

## PART I

# BASIC THERMODYNAMICS AND KINETICS OF PHASE TRANSFORMATIONS

The field of phase transitions is rich and 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 now being 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 core 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 allows more rigor for some topics, and makes it easier to incorporate some deeper concepts from Part II into descriptions of phase transitions in Part III and the online Advanced Topics.

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## 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 of 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.<sup>1</sup> 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, including atomic nuclei, traffic flow, and social networks. For many systems it is a challenge to find reliable models of the free energy, however, so thermodynamic analyses are not available.

**Interacting Components**

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? It is often useful to consider separately the components of the atoms:

- 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 components. For example, at low temperatures (microkelvin), the weak energy of interaction between spins at different nuclei can lead to a widespread alignment of nuclear spins. An ordered array of aligned nuclear spins may be favored thermodynamically at extremely low temperatures, but thermodynamics favors a disordered nuclear magnetic structure at modest temperatures. Order–disorder phase transitions have spawned several creative methods to understand how an order parameter, energy, and entropy depend on temperature.

<sup>1</sup> A brief review of free energy is given in Section 1.6.2.

Sometimes phase transitions involve multiple physical components. 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, for example. While these are 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.<sup>2</sup>

### Emergence of Macroscopic Behavior from the Atomistic

In a study of phase transitions, it is easy to lose track of the forest if we focus on the interesting trees. Throughout much of this text, the detailed interactions between the components of matter are replaced with simplifying assumptions that allow for straightforward analysis. Sometimes the essence of the phase transition is captured well with such a simple model. Other times the discrepancies prove interesting in themselves. Perhaps surprisingly, the same mathematical model reappears in explanations of phase transitions involving very different aspects of materials. The ordering of nuclear spins has a natural parallel with the ordering of electron spins in a ferromagnetic material, although the origin of the magnetic moments, their coupling, and the temperature of ordering are completely different. More surprisingly, there is a clear parallel between these spin-ordering problems and chemical ordering in an alloy, where a random distribution of two chemical elements on a crystal lattice evolves into a pattern such as a chessboard with decreasing temperature.

A phase transition is an “emergent phenomenon,” meaning that its large-scale features emerge from interactions between numerous individual components. Philosophers classify a phase transition as a type of “weak emergence” because the large-scale properties can be predicted from the interactions of the individual components.<sup>3</sup> How emergence occurs is a topic in itself. When a change in temperature or pressure favors a new phase, it can appear abruptly with macroscopic dimensions, or it can grow continuously from the atomic scale to the macroscopic. Although the atomic-scale processes are statistical, the averaged macroscopic behavior is quite consistent for the same material under the same conditions.

<sup>2</sup> At familiar temperatures the nuclear spins are completely disordered, and do not change in a way that affects the thermodynamics of the material. On the other hand, we might expect a coupling between chemical order and magnetic order if the energy scales of their internal interactions are comparable.

<sup>3</sup> “Strong emergence,” which cannot be predicted this way, may underlie the origin of consciousness or the soul.

The macroscopic behavior is usually predicted by assuming a material of infinite size, since Avogadro's number can often be approximated adequately as infinity.

## 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 have spatial patterns. 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 instantaneously 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. Once the electronic structure of a material is known, it is often possible to understand many properties of a material, especially its chemical, electronic, magnetic, and optical properties.

For many materials, accurate calculations of electronic structure have arrived. Many reliable quantum mechanical calculations are now routine, and more will be commonplace soon. Electronic structure calculations are an important but large topic that extends beyond the scope of this text. Some aspects of electronic energy are explained in Chapter 6, and other aspects are developed as needed to explain specific phase transformations in Part III. (Fortunately, there are many excellent references on electronic energy and chemical bonding of materials.) Entropy is the other thermodynamic function essential for understanding most phase transitions in materials. Both the energy and entropy of materials

### Box 1.1

#### Microstructure

Materials are made of atoms, but the structural arrangements of atoms are usually described by a hierarchy of features, each with its own characteristics. Mixtures of crystals and phases, with interfaces between them and defects inside them, are the "microstructure" of a material. One viewpoint is that a complete description of the structural features of microstructure is a full definition of the material. A second viewpoint adds excitations involving electrons, nuclei, or microstructure to the description of a material. The first viewpoint considers only matter, the second viewpoint adds energy to the definition of a material.

Control of microstructure is the means for controlling properties of a material – this is the central paradigm of materials science and engineering (see Fig. 1.1). Designing a microstructure is distinctly different from "Edisonian testing," which is another way to find materials with appropriate properties. Edisonian testing ignores the essence of a material, however, and is not materials science.

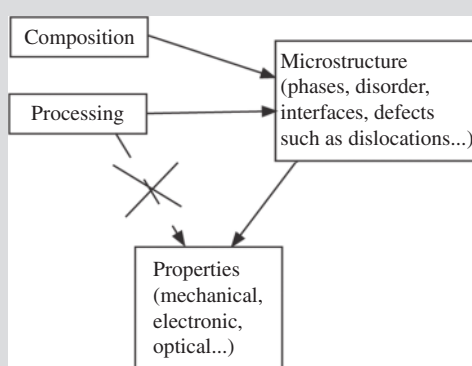


Figure 1.1

Paradigm of materials science. A direct processing-to-properties relationship, as Edison pursued when finding filament materials for incandescent light bulbs, is not materials science.

depend on the types of atoms and their mutual arrangements, parameterized as “state variables.” Careful selections of state variables are critical for developing predictive theories of phase transitions.

There are opportunities to control the states of matter through both thermodynamics and kinetics. Thermodynamic control tends to be the most reliable, at least when the atom motions are fast enough so that equilibrium can be approached in a reasonable time. Thermodynamic control involves selecting the chemical composition, and adjusting the intrinsic variables of temperature, pressure, and external fields. Control of temperature is usually the most accessible way to set the state of equilibrium, and has served us well through the bronze, iron, and silicon ages of humankind. Most of this book is concerned with phase transitions that are driven by temperature.

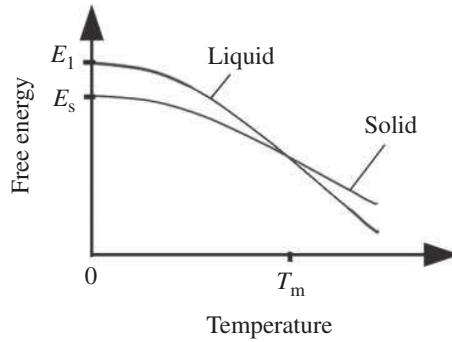
## 1.3 Pure Elements

### 1.3.1 Melting: A Discontinuous Phase Transition

A liquid and a crystal are fundamentally different owing to the symmetry of their atom arrangements. In Chapter 18 when the Landau–Lifshitz criterion for second-order phase transitions is developed, it is proved that melting must involve a discontinuity in the first derivative of the free energy,  $dF/dT$ , at the melting temperature. For now, please accept that it is not appropriate to use the same free energy function

$$F(T) = E - TS \quad (1.1)$$

for both the liquid and the solid phases. Instead, Fig. 1.2 shows two separate curves,  $F_s(T)$  and  $F_l(T)$ , for the solid and liquid phases of a pure element. The curve  $F_s(T)$  for the solid lies below that of the liquid at  $T = 0$  because the energy of the solid is lower than that of



**Figure 1.2** Free energy curves of a pure element when its atoms are arranged as a crystalline solid,  $F_s(T)$ , or as a liquid,  $F_l(T)$ .

the liquid.<sup>4</sup> As shown on the  $y$ -axis,  $E_s < E_l$ , and at  $T = 0$  there is no entropy contribution to the free energy. The free energy of the liquid decreases faster with temperature than that of the solid because  $S_s < S_l$ .<sup>5</sup> The two curves  $F_s(T)$  and  $F_l(T)$  cross at the melting temperature,  $T_m$ .

In equilibrium, an elemental material follows the solid curve of Fig. 1.2 at low temperatures, and switches to the liquid curve above  $T_m$ . At  $T_m$  there is a discontinuity in the first derivative of the free energy. A “first-order” phase transition occurs. This is rather catastrophic behavior, with the material changing from all liquid to all solid over an infinitesimal range of temperature across  $T_m$ .

Pure elements have well-defined melting temperatures that are set by the equality of the solid and liquid free energies,  $F_s(T_m) = F_l(T_m)$ . For constant  $E$  and  $S$ , a consequence is obtained quickly

$$F_s(T_m) = F_l(T_m), \quad (1.2)$$

$$E_s - T_m S_s = E_l - T_m S_l, \quad (1.3)$$

$$S_l - S_s = \frac{E_l - E_s}{T_m} = \frac{L}{T_m}, \quad (1.4)$$

where the latent heat,  $L$ , a positive quantity, is defined with the difference in entropy at  $T_m$

$$L \equiv [S_l(T_m) - S_s(T_m)] T_m. \quad (1.5)$$

The latent heat is absorbed at  $T_m$  during melting, and released during solidification.

Equation 1.4 for melting ignores the temperature dependences of  $E$  and  $S$ , which are important over a range of  $T$ . Nevertheless, if  $E$  and  $S$  in the solid and liquid vary slowly around  $T_m$ ,<sup>6</sup> the two curves in Fig. 1.2 can be approximated as straight lines. At

<sup>4</sup> Perhaps this is intuitive – the atoms in a crystalline solid have optimized their positions with respect to their neighbors, and all atoms are in such optimal positions. The liquid has bond distances and angles that are not at all uniform, meaning that some atoms are in configurations that are less favorable energetically.

<sup>5</sup> Again, perhaps this is intuitive – there are more equivalent ways  $\Omega$  of arranging the atoms in the liquid than in a crystalline solid, so the entropy,  $S = k_B \ln \Omega$ , is larger for the liquid.

<sup>6</sup> It is actually the differences,  $S_l - S_s$  and  $E_l - E_s$ , that should vary slowly with  $T$ , and this is more plausible.

temperatures very close to  $T_m$ , the difference in free energy of the liquid and solid is proportional to the undercooling

$$F_l(T) - F_s(T) = \frac{L(T_m - T)}{T_m} = \frac{L\Delta T}{T_m}, \quad (1.6)$$

with the undercooling defined as  $\Delta T \equiv T_m - T$  (see Problem 1.3). The sign is correct in Eq. 1.6 – when  $T < T_m$ , the  $F_s(T)$  is more negative (favorable) than  $F_l(T)$ .

The thermodynamics of melting (or solidification) illustrates some general truths:

- The low-energy phase is favored at low temperatures.
- The high-entropy phase is favored at high temperatures.
- If the low-energy phase has a lower entropy than the other phase, there will be a phase transition at a finite temperature.

We now take a short digression into kinetics. Although a liquid will eventually solidify at any temperature below  $T_m$ , the rate of solidification depends strongly on  $\Delta T$ . Equation 1.6 is useful for understanding the kinetics of solidification because it relates the undercooling below  $T_m$  to the difference in free energy of the liquid and solid. This difference in free energy is available to do work, such as overcoming any potential energy barriers that impede solidification. A larger undercooling makes it more probable for a small region of the liquid to overcome a nucleation barrier and become a solid,<sup>7</sup> and solidification speeds up considerably with undercooling. Equation 1.6 is based on thermodynamics, however. Kinetics requires additional information about the phase transformation. For example, Eq. 1.6 shows that the thermodynamics is symmetrical around  $T_m$  for solidification and melting (i.e.,  $F_l - F_s \propto \Delta T$  for both positive and negative  $\Delta T$ ), but the kinetics is not symmetrical. The enhanced kinetics of solidification with undercooling does not correspond to a more rapid melting with superheating. Melting does not have such a nucleation barrier.

### 1.3.2 Structural Symmetry and Continuous Phase Transitions

When the high-temperature phase and low-temperature phase have crystal structures with compatible symmetries, the phase transition can be continuous. Figure 1.3 is a map of the phases of cerium metal, charted in a space spanned by  $T$  and  $P$ , known as a “ $T$ – $P$  phase diagram.” Upon heating cerium at ambient pressure (0.0001 GPa), it transforms between four different crystalline phases before melting. Our present interest is in the phase transition between two of them, the  $\alpha$ - and  $\gamma$ -phases.<sup>8</sup> Curiously, both have the fcc crystal structure, but they differ in volume by about 17% at ambient pressure. Choose a pressure of 1 GPa (to avoid the  $\beta$ -phase), and follow a vertical path in Fig. 1.3b that starts at low temperature, with cerium in the  $\alpha$ -phase. Upon heating to a temperature near room

<sup>7</sup> Chapter 4 discusses how the nucleation barrier originates from unfavorable surface energy and the large surface-to-volume ratio of small particles.

<sup>8</sup> Solid phases, typically with different crystal structures, are designated by lower case Greek letters. The sequence of letters tends to follow their appearance in a phase diagram, or their sequence of discovery.



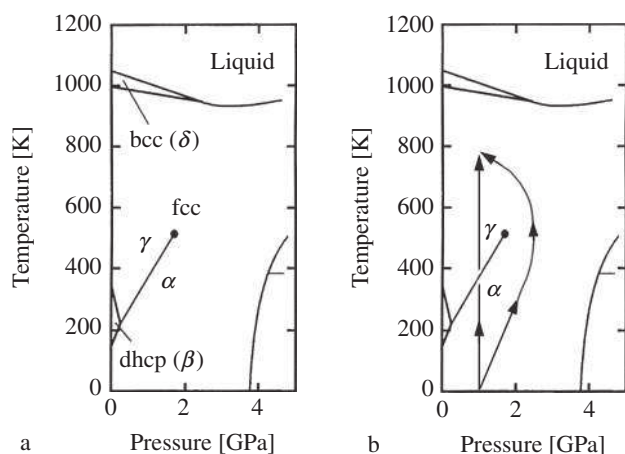


Figure 1.3

(a) Low-pressure region of the cerium  $T$ - $P$  phase diagram. The solid phases at zero pressure are fcc  $\alpha$ , double hcp  $\beta$ , fcc  $\gamma$ , bcc  $\delta$ . (b) Two paths through the phase diagram of part a. One path has a discontinuous expansion of the fcc unit cell, the other a continuous expansion.

temperature, the  $\alpha$ -phase undergoes a sudden expansion of its fcc unit cell as it transforms into the  $\gamma$ -phase. The how and why of this phase transition is not fully understood today, but its existence is not in doubt.<sup>9</sup>

Obviously the crystallographic symmetries of two fcc phases are the same, even if they differ in the sizes of their unit cells. With such a special relationship, we might ask if it is possible to go from one to the other in a continuous way, without a discontinuous change in volume. It turns out that this is indeed possible for cerium beyond a pressure of 2 GPa and a temperature of 500 K. The  $T$ - $P$  phase diagram of cerium metal has a “critical point,” beyond which the two fcc phases are indistinguishable. It is possible to change from a first-order discontinuous phase transition at lower pressures (or temperatures) to a second-order continuous phase transition by taking a path around the critical point in the phase diagram. If we start at  $T = 0$  K,  $P = 1$  GPa, and go up in temperature and pressure along a curved path that goes to the right of the critical point in Fig. 1.3b, the volume of the fcc unit cell will expand continuously.

It is perhaps better known that the  $T$ - $P$  phase diagram of water has a critical point, beyond which the liquid and gas phases become indistinguishable.<sup>10</sup> Evidently there can be a symmetry relationship between atom arrangements in gases and liquids that allows such continuous transitions.

<sup>9</sup> Cerium is the first element on the periodic table with an  $f$ -electron, and its electronic structure is a challenge to understand today. Its fcc-fcc transformation has attracted considerable attention, in part because of suggestions that its outer electrons become delocalized when the  $\gamma$ -phase collapses into the high-density  $\alpha$ -phase.

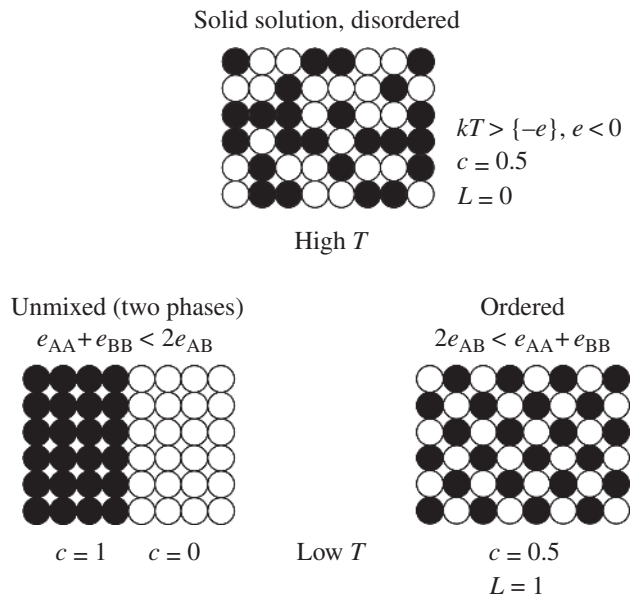
<sup>10</sup> Carbon dioxide also has a well-known critical point of its liquid and gas phases. When pushed beyond the critical point, “supercritical” carbon dioxide is an effective agent for dry cleaning clothes.

## 1.4 Alloys: Unmixing and Ordering

An “alloy,” which is a combination of two or more chemical elements, brings additional degrees of freedom to arrange the atoms, and more possibilities for energies and entropies. For millennia there has been interest in using temperature to alter the states of alloys. Today the equilibrium states of alloys are mapped on a chart of temperature versus composition called a “ $T$ - $c$  phase diagram.” Transitions between phases occur at specific temperatures and compositions, and knowing the boundaries of these phase transitions is of both fundamental and practical interest. Understanding  $T$ - $c$  phase diagrams is an important goal for this text.

Figure 1.4 shows two basic types of transitions from a high-temperature phase (at top) to a low-temperature phase or phases (at bottom). For clarity, all three atom configurations in Fig. 1.4 are based on an underlying square lattice. The problem is reduced to one of atom positions on an “Ising lattice,” where an Ising lattice is a graph of nodes connected by first-neighbor links. Each node (or site) is occupied by one atom of either species, with a probability dependent on the concentration. The links between nodes are chemical bonds, which have energies that depend on the specific atoms in each pair.

The high-temperature phase in Fig. 1.4 is a random (or nearly random) distribution of atoms called a “solid solution.” The two species of atoms are mixed together, or dissolved



**Figure 1.4** Three alloy states. At top is the expected high-temperature phase, a disordered solid solution. This phase is unstable at low temperatures when chemical bond energies overpower the disorder caused by thermal energy. Two low-temperature states are possible – an unmixed state of two phases (left), or an ordered compound (right). Chemical preferences usually select only one of these states. ( $L$  is the long-range order parameter, defined later.)