

3.21 Kinetics of Materials—Spring 2006

April 24, 2006

Lecture 24: Nucleation.

References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Chapter 19.

Key Concepts

- Nucleation is the process by which a metastable system initiates a discontinuous phase transformation. Nucleation requires localized fluctuations that are sufficiently large so that free energy decreases from the chemical driving force are large enough to offset those from creation of interphase boundary area and all other terms that resist the transformation (e.g., elastic strain energy).
- The main focus of nucleation theory is the prediction of the *steady-state nucleation rate* which results once the system has formed an equilibrium distribution of fluctuations, some of which eventually grow to exceed a critical size at which point they can grow spontaneously. In a supersaturated solution, steady-state nucleation will be achieved during the period before the system's supersaturation is appreciably changed. Growth and coarsening processes determine the subsequent evolution of the equilibrium phases and their microstructure.
- The chemical driving force for nucleation Δg_B in solutions can be determined from free energy vs. composition diagrams. For transformations at constant composition the *curve-to-curve* construction is used; for transformations involving a change of composition, the *curve-to-curve* construction is used.
- When nucleation occurs with equal probability at all sites in a transforming system, it is said to be *homogeneous nucleation*. If nucleation occurs preferentially at special sites, it is *heterogeneous nucleation*.
- The free energy change of transforming a small volume from phase α to phase β in the absence of elastic strain energy will have the form

$$\Delta \mathcal{G}_{\mathcal{N}} = \Delta \mathcal{G}_{\mathcal{N}}^{\text{bulk}} + \Delta \mathcal{G}_{\mathcal{N}}^{\text{interfacial}} = \mathcal{N}(\mu^{\beta} - \mu^{\alpha}) + \eta \mathcal{N}^{2/3} \gamma \quad (1)$$

and the size \mathcal{N}_c of the *critical nucleus* is found from the condition $\partial \Delta \mathcal{G}_{\mathcal{N}} / \partial \mathcal{N} = 0$.

- The steady-state nucleation rate is given by *KoM* Eq. 19.17 as $J = Z \beta_c N \exp[-\Delta \mathcal{G}_c / (kT)]$. For practically detectable nucleation rates in materials, the nucleation barrier $\Delta \mathcal{G}_c$ must be less than approximately $76kT$ (see *KoM* Section 19.1.7).
- In solids, elastic strain energy contributes to the nucleation barrier in a complex and often non-intuitive way. Depending on conditions, the elastic strain energy associated with a nucleus may be a function of the nucleus shape, making the calculation of the minimum-energy barrier one of minimizing $\Delta \mathcal{G}_{\mathcal{N}}$ with respect to several variables that describe particle size and shape (see *KoM* Section 19.1.3).

Related Exercises in *Kinetics of Materials*

Review Exercises 19.1–3, pp. 485–489.