PART I

BASIC THERMODYNAMICS AND KINETICS OF PHASE TRANSFORMATIONS

The field of phase transitions is rich, vast, and continues to grow. This text covers parts of the field relevant to materials physics, but many concepts and tools of phase transitions in materials are used elsewhere in the larger field of phase transitions. Likewise, new methods from the larger field are beginning to be applied to studies of materials.

Part I of the book covers essential topics of free energy, phase diagrams, diffusion, nucleation, and a few classic phase transformations that have been part of the historical backbone of materials science. In essence, the topics in Part I are the thermodynamics of how atoms prefer to be arranged when brought together at various temperatures, and how the processes of atom movements control the rates and even the structures that are formed during phase transformations. The topics in Part I are largely traditional ones, but formulating the development in terms of statistical mechanics and in terms of the kinetic master equation allows more rigor for some topics, and makes it easier to incorporate a higher level of detail from Part II into descriptions of phase transitions in Parts III and IV.

1 Introduction

1.1 What Is a Phase Transition?

A phase transition is an abrupt change in a system that occurs over a small range in a control variable. For thermodynamic phase transitions, typical control variables are the "intensive variables" of temperature, pressure, or magnetic field. Thermodynamic phase transitions in materials and condensed matter, the subject of this book, occur when there is a singularity in the free energy function of the material, or in one of the derivatives of the free energy function.[1] Accompanying a phase transition are changes in some physical properties and structure of the material, and changes in properties or structure are the usual way that a phase transition is discovered. There is a very broad range of systems that can exhibit phase transitions, extending from atomic nuclei to traffic flow or politics. For many systems it is a challenge to find reliable models of the free energy, however, so thermodynamic analyses are not available.

Our focus is on thermodynamic phase transitions in assemblages of many atoms. How and why do these groups of atoms undergo changes in their structures with temperature and pressure? In more detail, we often find it useful to consider separately:

- nuclei, which have charges that define the chemical elements,
- nuclear spins and their orientations,
- electrons that occupy states around the nuclei, and
- electron spins, which may have preferred orientations with respect to other spins.

Sometimes a phase transition involves only one of these entities. For example, at low temperatures (microKelvin), the weak energy of interaction between nuclear spins can lead to nuclear spin alignments. An ordered state of aligned nuclear spins may have the lowest energy, and may be favored thermodynamically at low temperatures. Temperature disrupts these delicate alignments, however, and thermodynamics favors a disordered nuclear magnetic structure at modest temperatures. The free energy, F, changes with temperature when the nuclear spins are aligned, but the functional form of this curve of $F_{\mathrm{ord}}(T)$ is not the same as $F_{\mathrm{dis}}(T)$ for the disordered state at higher temperature. At the critical temperature of the ordering transition there is a switch from one curve to another, or perhaps the second derivative $\mathrm{d}^2F/\mathrm{d}T^2$ has a kink. Order-disorder phase transitions are

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[1] A brief review of free energy is given in Sect. 1.6.2.

enlightening, and have spawned several creative methods to understand how an order parameter, energy, and entropy depend on temperature.

Sometimes phase transitions involve multiple physical entities. Electrons of opposite spin can be coupled together by a wave of nuclear vibration (a phonon). These Cooper pairs can condense into a superconducting state at low temperatures. Perhaps electron charge or spin fluctuations couple the electrons in high temperature superconductors, although the mechanism is not fully understood today. Much of the fascination with phase transitions such as superconductivity is with the insight they give into the interactions between the electrons and phonons, or the electron charges and spins. While these are indeed important subjects for study, they are to some extent diversions from the main topic of phase transitions. Likewise, delving deeper into the first example of nuclear spin alignments at low temperatures reveals that the information about the alignment of one nucleus is carried to a nearby nucleus by the conduction electrons, and these hyperfine interactions between nuclei and electrons are an interesting topic in their own right.

In a study of phase transitions, it is easy to lose track of the forest if we focus on the interesting trees within it. Throughout much of this text, the detailed interactions between the entities of matter are replaced with simplifying assumptions that facilitate mathematical modeling. Sometimes the essence of the phase transition is captured well with such a simple model. Other times the discrepancies prove interesting in their own right. Perhaps surprisingly, the same mathematical model reappears in explanations of phase transitions involving very different types of matter. A phase transition is an "emergent phenomenon," meaning that it displays features that emerge from interactions between numerous individual entities, and these large-scale features can occur in systems with very different microscopic interactions. The study of phase transitions has become a respected field of science in its own right, and Chapter 20, for example, presents some concepts from this field that need not be grounded in materials phenomena.

1.2 Atoms and Materials

An interaction between atoms is a precondition for a phase transition in a material (and, in fact, for having a material in the first place). Atoms interact in interesting ways when they are brought together. In condensed matter there are liquids of varying density, and numerous types of crystal structures. Magnetic moments form structures of their own, and the electron density can show spatial modulations. In general, chemical bonds are formed when atoms are brought together. The energy of interatomic interactions is dominated by the energy of the electrons, which are usually assumed to adapt continuously ("adiabatically") to the positions of the nuclei. The nuclei, in turn, tend to position themselves to allow the lowest energy of the material, which means that nuclei move around to let the electrons find low-energy states. Nevertheless, once we know the electronic structure of a