4 Nucleation

As discussed in Section 1.5.2, phase transformations can occur continuously or discontinuously. The discontinuous case begins with the appearance of a small but distinct volume of material having a structure and composition that differ from those of the parent phase.[1] A discontinuous transition can be forced by symmetry, as formalized for some cases in Sect. 14.4. There is no continuous way to rearrange the atoms of a liquid into a crystal, for example. The new crystal must appear in miniature in the liquid, a process called "nucleation." If the nucleation event is successful, this crystal will grow. The process of nucleation is an early step for most phase transformations in materials. It has many variations, but two key concepts can be appreciated immediately.

- Because the new phase and the parent phase have different structures, there must be an interface between them. The atom bonding across this interface is not optimal,[2] so the interfacial energy must be positive. This surface energy is most significant when the new phase is small, because a larger fraction of its atoms are at the interface. Surface energy plays a key role in nucleation.
- For nucleation of a new phase within a solid, a second issue arises when the new phase differs in shape or specific volume from the parent phase. The mismatch creates an elastic field that costs energy. This is not an issue for nucleation in a liquid or gas, since the surrounding atoms can flow out of the way.

An issue for nucleation with chemical unmixing is the time required for diffusion of the different chemical species of atoms, and this time can be long if atoms must move long distances between incipient nuclei (sometimes called "embryos"). The addition of atoms to embryos is largely a kinetic phenomenon, although the tendency of atoms to remain on the embryos is a thermodynamic one. A steady-state rate of forming "critical" nuclei that can grow is calculated. The chapter ends with a discussion of the transient time after a quench from high temperature when the distribution of solute relaxes towards the equilibrium distribution for steady-state nucleation.

---

[1] The nucleus may or may not have the structure and composition of the final phase because the transformation may occur in stages.

[2] If the structure of the interfacial atoms and bonds were favorable, the new phase would take this local atomic structure.

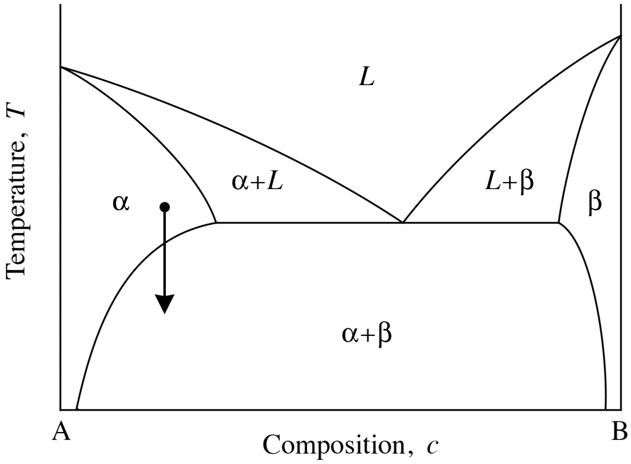

Fig. 4.1 Binary phase diagram depicting a quench path from a temperature with pure α-phase to a temperature where some β-phase will nucleate.

4.1 Terminology and Issues

Nucleation can occur without a change in crystal structure. Consider an A-rich A-B alloy having the α-phase at high temperature, as shown in the unmixing phase diagram of Fig. 2.10. Suppose the alloy is quenched (cooled quickly) to a temperature such as $0.4zV/k_B$, where the equilibrium state would have mostly A-rich α'-phase, plus some B-rich α''-phase. For some compositions, the B-rich α''-phase may nucleate as small zones or "precipitates" in an A-rich matrix.[3] In this case, the underlying crystal lattice remains the same while the solute atoms coalesce. A different case is shown with Fig. 4.1 for the unmixing of solute in a eutectic alloy. Here the precipitation of β-phase in an alloy cooled rapidly from the α-phase requires both a redistribution of chemical elements and a different crystal structure. In both these examples of nucleation, the parent phase is "supersaturated" immediately after the quench, and is unstable against forming the new phase.

"Homogeneous" nucleation occurs when nuclei form randomly throughout the bulk material; i.e. without preference for location. "Heterogeneous" nucleation refers to the formation of nuclei at specific sites. In solid→solid transformations, heterogeneous nucleation occurs on grain boundaries, dislocation lines, stacking faults, or other defects or heterogeneities. When freezing a liquid, the wall of the container is a common heterogeneous site. For the nucleation of solid phases, heterogeneous nucleation is more common than homogeneous.

The precipitate phase can be "coherent" or "incoherent" with the surrounding matrix. Figure 4.2a illustrates an incoherent nucleus. The precipitating β-phase has a crystal structure different from the parent α-phase, and there is little registry of

---

[3] A "matrix" is an environment in which a new phase develops.