3.205 Thermodynamics and Kinetics of Materials—Fall 2006

November 16, 2006

Kinetics Lecture 7A: Nucleation Theory—I. Homogeneous

Lecture References

1. Porter and Easterling, *Phase Transformations in Metals and Alloys*, Van Nostrand Reinhold (International), Wokingham, 1988. Sections 4.1–4.1.2, pp. 186–193.

2. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 19.1, "Homogeneous Nucleation."

Key Concepts

- *Phase transformations* can occur whenever a materials system is not at equilibrium. An *unstable* system (e.g., one within the *spinodal region* can find a transformation path that allows for a continuous decrease of free energy, even for infinitesimal fluctuations about the unstable state. A *metastable* system can only transform to a more stable state by surmounting a free-energy barrier.

- The *nucleation regime* is the earliest stage of a transformation from a metastable to a more stable state. A common example is *precipitation* from a supersaturated solution. The initial solution is compositionally homogeneous, and during nucleation clusters of different composition form that are of sufficiently large size to become unstable to further growth. Nucleation theory describes the configuration, energetics, and kinetics of formation of these *critical nuclei*.

- The most important barrier to nucleation is the free energy of the interface between the bulk solution and the nucleus. In solids, elastic strain energy can also contribute significantly to the nucleation barrier.

- In fluid solutions, there is no strain energy and the interfacial energy is isotropic. The barrier to nucleation is determined by the chemical free energy change (per unit volume) of transforming the nucleus, Δg_B, and the interfacial free energy per unit area, γ. Δg_B is negative in the nucleation regime and it provides the *driving force* for the transformation. γ is positive and it opposes the transformation. The free energy change of forming the nucleus, $\Delta \mathcal{G}$, is dominated by the interfacial energy at small sizes and by the chemical driving force at larger sizes—thus, there is a *critical size* and a critical free energy barrier $\Delta \mathcal{G}_c$ at which the critical nucleus can grow spontaneously.

- The theory of nucleation kinetics provides a useful guide to the largest critical free-energy change, $\Delta \mathcal{G}_c$, that will allow practically observable nucleation rates: for typical materials processes, nucleation will only occur in reasonable times when $\Delta \mathcal{G}_c < 76kT$.