<u>Last time</u>
<u>Order Parameters</u>

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<u>Continuous and Discontinuous Transformations</u>

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<u>Free Energy Changes for Conserved and Non-conserved Order Parameters</u>

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<u>Free Energy Density and Diffuse Interfaces</u>

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3.21 Spring 2002: Lecture 23

<u>Continuous Phase Transformations—Kinetics</u>

The functional gradient is the starting point for the kinetic equations for conserved and non-conserved parameter fields. From an integral over the homogeneous free energy density and a gradient energy term:

$$F[y(x)] = \int_\Omega (f(y) + \frac{K}{2}\nabla y \cdot \nabla y)dV \tag{23-1}$$

This is the free energy for a domain Ω for an arbitrary field $y(\vec{x})$ representing an order parameter.

Supposing the the order parameter field is changing (or, flowing) with velocity field $v(\vec{x})$, the free energy as a function of time is $F(y+vt)$ and the instantaneous rate of total free energy change:

$$\left.\frac{\partial F}{\partial t}\right|_{t=0} = \int_{\Omega} (f'(y) - K\nabla^2 y)v dV \tag{23-2}$$

from this equation, it follows that the fastest[33] decrease in total free energy if the flow field $v(\vec{x})$ is chosen so that it is 'parallel' to (minus) the functional gradient $-\delta F/\delta y$ which is defined by:

$$\frac{\delta F}{\delta y} \equiv f'(y) - K\nabla^2 y \tag{23-3}$$

Kinetics of Non-conserved Order Parameters: The Allen-Cahn Equation

For a non-conserved order parameter $\eta(\vec{x})$, Eq. 22-15 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 η. 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:

$$\frac{\partial \eta}{\partial t} = M_\eta[K_\eta\nabla^2\eta - f'(\eta)] \tag{23-4}$$

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 $\eta = \pm 1$:

$$f(\eta) = f_s((1+\eta)(1-\eta))^2 \tag{23-5}$$

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

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[33] "Fastest" requires the definition of a norm. Considerations of norms and their connection to kinetics can be found in, Carter W.C, Taylor J.E., and Cahn J.W., "Variational methods for microstructural-evolution theories" Journal of Materials, pp 30–36 (1997).

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. 23-5 into Eq. 23-4, and keeping the lowest order terms in $\delta(t)$:

$$\frac{d\delta(t)}{dt} = M_\eta(4f_s - K_\eta\omega^2)\delta(t) \tag{23-6}$$

so that

$$\delta(t) = \delta(0)\exp[M_\eta(4f_s - K_\eta\omega^2)t] \tag{23-7}$$

The perturbations grow if

$$\lambda > \lambda_{crit} = \pi\sqrt{\frac{K_\eta}{f_s}} \tag{23-8}$$

which is approximately equal to the interface width.

Note that the amplification factor is a weakly increasing function of wavelength (asymptotically approaching $4M_\eta f_s$ 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.

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 22-15 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. 22-15:

$$\vec{J}_c = -M_c \nabla [f'(c(\vec{x})) - K_c \nabla^2 c] \tag{23-9}$$

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.

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

$$\frac{\partial c}{\partial t} = \nabla \cdot M_c \nabla [f'(c(\vec{x})) - K_c \nabla^2 c(\vec{x})] \tag{23-10}$$

if M_c is constant, then

$$\frac{\partial c}{\partial t} = M_c [\nabla^2 f'(c(\vec{x})) - K_c \nabla^4 c(\vec{x})] \tag{23-11}$$

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. 23-11 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.

<u>Cahn-Hilliard: Critical and Kinetic Wavelengths</u>

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

$$f(c) = \frac{16 f_s}{(c_\beta - c_\alpha)^4}[(c - c_\alpha)(c - c_\beta)]^2 \tag{23-12}$$

which has minima at concentrations c_α and c_β 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. 23-11 and keeping the lowest-order terms in $\epsilon(t)$,

$$\frac{d\epsilon}{dt} = \frac{M_c\omega^2}{(c_\beta - c_\alpha)^2}[16f_s - K_c\omega^2(c_\beta - c_\alpha)^2]\epsilon \tag{23-13}$$

Therefore any wavelength λ will grow if

$$\lambda > \lambda_{crit} \equiv \frac{\pi}{2}(c_\beta - c_\alpha)\sqrt{\frac{K_c}{f_s}} \tag{23-14}$$

Taking the derivative of the amplification factor in Eq. 23-13 with respect to ω and setting it equal to zero, we find the fastest growing wavelength:

$$\lambda_{max} = \sqrt{2}\lambda_{crit} = \frac{\sqrt{2}\pi}{2}(c_\beta - c_\alpha)\sqrt{\frac{K_c}{f_s}} \tag{23-15}$$

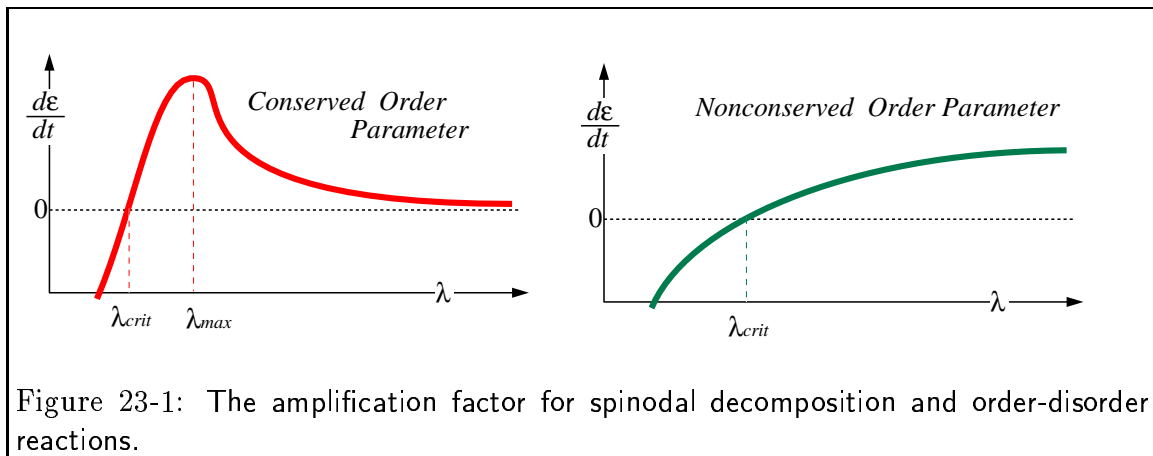It is expected that domain size in the early stage of spinodal decomposition will be approximately λ_{max}.

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

Figure 23-1: The amplification factor for spinodal decomposition and order-disorder reactions.

Simulations

Below are simulations of Eqs. 23-4 and 23-11 with initial conditions taken as a small perturbation about the unstable (or saddle) point.

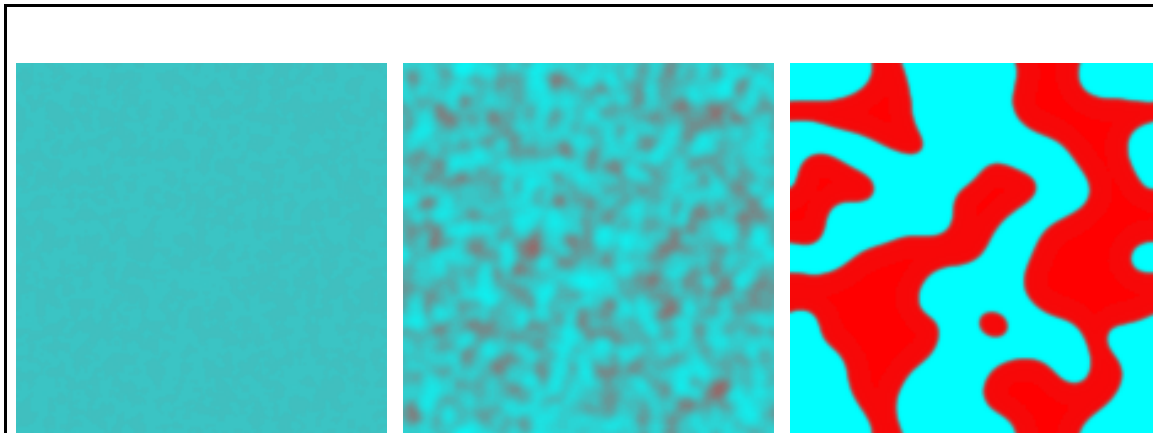Can you determine, by observation, which simulation corresponds to which type of kinetics?

Figure 23-2: A simulation—can you determine which type of kinetics? If you are viewing in HTML, click on the figure to see the simulation.
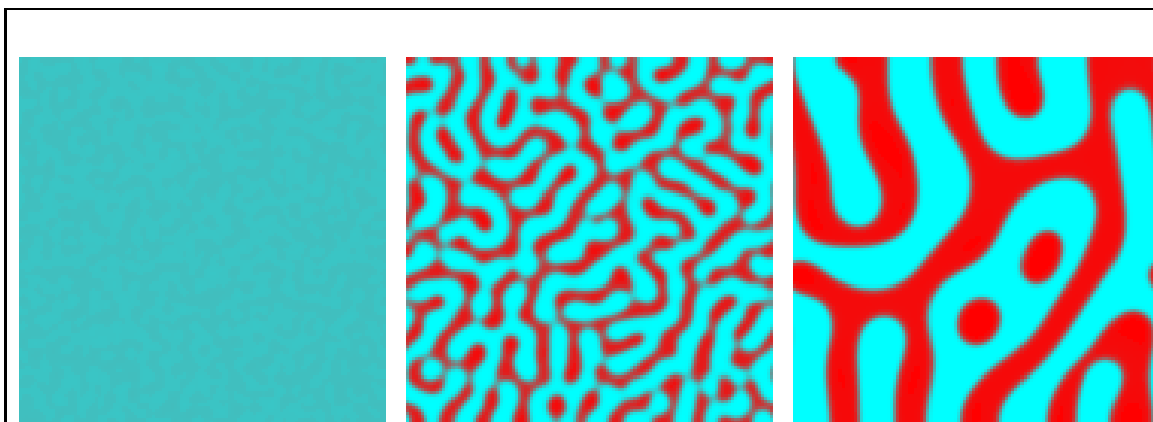

Figure 23-3: A simulation—can you determine which type of kinetics? If you are viewing in HTML, click on the figure to see the simulation.