

Lecture 24: Spinodal Decomposition: Part 3: kinetics of the composition fluctuation

Today's topics

- Diffusion kinetics of spinodal decomposition in terms of the concentration (composition) fluctuation as a function of time: $c(x,t) - c_0 = A_m(\beta, 0) \cdot \exp[R(\beta)t] \cdot \cos \beta x$, where

$$R(\beta) = -\frac{M}{N_0} \cdot \beta^2 \cdot \left[\frac{\partial^2 g}{\partial c^2} \Big|_{c_0} + 2K \beta^2 \right]$$

- Learn how to derive above equation from the Fick's second law, for which how to deduce the term $\frac{\partial g}{\partial c}$ is critical, $\frac{\partial g}{\partial c} = \frac{\partial^2 g}{\partial c^2} \Big|_{c_0} (c - c_0) - 2K \frac{d^2 c}{dx^2}$.
- Understand the critical wavelength λ_c (or wave number β_c) for the composition fluctuation: for $\beta < \beta_c$ (or $\lambda > \lambda_c$), then $R(\beta) > 0$, the composition fluctuations (amplitude) will grow --- thermodynamically favorable.
- Understand the maximal wavelength λ_m (or wave number β_m), at which the composition fluctuations (amplitude) will grow the fastest: when $\beta \ll \beta_m$ (or $\lambda \gg \lambda_m$), the growth becomes diffusion limited.

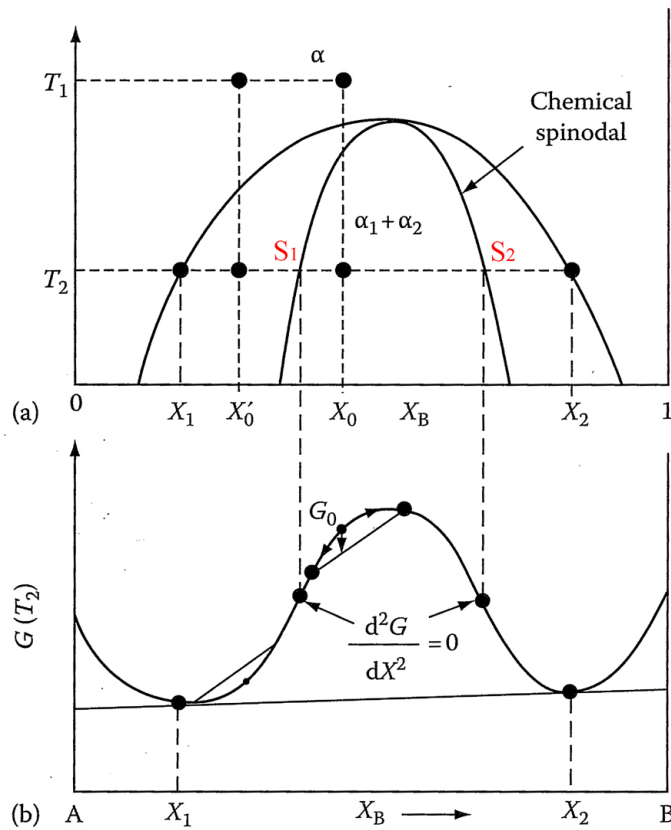
Phase diagram and free energy plot of Spinodal Decomposition

As a special case of phase transformation, **spinodal decomposition** can be illustrated on a phase diagram exhibiting a miscibility gap (see the diagram below). Thus, phase separation occurs whenever a material transitions into the unstable region of the phase diagram. The boundary of the unstable region, sometimes referred to as the binodal or coexistence curve, is found by performing a common tangent construction of the free-energy diagram. Inside the binodal is a region called the spinodal, which is found by determining where the curvature of the free-energy curve is negative. The binodal and spinodal meet at the critical point. It is when a material is moved into the spinodal region of the phase diagram that spinodal decomposition can occur.

If an alloy with composition of X_0 is solution treated at a high temperature T_1 , and then quenched (rapidly cooled) to a lower temperature T_2 , the composition will initially be the same everywhere and its free energy will be G_0 on the G curve in the following diagram. However, the alloy will be immediately unstable, because small fluctuation in composition that produces A-rich and B-rich regions will cause the total free energy to decrease. Therefore, "up-hill" diffusion (as shown) takes place until the equilibrium

compositions X_1 and X_2 are reached. *How such small composition fluctuation leads to the spinodal phase separation is today's and next two lectures' topics.*

The free energy curve is plotted as a function of composition for the phase separation temperature T_2 . Equilibrium phase compositions are those corresponding to the free energy minima. Regions of negative curvature ($d^2G/dc^2 < 0$) lie within the inflection points of the curve ($d^2G/dc^2 = 0$) which are called the spinodes (as marked as S_1 and S_2 in the diagram above). For compositions within the spinodal, a homogeneous solution is ***unstable against microscopic fluctuations in density or composition, and there is no thermodynamic barrier to the growth of a new phase, i.e., the phase transformation is solely diffusion controlled.***



In last two lectures (#22, 23):

For a homogeneous solid solution of composition C_0 , when a composition perturbation (or fluctuation) is created such that the composition is a function of position (*although the average composition is still c_0*), the spinodal decomposition will initiated.

The composition fluctuation can be described as

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

where A_m = amplitude, and $\beta = \frac{2\pi}{\lambda}$ = wave number

Let concentration (molar fraction) of B atom is c , the concentration of A atom is $(1-c)$,

Then the interdiffusion coefficient can be expressed as:

$$\tilde{D} = \frac{c(1-c)}{N_0} \{cM_A + (1-c)M_B\} \frac{\partial^2 g}{\partial c^2} \quad (N_0 \text{ is the Avogadro constant, } k_B \text{ is the Boltzmann constant.})$$

Where $\frac{D_A}{k_B T} = M_A$ and $\frac{D_B}{k_B T} = M_B$, M_A and M_B are **mobilities** of A and B, respectively.

Defining $M = [cM_A + (1-c)M_B] \cdot c \cdot (1-c)$

Then, $\tilde{D} = \frac{M}{N_0} \cdot \frac{\partial^2 g}{\partial c^2}$ (Inside the spinodal, $\tilde{D} < 0$.)

Today's Lecture:

Fick's first law gives.

$$J = -\tilde{D} \cdot \frac{\partial c}{\partial x} = -\frac{M}{N_0} \cdot \frac{\partial^2 g}{\partial c^2} \cdot \frac{\partial c}{\partial x}$$

Rewrite the above as

$$\begin{aligned} J &= -\tilde{D} \cdot \frac{\partial c}{\partial x} = -\frac{M}{N_0} \cdot \frac{\partial}{\partial c} \left(\frac{\partial g}{\partial c} \right) \cdot \frac{\partial c}{\partial x} \\ &= -\frac{M}{N_0} \cdot \frac{\partial}{\partial x} \left(\frac{\partial g}{\partial c} \right) \end{aligned}$$

Then, Fick's second law becomes

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial}{\partial x} \left[\frac{M}{N_0} \cdot \frac{\partial}{\partial x} \left(\frac{\partial g}{\partial c} \right) \right]$$

In general, M depends on the composition, but here for simplicity, we assume such composition dependence is ignorable, so that M remains constant.

$$\text{Thus, } \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[\frac{M}{N_0} \cdot \frac{\partial}{\partial x} \left(\frac{\partial g}{\partial c} \right) \right] = \frac{M}{N_0} \cdot \frac{\partial^2}{\partial x^2} \left(\frac{\partial g}{\partial c} \right)$$

From Lecture 23, we know total free energy $G(c)$ along one dimension can be expressed as

$$G(c) = \int_x g(c) dx = \int_x \left[g(c_0) + \left. \frac{\partial g}{\partial c} \right|_{c_0} (c - c_0) + \frac{1}{2} \left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} (c - c_0)^2 + K \left(\frac{dc}{dx} \right)^2 \right] dx$$

Where $g(c)$ is free energy per volume defined along one dimension.

Taking a variational derivative

$$\begin{aligned} \delta G(c) &= \int_x \frac{\partial g}{\partial c} \cdot \delta c \cdot dx \\ &= \int_x \left[\left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} (c - c_0) \cdot \delta c + K \delta \left(\frac{dc}{dx} \right)^2 \right] dx \end{aligned} \quad (1)$$

Now, let us evaluate the term $\int_x K \delta \left(\frac{dc}{dx} \right)^2 dx$

Note $\delta \left(\frac{dc}{dx} \right)^2 dx = 2 \frac{dc}{dx} \cdot \delta \left(\frac{dc}{dx} \right) dx = 2 \left(\frac{dc}{dx} \right) \cdot \delta(dc)$

Thus, $\int_x K \delta \left(\frac{dc}{dx} \right)^2 dx = \int_x 2K \left(\frac{dc}{dx} \right) \cdot \delta(dc)$ (2)

Integration by parts gives

$$\int_x 2K \left(\frac{dc}{dx} \right) \cdot \delta(dc) = 2K \left(\frac{dc}{dx} \right) dc - 2K \int_x \left(\frac{d^2c}{dx^2} \right) \cdot dx \delta c$$

Then, Eq. (2) can be re-written as:

$$\int_x K \delta \left(\frac{dc}{dx} \right)^2 dx = \int_x 2K \left(\frac{dc}{dx} \right) \cdot \delta(dc) = 2K \left(\frac{dc}{dx} \right) dc - 2K \int_x \left(\frac{d^2c}{dx^2} \right) \cdot dx \delta c \quad (3)$$

What is integration by parts:

In calculus, and more generally in mathematical analysis, integration by parts is a rule that transforms the integral of products of functions into other (ideally simpler) integrals. The rule arises from the product rule of differentiation.

If $u = f(x)$, $v = g(x)$, and the differentials $du = f'(x) dx$ and $dv = g'(x) dx$, then the product rule in its simplest form is:

$$\int u \frac{dv}{dx} dx = uv - \int v \frac{du}{dx} dx$$

At the very early stage of spinodal decomposition, composition variation is very small, $\frac{dc}{dx} \approx 0$

So, Eq. (3) becomes

$$\int_x K \delta \left(\frac{dc}{dx} \right)^2 dx = - \int_x 2K \left(\frac{d^2c}{dx^2} \right) \cdot \delta c \cdot dx \quad (4)$$

Thus, Eq. (1) becomes

$$\delta G(c) = \int_x \frac{\partial g}{\partial c} \delta c dx = \int_x \left[\frac{\partial^2 g}{\partial c^2} \Big|_{c_0} (c - c_0) - 2K \frac{d^2c}{dx^2} \right] \delta c dx \quad (5)$$

$$\text{That is } \frac{\partial g}{\partial c} = \frac{\partial^2 g}{\partial c^2} \Big|_{c_0} (c - c_0) - 2K \frac{d^2c}{dx^2}$$

Now, Fick's first law above can be written as

$$J = - \frac{M}{N_0} \cdot \frac{\partial}{\partial x} \cdot \left(\frac{\partial g}{\partial c} \right) = - \frac{M}{N_0} \left(\frac{\partial^2 g}{\partial c^2} \Big|_{c_0} \frac{\partial c}{\partial x} - 2K \frac{\partial^3 c}{\partial x^3} \right) \quad (6)$$

And, Fick's second law above can be written as

$$\frac{\partial c}{\partial t} = - \frac{\partial J}{\partial x} = \frac{M}{N_0} \cdot \left\{ \frac{\partial^2 g}{\partial c^2} \Big|_{c_0} \frac{\partial^2 c}{\partial x^2} - 2K \frac{\partial^4 c}{\partial x^4} \right\} \quad (7)$$

The above is known as **Cahn's diffusion equation**, which also accounts for the "pseudo" interfacial energy, the term containing K (see Lecture 23). This term (as discussed for the nucleation) opposes phase separation, but favors concentration amplitude growth in spinodal decomposition as discussed below.

We have assumed that the composition fluctuation is of the type

$$c(x) - c_0 = A_m \cos \beta x$$

where A_m = amplitude, and $\beta = \frac{2\pi}{\lambda}$ = wave number, and λ is the wavelength.

Assuming the wavelength to be independent of time, then the time dependence must be in the amplitude, that is

$$c(x, t) - c_0 = A_m(\beta, t) \cos \beta x$$

By inspection, it is seen that a solution to the diffusion equation (Eq. 7) has the following form:

$$c(x, t) - c_0 = A_m(\beta, 0) \cdot \exp[R(\beta)t] \cdot \cos \beta x \quad (8)$$

where $R(\beta) = -\frac{M}{N_0} \cdot \beta^2 \cdot \left[\frac{\partial^2 g}{\partial c^2} \Big|_{c_0} + 2K \beta^2 \right]$ (9)

$R(\beta)$ is termed amplification factor. As long as the term inside the parentheses is negative (note: $\frac{\partial^2 g}{\partial c^2} \Big|_{c_0}$

< 0 in the spinodal), $R(\beta) > 0$, and the amplitude will grow (see the diagram below) --- **the critical β is thus**

defined as: $\beta_c = \left(-\frac{\partial^2 g}{\partial c^2} \Big|_{c_0} / 2K \right)^{1/2}$, and $\lambda_c = 2\pi/\beta$, or $\lambda_c = \frac{2\pi}{\beta_c} = \left[\frac{1}{8\pi^2 K} \left(-\frac{\partial^2 g}{\partial c^2} \Big|_{c_0} \right) \right]^{-1/2}$

i.e., the largest β (or smallest λ) possible for the composition (c_0) at a temperature to vary.

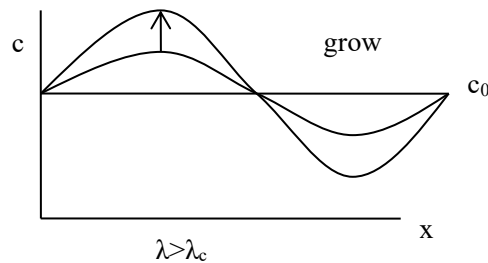
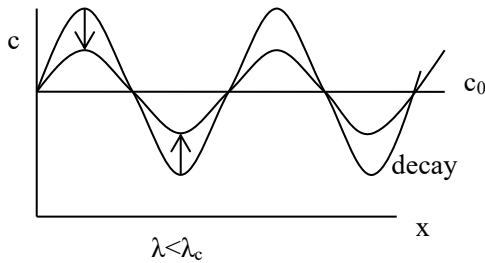
---this is consistent with what we learned in Lecture 23, where

To have $\Delta g = \frac{A_m^2}{4} \left\{ \frac{\partial^2 g}{\partial c^2} \Big|_{c_0} + 2K \beta^2 \right\} \leq 0$, i.e., to assure spontaneous process,

We deduced the same $\beta_c = \left(-\frac{\partial^2 g}{\partial c^2} \Big|_{c_0} / 2K \right)^{1/2}$, and $\lambda_c = \frac{2\pi}{\beta_c} = \left[\frac{1}{8\pi^2 K} \left(-\frac{\partial^2 g}{\partial c^2} \Big|_{c_0} \right) \right]^{-1/2}$

Clearly, inside the spinodal,

- when $\beta < \beta_c$ (or $\lambda > \lambda_c$), then $R(\beta) > 0$, the concentration fluctuations (amplitude) will grow;
- when $\beta > \beta_c$ (or $\lambda < \lambda_c$), then $R(\beta) < 0$, the concentration fluctuations will decay away.



As clearly seen from Eq. (8), the value of β which maximizes $R(\beta)$ will grow the fastest.

From Eq. (9), the maximum $R(\beta)$ is given by

$$\frac{dR}{d\beta} = 0 = -\frac{M}{N_0} \left[2\beta_m \cdot \frac{\partial^2 g}{\partial c^2} \Big|_{c_0} + 8K \beta_m^3 \right]$$

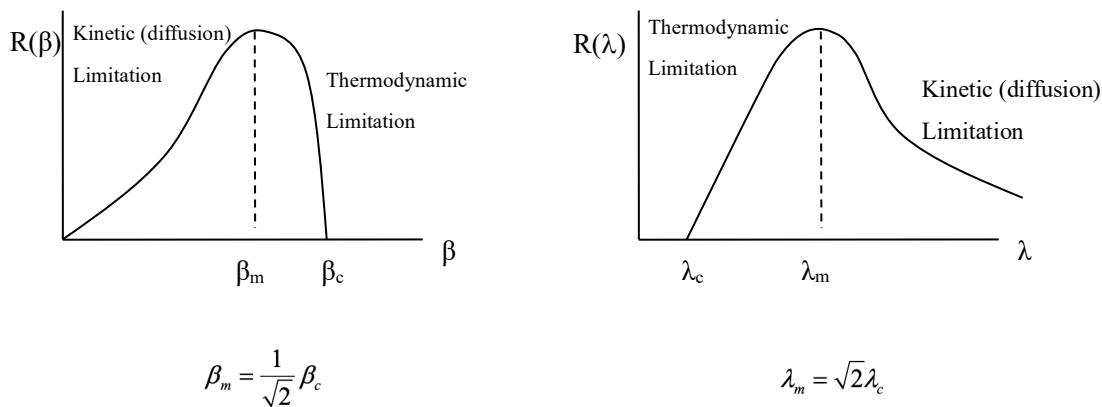
$$\text{so, } \beta_m = \sqrt{\frac{-\left.\frac{\partial^2 g}{\partial c^2}\right|_{c_0}}{4K}} = \frac{1}{\sqrt{2}} \beta_c$$

$$\text{or, } \lambda_m = \sqrt{2} \lambda_c$$

--- **R(β) is maximum at $\beta_m = \beta_c / \sqrt{2}$ or at $\lambda_m = \sqrt{2} \lambda_c$.**

In other words, composition fluctuation of wavelength λ (or wave number β) very close to λ_m (β_m) grow much more rapidly than the rest (i.e., very much kinetically favorable). As a result, the microstructure formed in spinodal decomposition is very **uniform and fine**. The typical values of λ_m are on the order of 20 to 100Å in the early stage. Small angle x-ray scattering and electron diffraction are suitable techniques to study the microstructure formed in spinodal decomposition.

As shown in the plots of R(β) vs. β or R(λ) vs. λ below: **the maximal growth rate occurs as a compromise between the thermodynamic factor and kinetic factor.**



Note the similarity with the Eutectoid phase transformation (a typical cellular precipitation as learned in Lecture 20), wherein the lamellar spacing (λ^*) corresponding to the maximum growth rate is **twice** that of the minimum possible λ_{\min} .

As learned from Lecture 23, for the fluctuation to be stable (thermodynamically favorable) in relation to the original, homogeneous solid solution, we must have

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

$$\text{This also gives the critical } \beta \text{ and } \lambda, \quad \beta_c = \left[\frac{1}{2K} \left(- \left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} \right) \right]^{1/2}, \quad \lambda_c = \frac{2\pi}{\beta_c} = \left[\frac{1}{8\pi^2 K} \left(- \left. \frac{\partial^2 g}{\partial c^2} \right|_{c_0} \right) \right]^{-1/2}$$

Meaning, when $\lambda < \lambda_c$, or $\beta > \beta_c$, Δg will become > 0 , not thermodynamically favorable for the fluctuation

to be stable, i.e., for the Spinodal decomposition to proceed.

Lecture 20: Eutectoid phase transformation (a typical cellular precipitation): γ -iron \rightarrow α -iron + cementite

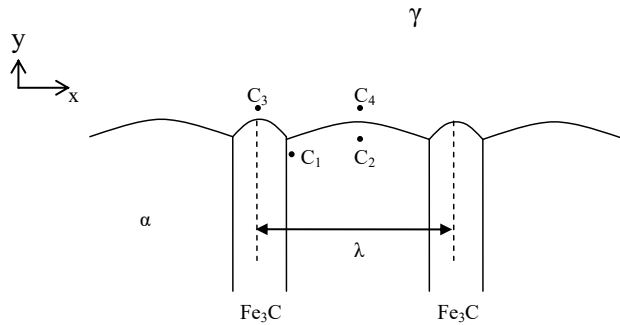
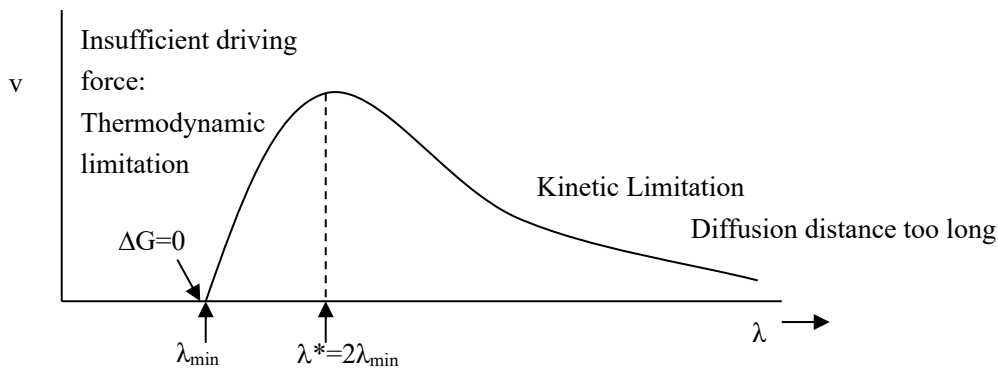


FIGURE 5.60
Pearlite colony advancing into an austenite grain. (After Darken, L.S. and Fisher, R.M., in *Decomposition of Austenite by Diffusional Processes*, Interscience, New York, 1962.)

This gives $\lambda^* = 2\lambda_{\min}$ corresponding to the maximum growth rate as depicted below.



Brief summary of Spinodal decomposition vs. Eutectoid transformation

Three unique features shared by eutectoid transformation and spinodal decomposition

1. structure uniformness, due to the maximal transformation rate determined by (favored at) a specific λ size, for the eutectoid transformation, $\lambda^* = 2\lambda_{\min}$, for spinodal decomposition, $\lambda_m = \sqrt{2}\lambda_c$
2. large area uniformness: because both phase transformation initiated throughout the whole phase, with eutectoid transformation initiated from local grain boundaries and defects, and spinodal decomposition from concentration fluctuation in the whole phase.
3. Diffusion: both local, short range

major differences:

1. During the eutectoid transformation the original phase (here γ) maintains though being consumed, whereas in spinodal decomposition the original phase is no longer there when cooled down to lower temperature T_2 , since the composition fluctuation changes the composition throughout the phase.

2. During the process of phase transformation, the new phases formed in eutectoid transformation keep constant concentrations (fixed composition), whereas in spinodal decomposition the composition keeps changing (building up the concentrations).
3. The diffusion in eutectoid transformation is along the concentration gradient, but the diffusion of spinodal decomposition is against (uphill) the concentration gradient.
4. eutectoid transformation terminates suddenly, with impingement of the cells to finish the phase transformation. spinodal decomposition stops by the local uphill diffusion.
5. The specific λ size that gives the maximal rate is different for spinodal decomposition and Eutectoid transformation.