VIII. Phase Transformations

Lecture 38: Nucleation and Spinodal Decomposition

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In this lecture we will study the onset of phase transformation for phases that differ only in their equilibrium composition, keeping in mind that it is possible for phases to differ in other physical quantities such as density, crystal structure, magnetization, etc.

Consider a regular solution model for free energy, illustrated in figure 1. Suppose a homogeneous system is in region of its phase diagram (P,T,c)

Regular solution model

Figure 1

where the homogeneous phase is unstable thermodynamically. The system can lower its free energy by separating into two phases with an interface in between. In figure 1, c_- and c_+ are common tangent points that mark the boundaries of the miscibility gap. For any composition inside the miscibility gap (between c_- and c_+), a phase separated system is energetically favorable.

Outside the miscibility gap, the system remains homogeneous at equilibrium no matter what the composition.

In his classical treatment of phase transformations, Gibbs distinguished between two types of transformations: those that are small in degree and large in extent (spinodal decomposition, linear instability), and those that are large in degree and small in extent (nucleation, nonlinear instability). Let's examine both in a bit more detail.

1   Spinodal decomposition

Compositions between c_{s-} and c_{s+} lie within the chemical spinodal, a region of linear instability where $g''(c) < 0$ and small fluctuations will grow spontaneously through a process called spinodal decomposition. Previously we showed that $\bar{g}''(c) < 0$ is the condition for linear instability by graphical construction (ignoring variations of μ with ∇c). Spontaneous phase separation is favored when the chord to a free energy curve is lower everywhere than the curve itself:
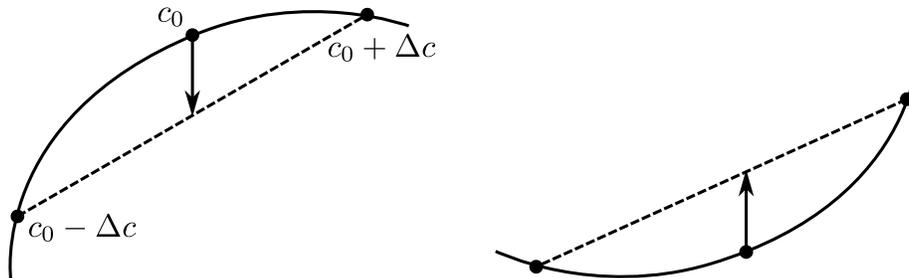
(a) $g''(c) < 0$ promotes spinodal decomposition. Spontaneous separation into $c_0 + \Delta c$ and $c_0 - \Delta c$ lowers the total free energy ($\Delta c << c_0$).

(b) $g''(c) > 0$ does not promote spontaneous phase separation. Small composition fluctuations raise the total free energy.

2   Classical nucleation

Nucleation is a nonlinear instability that requires the formation of a large enough nucleus of the nucleating phase. The creation of a nucleus of the low-energy phase with concentration c_+ form a matrix of concentration c_* (where $c_- < c_* < c_{s-}$), is illustrated in figure 2a. There is a decrease in free energy $\Delta \bar{g}$ associated with the conversion of c_* to c_+, and an increase in free energy due to the interfacial energy γ. There is a critical radius where these

(a) A simple spherical nucleus with a sharp interface.

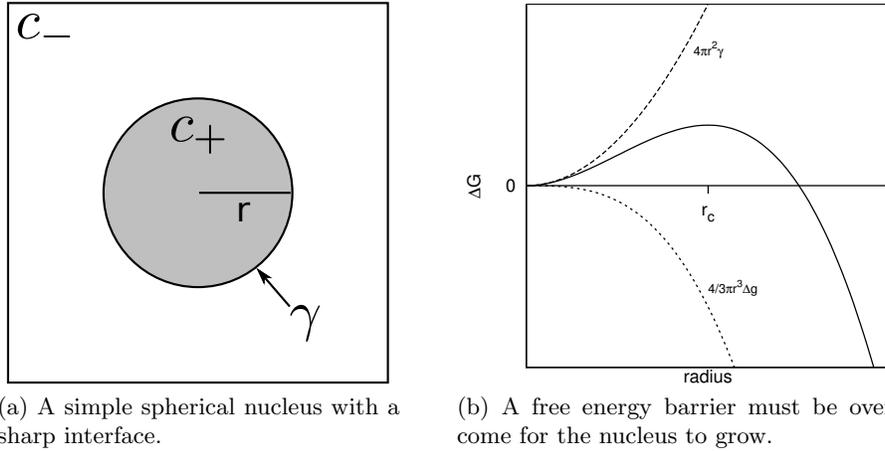(b) A free energy barrier must be overcome for the nucleus to grow.

Figure 2

two opposing effects exactly balance each other, as illustrated in figure 2b. Recall that the surface area of a sphere is proportional to r^2, but its volume is proportional to r^3. A nucleus larger than the critical radius will grow due to the volume free energy decrease, and a nucleus smaller than the critical radius will shrink due to its proportionally high surface area. The growth rate of a nucleus is proportional to $e^{-\frac{\Delta G}{kT}}$.

The free energy change for the creation of a nucleus with radius r is:

$$\Delta G = V\Delta\bar{g} + A\gamma$$
$$= \frac{4}{3}\pi r^3 \Delta\bar{g} + 4\pi r^2 \gamma \tag{1}$$

where $\Delta\bar{g} = \bar{g}(c_+) - \bar{g}(c_*)$ is the volume free energy savings (thus $\Delta\bar{g} < 0$) and γ is the surface energy. The particle will grow when $\frac{d\Delta G}{dr} > 0$ and shrink when $\frac{d\Delta G}{dr} < 0$. At the critical radius:

$$\frac{d\Delta G}{dr} = 4\pi r^2 \Delta\bar{g} + 8\pi r\gamma = 0 \tag{2}$$

The critical radius is:

$$\boxed{r = r_c = \frac{2\gamma}{|\Delta\bar{g}|}} \tag{3}$$

Unfortunately, the classical nucleation model generally does not agree well with experiment. Treating interfacial energy as a constant and modeling the interface as a sharp discontinuity are too simplistic. The discrepancy

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remained until Cahn and Hilliard introduced a model that treated the interface as a smoothly varying, diffuse quantity.

3   The Cahn-Hilliard model

The Cahn-Hilliard model adds a correction to the homogeneous free energy function to account for spatial inhomogeneity. This correction comes from a Taylor expansion of $\bar{g}$ in powers of ∇c combined with symmetry considerations. Similar models were used by Van der Walls to model liquid-vapor interfaces, and by Landau to study superconductors.

While composition in a homogeneous system is a scalar, composition becomes a field for an inhomogeneous system. Thus the Cahn-Hilliard free energy is a functional of the composition field:

$$G[c(x)] = N_V \int_V \bar{g}(c) + \frac{1}{2}\kappa(\nabla c)^2 dV \qquad (4)$$

$\bar{g}(c)$ is the homogeneous free energy, and N_V is the number of sites per volume. $\kappa \nabla^2 c$, the so-called gradient energy, is the first-order correction for inhomogeneity which introduces a penalty for sharp gradients, allowing interfacial energy to be modeled.

3.1   Chemical potential

Chemical potential is a scalar quantity that is only defined at equilibrium. Here we will introduce a chemical potential that is defined for an inhomogeneous system, away from equilibrium. If we assume local equilibrium, we can define this potential field by employing the calculus of variations:

$$\mu = \frac{\delta G}{\delta c} = \lim_{\epsilon \to 0} \frac{G[c(x) + \epsilon \delta_\epsilon(x - y)] - G[c(x)]}{\epsilon} \qquad (5)$$

See 2009 notes for mathematical details. The variational derivative may be found by applying the Euler-Lagrange equation:

$$\frac{\delta G}{\delta c} = \frac{\partial I}{\partial c} - \frac{d}{dx}\frac{\partial I}{\partial \nabla c} \qquad (6)$$

where I is the integrand of $G[c(x)]$. The functional derivative of Eq. 4 is:

$$\mu = \bar{g}'(c) - \kappa \nabla^2 c \qquad (7)$$

3.2 Anisotropy

For a crystal, κ is anisotropic and must be represented as a tensor $\mathbf{K}$. The free energy functional and corresponding chemical potential are:

$$G = N_V \int_V \bar{g}(c) + \frac{1}{2} \nabla c \cdot \mathbf{K} \nabla c \, dV \tag{8a}$$

$$\mu = \frac{\delta G}{\delta c} = \bar{g}'(c) - \nabla \cdot \mathbf{K} \nabla c \tag{8b}$$

3.3 Evolution equation for c

In previous lectures we have arrived at a generalized expression for the flux of concentration:

$$\vec{F} = -Mc\nabla\mu \tag{9}$$

Since c is a conserved quantity, it obeys a conservation law:

$$\frac{\partial c}{\partial t} + \nabla \cdot \vec{F} = 0 \tag{10}$$

Combining equations 7, 9, and 10, we arrive at the Cahn-Hilliard equation:

$$\boxed{\frac{\partial c}{\partial t} = \nabla \cdot \left(Mc\nabla \left(\bar{g}'(c) - \kappa\nabla^2 c \right) \right)} \tag{11}$$

3.4 The equilibrium phase boundary

Without the gradient penalty, the Cahn-Hilliard model describes nonlinear diffusion where equilibrium (constant μ, zero flux) implies a uniform concentration, if $\bar{\mu}(c)$ is monotonic. If $\bar{\mu}(c)$ is non-monotonic or $\bar{g}(c)$ has multiple minima, the equilibrium states can have solutions of piecewise constant c representing different phases, with sharp (discontinuous) interfaces.

The Cahn-Hilliard gradient penalty leads to diffuse phase boundaries of width λ, controlled by $\mathbf{K}$. Mathematically, this occurs because $\mu = const.$ becomes an ODE in 1D (a PDE in 2D, the Beltrami equation) rather than an algebraic equation:

$$\bar{g}'(c) - \kappa\nabla^2 c = const. \tag{12}$$

The constant is the first integral for the system which may be obtained from thermodynamics (i.e. an Euler integral, $G = \sum_i c_i \mu_i$), or by considering boundary conditions: $c(-\infty) = c_-, \nabla c(-\infty) = 0, c(\infty) = c_+, \nabla c(\infty) = 0$.
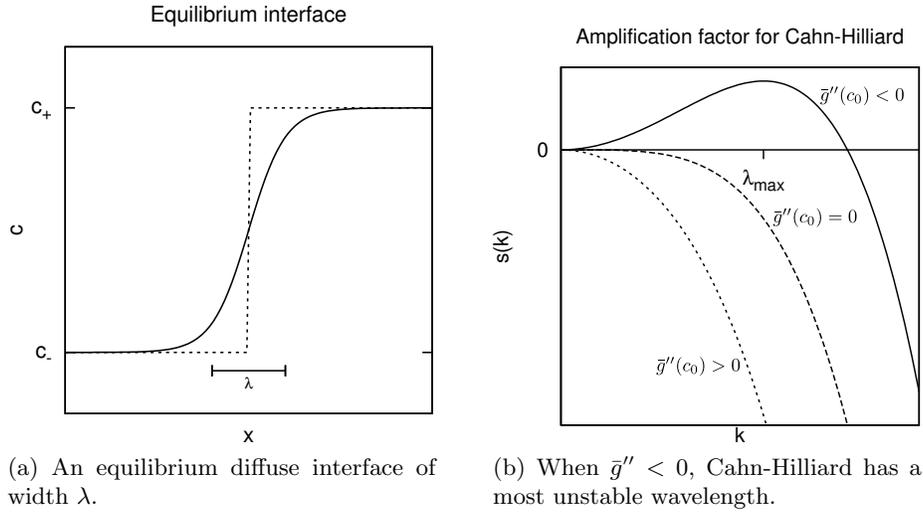
Equilibrium interface

Amplification factor for Cahn-Hilliard

(a) An equilibrium diffuse interface of width λ.

(b) When $\bar{g}'' < 0$, Cahn-Hilliard has a most unstable wavelength.

Figure 3

This equation may be integrated once to obtain a first-order separable ODE (for a 1D system) that can be be solved by integration:

$$\bar{g}'(c) + \frac{1}{2}\kappa(\nabla c)^2 = const. \tag{13}$$

For $\bar{g}(c) = (1-c^2)^2$, the constant is zero and the solution is $c(x) = \tanh\left(\frac{x}{\lambda}\right)$.

The shape of the critical nucleus as well as the nucleation barrier energy may also be calculated by examining the metastable solutions of Eq. 13 in a region of nonlinear instability. Cahn and Hilliard studied this diffuse critical nucleus and found much better agreement with experiment than with the "classic" nucleation model.

3.5   Interfacial width

Suppose $\bar{g}$ has scale a (e.g. a regular solution), where $a \gtrsim kT$. Equating units in Eq. 11 we can estimate the interfacial width λ:

$$\bar{g} \sim \kappa(\nabla c)^2 \rightarrow a \sim \kappa\left(\frac{\Delta c}{\lambda}\right)^2 \tag{14a}$$

$$\lambda = \Delta c\sqrt{\frac{\kappa}{a}} \tag{14b}$$

whereΔ $c = c_+ - c_-$, the width of the miscibility gap.

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3.6   Interfacial tension

We can also estimate the effective interfacial tension of the diffuse phase boundary. $\gamma = $ (interfacial width) $\times$ (gradient energy/volume):

$$\gamma \sim \lambda \kappa \left(\frac{\Delta c}{\lambda} \right)^2 = \kappa \frac{(\Delta c)^2}{\lambda} \tag{15a}$$

$$\boxed{\gamma = \Delta c \sqrt{\kappa a}} \tag{15b}$$

4   Dynamics of spinodal decomposition

Now let's use the Cahn-Hilliard model to describe the dynamics of spinodal decomposition. For small perturbations of a uniform concentration, we can interpret the gradient penalty not as a diffuse interfacial tension, but rather as the leading term in a Taylor expansion of the free energy per volume that approximates non-local effects.

It is important to remember that Cahn-Hilliard is still an LDA theory. The miracle of the Cahn-Hilliard model is that the same gradient term gives a reasonable description in both extremes - small perturbation of a uniform c and large perturbations that nucleate a phase boundary. In one regime, κ models weak short range interactions, and in the other regime, interfacial tension between two different phases. As a result of this ambiguity, there is no clear molecular definition of κ.

4.1   Linear stability analysis

Let $c(x,t) = c_0 + \nu$, where c_0 is a constant and $\nu = \epsilon e^{ikx} e^{st}$ is a small perturbation. We want to find the amplification factor s in terms of the wave number k to determine which frequencies will be amplified. Substitute $c = c_0 + \nu$ into the Cahn-Hilliard equation (Eq. 11) produces:

$$\frac{\partial (c_0 + \nu)}{\partial t} = \nabla \cdot \left(M(c_0 + \nu) \nabla \left(\bar{g}'(c_0) + \nu \bar{g}''(c_0) - \kappa \nabla^2 (c_0 + \nu) \right) \right)$$
$$\frac{\partial \nu}{\partial t} = \nabla \cdot \left(M(c_0 + \nu) \nabla \left(\nu \bar{g}''(c_0) - \kappa \nabla^2 \nu \right) \right) \tag{16}$$

Substituting $\nu = \epsilon e^{ikx} e^{st}$ and keeping only the linear $O(\epsilon)$ terms, we obtain:

$$\boxed{s = -Mc_0 \left(\bar{g}''(c_0)k^2 + \kappa k^4 \right)} \tag{17}$$

(a) $c \approx c_0$ inside the spinodal region. $t \approx 0$

(b) Spinodal decomposition. $t = \tau_{sp}$

(c) Ostwald ripening - coarsening driven to reduce interfacial area. The length scale grows as $l \sim t^{\frac{1}{3}}$, and $t >> \tau_{sp}$.
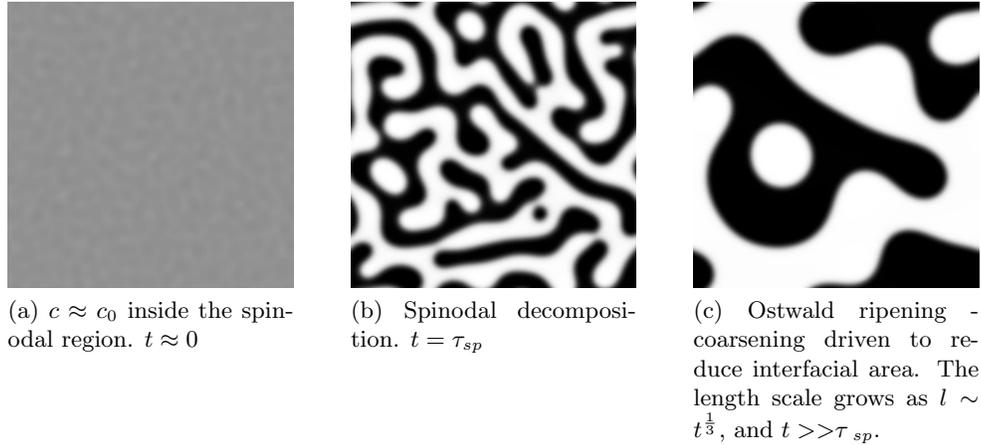
Figure 4

growth rate of a perturbation of wavenumber k. In this case, the most unstable wavelength is:

$$\lambda_{max} = \frac{2\pi}{k_{max}} = 2\pi\sqrt{\frac{2\kappa}{|\bar{g}''(c_0)|}} \tag{18}$$

The existence of a most unstable wavelength $\lambda_{max} > 0$ means that random fluctuations will decompose into a pattern with a characteristic length scale, as illustrated in figure 4. Note: If we estimate $|\bar{g}''(c_0)| \sim \frac{a}{(\Delta c)^2}$, then $\lambda_{max} \sim \lambda$ = phase boundary width.

The time scale for growth of the most unstable mode is:

$$\tau_{sp} = \frac{1}{s(k_{max})} = \frac{4\kappa}{|\bar{g}''|^2 Mc_0} \tag{19}$$

Now substitute Eq. 18 and the Einstein relation $D = MkT$:

$$\boxed{\tau_{sp} = \frac{4\pi^2\lambda_{max}^2}{D}\left(\frac{2kT}{c_0|\bar{g}''(c_0)|}\right)} \tag{20}$$

The physical interpretation of τ_{sp} is the time for a particle to diffuse across a distance λ_{max} divided by the thermodynamic driving force (of order T/T_c).

10.626 Electrochemical Energy Systems

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