3.21 Spring 2001: Lecture 33

Macroscopic Theories for Decomposition and Order/Disorder Kinetics

Background: Changes in Density of Extensive Functions for Conserved and Non-Conserved Quantities

Figure 33-1: Illustration of the change in molar free energy from a composition $c_0$. If the system is closed so the composition is fixed, then the change in any molar extensive quantity (e.g. molar free energy) is $\Delta F_c$ for every mole which forms at composition $c'$. If the system is open and the composition is free to change its value—or if the quantity associated with the transformation is non-conserved, then $\Delta F_{\text{trans}}$ is the change per mole transformed.
Results for Small Variations

- **Non-conserved quantities:** If $\eta$ is a non-conserved quantity, like spin, or crystalline order, then for small changes in $\eta$ given by $\delta \eta$:

$$\Delta G = \delta \eta \left. \frac{dG}{d\eta} \right|_{\eta=\eta_0}$$

(33-1)

Therefore, an order parameter can always decrease the free energy by picking a variation $\delta \eta$ with a sign that makes the product in Eq. 33-1 negative. An non-conserved order parameter has no barrier against reaching a value which makes the free energy a local minimum.

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- **Conserved quantities:** If $c$ is a non-conserved quantity, like concentration, then for small changes in $c$ given by $\delta c$:

$$\Delta G = \frac{1}{2} (\delta c)^2 \left. \frac{d^2G}{dc^2} \right|_{c=c_0}$$

(33-2)

Therefore, a barrier to the growth of small variations exists whenever the second derivative in Eq. 33-2 is positive. Thus, nucleation is required for a transformation outside of the spinodal curves.

In fact, it can be shown that the sign of the diffusivity, $D$, for concentration flux is given by the second derivative $\partial^2G/\partial c^2$. This has the effect of causing “up-hill” diffusion.

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**Macroscopic Theories for Decomposition Kinetics**

It is possible, but currently impractical, to model the kinetics of an order/disorder reaction or a spinodal decomposition by simulating the motions of individual atoms. In this section, a coarse-graining procedure is developed and partial differential equations are developed for the evolution of the coarse-grained parameters.\(^{39}\)

\(^{39}\)Some material for this section appeared in the previous lecture notes.
It is possible to derive the kinetics of order/disorder and spinodal decomposition from the same underlying principles. In the case of spinodal decomposition, extra considerations for the locally conserved composition field will result in a different kinetic relation.

Let \( y(\vec{x}) \) represent either a conserved or non-conserved quantity, and consider how an arbitrary distribution \( y(\vec{x}) \) evolves towards equilibrium.

We will take a variational calculus approach of writing down an expression for the total free energy in terms of \( y \) and its gradients.

The total free energy of the entire system (occupying the domain \( \Omega \)) is:

\[
F[y(x)] = \int_{\Omega} (f(y) + \frac{K}{2} \nabla y \cdot \nabla y) dV \tag{33-3}
\]

which defines \( F \) as a functional with the argument \( y(\vec{x}) \). The function \( y(\vec{x}) \) will also have specified boundary conditions on \( \partial \Omega \) (the boundary of \( \Omega \)); for instance, \( y(\partial \Omega) \) will have fixed values or fixed derivatives.

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\[^{40}\text{A functional is a function of a function; in this case, it takes a function and maps it to a scalar which is numerically equal to the total free energy of the system.}\]
If the field \( y(\vec{x}) \) is changing with velocity \( v(\vec{x}) \), the is the rate of change of \( F \) is

\[
F(y + vt) = \int_{\Omega} \left[ f(y + vt) + + \frac{K}{2} (\nabla y \cdot \nabla y + 2t \nabla v \cdot \nabla v + \partial^2 \nabla v \cdot \nabla v) \right] dV
\]

(33-4)

and it can be shown\(^{41}\)

\[
\frac{\partial F}{\partial t} \bigg|_{t=0} = \int_{\Omega} (f'(y) - K \nabla^2 y) v dV
\]

(33-5)

The change in total energy in Eq. 33-5 is the sum of local variations: \((f'(y) - K \nabla^2 y) v\). Therefore, the **largest possible increase** of \( F \) is when the flow, \( v(\vec{x}) \) is proportional to (minus) the other factor in the integrand of Eq. 33-5:

\[
v(\vec{x}) = -M f'(y) - K \nabla^2 y
\]

(33-6)

Therefore, The right-hand-side of Eq. 33-6 is the functional gradient of \( F(y) \) and can be associated with the local potential for changing the field \( y \) so as to reduce the total energy \( F[y] \).

The functional gradient is the starting point for the kinetic equations for conserved and non-conserved parameter fields.

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**Kinetics of Non-conserved Order Parameters:**

**The Allen-Cahn Equation**

For a non-conserved order parameter \( \eta(\vec{x}) \), Eq. 33-6 is the local rate of increase of free energy for a small change \( \delta \eta(\vec{x}) \); therefore \(- (f'(\eta) - K \eta \nabla^2 \eta)\) is the driving force to change \( \eta \). No long-range diffusion is required (in other words, the order parameter can change with no flux of order into an element \( dV \)). Therefore, assuming kinetics that are linear in the driving force:

\[
\frac{\partial \eta}{\partial t} = M \eta [K \nabla^2 \eta - f'(\eta)]
\]

(33-7)

\(^{41}\)See last lecture for details. However, it is not important that you know the mathematics, only the concepts.
which is known as the Allen-Cahn equation for describing order-disorder kinetics. It is also called Model A or the non-conserved Ginsberg-Landau equation.

Allen-Cahn: Critical Microstructural Wavelengths
Consider a system where \( f(\eta) \) has two minima at \( \eta = \pm 1 \):

\[
f(\eta) = f_s((1 + \eta)(1 - \eta))^2
\]

(33-8)

where \( f_s \) is the height at the unstable saddle point at \( \eta = 0 \). Suppose the system is initially uniform at unstable point \( \eta = 0 \) (for instance, the system may have been quenched from a higher temperature, disordered state and \( \eta = \pm 1 \) represent two equivalent ordering variants). If the system is perturbed a small amount by a planar perturbation in the z-direction, \( \eta(\vec{x}) = \delta(t) \sin(\omega z) \). Putting this and Eq. 33-8 into Eq. 33-7, and keeping the lowest order terms in \( \delta(t) \):

\[
\frac{d\delta(t)}{dt} = M_\eta(4f_s - K_\eta\omega^2)\delta(t)
\]

(33-9)

so that

\[
\delta(t) = \delta(0) \exp[M_\eta(4f_s - K_\eta\omega^2)t]
\]

(33-10)

The perturbations grow if

\[
\lambda > \lambda_{\text{crit}} = \pi \sqrt{\frac{K_\eta}{f_s}}
\]

(33-11)

which is approximately equal to the interface width.
Note that the amplification factor is a weakly increasing function of wavelength (asymptotically approaching $4M_\eta f_\ast$ at long wavelengths). This would predict that the longest wavelengths would dominate the morphology of an order-disorder phase transition. However, the probability of finding a long wavelength perturbation is a decreasing function of wavelength and this also has an effect on morphology.

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**The Kinetics of Conserved Parameters: The Cahn-Hilliard Equation**

Because $c(x)$ is a (locally) conserved parameter, the flux of $c$ from one volume element to its neighbor will affect the kinetics. $c(\bar{x})$ is guaranteed to be conserved if $\partial c/\partial t$ is the divergence of a flux.

Equation 33-6 is the local increase of free energy density due to a local addition $\delta c(\bar{x})$. The flux is assumed to be linear in the gradient of Eq. 33-6:

$$\vec{J}_c = -M_c \nabla [f'(c(\bar{x})) - K_c \nabla^2 c]$$

(33-12)

This is equivalent to the linear assumption in Fick's law. The proportionality factor $M_c$ is related to the interdiffusion coefficient. However, $M_c$ is necessarily positive.

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Therefore, the local rate of increase of the composition is given by (minus) the divergence of the flux:

$$\frac{\partial c}{\partial t} = \nabla \cdot M_c \nabla [f'(c(\bar{x})) - K_c \nabla^2 c(\bar{x})]$$

(33-13)

if $M_c$ is constant, then

$$\frac{\partial c}{\partial t} = M_c [\nabla^2 f'(c(\bar{x})) - K_c \nabla^4 c(\bar{x})]$$

(33-14)

which is known as the Cahn-Hilliard equation describing the kinetics of spinodal decomposition. It is also called *Model B* or the *conserved Ginsberg-Landau equation*.
The first term on the right-hand side of Eq. 33-14 looks like the classical diffusion equation in regions where \( f(c) \) can be reasonably approximated by a quadratic function, (for instance near the minima of \( f \)). The fourth-order term has the effect of stabilizing the shortest wavelengths when \( f'' < 0 \), as discussed below.

Cahn-Hilliard: Critical and Kinetic Wavelengths

Consider the following function as an approximation to the regular solution model:

\[
f(c) = \frac{16f_s}{(c_\beta - c_\alpha)^2}[(c - c_\alpha)(c - c_\beta)]^2
\]

(33-15)

which has minima at concentrations \( c_\alpha \) and \( c_\beta \) and a maximum of height \( f_s \) at \( c = c_{\text{avg}} \equiv (c_\alpha + c_\beta)/2 \). Suppose we have an initially uniform solution at \( c = c_{\text{avg}} \) and that we perturb the concentration with a small plane wave: \( c(\vec{x}) = c_{\text{avg}} + \epsilon(t) \sin \omega z \). Putting this into Eq. 33-14 and keeping the lowest-order terms in \( \epsilon(t) \),

\[
\frac{d\epsilon}{dt} = \frac{M c \omega^2}{(c_\beta - c_\alpha)^2}[16f_s - K_c \omega^2(c_\beta - c_\alpha)^2] \epsilon
\]

(33-16)

Therefore any wavelength \( \lambda \) will grow if

\[
\lambda > \lambda_{\text{crit}} \equiv \frac{\pi}{2}(c_\beta - c_\alpha)\sqrt{\frac{K_c}{f_s}}
\]

(33-17)
Taking the derivative of the amplification factor in Eq. 33-16 with respect to \( \omega \) and setting it equal to zero, we find the fastest growing wavelength:

\[
\lambda_{\text{max}} = \sqrt{2} \lambda_{\text{crit}} = \sqrt{\frac{2\pi}{2}} (c_{\beta} - c_{\alpha}) \sqrt{\frac{K_c}{f_s}}
\]

(33-18)

It is expected that domain size in the early stage of spinodal decomposition will be approximately \( \lambda_{\text{max}} \).

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Note that this approach for conserved order parameter is analogous to the case of kinetic and thermodynamic stability of a cylinder with axial perturbations:

![Graphs](image)

**Figure 33-3:** The amplification factor for spinodal decomposition and order-disorder reactions.

**Simulations**

Below are simulations of Eqs. 33-7 and 33-14 with initial conditions taken as a small perturbation about the unstable (or saddle) point.

Can you determine, by observation, which simulation corresponds to which type of kinetics?

![Simulation Images](image)

**Figure 33-4:** A simulation—can you determine which type of kinetics? If you are viewing in HTML, click on the figure to see the simulation.
Figure 33-5: A simulation—can you determine which type of kinetics? If you are viewing in HTML, click on the figure to see the simulation.