# Lecture 23: Spinodal Decomposition: *Part 2: regarding free energy change and interdiffusion coefficient inside the spinodal*

Today's topics

- Continue to understand the basic kinetics of spinodal decomposition.

- Within the spinodal, $d^2G/dc^2 < 0$ and interdiffusion coefficient ($\tilde{D}$)<0; how to interpret this regarding the free energy change.

"c" or "X" here refers to the concentration of components.
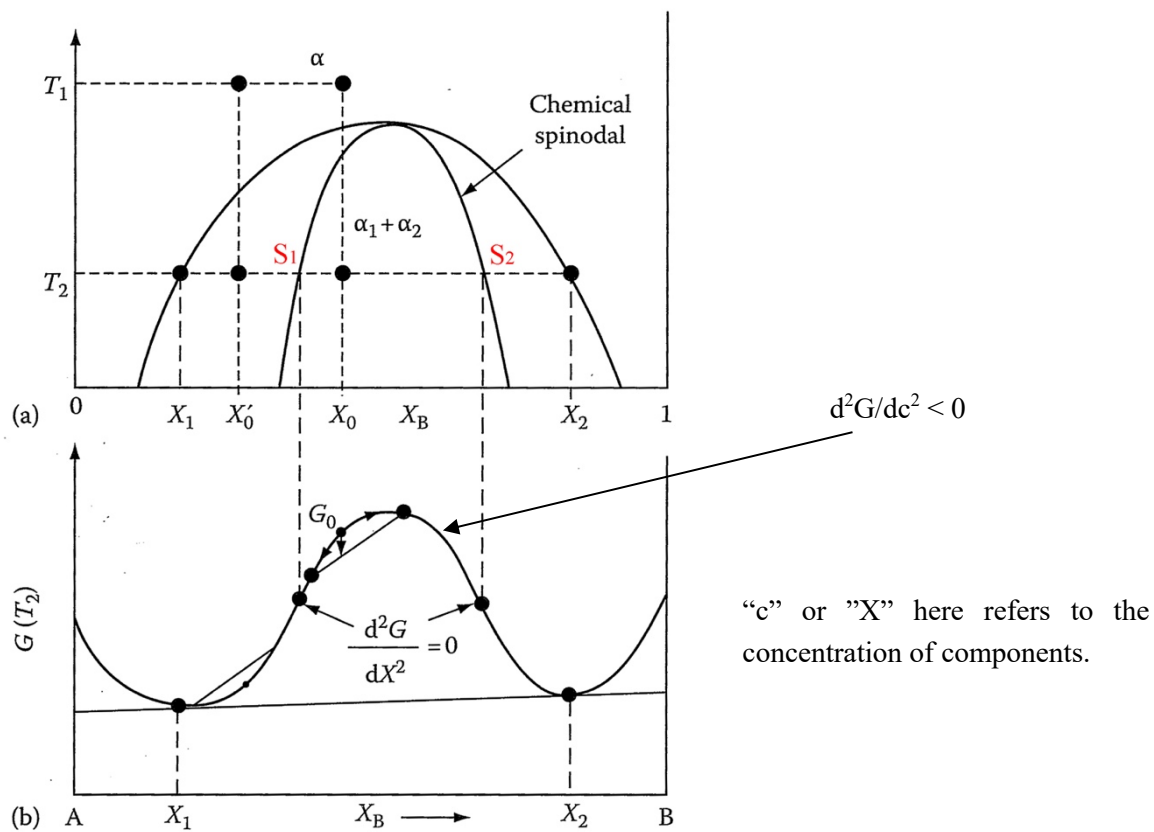
The starting point for the analysis is the Cahn-Hilliard equation for the total free energy (G) of a solid solution.

$$G = N_V \int [g(c) + K(\nabla C)]dV$$

or, in one dimensional composition variation (composition gradient in one dimension):

$$G = AN_V \int [g(c) + K(\frac{dc}{dx})^2]dx$$

where A is the cross-sectional area perpendicular to the x-axis,

Nᵥ is the number of atoms/unit volume.

Also, g(c) and K are quantities defined on a per atom/molecule basis.

If we define g(c) and K on a per unit volume basis, then we have

$$G = A \int [g(c) + K(\frac{dc}{dx})^2] dx \qquad \textbf{(1)}$$

In the following, concentration "c" will be used to represent atom or molar fraction.

Note: The above equation was derived by "local density" approximation --- that is, by expanding 'g' as a function of c, $\frac{dc}{dx}, \frac{d^2c}{dx^2}$ ..., about a locally homogeneous (uniform) solution, for which c = constant,

$$\frac{dc}{dx} = 0, \frac{d^2c}{dx^2} = 0, ...$$

Now consider a homogeneous solid solution of composition C_0, the free energy of a volume A·L (L = length along x) is

$$G(c_0) = A \cdot L \ g(c_0) \qquad (\frac{dc}{dx} = 0).$$

Now, let us assume that somehow a composition perturbation (or fluctuation) is created such that the composition is a function of position, *although the average composition is still c_0*.

Then, we can expand g(c) about the average composition. That is

$$g(c) = g(c_0) + \frac{\partial g}{\partial c}\bigg|_{c_0} (c - c_0) + \frac{1}{2}\frac{\partial^2 g}{\partial c^2}\bigg|_{c_0} (c - c_0)^2 + ...$$

Thus, Gibbs free energy for an alloy of average composition c_0, but with a spatially varying composition is (Eq. (1) →)

$$G = A \int [g(c_0) + \frac{\partial g}{\partial c}\bigg|_{c_0} (c - c_0) + \frac{1}{2}\frac{\partial^2 g}{\partial c^2}\bigg|_{c_0} (c - c_0)^2 + ... + K(\frac{\partial c}{\partial x})^2] dx \qquad \textbf{(2)}$$

Note that any composition variation can be given in terms of a Fourier series. We will simply assume that the entire composition variation can be described by a single sinusoidal wave of wavelength 'λ'. Specifically, let us assume that the composition fluctuation is given by

$$c(x) - c_0 = A_m \cos(\frac{2\pi x}{\lambda}) = A_m \cos \beta x \qquad \textbf{(3)}$$

where A_m = amplitude, and $\beta = \frac{2\pi}{\lambda}$ = wave number
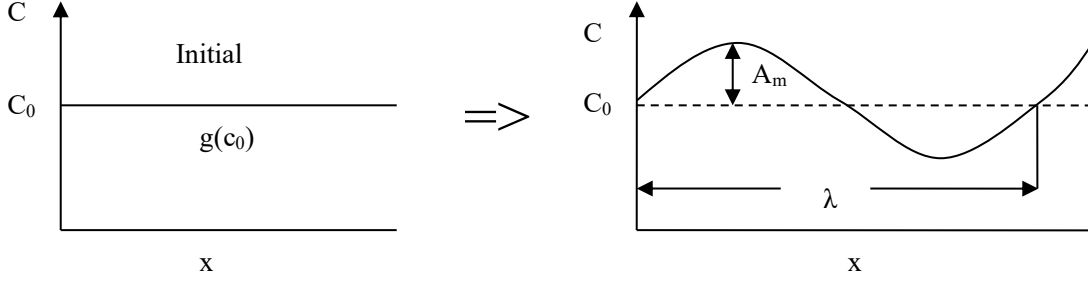
Thus, when such a composition fluctuation exists, the free energy per unit volume can be deduced as follows:
First from Eq. (2), we have

$$\frac{G}{A\lambda} = g(c) = \frac{1}{\lambda}\int_0^{\lambda}[g(c_0) + \frac{\partial g}{\partial c}\Big|_{c_0}(c - c_0) + \frac{1}{2}\frac{\partial^2 g}{\partial c^2}\Big|_{c_0}(c - c_0)^2 + K(\frac{dc}{dx})^2]dx$$

Second, substitute for c with Eq. (3), we get

$$g(c) = \frac{1}{\lambda}\int_0^{\lambda}[g(c_0) + \frac{\partial g}{\partial c}\Big|_{c_0}A_m\cos(\frac{2\pi}{\lambda}x) + \frac{1}{2}\frac{\partial^2 g}{\partial c^2}\Big|_{c_0}A^2_m\cos^2(\frac{2\pi}{\lambda}x) + K(\frac{2\pi}{\lambda})^2 A^2_m\sin^2(\frac{2\pi}{\lambda}x)]dx$$

$$g(c) = g(c_0) + \frac{A_m}{\lambda}\frac{\partial g}{\partial c}\Big|_{c_0}\int_0^{\lambda}\cos(\frac{2\pi}{\lambda}x)dx + \frac{A_m^2}{2\lambda}\frac{\partial^2 g}{\partial c^2}\Big|_{c_0}\int_0^{\lambda}\cos^2(\frac{2\pi}{\lambda}x)dx + K(\frac{2\pi}{\lambda})^2\frac{A_m^2}{\lambda}\int_0^{\lambda}\sin^2(\frac{2\pi}{\lambda}x)dx$$

now, write $\quad \theta = \frac{2\pi}{\lambda}x, \quad$ then, $\quad d\theta = \frac{2\pi}{\lambda}dx, \quad\quad dx = \frac{\lambda}{2\pi}d\theta, \quad \begin{array}{l} x = 0 \rightarrow \theta = 0 \\ x = \lambda \rightarrow \theta = 2\pi \end{array}$

Then,

$$g(c) = g(c_0) + \frac{A_m}{2\pi}\frac{\partial g}{\partial c}\Big|_{c_0}\int_0^{2\pi}\cos\theta d\theta + \frac{A_m^2}{2}\frac{1}{2\pi}\frac{\partial^2 g}{\partial c^2}\Big|_{c_0}\int_0^{2\pi}\cos^2\theta d\theta + K(\frac{2\pi}{\lambda})^2\frac{A_m^2}{2\pi}\int_0^{2\pi}\sin^2\theta d\theta$$

Now $\quad \int_0^{2\pi}\cos\theta d\theta = 0, \quad \int_0^{2\pi}\cos^2\theta d\theta = \int_0^{2\pi}\sin^2\theta d\theta = \pi$

$$g(c) = g(c_0) + \frac{A_m^2}{4}\frac{\partial^2 g}{\partial c^2}\Big|_{c_0} + \frac{KA_m^2}{2}(\frac{2\pi}{\lambda})^2$$

Or

$$g(c) = g(c_0) + \frac{A_m^2}{4}\frac{\partial^2 g}{\partial c^2}\Big|_{c_0} + \frac{KA_m^2\beta^2}{2} = g(c_0) + \frac{A_m^2}{4}\{\frac{\partial^2 g}{\partial c^2}\Big|_{c_0} + 2K\beta^2\} \qquad (4)$$

The above gives the free energy per unit volume of a solid solution having a composition fluctuation described by

$$c(x) - c_0 = A_m\cos(\frac{2\pi}{\lambda}x) = A_m\cos\beta x \qquad (3)$$

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Eq.(3) tells us: For a <u>homogeneous solid solution</u> of composition C_0, if a <u>composition perturbation</u> (or fluctuation) is created such that the composition is a function of position, *although the average composition is still c_0.*

Now, lets continue to analyze the above equation to interpret the spinodal decomposition, wherein $\Delta g \leq 0$ and interdiffusion coefficient ($\tilde{D}$)<0.

With the composition fluctuation given by $c(x) = c_0 + A_m \cos \beta x$ developed within the initially homogeneous solid solution of composition c_0, the change in free energy can be written (from Eq. 4 above) as

$$\Delta g = g(c) - g(c_0) = g(c_0 + A_m \cos \beta x) - g(c_0) = \frac{A^2_m}{4} \{ \left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} + 2K\beta^2 \}$$

For the fluctuation to be stable in relation to the original, homogeneous solid solution, we must have

$$\Delta g = \frac{A^2_m}{4} \{ \left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} + 2K\beta^2 \} \leq 0$$

Now, K is always >0, and β^2>0, thus, $2K\beta^2$>0. Also, A^2_m always >0.

Therefore, for $\Delta g \leq 0$, it is necessary that $\left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} < 0.$

We have seen that inside the miscibility gap (the diagram on page 2), the free energy of the original solid solution is possible to have $\left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} < 0$. The two points ($S_1$ and S_2) at which $\left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} = 0$ are defined as spinodes (i.e., inflection points of the g curve), and the boundary of $\left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} = 0$ in the phase diagram is defined as the spinodal, as shown in the diagram above.

Thus, if the temperature is such that $\left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} < 0$***, i.e., inside the spinodal, and for the value of β to be sufficiently small (λ sufficiently large), it is possible to have Δg to be negative***

$$\Delta g = \frac{A^2_m}{4} \{ \left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} + 2K\beta^2 \} < 0$$

Then, the fluctuation is more stable composition compared to the homogeneous solid solution, i.e., $\Delta g < 0$.
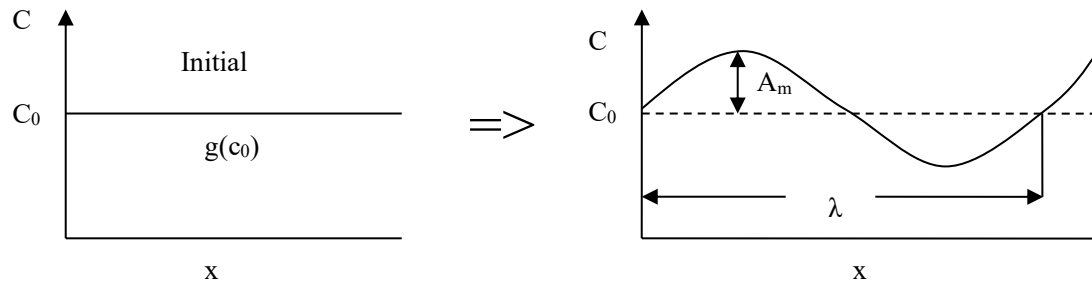
The above equation shows that the sign of Δg does not depend on the magnitude of A_m.

The largest possible β (lowest λ) such that the fluctuation is stable with respect to the homogeneous solid solution (i.e., as required by $\Delta g < 0$), is given by β_c,

$$\left.\frac{\partial^2 g}{\partial c^2}\right|_{c_0} + 2K\beta^2{}_c = 0$$

$$\beta_c = [\frac{1}{2K}(-\left.\frac{\partial^2 g}{\partial c^2}\right|_{c_0})]^{1/2}$$

or $\quad \lambda_c = \frac{2\pi}{\beta_c} = [\frac{1}{8\pi^2 K}(-\left.\frac{\partial^2 g}{\partial c^2}\right|_{c_0})]^{-1/2}$

Positive, real values of β_c and λ_c are possible only inside the spinodal so that $\frac{\partial^2 g}{\partial c^2} < 0$

The lower limitation λ (i.e., λ_c) is due to the **gradient energy term (K)**, which implies that the fluctuation (and eventual decomposition) cannot occur on too fine a scale. As we see later, there are certain similarities between the phenomenon of spinodal decomposition and cellular precipitation, mainly from the standpoint of the role of bulk free energy and the interfacial energy (gradient energy).

The Kinetics of Spinodal Decomposition:
Uphill Diffusion (against concentration gradient), and understanding based on Chemical diffusion coefficient ($D_A{}^C$), and Inter-diffusion coefficient ($\tilde{D}$)

As we learned before in **Lecture 5**, the chemical diffusion coefficient (e.g., $D_A{}^C$) depends on $\frac{\partial^2 g}{\partial c^2}$, as expressed by the following equations:

$$D_A^C = D_A\{1+\frac{\partial \ln \gamma_A}{\partial \ln c_A}\} = \frac{D_A c_A c_B}{RT} \cdot \frac{\partial^2 G}{\partial c_A^{\,2}} = \frac{D_A c_A c_B}{RT} \cdot \frac{\partial^2 G}{\partial c_B^{\,2}} \quad \text{(per mole)}$$

$$D_B^C = D_B\{1+\frac{\partial \ln \gamma_B}{\partial \ln c_B}\} = \frac{D_B c_A c_B}{RT} \cdot \frac{\partial^2 G}{\partial c_B^{\,2}} = \frac{D_B c_A c_B}{RT} \cdot \frac{\partial^2 G}{\partial c_A^{\,2}} \quad \text{(per mole)}$$

Let **c = concentration of B atom or mole fraction**, then the above equations may also be written as

$$D_A^C = \frac{D_A c_A c_B}{N_0 k_B T} \cdot \frac{\partial^2 g}{\partial c_B^{\,2}} = \frac{D_A c(1-c)}{N_0 k_B T} \cdot \frac{\partial^2 g}{\partial c^2} \quad \text{(per unit volume)}$$

$$D_B^C = \frac{D_B c_A c_B}{N_0 k_B T} \cdot \frac{\partial^2 g}{\partial c_B^{\,2}} = \frac{D_B c(1-c)}{N_0 k_B T} \cdot \frac{\partial^2 g}{\partial c^2} \quad \text{(per unit volume)}$$

Where N_0 is the Avogadro constant, k_B is the Boltzmann constant.

From Nernst-Einstein Equation:

$$\frac{D_A}{k_B T} = M_A \quad \text{and} \quad \frac{D_B}{k_B T} = M_B, \quad \text{where } M_A \text{ and } M_B \text{ are } \textbf{mobilities} \text{ of A and B, respectively.}$$

So,
$$D_A^C = \frac{M_A c(1-c)}{N_0} \cdot \frac{\partial^2 g}{\partial c^2}, \quad D_B^C = \frac{M_B c(1-c)}{N_0} \cdot \frac{\partial^2 g}{\partial c^2}$$

Let us assume that the interdiffusion coefficient ($\tilde{D}$) obeys Darken's equation (**Lecture 6**), then,

$$\tilde{D} = c D_A^C + (1-c) D_B^C$$

$$= \frac{M_A c^2(1-c)}{N_0} \cdot \frac{\partial^2 g}{\partial c^2} + \frac{M_B c(1-c)^2}{N_0} \cdot \frac{\partial^2 g}{\partial c^2}$$

$$= \frac{c(1-c)}{N_0} \{c M_A + (1-c) M_B\} \frac{\partial^2 g}{\partial c^2}$$

write, $M = [c M_A + (1-c) M_B] \cdot c \cdot (1-c)$

so, $\tilde{D} = \dfrac{M}{N_0} \cdot \dfrac{\partial^2 g}{\partial c^2}$

Inside the spinodal, $\dfrac{\partial^2 g}{\partial c^2} < 0$

so, $\tilde{D} < 0.$

Now, as we learned in Lecture 6, the Fick's first Law gives:

$$J_A = - \tilde{D} \ \frac{\partial c_A}{\partial x} , \qquad J_B = - \tilde{D} \ \frac{\partial c_B}{\partial x}$$

As the diffusion flux (J_A, J_B) must be positive, this means (dC_A/dx, or dC_B/dx) must be positive, i.e., the diffusion is up against concentration gradient, though still along chemical potential or free energy gradient, $\Delta G < 0$.