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**OVERVIEW** 

*In our experience, the study of statistical mechanics elicits a transition from a phase of ignorance to a phase of bliss.* 

The existence of phase transitions is a remarkable fact of nature. Unlike most other phenomena in physics, phase transitions can involve a dramatic change in the properties of a material. Water can boil. Steam can condense back into water. A piece of iron can become magnetized. And most pure metals, when cooled sufficiently close to absolute zero, gain the ability to superconduct—to conduct electricity without any resistance at all.

Phase transitions are among the clearest and best understood examples of emergent properties—properties that involve the collective behavior of many constituent parts. When water boils, nothing intrinsic about its molecules is affected. Studying the details of the molecular interaction does not lead to insight about the nature of boiling. To properly appreciate the striking transformation from liquid to gas, a macroscopic point of view is required—a view that takes into account the statistical properties of the vast numbers of water molecules and their interactions with one another. This is the approach we will take in this book.

In this chapter, we will start with a bird's-eye overview about phases of matter, their transitions, and the way they are characterized. We begin with a qualitative description. Along the way, we will see how ideas from statistical mechanics can help us build an understanding of these phenomena. We assume that students have already been introduced to the basic ideas of statistical mechanics—the prerequisite knowledge is reviewed in Chapter 2.

## 1.1 Phases

In childhood we are taught of three phases of matter: solid, liquid, and gas. Each of these phases is characterized by a distinct set of physical properties: a gas is highly compressible, a liquid has fixed volume but still can flow, and a solid is rigid.<sup>1</sup> These physical qualities are emergent—an individual molecule cannot "flow" or "be rigid";

<sup>1.</sup> As we will discuss in Section 1.2.2, liquids and gases are not truly distinct phases of matter.

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only a large collection of molecules can. A phase of matter is a collective effect that only makes sense if there are a lot of particles.

There are, in fact, many more phases of matter beyond these three, each with its own fascinating and mysterious properties. The superconducting phase has zero electrical resistance; a superfluid flows without any viscous damping. In ferromagnets, the spins of the electrons align preferentially in one direction, giving rise to an overall magnetic dipole moment. In a nematic liquid crystal (the material behind many modern-day digital screens), rod-like molecules are oriented preferentially in one direction, yet they freely flow past one another. All these ordered phases of matter share the same property that their individual constituents are organized with some form of collective "long-range order."

## 1.1.1 Phase Diagrams

The phase diagram of water is shown in Figure 1.1. A phase diagram maps out the equilibrium phases of a system as a function of a set of external control parameters in this case, the temperature *T* and the pressure *P*. Depending on the control parameters, the properties of the material, such as its density  $\rho$  and its compressibility  $\kappa$ , will vary. By measuring these properties at different points on the phase diagram, we can obtain equations of state such as  $\rho = \rho(T, P)$  describing how a



# FIGURE 1.1. A schematic phase diagram of water. Note that the region of the phase diagram labeled "solid" actually comprises many structurally distinct crystalline phases. The colored dotted lines represent distinct "trajectories" through the phase diagram. Trajectory B represents the heating of water past its boiling point; a phase transition from liquid to gas occurs where it intersects the phase boundary, indicated by the magenta line. There is no phase transition encountered along trajectories A and C.

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FIGURE 1.2. At a phase transition, observable properties have nonanalytic behavior. At atmospheric pressure, water boils at 100°C, hence both the density (A) and the compressibility (B) change discontinuously as a function of temperature. At the critical pressure,  $P_c$ , the density (C) varies continuously through the transition, whereas the compressibility (D) diverges.

material's observable quantities depend on the control parameters. Similarly, other thermodynamic quantities such as the free energy F(T, P) may be obtained as functions of the control parameters.

## 1.1.2 Phase Transitions

Within a phase, all observables change smoothly as the control parameters are varied. To be precise, the equations of state are analytic functions. (An analytic function is one which is well behaved in the sense that it is continuous, has derivatives to all orders, and converges to its Taylor expansion.) This is the case, for example, along the blue path A in Figure 1.1.

In contrast, at phase boundaries, material properties can undergo discontinuous changes. One dramatic (yet familiar) example is the boiling of water, the brown path B in Figure 1.1. At atmospheric pressure, a minute change in temperature from 99.999°C to 100.001°C causes a sudden, striking transformation: the molecules fly apart, the density plummets by a thousand-fold, and the essentially incompressible water becomes highly compressible steam.

Such changes in the material properties are illustrated in Figures 1.2A and B, where we show the density  $\rho$  and the compressibility  $\kappa$  along a path through the phase diagram corresponding to the brown path B in Figure 1.1. The discontinuities in  $\rho(P, T)$  and  $\kappa(P, T)$  occur at the liquid-gas phase boundary. In contrast, along any path on the phase diagram that avoids all phase boundaries, such as the blue path A or the green path C, the evolution of physical quantities is everywhere smooth, without discontinuities in any thermodynamic observable.

#### 1.1.3 The Critical Point

A particularly interesting feature of the phase diagram of water is the critical point at  $(P_c, T_c) = (218 \text{ atm}, 374^{\circ}\text{C})$ , where the liquid-gas phase boundary ends. Across any point on the phase boundary, there is a discontinuous jump in the density

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 $\Delta \rho \equiv \rho_{liquid} - \rho_{gas}$  between the liquid and gas phase, as illustrated in Figure 1.2A. At successively higher points along the phase boundary, the liquid and gas become more similar in density, i.e.,  $\Delta \rho$  becomes smaller and smaller, eventually reaching zero at the critical point (Figure 1.2C). Beyond this point, the distinction between the liquid and the gas disappears.

The critical point exhibits many unusual properties. For instance, upon approaching the critical point, the density becomes extremely susceptible to even slight variations in pressure, i.e., the compressibility diverges (Figure 1.2D). Additionally, a fluid near its critical point appears turbid, like a saturated culture of bacteria. This is visible evidence that the fluctuations in density become extremely pronounced near the critical point; when local regions of higher or lower density grow so large that they scatter visible light, this gives rise to a milky appearance.

## **1.1.4 Continuous and Discontinuous Transitions**

The two cases we have described—the liquid-gas transition and the critical point are examples of a discontinuous and a continuous phase transition, respectively. This classification of phase transitions, after Ehrenfest, stems from the fact that the free energy is always a continuous function of parameters, even at the point of a phase transition.<sup>2</sup> Transitions are classified as either discontinuous or continuous depending on whether or not any first derivatives of *F* (e.g., density or entropy) are discontinuous.

Continuous phase transitions share many properties with the critical point of water. There is a divergence in a susceptibility, indicating extreme sensitivity to external perturbations. Additionally, fluctuations (such as those responsible for critical opalescence) become relevant on all lengthscales.

Discontinuous phase transitions, such as a liquid-gas transition, have a host of different properties. The defining characteristic is that there is a discontinuity in a first derivative of the free energy, e.g., as water vaporizes its density plummets discontinuously (Figure 1.2A). Another characteristic of a discontinuous transition is a nonzero latent heat: upon crossing the phase transition, a particular amount of heat per unit volume is absorbed or released.<sup>3</sup> Furthermore, discontinuous transitions can exhibit metastability: water can be chilled below its freezing point without the formation of any ice crystals, which is known as supercooling (Section 4.4.3).

<sup>2.</sup> Formally, the continuity of the free energy follows from the fact that it is a bounded, convex function. Physically, since its derivatives are state functions (such as the entropy or the magnetization), these must everywhere be well-defined (although possibly themselves discontinuous) functions.

<sup>3.</sup> The latent heat of water vapor is the reason why the steam over a pot of soup feels so hot: the water vapor releases heat as it condenses. It is also why it feels so cold to get out of a swimming pool on a windy day: the water absorbs heat as it evaporates off your skin, a process accelerated by the wind!

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For historical reasons, discontinuous and continuous transitions are also known as 1st-order and 2nd-order transitions, respectively. This nomenclature comes from thermodynamics: the density  $\rho$  is a first derivative of the free energy, whereas the compressibility  $\kappa$  is a second derivative. At a 1st-order (discontinuous) transition such as the boiling of water, the first derivative  $\rho$  jumps discontinuously, whereas at a 2nd-order (continuous) transition such as the critical point, the second derivative  $\kappa$  diverges.

## 1.1.5 Distinction between Phases

In the phase diagram of water (Figure 1.1), the liquid-gas phase boundary does not extend indefinitely: there is no phase boundary past the critical point. This means the liquid and gas phases are not truly distinct. By choosing a path in the T - P plane that circles beyond the critical point (e.g., the green path C in Figure 1.1), it is possible to start in the "liquid" phase and end in the "gas" phase without ever crossing a phase boundary. In this sense, the two are really part of the same fluid phase! In contrast, the solid phase is distinct from the fluid phase because the two are always separated by a phase boundary.

In order to classify the phases of matter in an unambiguous way, a clear distinguishing criterion must be established. It may be tempting to define a gas as a "highly compressible" fluid, but since even liquids are somewhat compressible, there is no clear threshold number that can be used to make this definition precise. Phases must be defined by a clear-cut property—something which is either present or absent, with no in-between. To this end, phases are often classified on the basis of symmetry.<sup>4</sup>

## 1.2 Symmetries

Symmetry can seem abstract, but we will come to appreciate it as a powerful and precise way to make sense of the phases of matter. As you may recall, the very laws of physics have a set of fundamental symmetries. For example, when light passes through empty space, its speed is the same regardless of the direction of propagation. This reflects the rotational symmetry of space. Likewise, there is translation and reflection symmetry of space, and translation and reversal symmetry of time.

Phases of matter, however, are often less symmetric than are the laws of physics. If light passes through a piece of ice, its speed depends on the direction of propagation:

<sup>4.</sup> Any property that is binary, in the sense that a phase either exhibits it or does not, can in principle be used to distinguish phases of matter. As an aside, we list (without explanation) some examples of other features that can characterize a phase of matter other than its symmetries: A system can be a fluid (able to flow) or a solid (able to support a shear). A collection of electrons can form a "metal" (with a finite resistance in the limit  $T \rightarrow 0$ ), an "insulator" (with a diverging resistance in the limit  $T \rightarrow 0$ ), or a "superconductor" (with a vanishing resistance for  $T < T_c$ ). In gauge theories, for instance of the strong interaction, there are "confining" phases (in which quarks are confined), and "deconfined" phases, which are distinguished by a form of "topological order."

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FIGURE 1.3. An illustration of cubic symmetry (above) and tetragonal symmetry (below). In both cases the action of three transformations is depicted, corresponding to a 90 degree rotation about each of the three axes. A check mark or a cross indicates whether or not a transformation is a symmetry.

the index of refraction depends on how the beam of light is oriented with respect to the axes of the crystal. Crystalline solids such as ice, manifestly, do not have the same rotational symmetry as empty space.

## 1.2.1 The Cubic-to-Tetragonal Transition

As a first example of how symmetry can differentiate phases of matter, consider a crystal with cubic symmetry, such as common table salt. On a microscopic level, the atoms in a crystal are arranged in a regular lattice with a basic repeating unit, known as a unit cell. In a cubic lattice, the unit cell is a cube, as shown in Figure 1.3. The three axes of the crystal are equivalent and mutually perpendicular, and the lengths of the sides of the unit cell (lattice parameters) are identical.

If a crystal is heated, it undergoes thermal expansion (until at high enough temperatures it melts). On the basis of symmetry, the three axes in a cubic crystal should each lengthen in exactly the same way. If a cubic crystal is cooled, we might expect it to also contract isotropically—but this is not always the case! Rather, in

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certain crystals, one of the lattice parameters can become distinct from the other two, transforming the lattice from cubic symmetry to *tetragonal* symmetry. This shape-shifting behavior is illustrated in Figure 1.3. In a tetragonal crystal, two of the three axes are identical and the third one is either longer or shorter. All axes are perpendicular.

The transition from a cubic to a tetragonal phase involves a change in the symmetry of the crystal. As such, it must occur at a well-defined critical temperature,  $T_c$ , because symmetry is crisply defined: either all three axes are equivalent, or only two of them are. (You could also imagine that at an even lower temperature,  $T'_c$ , the two equivalent axes in a tetragonal crystal could become different, yielding an orthorhombic crystal with three distinct axes. We will return to this point when we discuss other sorts of structural phase transitions in Section 5.2.2).

Intuitively it is pretty clear that some sort of symmetry has been lost in going from the cubic to the tetragonal phase. What this means mathematically is the following: there are certain transformations which preserve the symmetry of the cubic lattice. Such a transformation, when applied to a cubic lattice, leave the system indistinguishable from its initial state. For example, if we chose one of the three axes and rotated the crystal by 90 degrees around that axis, the lattice would look exactly the same after the rotation, as illustrated in the top right of Figure 1.3. However, this is not the case for a tetragonal lattice. As illustrated in the bottom right of Figure 1.3, only for one of the three axes is a rotation by 90 degrees a symmetry transformation. Evidently, a tetragonal lattice has a smaller set of symmetry transformations than a cubic lattice. We will come to see this as a general pattern of phases of matter: low-temperature phases tend to have reduced symmetry compared to high-temperature phases.

Finally, observe that there was nothing *intrinsic* in the cubic crystal about which of the three axes becomes unique—after all, above  $T_c$ , the three axes are equivalent in every conceivable manner. Rather, it is a random occurrence as to which axis will become distinct as the crystal is cooled below  $T_c$ . The symmetry is broken *spontaneously*. However, it is possible to force one axis to become the longer one by pulling the crystal along that axis as it is cooled. Such an external perturbation which favors one symmetry-broken state over the others is called a symmetry-breaking field.<sup>5</sup> Even if a symmetry-breaking field is then removed after the system is below  $T_c$ , that axis will remain elongated; the system remembers its thermal history.

## 1.2.2 Solids, Liquids, and Gases

From the perspective of symmetry, we can explain why the liquid and gas "phases" are actually the same phase of matter while the solid phase is definitively distinct.

<sup>5.</sup> Here a "field" refers to a physical quantity that acts over a region of space, such as electric/magnetic fields or more general quantities such as strain.

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The question to ask is "what symmetry transformations leave these phases of matter invariant?"

The solid state is invariant under a smaller set of spatial translations than the liquid or the gas. A spatial translation is a transformation in which all the atoms in a material are uniformly shifted by a displacement,  $\vec{r} \rightarrow \vec{r} + \vec{R}$ . Since liquids and gases are homogeneous in space, they are invariant under translations of arbitrary magnitude and direction, i.e.  $\vec{R}$  can be any three-dimensional vector. In contrast, in a crystalline solid, only certain translations are symmetries. Because the average position of atoms in a crystal is regular and periodic, a translation will leave a crystal invariant only if it places each unit cell in a new location where it overlaps with an identical copy. Consequently, in a crystal,  $\vec{R}$  must be a lattice vector of the form  $\vec{R} = n_a \vec{a} + n_b \vec{b} + n_c \vec{c}$ , where  $\vec{a}, \vec{b}, \vec{c}$  are basis vectors of the lattice, and  $n_a, n_b, n_c$  are integers representing the number of units to translate along each direction. The translation symmetry of free space is spontaneously broken in a crystal.

Stated more precisely, in a crystal, the probability of finding an atom at a given point in space is a periodic function of position, with a periodicity represented by the crystalline lattice. In contrast, in a fluid state, the probability of finding an atom at any point in space is the same as at any other (indeed, all thermodynamic quantities are independent of position). Therefore the symmetry of the crystal is lower than that of liquids and gases: a fluid is invariant with respect to any translation, while the crystal is invariant only with respect to a discrete subset of translations. There is no symmetry-based distinction between a liquid and a gas.

Beyond the translational symmetries we have discussed, a crystal also spontaneously breaks the rotational symmetry of free space. For example, if a liquid were to freeze into a tetragonal crystal, it would no longer be invariant under arbitrary rotations—it would have a reduced, 4-fold discrete rotational symmetry (rotations by  $0^{\circ}$ ,  $90^{\circ}$ ,  $180^{\circ}$ , and  $270^{\circ}$  about the tetragonal axis). The transition from a liquid to a crystal is an example where a continuous symmetry is spontaneously broken. If, upon further cooling, the tetragonal crystal were to enter an orthorhombic phase (where all three axes are distinct), the rotational symmetry would be reduced to an even smaller subset ( $0^{\circ}$  and  $180^{\circ}$ ). In this example a discrete symmetry is spontaneously broken.

#### 1.2.3 Ferromagnets

Ferromagnets are materials that spontaneously develop a net magnetization below a certain temperature (known as the Curie point). Since the north pole of a ferromagnet points in a particular direction, the ferromagnetic phase manifestly breaks the rotational symmetry of space. If ferromagnetic order develops in a liquid (a ferrofluid), it will break the continuous rotational symmetry of free space; if it develops in a crystal, it will break the discrete rotational symmetry of the crystal. As discussed

#### 1.3. UNIVERSALITY 9

Heisenberg

Table 1.1. I ferromagne	Names of a few cor ets where the magr	mmon models of netization is an			
V-dimensional vector.					
N = 1	<i>N</i> = 2	N = 3			

XY

Ising

in Section 5.2.5, the ferromagnetic phase also spontaneously breaks time-reversal symmetry.

The microscopic origin of ferromagnetism comes from quantum mechanics. At a cartoon level, each atom can be thought of as having a miniature magnetic dipole moment, arising from the quantum mechanical spin of an unpaired electron (see Section 5.2.5). In a ferromagnetic material, the spins of neighboring atoms have a strong enough tendency to align in the same direction that, at low temperatures, the spins are aligned over macroscopic scales. At high temperatures, the thermal energy always randomizes the spin orientations so that on average there is no net magnetization.

There are a handful of common models to describe different categories of ferromagnets, summarized in Table 1.1. The simplest one is an Ising<sup>6</sup> ferromagnet, where the spins preferentially point along an "easy axis"; below the Curie point, the average spin is either up or down along this axis. In an XY ferromagnet, the spins are confined to lie in an "easy plane"; in this case, for  $T < T_c$  the magnetization is a twodimensional vector in the easy plane. In a Heisenberg ferromagnet, the spins are free to point in all directions equivalently, and so the magnetization is specified by a three-dimensional vector. In all these cases, the magnetization is representable by an *N*-dimensional vector.

In many ferromagnetic crystals, including the strong rare earth magnets, the spins are Ising-like because of the strong, anisotropic interactions between the spins and the crystal lattice (known as spin-orbit coupling). There are no real examples of XY ferromagnets—though, remarkably, a superfluid can be thought of as some kind of XY ferromagnet (see Section 5.2.6). A ferrofluid has Heisenberg symmetry. The connection between these models and real ferromagnets is discussed more in depth in Chapter 5.

## 1.3 Universality

The overall features of the phase diagram of water are not unique to water. They are common to many fluids. For instance, xenon also exhibits a liquid-gas phase boundary terminating at a critical point. The difference is that the critical pressure

<sup>6.</sup> Named after the German physicist Ernst Ising (1900-1998), who apparently did little physics after working on his eponymous model.

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	Ne	Ar	Kr	Xe	$N_2$	O <sub>2</sub>	СО	$CH_4$
$T_c$ (K)	44.8	150.7	209.4	289.8	126.0	154.3	133.0	190.3
$P_c$ (atm)	26 9	48.0	54.1	58.2		49.7	34 5	45.7

Table 1.2. The critical temperature and pressure of a selection of fluids.

and temperature of xenon are  $P_c = 58$  atm and  $T_c = 290$  K. The critical points of some common fluids are listed in Table 1.2.

In Figure 1.4, we have plotted the phase diagram of a number of fluids in the  $\rho - T$  plane, with a special choice of units: for each fluid, we have divided  $\rho$  by  $\rho_c$  and T by  $T_c$ .<sup>7</sup> Astoundingly, if we do this, the shape of the phase boundary is almost exactly the same for all fluids! This is especially remarkable considering how these materials differ in other respects—carbon monoxide is poisonous, methane flammable, and neon inert. Despite this, they share a qualitative similarity—in terms of the existence of a critical point—and a semi-quantitative one as well, in the shape of the phase boundary. As far as phases are concerned, the only differences between these fluids seem to be their numerical values of  $\rho_c$  and  $T_c$ .

Even more remarkably, a completely different physical system, a uniaxial ferromagnet (or Ising ferromagnet), has a phase diagram similar enough to the fluid phase diagram to warrant a comparison. Its phase diagram in the T - H plane is shown in the right panel of Figure 1.5. Here H is the strength of an external magnetic field applied along the easy axis of the sample. The magnetic field gives the spins an energetic bias to align in the same direction as H. At low temperature, this effect leads to a discontinuous phase boundary between the "up phase" and the "down phase." (This is analogous to the liquid-gas phase boundary.) However, the up and down phases are not truly distinct phases in the T - H phase diagram because the distinction between them disappears above the Curie point. Above this temperature, the magnetization encounters no abrupt jump as the sign of the external magnetic field is changed. Comparing the schematic phase diagrams in Fig. 1.5, it is apparent that the fluid and the uniaxial ferromagnet share a topological similarity.

## 1.3.1 Critical Exponents

The correspondence between these two seemingly unrelated systems extends beyond qualitative similarities. Consider measuring the fluid density in the vicinity of the liquid-gas critical point. At temperatures slightly below  $T_c$ , the density of the two coexisting phases varies as

$$\rho(T) - \rho_c \sim \pm |T_c - T|^{\beta}, \quad \beta \simeq 1/3, \tag{1.1}$$

<sup>7.</sup> For any  $T < T_c$ , there are two "phases"—the liquid phase and the vapor phase—with densities  $\rho_{\text{liquid}}(T)$  and  $\rho_{\text{gas}}(T)$ , respectively. The critical temperature is the point at which  $\rho_{\text{liquid}}(T_c) = \rho_{\text{gas}}(T_c) \equiv \rho_c$ .



FIGURE 1.4. (top) The phase diagram of eight different fluids in the  $\rho - T$  plane. The two branches of the curves indicate the densities of the two phases that coexist at a given T—the gas (small  $\rho$ ) and the liquid (large  $\rho$ ). The critical points of different fluids occur at different values of  $\rho_c$  and  $T_c$ . However, the values of  $\rho$  and T have here been scaled by their critical values listed in Table 1.2; remarkably this rescaling results in the phase boundaries all lying on the same curve. (bottom) An analogous phase diagram of a uniaxial ferromagnet. The curves indicate the magnetization at a given T. This figure has been reproduced with permission from James P. Sethna's textbook, *Statistical Mechanics: Entropy, Order Parameters, and Complexity* (Oxford University Press, Oxford, 2021).

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FIGURE 1.5. Schematic phase diagrams of a fluid (left) and a ferromagnet (right) near their critical points. The pressure *P* exerted on a fluid is analogous to the external magnetic field *H* applied to a ferromagnet. In both cases there is a discontinuous phase boundary which terminates at a critical point.

with a + for the liquid phase and – for the gaseous phase. The small value of  $\beta$  is reflected in the very flat top of the phase boundary in the top panel of Figure 1.4. As illustrated in the bottom panel of Figure 1.4, the analogous measurement for a uniaxial ferromagnet—measuring the magnetization *m* as a function of the temperature below the critical point—yields

$$m(T) \propto |T - T_c|^{\beta}, \quad \beta \simeq 1/3,$$
 (1.2)

with the same critical exponent  $\beta$  within experimental error!

The commonality between the liquid-gas and the uniaxial ferromagnet critical points extends further. If a fluid is held at its critical pressure, the compressibility  $\kappa$  diverges (Figure 1.2D) as the critical temperature is approached from above, with a functional dependence of

$$\kappa \propto |T - T_c|^{-\gamma}, \quad \gamma = 1.24.$$
 (1.3)

This is the same power law observed for the magnetic susceptibility in a uniaxial ferromagnet,

$$\chi \propto |T - T_c|^{-\gamma}, \quad \gamma = 1.24 \tag{1.4}$$

as  $T \to T_c^+!$ 

Not all continuous phase transitions have exactly these same exponents. For instance, for an XY ferromagnet the exponent  $\beta$  is 0.35. Mysteriously, this value of  $\beta$  is identical to an analogous exponent observed in the transition to the superfluid phase of Helium-4!

In general, physical quantities in the vicinity of a critical point often take the form of power laws

$$y \propto |x|^z, \tag{1.5}$$

where *x* is a control parameter (like  $T - T_c$ ) and *y* is a measurable thermodynamic quantity (such as a susceptibility). The critical exponent *z* describes the nature of the singularity.<sup>8</sup> In Worksheet W1.1, you get to work through some examples of power laws.

Certainly, we will want to understand the origin of these power laws at critical points, why they are so universal, and why certain transitions have the same or different critical exponents. Ideally, we would like to be able to predict the values of these critical exponents.

#### 1.3.2 Universality Classes

In the 1970s and 1980s, many of the mysteries of continuous transitions came to be successfully understood. Today, we have a unified framework for understanding a variety of phase transitions.

Phase transitions can be classified into various universality classes. All the phase transitions within a universality class share the same values of critical exponents and share additional universal features. For instance, the uniaxial ferromagnet and the liquid-gas transition both fall into the 3D ISING universality class. Other phase transitions in this universality class, such as the order-disorder transition of  $\beta$ -brass (see Section 5.2.1), have the same 3D ISING critical exponents. The easy-plane ferromagnet and the superfluid, on the other hand, fall in the 3D XY class and have their own set of exponents. The transition to a ferromagnetic state in a ferrofluid falls in yet another class, the 3D HEISENBERG class.

What determines the universality class of a transition is somewhat abstract. We will return to this topic throughout the book. In the end we will find that it depends on some very general features of the broken symmetries and on the dimension of space, but on no other details of the system involved.

One of the shared properties within a universality class is the exponents of various power laws (Eq. 1.5). Conventionally, the critical exponents are represented by various Greek letters. We will encounter a whole bunch of other critical exponents throughout the text, summarized in Table 1.3. The values of these critical exponents have been determined theoretically, either by exact solution of model problems or by extensive numerical simulation of such models. They are summarized in Table 1.4. Notice that the values depend on both the symmetry index N as well as the spatial dimensionality d. In many cases these theoretical predictions agree well with experiments in a variety of systems.

One of our goals in the book, in addition to understanding the existence of distinct phases of matter and sharply defined phase transitions between them, is to understand the origin of these critical exponents and why they are universal.

<sup>8.</sup> A singularity is a point where a function is nonanalytic—a cusp, a discontinuity, a divergence, ....

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Table 1.3. A summary of the critical exponents discussed in this text. The reduced temperature  $t = (T - T_c)/T_c$  is a dimensionless measure of distance from a critical point. Exponents  $\delta$  and  $\eta$  are defined for t = 0. G(r) is the correlation function (Eq. 2.28) and  $\xi$  is the correlation length (Eq. 2.31).

Exponent	Definition	Name	First Seen
α	$c \sim  t ^{-\alpha}$	specific heat	Eq. 10.8
$\beta$	$m \sim  t ^{eta}$	magnetization	Eq. 1.1
$\gamma$	$\chi \sim  t ^{-\gamma}$	susceptibility	Eq. 1.3
$\delta$	$m \sim h^{1/\delta}$	magnetization	Eq. 4.39
$\eta$	$G(r) \sim r^{-(d-2+\eta)}$	anomalous dimension	Eq. 10.1
ν	$\xi \sim  t ^{-\nu}$	correlation length	Eq. 7.28

Table 1.4. Critical exponents of various models in different numbers of spatial dimensions. Numbers given as rational fractions are obtained from exact analytic approaches while those given as decimals are from accurate numerical simulations, rounded to two decimal places.

Universality Class	α	β	$\gamma$	δ	$\eta$	ν
2D Ising	0	1/8	7/4	15	1/4	1
3D Ising	0.11	0.32	1.24	4.79	0.04	0.63
4D Ising	0	1/2	1	3	0	1/2
3D XY	-0.01	0.35	1.32	4.78	0.04	0.67
4D XY	0	1/2	1	3	0	1/2
3D Heisenberg	-0.12	0.36	1.39	4.91	0.04	0.71
4D Heisenberg	0	1/2	1	3	0	1/2

## 1.4 Problems

- 1.1. *Phase diagram of simple polynomials.* The qualitative properties of a polynomial—for instance, the number of distinct real-valued roots—depend on the values of its coefficients.
  - (a) Draw a phase diagram that maps out the number of real-valued roots of the polynomial  $f(x) = x^2 ax + b$  as a function of *a* and *b*. How many phases are there? What is the functional form of the phase boundary?
  - (b) Now consider the polynomial g(x) = x<sup>3</sup> cx + d. Draw a phase diagram in the c d plane displaying the number of real-valued roots, and determine the functional form of the phase boundary. There is a special point on the phase boundary; what is special about it? *Hint:* At the special point on the phase boundary, the extremum of the function is simultaneously a root: g(x\*) = g'(x\*) = 0.

(c) We can draw a different (more interesting!) phase diagram with the same polynomial,  $g(x) = x^3 - cx + d$ . Consider the *largest real root* of g(x),

$$x_{max} = \max\{x | g(x) = 0\},$$
 (1.6)

as a function of the control parameters *c* and *d*. Draw the phase diagram of  $x_{max}$ . What is different about this phase boundary compared to parts (a) and (b)? Does the overall topology of the phase diagram resemble any of the physical systems discussed in this chapter?

Remarkably, the phase diagrams of many physical systems can be approximately determined using simple polynomials, as we have done here. The reason is that, near to a critical point, the free energy may be approximated by a Taylor expansion, i.e., a simple polynomial. We discuss this concept in Chapter 6.

- 1.2. *Power laws and universality*. Near critical points, thermodynamic quantities are often well described by power laws of the form  $y = ax^{z}$ . The pre-factor *a* depends on the details of the physical system, but the exponent *z* is universal.
  - (a) Give a few examples of power laws from prior physics classes.
  - (b) What is the area of a square with side length *l*? Of a triangle? Of a circle with diameter *l*? What is common among these formulas, and what is different?
  - (c) What is the volume of a cube with side length *l*? Of a sphere with diameter *l*? What is different from part (b)?
  - (d) In *d* dimensions, what is the formula for a shape's hypervolume *V* as a function of its side length? You may leave the answer in terms of an arbitrary constant *a* which depends on the details of the shape.
- 1.3. *Scale invariance and fractals.* Consider the effect of a scale transformation  $\ell \mapsto b\ell$ , whereby all lengths are scaled up by a factor of *b*, akin to the action of a magnifying glass.
  - (a) What happens to the hypervolume of a *d*-dimensional shape upon a rescaling  $\ell \mapsto b\ell$ ?

Remarkably, a physical system at its critical point *remains unchanged* upon a change of scale: it is scale invariant. This property is reminiscent of the self-similarity of *fractals*, which are sometimes encountered in recreational mathematics. An example is the Sierpinski triangle, which is formed by starting with an equilateral triangle, dividing it into four equally sized equilateral triangles, removing the central triangle, and repeating the process for each of the remaining triangles ad infinitum.

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  - (a) The Sierpinski triangle is not scale invariant, but it is self-similar: there are *particular* values of *b* which leave the shape unchanged under *l* → *bl*. What are they?
  - (b) What is the dimensionality of the Sierpinski triangle? *Hint*: Under a scaling by *b*, the triangle generates *c* copies of itself. Find *b* and *c*, and use the relation from part (a).

A system at a critical point exhibits patterns with fractal-like shapes, with structures on all lengthscales. The dimension of a fractal need not be an integer; it can even be an irrational number.

- 1.4. Universality in a random walk. Consider a particle on a 1D line which starts at x = 0. Suppose that at each time step, it can either step to the left,  $s_i = -a$ , with probability 1/2, or it can step to the right,  $s_i = +a$ , with probability 1/2. After *N* steps, the position of the particle is  $S = \sum_{i=1}^{N} s_i$ .
  - (a) How does the mean squared displacement,  $\langle S^2 \rangle$ , depend on the number of steps *N*?
  - (b) For large *N*, what is the probability distribution of *S*? *Hint:* Consider the central limit theorem.

Now consider a different random walk where each step is distributed as

$$r_{i} = \begin{cases} -2a & \text{with probability } 1/2; \\ a & \text{with probability } 1/4; \\ 3a & \text{with probability } 1/4. \end{cases}$$
(1.7)

- (c) After many steps  $N \gg 1$ , what is the distribution of the position of the particle,  $R = \sum_{i=1}^{N} r_i$ ?
- (d) Compare and contrast the distributions of the *R* random walk and the *S* random walk after a few steps and after very many steps.

This is an example of universality: the *R* and *S* random walks have different microscopic behaviors, but after very many steps, they converge to the same asymptotic behavior.

## 1.5 Worksheets for Chapter 1

## W1.1 Critical Exponents

If we plot certain properties of materials as a function of a tuning parameter close to a phase transition, the functional dependence can often be described by some power law. Here let us gain some familiarity with the shapes of various power laws, and identify the correct power laws from real experimental data.

- 1. Sketch the following power laws:
  - (a)  $m \propto (T_C T)^{\beta}$ , where  $0 < \beta < 1$ .
  - (b)  $c \propto |T T_C|^{-\alpha}$ , where  $0 < \alpha < 1$ .

When you have access to graphing tools, try plotting out these power laws and observe how they change as you vary  $\alpha$  and  $\beta$ !

- 2. A phase transition is considered "continuous" if the first derivative of the free energy is continuous across the phase boundary. Are the above transitions continuous given that:
  - (a) *m* is a first derivative of the free energy with respect to an applied field, *h*?
  - (b) c is a second derivative of the free energy with respect to temperature T?
- 3. A critical exponent and the associated power law describe the behavior of various physical quantities *close to* the critical point. Let us see what this means in practice.

Suppose we have a magnet whose normalized magnetization close to  $T = T_c$  behaves as:

$$m(T) = \sqrt{1 - (T/T_c)^2}$$
 for  $T < T_c$ . (1.8)

- (a) What is the meaning of the temperature scale  $T_c$ ?
- (b) Close to the phase boundary  $(0 < 1 |T/T_c| \ll 1)$ , the normalized magnetization can be written as:

$$m(T) = a(T_c - T)^{\beta}.$$
 (1.9)

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Find the value of the constant of proportionality a and the critical exponent  $\beta$  such that Eq. 1.9 correctly describes the behavior of Eq. 1.8 close to the phase boundary (see Figure W1.1).

*Hint:* Find the quantity that is small close to  $T_c$ , and expand Eq. 1.8 w.r.t. that quantity.



FIGURE W1.1. Full functional dependence vs. power-law description near phase boundary.

With the correct values for *a* and  $\beta$ , the power-law description very accurately describes the behavior near the phase boundary, but deviates quickly away from it. Moving forward, we must remember that many descriptions of critical phenomena are (approximately) correct only near phase boundaries!

4. Below is a plot of the superconducting gap energy of Tantalum close to the critical temperature as a function of the rescaled temperature  $t = T/T_c$ .



TABLE 1.5. Tantalum gap energy
temperature dependence.

$T/T_c$	$\Delta(T)/\Delta(0)$		
0.9904	0.1833		
0.9895	0.1522		
0.9858	0.2112		
0.9843	0.2485		
0.9781	0.2718		
0.9689	0.3013		
0.9674	0.3339		
0.9612	0.3478		
0.9542	0.3711		
0.9458	0.4084		
0.9349	0.4394		
0.9249	0.4580		

FIGURE W1.2. Superconducting gap of Tantalum close  $T_c$ .

- (a) Judging from the plot, what is the form of the normalized gap  $\Delta(T)/\Delta(0)$  close to t = 1?
- (b) Plotting the data on log-log axes, estimate the critical exponent, as well as the constant of proportionality.

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FIGURE W1.3. Log-log plot of Tantalum superconducting energy gap.

Is the theory a good description close to criticality? Close to  $T_c$  the theoretical value is  $\Delta(T)/\Delta(0) = 1.74\sqrt{1 - T/T_c}$ .

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