3.205 Thermodynamics and Kinetics of Materials—Fall 2006

November 16, 2006

Kinetics Lecture 7B: Nucleation Theory—II. Heterogeneous

Lecture References

1. Balluffi, Allen, and Carter, *Kinetics of Materials*, Section 19.2, "Heterogeneous Nucleation."

2. Porter and Easterling, *Phase Transformations in Metals and Alloys*, Van Nostrand Reinhold (International), Wokingham, 1988. Section 4.1.3, pp. 193–197.

Key Concepts

- The theory of nucleation kinetics is closely linked with fluctuation theory and the theory of activated processes. The *steady-state nucleation rate*, J, is the rate of formation of "supercritical" nuclei that form per unit volume, and it has the form $J = Z\beta_c N \exp[-\Delta\mathcal{G}_c/(kT)]$, where N is the number of available sites for nucleation, Z is called the Zeldovich non-equilibrium factor and is approximately 10^{-1}, β_c is a term that relates to the diffusivity of atoms to a subcritical nucleus, and $\Delta\mathcal{G}_c$ is the free-energy barrier that needs to be overcome to form a critical nucleus. Using typical values of N, Z, and β_c, and assuming a reasonable value for a minimum detectable nucleation rate, one can show that $\Delta\mathcal{G}_c$ must be less than about $76kT$ for observable nucleation.

- $\Delta\mathcal{G}_c$ plays a critical role in nucleation kinetics. It is typically strongly dependent on undercooling and on interphase boundary structure. In solids, interfacial structure may be incoherent, semi-coherent, or coherent. Coherent interfaces have the lowest γ, on the order of 100 mJ/m^2, and are thus more likely at the nucleation stage. Coherent particles that form in systems in which the molar volume of the nucleus and the matrix differ also can have an elastic strain energy Δg_ε that impedes nucleation.

- *Heterogeneous nucleation* uses pre-existing imperfections to lower $\Delta\mathcal{G}_c$ for nucleation on special sites. Competition between homogeneous and heterogeneous nucleation is easily understood with the equation for steady-state nucleation kinetics. The lower value of $\Delta\mathcal{G}_c$ favors heterogeneous nucleation, but the far larger value of N (the number of sites available for nucleation) favors homogeneous nucleation. Heterogeneous nucleation is very common in materials. Preferred sites include container walls, free surfaces, "foreign" inclusion particles, and crystalline imperfections such as dislocations, stacking faults, and grain boundaries.