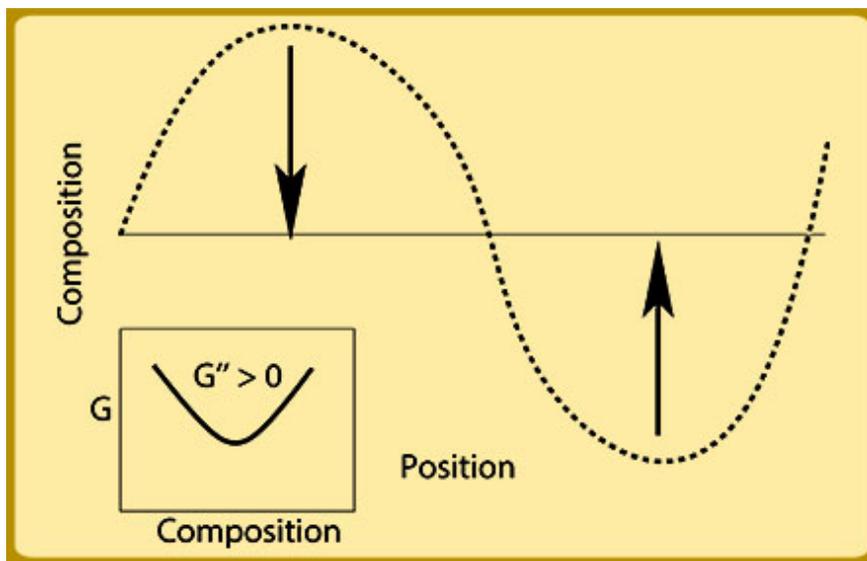


Figure 8: Evolution of composition during homogenisation and phase separation. By combining the signs of the curvature of the composition profile and free energy versus composition curve, we can explain both.

1.3 Spinodal decomposition

Consider a system with an interdiffusion coefficient D and undergoing spinodal decomposition. Within the spinodal region, the composition fluctuations grow as shown in Fig. 5; the fluctuations grow with a characteristic time constant $\tau = -\lambda^2/4\pi^2D$ where λ is the wavelength of the composition modulation (assuming one-dimensional modulations). Thus, for smaller λ , the rate of transformation becomes high; however, there is a minimum λ below which spinodal decomposition cannot occur; this is because, during spinodal decomposition, as A and B-rich regions are forming, there are also interfaces between these regions where AB bonds are formed which are energetically costlier; these regions give rise to an increase in free energy; the ‘incipient’ interfacial energy associated with the formation of these regions with large AB bonds are the ones which set the lower wavelength limit. The lower limit on the wavelength λ can be obtained using the following argument.

Consider a homogeneous alloy of composition x_B^0 decomposing into two parts: one with composition $x_B^0 + \Delta x$ and another with composition $x_B^0 - \Delta x$. It can be shown that the total free energy change associated with this decomposition is

$$\Delta G_{chem} = \frac{1}{2} \frac{d^2 G}{dx_B^2} (\Delta x)^2 \quad (5)$$

As noted earlier, the AB bonds in the incipient interface regions also contribute to the free energy; this free energy contribution, thus, is associated with the gradients in composition. Consider a sinusoidal composition modulation of wavelength λ and amplitude Δx ; the maximum composition gradient is thus $\Delta x/\lambda$ and the gradient energy contribution is

$$\Delta G_{grad} = \kappa \left(\frac{\Delta x}{\lambda} \right)^2 \quad (6)$$

where

$$\Delta G_{grad} = \kappa \left(\frac{\Delta x}{\lambda} \right)^2$$

is a proportionality constant which is dependent on the difference between AB and AA and BB bond energies.

The total change in free energy associated with a composition fluctuation of wavelength λ is thus given by the addition of the chemical and gradient terms (Eqns. 5 and 6):

$$\Delta G = \Delta G_{chem} + \Delta G_{grad} = \left(\frac{d^2 G}{dx_B^2} + \frac{2\kappa}{\lambda^2} \right) \frac{(\Delta x)^2}{2} \quad (7)$$

From the above expression, it is clear that for spinodal decomposition

$$-\frac{d^2 G}{dx_B^2} > \frac{2\kappa}{\lambda^2} \quad (8)$$

Or,

$$\lambda^2 > -\frac{2\kappa}{\frac{d^2 G}{dx_B^2}} \quad (9)$$

1.4 Tutorial problems and questions

- Derive the lower limit on the wavelength λ for spinodal decomposition including the effect of coherency elastic stress effects.

1.5 Solutions to the tutorial

- Let us consider the coherency strain associated with composition fluctuations: the change in lattice parameter with composition is given by $\frac{da}{dx}$; thus, for a total composition change of Δx , molar volume V_m , ΔG_{coh} is given by

$$\Delta G_{coh} = \eta^2 (\Delta x)^2 V_m E' \quad (10)$$

where

$$\eta = \frac{1}{a} \frac{da}{dx} \quad (11)$$

and

$$E' = \frac{E}{1 - \nu} \quad (12)$$

Adding the above energy ΔG_{coh} to Eq. 7, one obtains the equation

$$\begin{aligned} \Delta G &= \Delta G_{chem} + \Delta G_{grad} + \Delta G_{coh} \\ &= \left(\frac{d^2 G}{dx_B^2} + \frac{2\kappa}{\lambda^2} + 2\eta^2 E' V_m \right) \frac{(\Delta x)^2}{2} \end{aligned} \quad (13)$$

from which the condition for spinodal is derived as

$$-\frac{d^2 G}{dx_B^2} > \frac{2\kappa}{\lambda^2} + 2\eta^2 E' V_m \quad (14)$$

1.6 Supplementary information

Some sections of this module is based on a Module 3 in Part IV of the NPTEL course, Computational Methods in Materials Science and Engineering; as shown in that module, even though the accounting of the curvature of free energy versus composition curve can explain the phase separation process in terms of concentration changes, the Eq. 4 is not sufficient to describe the process of spinodal phase separation. This is because when phase separation happens, even though the system prefers AA and BB bonds, there are incipient interfaces between the A and B-rich phases which contain AB bonds. Hence there is an increase in interfacial energy which is not accounted for in the classical picture, and as noted above, it can be accounted for using the gradient energy coefficient κ . Including this contribution of incipient interfaces and deriving the non-classical diffusion equation involves calculus of variations; the equation, when derived is known as the Cahn-Hilliard equation. In the Computational Methods in Materials Science and Engineering course module referred to above, the Cahn-Hilliard equation as well as a way of solving it numerically are shown.