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3.21 Kinetics of Materials—Spring 2006

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Lecture 23: Spinodal Decomposition Kinetics.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapter 18.
2. *Mathematica* notebook for Lecture 23, which extends the notebook for Lecture 22 to include treatment of kinetics.

Key Concepts

- The amplification factor $R(\beta)$ in the linear theory of spinodal decomposition determines the growth or dissolution rate of composition fluctuations, as $c - \langle c \rangle = \exp[R(\beta)t]\,\cos(\beta x)$. Substitution of this solution into the Cahn–Hilliard equation gives the expression

$$R(\beta) = -M_c \left[f'' + 2K_c\beta^2\right]\beta^2 \tag{1}$$

  The non-trivial zero of this fourth order polynomial in β gives the critical wavenumber β_{crit}, and the maximum in the function gives the kinetic wavenumber β_{max} that receives maximum amplification. β_{max} sets the length scale of the resulting microstructure, to a good approximation, resulting in the relations:

$$\beta_{\text{crit}} = \sqrt{-\frac{f''}{2K_c}} \qquad \beta_{\text{max}} = \sqrt{-\frac{f''}{4K_c}} \qquad \beta_{\text{crit}} = \sqrt{2}\beta_{\text{max}} \tag{2}$$

- The characteristic time for the development of a spinodal microstructure can be estimated from $1/R(\beta_{\text{max}})$.

- The temperature dependence of spinodal decomposition arises primarily from that of M_c, which obeys an Arrhenius law, and from that of f'', which varies linearly with temperature in the Bragg–Williams (regular solution) model. The theory is easily shown to give these trends: (1) λ_{max} decreases with increasing undercooling below the spinodal temperature at which $f'' = 0$; (2) the rate of spinodal decomposition goes through a maximum as the decomposition temperature decreases. On a time–temperature–transformation diagram, the transformation exhibits "C-curve" kinetics. See the Mathematica notebook for today's lecture, and *KoM* Exercise 18.4.

- Non-linear effects in spinodal decomposition include the approach to equilibrium compositions of the phases, the approach to equilibrium volume fractions of the phases, and coarsening of the microstructure. In order to capture the phase compositions and volume fractions, the composition dependence of f'' must be included. Coarsening of the microstructure arises from interactions between growing waves with different wavelengths and wave vectors. Cahn's 1968 paper on these topics is instructive.

Related Exercises in *Kinetics of Materials*

Review Exercises 18.2–4, pp. 454–458.