

3.205 Thermodynamics and Kinetics of Materials—Fall 2006

November 30, 2006

Kinetics Lecture 10: Spinodal Decomposition

Lecture References

1. Porter and Easterling, *Phase Transformations in Metals and Alloys*, Van Nostrand Reinhold (International), Wokingham, 1988. Section 5.5.5, pp. 308–314.
2. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapters 17 and 18 (advanced treatment; also includes discussion of continuous order-disorder transformations—not covered in 3.205).

Key Concepts

- Spinodal decomposition is the name of the mechanism by which an initially uniform but compositionally unstable solution can transform to the equilibrium two-phase mixture. A homogeneous solution is unstable inside the “spinodal” region defined by  $\partial^2 f / \partial c^2 < 0$ , where  $f$  is an appropriate free energy per unit volume for the homogeneous solution. In the absence of elastic strain energy accompanying compositional variations,  $f$  is the solution’s chemical free energy per unit volume and  $\partial^2 f / \partial c^2 = 0$  defines the “chemical spinodal.”
- As a system inside the spinodal region develops composition variations, the regions where there are *composition gradients* make an extra contribution to the system’s free energy, such that the total free energy of a system with an arbitrary one-dimensional composition profile  $c(x)$  is given by

$$F[c(x)] = A \int_{-\infty}^{\infty} \left[ f(c) + K (dx/dx)^2 \right] dx \quad (1)$$

where  $K$  is a positive constant known as the *gradient-energy coefficient*.

- When gradient energy makes a significant contribution to the system’s free energy (i.e., when the density of regions with composition gradients is high), gradient energy consumes some of the available driving force for diffusion, and the appropriate diffusion equation becomes

$$\frac{\partial c}{\partial t} = \tilde{D} \left[ \frac{\partial^2 c}{\partial x^2} - \left( \frac{2K}{\partial^2 f / \partial c^2} \right) \frac{\partial^4 c}{\partial x^4} \right] \quad (2)$$

- Inside the spinodal region where  $\partial^2 f / \partial c^2 < 0$ , (??) will have solutions obtainable by separation of variables, with the form

$$c = c_0 + e^{R(\beta)t} \cos \beta x \quad (3)$$

and substitution into the diffusion equation shows that the *amplification factor*  $R(\beta)$  must obey

$$R(\beta) = -\tilde{D}\beta^2 \left[ 1 + \left( \frac{2K}{\partial^2 f / \partial c^2} \right) \beta^2 \right] \quad (4)$$

At a given temperature within the spinodal region, the maximum rate of spinodal decomposition will occur for waves with  $\beta = \beta_{\max}$  at which  $dR(\beta)/d\beta = 0$ .