Last time
Heterogeneous Nucleation

Decomposition versus Order/Disorder Kinetics

Simulations on a Square Lattice

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 $\Delta F_u$ 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 $\delta \eta$:

$$\Delta G = \delta \eta \frac{dG}{d\eta} \bigg|_{\eta=\eta_0}$$  \hspace{1cm} (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.

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

$$\Delta G = \frac{1}{2}(\delta c)^2 \frac{d^2G}{dc^2} \bigg|_{c=c_0}$$  \hspace{1cm} (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 $\partial^2 G/\partial c^2$. 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.\(^\text{39}\)

\(^{39}\)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 $y(x)$ represent either a conserved or non-conserved quantity, and consider how an arbitrary distribution $y(x)$ 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:

$$F[y(x)] = \int_{\Omega} \left( f(y) + \frac{K}{2} \nabla y \cdot \nabla y \right) dV$$  \hspace{1cm} (33-3)

which defines $F$ as a functional with the argument $y(x)^{40}$. The function $y(x)$ 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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\textsuperscript{40} A functional is a \textit{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

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

(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:

$$v(\vec{x}) = -Mf'(y) - K\nabla^2 y$$

(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:

$$\frac{\partial \eta}{\partial t} = M_\eta[K_\eta \nabla^2 \eta - f'(\eta)]$$

(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 \( \eta = \pm 1 \):

\[
f(\eta) = f_s((1 + \eta)(1 - \eta))^2 \quad (33-8)
\]

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 \( \delta(t) \):

\[
\frac{d\delta(t)}{dt} = M_\eta(4f_s - K_\eta \omega^2)\delta(t) \quad (33-9)
\]

so that

\[
\delta(t) = \delta(0) \exp[M_\eta(4f_s - K_\eta \omega^2)t] \quad (33-10)
\]

The perturbations grow if

\[
\lambda > \lambda_{\text{crit}} = \pi \sqrt{\frac{K_\eta}{f_s}} \quad (33-11)
\]

which is approximately equal to the interface width.
Note that the amplification factor is a weakly increasing function of wavelength (asymptotically approaching $4M_qf_s$ 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. $c(x)$ 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 $\delta c(x)$. The flux is assumed to be linear in the gradient of Eq. 33-6:

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

(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:

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

(33-13)

if $M_c$ is constant, then

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

(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:

\[
 f(c) = \frac{16f_s}{(c_\beta - c_\alpha)^4}[(c - c_\alpha)(c - c_\beta)]^2 \tag{33-15}
\]

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

\[
 \frac{d\epsilon}{dt} = \frac{M_{c} \omega^2}{(c_\beta - c_\alpha)^2}[16f_s - K_c \omega^2 (c_\beta - c_\alpha)^2] \epsilon \tag{33-16}
\]

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

\[
 \lambda > \lambda_{crit} \equiv \frac{\pi}{2} (c_\beta - c_\alpha) \sqrt{\frac{K_c}{f_s}} \tag{33-17}
\]
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:

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

(33-18)

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

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

![Conserved and nonconserved order parameters](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.