

3.21 Kinetics of Materials—Spring 2006

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Lecture 22: Spinodal Decomposition and Continuous Ordering.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapter 18.

Key Concepts

- The interdiffusion flux in a binary alloy in the volume-fixed frame is given by *KoM* Eq. 18.9 as

$$\bar{J}_B^V = -M\nabla(\mu_B - \mu_A) = -\frac{M\Omega}{N_o} \frac{\partial^2 F}{\partial X_B^2} \nabla c_B = \tilde{D} \nabla c_B \quad (1)$$

and thus inside the spinodal $\tilde{D} < 0$ and the usual form of Fick's second law is *ill-posed*. The condition $\tilde{D} < 0$ leads to *uphill diffusion*, consistent with separation of an initially uniform solution into two bulk phases with different compositions.

- During continuous phase separation on a very fine scale, significant free energy is dissipated by the formation of *concentration gradients* in the system. This *gradient energy* modifies the diffusion potential for transformations. The free energy becomes a *functional* of the order parameter field $\xi(\vec{r})$ and the local diffusion potential is given by *KoM* Eq. 18.22:

$$\Phi(\vec{r}) = \frac{\partial f^{\text{hom}}}{\partial \xi} - 2K\nabla^2 \xi \quad (2)$$

- For conserved order parameters, the modified diffusion potential leads to the evolution equation known as the Cahn–Hilliard equation, *KoM* Eq. 18.25:

$$\frac{\partial c_B}{\partial t} = M_o \left[\frac{\partial^2 f^{\text{hom}}}{\partial c_B^2} \nabla^2 c_B - 2K_c \nabla^4 c_B \right] \quad (3)$$

When gradient-energy effects can be ignored, this is equivalent to Fick's second law.

- For non-conserved order parameters, the modified diffusion potential leads to the evolution equation known as the Allen–Cahn equation, *KoM* Eq. 18.26:

$$\frac{\partial \eta}{\partial t} = -M_\eta \left\{ \frac{\partial f^{\text{hom}}}{\partial \eta} - 2K_\eta \nabla^2 \eta \right\} \quad (4)$$

- The solution to the Cahn–Hilliard equation for a one-dimensional system takes the simple form $c - \langle c \rangle = \exp[R(\beta)t] \cos(\beta x)$ where $\beta = 2\pi/\lambda$ is the wavenumber and $R(\beta)$ is the *amplification factor*. The initial stage of spinodal decomposition thus involves growth of composition modulations when $R(\beta) > 0$. The model gives simple expressions for the thermodynamic and kinetic wave-numbers, β_{crit} and β_{max} (see *KoM* Fig. 18.9).

- For crystalline systems undergoing spinodal decomposition, the lattice constant is generally a function of the composition of the solution and this can give rise to significant *coherency strain energy* that adds an additional term to the diffusion potential and thus to the Cahn–Hilliard equation. Two effects are commonly observed: first, the region of spinodal decomposition lies within the *coherent spinodal* defined by $f'' + 2a_c^2 Y = 0$, where $a_c = (1/a)da/dc_B$ and Y is an elastic modulus that in anisotropic crystals depends on orientation of the composition wave (i.e., its wave vector); second, when Y is anisotropic, there will be specific directions in the crystal along which growth of composition waves is favored (in cubic crystals it is usually along $\langle 100 \rangle$ directions).
- The microstructure of spinodally decomposed materials consists of spatially periodic composition modulations (see *KoM* Figs. 18.4 and 18.13). In crystalline materials the microstructure generally shows crystallographic alignment. Periodic variations of composition give rise to “satellite” reflections in diffraction patterns, allowing easy measurement of the decomposition wavelength by small-angle scattering experiments.
- The microstructure of continuously ordered materials consists of interconnected antiphase boundaries which coarsen rapidly (see *KoM* Fig. 18.5) with a $\langle R \rangle^2 \sim t$ law (the same law as for grain growth).
- Stationary solutions to the Allen–Cahn equation give the equilibrium structure and energy of diffuse antiphase boundaries. Non-stationary solutions give ordering kinetics and allow modeling antiphase boundary motion by “interface tracking” methods.
- Interface tracking methods are the basic approach to the “phase-field” approach to modeling a great variety of phase transformation phenomena via coupled Cahn–Hilliard and Allen–Cahn evolution equations.

Related Exercises in *Kinetics of Materials*

Review Exercises 18.2–4, pp. 454–458.