

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 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.

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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 $F_{\text{ord}}(T)$ is not the same as $F_{\text{dis}}(T)$ 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 d^2F/dT^2 has a kink. Order–disorder phase transitions are enlightening, and

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

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 themselves. 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 material, it is often possible to understand many properties of a material, especially its chemical, electronic, magnetic, and optical properties.

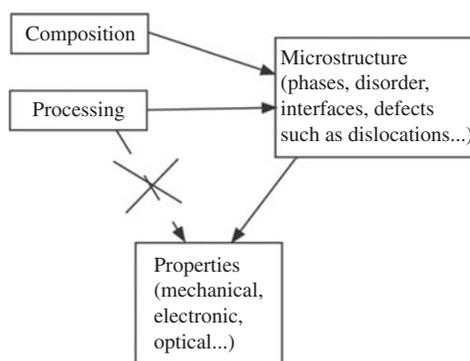


Fig. 1.1 Paradigm of materials science. A direct processing-to-properties relationship, as Edison pursued when finding filament materials for incandescent light bulbs, is not materials science.

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.

For many materials, reliable calculations of electronic structure have arrived. Some types of accurate calculations are routine today, 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 depend on the types of atoms and their mutual arrangements. Careful selections of variables to describe states of a material 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. Temperature is usually the most

accessible means for controlling 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 crystalline solid are fundamentally different owing to the symmetry of their atom arrangements. In Chapter 14 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 the liquid.² 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 $S_s < S_l$.³ 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

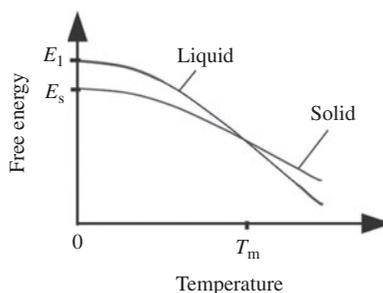


Fig. 1.2 Free energy curves of a pure element when its atoms are arranged as a crystalline solid, $F_s(T)$, or as a liquid, $F_l(T)$.

² 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.

³ Again, perhaps this is intuitive – there are more equivalent ways Ω 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.

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 .

The free energies are equal at the melting temperature, $F_s(T_m) = F_l(T_m)$. 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 , 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 freezing.

The expression for melting in Eq. 1.4 has ignored the temperature dependence of E and also S . There are many effects to consider, and any quantitative thermodynamic calculation of T_m might require a detailed understanding of E_s , E_l , S_s , and S_l .⁴ Nevertheless, pure elements do have well-defined melting temperatures. Another useful result is obtained by working at temperatures very close to T_m . Over a small range of T , (1) the changes in $E(T)$ and $S(T)$ for both solid and liquid phases are small and can be ignored, and (2) the two curves in Fig. 1.2 can be approximated as straight lines. At temperatures very close to T_m , the difference in free energy of the two phases is

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

Equation 1.6 is a linear relation between the difference in free energy between the solid and liquid, and the difference in temperature from T_m . It turns out that the “driving force” for freezing is this difference in free energy of the solid and liquid, so Eq. 1.6 tells us that this driving force increases linearly with the undercooling below T_m . This seems correct intuitively. Incidentally, the sign is correct in Eq. 1.6 – when $T > T_m$, the $F_l(T)$ is more negative (favorable) than $F_s(T)$. The thermodynamics of melting (or freezing) 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 low entropy compared with the other phase, there will be a phase transition at a finite temperature.

1.3.2 Structural symmetry and continuous phase transitions

When the symmetries of the high-temperature phase and low-temperature phase have special relationships, the phase transition can be continuous. Sometimes a discontinuous phase

⁴ For example, as atoms in a crystal vibrate from their periodic positions, the electron energy levels may change somewhat, and there is an increasing entropy of vibrations. Liquids are even more complicated – Chapter 10 attempts to discuss their structure and degrees of freedom.

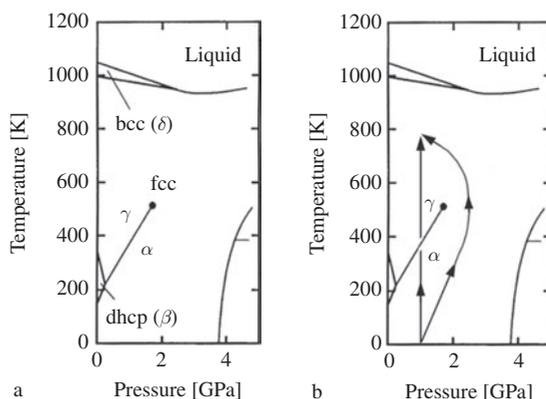


Fig. 1.3

(a) Low-pressure region of the cerium T - P phase diagram. The solid phases at zero pressure are: fcc α , double hcp β , fcc γ , bcc δ . (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.

transition can be changed to a continuous one by adding another thermodynamic variable such as pressure. 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 atmospheric pressure, it transforms between four different crystalline phases before melting. Our present interest is in two of them, the α - and γ -phases.⁵ Curiously, both have the fcc crystal structure, but they differ in volume by about 17% at ambient pressure. Let us start at a pressure of 1 GPa (to avoid the β -phase), and follow a vertical path in Fig. 1.3b that starts at low temperature, with cerium in the α -phase. Upon heating to a temperature near room temperature, the α -phase undergoes a sudden expansion of its fcc unit cell as it transforms into the γ -phase. The how and why of this phase transition is not fully understood today, but its existence is not in doubt.⁶

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.

⁵ Solid phases, typically with different crystal structures, are designated by Greek letters. The sequence of letters tends to follow their appearance in a phase diagram, or their sequence of discovery.

⁶ 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 γ -phase collapses into the high-density α -phase.

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.⁷ Evidently there can be a symmetry relationship between atom arrangements in gases and liquids that allows such continuous transitions.

1.4 Alloys: unmixing and ordering

“Alloying,” the mixing of two or more chemical species of atoms, 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 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. Explaining T - c phase diagrams is an important goal of 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). Note that all three atom configurations in Fig. 1.4 are based on an underlying square lattice, simplifying the geometry. 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

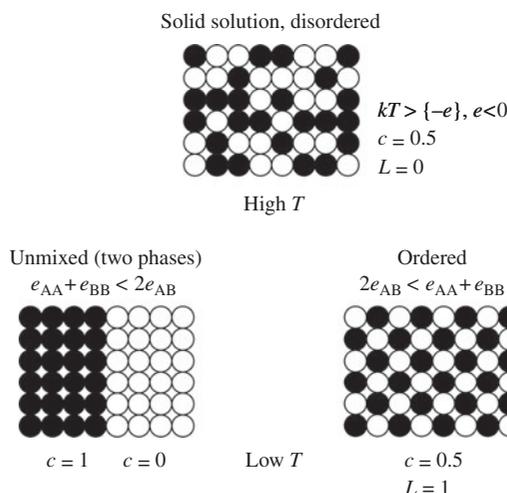


Fig. 1.4

Three alloy phases. 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 expected – an unmixed state of two phases (left), or an ordered compound (right). Only one of these states is expected, owing to chemical preferences. (L is the long-range order parameter, defined later.)

⁷ 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.

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 in each other. Some A–B alloys mix better than others, much like “liquid solutions” of ethanol and water, as opposed to oil and water. With many equivalent configurations, a solid solution phase has a high configurational entropy, S_{conf} , favoring it at high temperatures.

At low temperatures, two phases of low S_{conf} are possible:

- The lower left shows an unmixed alloy, where the B-atoms separate from the A-atoms. Unmixing is expected if atoms prefer their same species as neighbors more than they prefer unlike atoms as neighbors. Unmixing may lead to small regions, rich in solute, called “precipitates.”⁸
- The lower right shows the case of an ordered structure. Ordering is expected if unlike atoms are preferred as neighbors because this ordered structure maximizes the numbers of unlike neighbor pairs.

These unmixing and ordering transitions are usually more complicated than the extremes depicted in Fig. 1.4. At intermediate temperatures there is usually partial unmixing, or partial ordering.⁹ It is also possible, for example, for a solid solution to be in equilibrium with a partially ordered phase. Nevertheless, the two phase transitions from low to high temperature indicated in Fig. 1.4 are essential ones, and we consider them first.

It turns out that a simplified problem of a two-dimensional square lattice with fixed first-neighbor interactions is the only problem with an exact solution for the free energy through the critical temperature. The solution was reported by Onsager in 1944, and is an impressive achievement, well beyond the scope of this text. Unfortunately, the Onsager solution seems to be a special case, and efforts to extend it beyond the square lattice have not been successful. The difficulty is that the problem is a multibody one, where the energies of all atoms depend on the configurations of all others. Consider an alloy that develops chemical order. Although the free energy of the fully ordered state and the fully disordered solid solutions are reasonably straightforward to understand, the intermediate states near the critical temperature are not. As disorder begins to develop in an ordered structure, the neighborhoods of individual atoms differ. The energy of each atom depends on its bonds to the surrounding atoms, but the types of these atoms change with disorder. Sadly, it is not enough to consider only an average neighborhood about a typical atom. Likewise, the neighbors of the neighbors (some of which are the original atom and its neighbors) influence the types of atoms in neighboring positions.

The interaction of an atom with its neighbors, whose identities depend on how they interact with their own neighbors, leads to cooperative behavior in a phase transition. In essence, with increasing temperature the alloy tends to hold its order locally, but the quality of order over longer distances deteriorates more rapidly. At the critical temperature the long-range order is lost, but the short-range order is not, and persists to higher temperatures. Short-range order is often best treated with its own, independent order

⁸ This is much like a precipitation reaction in a liquid solution, but of course the precipitates in solids cannot fall to the bottom of a test tube under gravity.

⁹ An “order parameter” is usually necessary to describe how the quality of order changes with temperature.