

Last timeHeterogeneous Nucleation


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Decomposition versus Order/Disorder Kinetics


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Simulations on a Square Lattice


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## 3.21 Spring 2001: Lecture 33

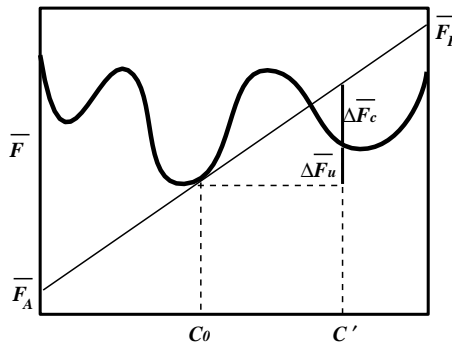
Macroscopic Theories for Decomposition and Order/Disorder KineticsBackground: Changes in Density of Extensive Functions for Conserved and Non-Conserved Quantities

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  $\Delta \bar{F}_c$  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  $\Delta \bar{F}_u$  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  $\delta\eta$ :

$$\Delta G = \delta\eta \left. \frac{dG}{d\eta} \right|_{\eta=\eta_0} \quad (33-1)$$

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. A 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  $\delta c$ :

$$\Delta G = \frac{1}{2}(\delta c)^2 \left. \frac{d^2 G}{dc^2} \right|_{c=c_0} \quad (33-2)$$

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.<sup>39</sup>

<sup>39</sup>Some material for this section appeared in the previous lecture notes.

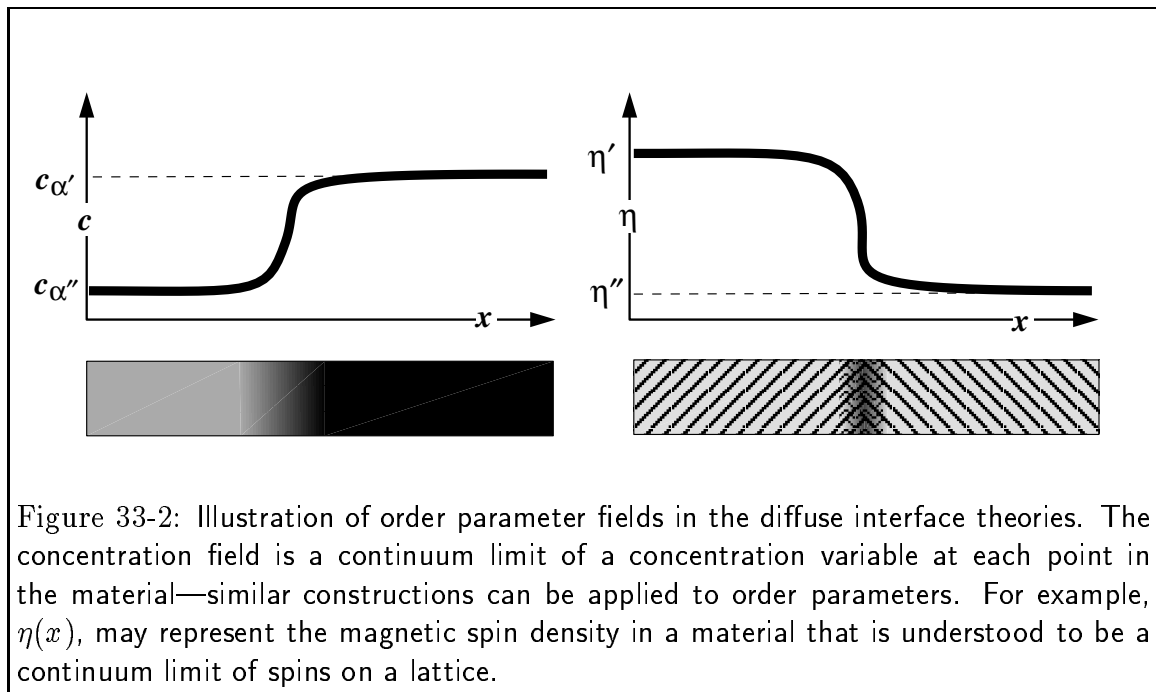


Figure 33-2: Illustration of order parameter fields in the diffuse interface theories. The concentration field is a continuum limit of a concentration variable at each point in the material—similar constructions can be applied to order parameters. For example,  $\eta(x)$ , may represent the magnetic spin density in a material that is understood to be a continuum limit of spins on a lattice.

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:

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

which defines  $F$  as a functional with the argument  $y(\vec{x})$ <sup>40</sup>. 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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<sup>40</sup>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

$$F(y + vt) = \int_{\Omega} [f(y + vt) + \frac{K}{2}(\nabla y \cdot \nabla y + 2t\nabla y \cdot \nabla v + t^2\nabla v \cdot \nabla v)]dV \quad (33-4)$$

and it can be shown<sup>41</sup>

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$$\left. \frac{\partial F}{\partial t} \right|_{t=0} = \int_{\Omega} (f'(y) - K\nabla^2 y)v dV \quad (33-5)$$

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:

$$v(\vec{x}) = -M f'(y) - K\nabla^2 y \quad (33-6)$$

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:

$$\frac{\partial\eta}{\partial t} = M_{\eta}[K_{\eta}\nabla^2\eta - f'(\eta)] \quad (33-7)$$

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<sup>41</sup>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*.

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### 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  $\delta(t)$ :

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

so that

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

The perturbations grow if

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

which is approximately equal to the interface width.

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Note that the amplification factor is a weakly increasing function of wavelength (asymptotically approaching  $4M_\eta f_s$  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.  $c(\vec{x})$  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  $\delta c(\vec{x})$ . The flux is assumed to be linear in the gradient of Eq. 33-6:

$$\vec{J}_c = -M_c \nabla [f'(c(\vec{x})) - K_c \nabla^2 c] \quad (33-12)$$

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:

$$\frac{\partial c}{\partial t} = \nabla \cdot M_c \nabla [f'(c(\vec{x})) - K_c \nabla^2 c] \quad (33-13)$$

if  $M_c$  is constant, then

$$\frac{\partial c}{\partial t} = M_c [\nabla^2 f'(c(\vec{x})) - K_c \nabla^4 c] \quad (33-14)$$

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*.

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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.

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### Cahn-Hilliard: Critical and Kinetic Wavelengths

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

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


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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  $\epsilon(t)$ ,

$$\frac{d\epsilon}{dt} = \frac{M_c \omega^2}{(c_\beta - c_\alpha)^2} [16f_s - K_c \omega^2 (c_\beta - c_\alpha)^2] \epsilon \quad (33-16)$$

Therefore any wavelength  $\lambda$  will grow if

$$\lambda > \lambda_{crit} \equiv \frac{\pi}{2} (c_\beta - c_\alpha) \sqrt{\frac{K_c}{f_s}} \quad (33-17)$$


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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:

$$\lambda_{max} = \sqrt{2}\lambda_{crit} = \frac{\sqrt{2}\pi}{2}(c_\beta - c_\alpha)\sqrt{\frac{K_c}{f_s}} \quad (33-18)$$

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

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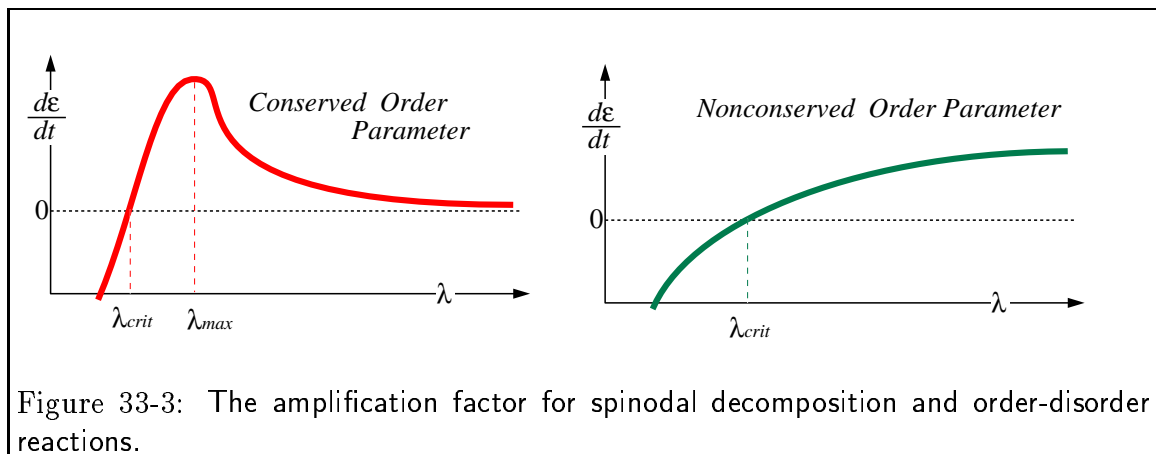


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Note that this approach for conserved order parameter is analogous to the case of kinetic and thermodynamic stability of a cylinder with axial perturbations:



### 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?

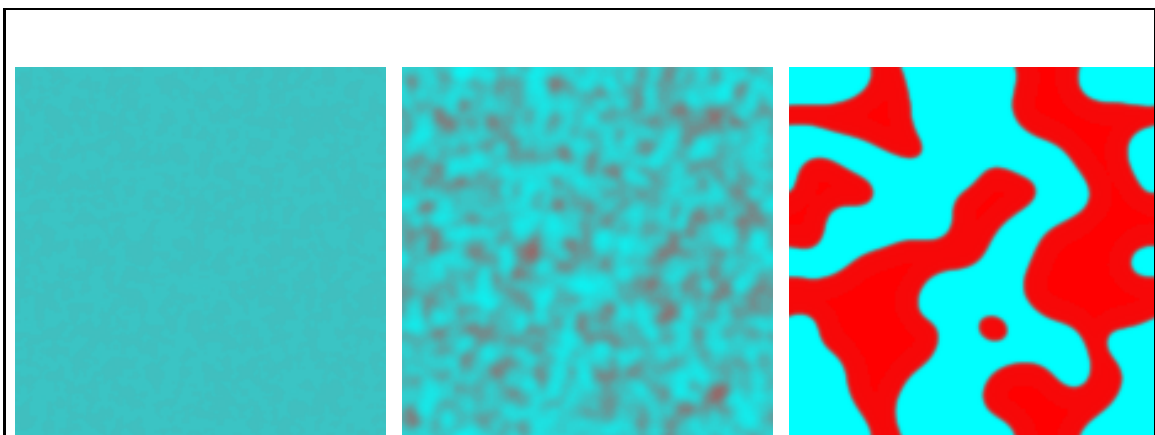


Figure 33-4: A simulation—can you determine which type of kinetics? If you are viewing in HTML, click on the figure to see the simulation.



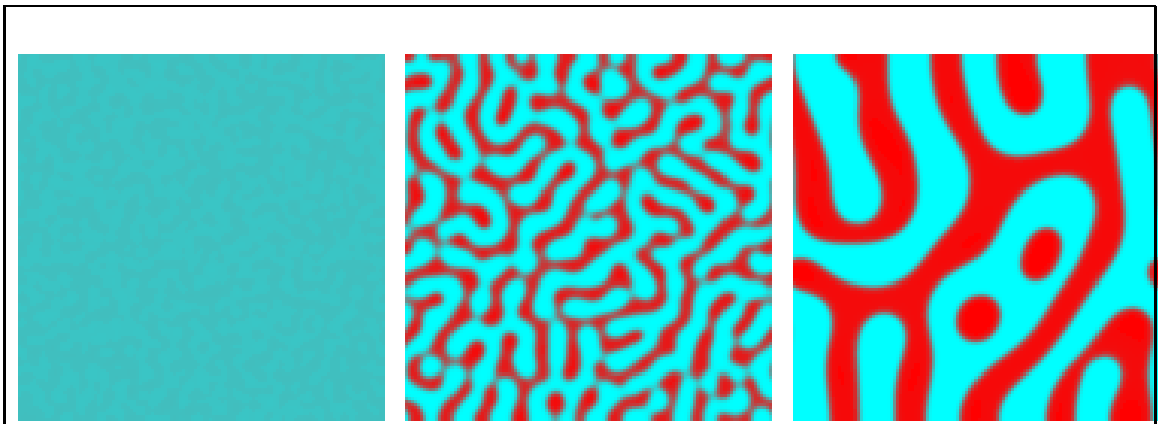


Figure 33-5: A simulation—can you determine which type of kinetics? If you are viewing in HTML, click on the figure to see the simulation.