SECOND EDITION

Fundamentals of Soft Matter Science

Linda S. Hirst

Contents

Preface

The goal of this book is to provide a comprehensive introduction to the science of soft materials. The study of different soft matter systems has a long history but, until relatively recently, the subject was not consolidated into a distinct field. The idea that common physical principles underlie many of the once-separate soft matter topics was pioneered by 1991 Nobel Laureate Pierre-Gilles de Gennes. His theoretical work inspired a new way to approach and define soft matter, inspiring huge interest and growth in this fascinating subject. In addition, the parallel rapid growth of biophysics and polymer science over the past few decades has produced an explosion of focused soft matter research groups worldwide. Nowadays, soft materials are at the forefront of many contemporary technologies such as novel flexible displays, tissue engineering scaffolds, lab-on-a-chip biotechnology applications, and cutting-edge food science.

Recently it has become increasingly common for professors to include soft matter topics in their classes, or to offer complete courses, either at the graduate or undergraduate level. This development is extremely positive for the field of soft materials. Consequently, soft materials such as polymers, rubbers, gels, colloids, and liquid crystals touch every aspect of our lives and should be a standard part of the undergraduate curriculum. How can students understand the properties of everyday materials without an introduction to the fundamental science behind molecular self-assembly and the physics of soft materials?

Therefore, my goal was to write a readable book designed to be understandable at the undergraduate level for students with a background in introductory college-level physical and chemical sciences. The book is designed to be used as a textbook introduction for mid- to upper-level undergraduates and also to act as a useful resource for graduate students or more senior scientists of all levels new to the field of soft matter.

With these goals in mind, the book puts an emphasis on conceptual understanding and tends to avoid a lot of mathematical derivations. Lower division/introductory college course knowledge in physics, chemistry, and math is assumed throughout, with some refreshers and the appendices fill in some mathematical details. The aim is not to provide a rigorous theoretical description of any particular subject because this work has already been done very well by many authors at a graduate level in the specialized books among those referenced at the end of each chapter.

I have broadly defined the materials into several classifications. These classifications are by no means distinct, however, and there are many soft materials around that can span over a couple of chapters in this book. There are also many crossovers between subject areas in terms of theoretical descriptions and experimental techniques. In fact, one of the most fascinating aspects of soft matter science lies in the many conceptual connections that can be drawn between different materials. For example, much of the chapter on surfactants could potentially be classified as part of the liquid crystals chapter, and certain topics in the biomaterials chapter could equally find a home as part of the surfactant or polymer chapters. One important concept to understand from this book is the universality of the physics we use to describe soft materials. Although scientists and students may identify with one or more of the main topics presented here, there is much overlap and flexibility in how materials can be described and classified.

Each chapter in the book is dedicated to a different group of soft materials. Through the book we will look at liquid crystals, surfactants, polymers, colloids, and selections of soft biomaterials. For each

subject, I discuss the essential concepts of the subfield: material structures and physical characteristics, some simple theoretical ideas, and important experimental methods. Italicized terms can be found in the glossary for quick reference. As there is a natural overlap in experimental techniques between the chapters I have tried to find the most comfortable home for each technique.

At the end of each chapter, a further reading section will guide the reader toward more in-depth future study, including some of the detailed graduate-level texts currently available. My hope is that this book will serve as a springboard for students of all levels to initiate and expand their knowledge of soft matter, and perhaps even consider a future career or new research program specializing in some aspect of this fascinating subject.

Acknowledgments

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About the Author

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Trevor Hirst read Law at the Victoria University of Manchester, went on to train as a solicitor (attorney), and was admitted to the Roll of Solicitors of the Supreme Court of England and Wales in 1999, practicing civil litigation in Altrincham, Cheshire, UK. He and his wife, Linda, emigrated to California in early 2002, whereupon Trevor changed careers from litigation to education and began to follow more creative pursuits such as photography and illustration.

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Introduction

1.1 WHAT IS SOFT MATTER?

Soft matter science is the study of materials that are physically "soft," and this book is an introduction to the science behind these materials. But, what does it mean to be soft? The concept of a soft material can be applied to many different substances, ranging from relatively hard plastics and rubbers all the way to a variety of apparently liquid-like materials, such as polymer solutions or colloidal suspensions. A more precise definition of a soft material is therefore complicated somewhat by the huge range of physical properties observed in these systems. Pierre-Gilles De Gennes, the Nobel Prize-winning theoretical physicist, characterized soft matter as a class of materials that give a "large response to small perturbations."[1] This idea provides us with a clear and straightforward description. Any material that deforms easily under an external stimulus (e.g., mechanical forces, electric or magnetic fields, etc.) is "soft."

Another helpful concept that can help us to understand and identify soft matter is linked to thermal energy and intermolecular interactions. Soft materials are held together by weak intermolecular interactions and have a structure that can be significantly affected by energies close to the thermal energy $k_B T$, where k_B is the Boltzmann constant (1.38×10^{-23} m^2 kg/s^2 K), and T is the material's temperature measured in Kelvin. At room temperature, $k_B T$ has a value of about 26 me V (or 4.2×10^{-21} Joules)—much smaller than the energies that hold atoms together in a crystalline solid. Therefore, one of the most important characteristics of a soft material is that its structure can be easily altered at relatively low temperatures.

A third characteristic of soft materials is that they often have some degree of self-assembled non-crystalline structure. The basic component units of the material are arranged in a non-random fashion, although this ordering is typically short-range in comparison to the long-range regular atomic structure of a solid crystalline material. In terms of their structure, soft materials exist in a relatively disordered state with a molecular arrangement somewhere between a crystalline solid and a conventional liquid.

When we study the structure of materials, we usually first learn about the three basic phases of matter: solids, liquids, and gases. While these definitions provide an essential scientific foundation, they fail to describe adequately the majority of familiar materials we see around us and interact with in our everyday lives, including plastics, gels, rubbers, soaps and other detergent products, paints, most foods, and most of the human body (Figure 1.1). The aim of this book is to introduce a new flavor of materials

science focused on these soft materials. Through descriptions of the different classifications of soft materials and their structures, we will also provide an overview of some common experimental techniques and basic theoretical ideas.

There are several physical concepts that will be important to your understanding of the material in this book:

1. Basic thermal physics and phase transitions
2. Intermolecular forces
3. Self-assembly
4. Mechanical properties of materials
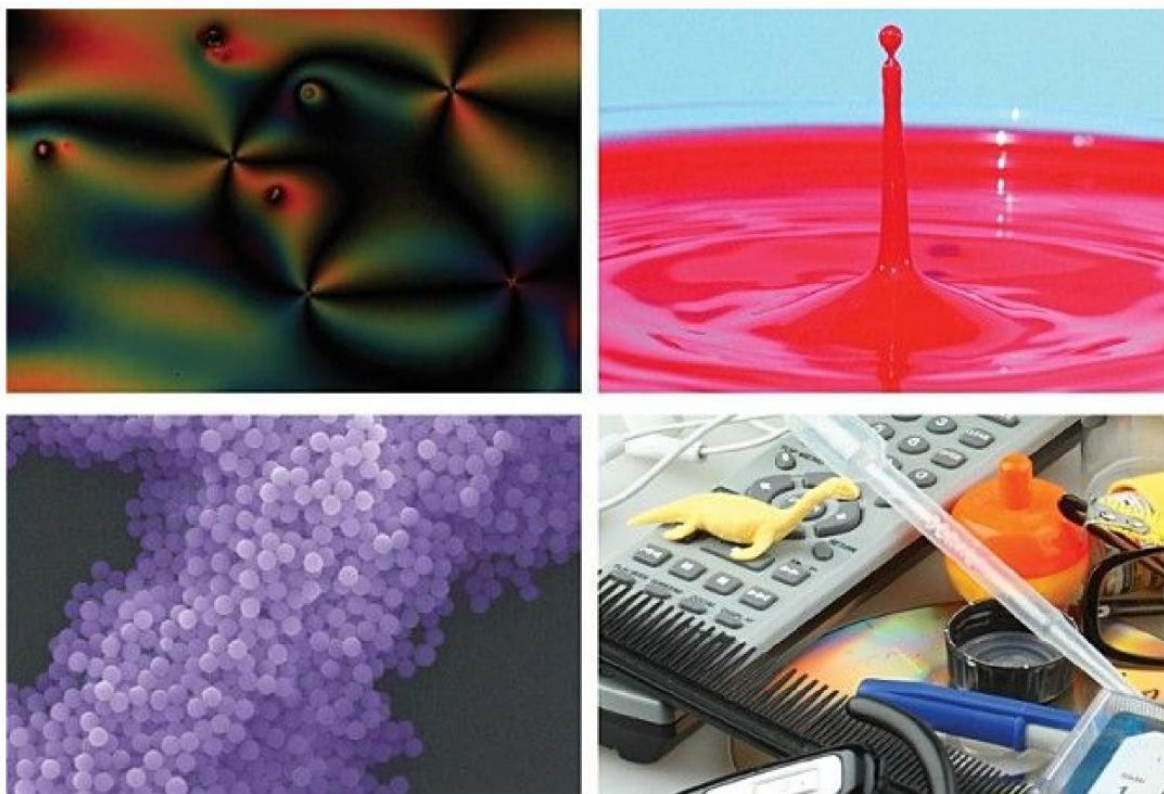
FIGURE 1.1 Examples of some of the different soft materials explored in this book.

As these ideas are so important and commonly encountered throughout the field of soft matter science, we will review them over the first two chapters of this book. In this first introductory chapter, we will spend some time on important concepts from thermal physics, including temperature, phase transitions, and phase diagrams.

1.2 BASIC THERMAL PHYSICS

Temperature is perhaps the most important experimental parameter for soft matter science because the structures of soft materials are so sensitive to energy changes on the order of $k_B T$. (4.2×10^{-21} J or 0.026 eV at 300 K). Because soft materials can be so sensitive to small temperature changes, random thermal molecular motions act to define phase behavior and structure. The concepts of thermal equilibrium, phase behavior, and statistical physics are central to both a basic and a more advanced understanding of this field, so we must begin there.

1.2.1 EQUILIBRIUM

In general, when two objects are in good thermal contact with each other (i.e., heat can transfer readily between them), they will eventually come to same temperature. At that point, the objects have reached a state we call *thermal equilibrium*. The timescale over which this occurs is known as the *relaxation time*. For example, if a metal cube is heated to 90°C and placed into a glass of water at 20°C, the two materials will come to thermal equilibrium. The temperature of the water will increase and the temperature of the metal cube will decrease until a common temperature is reached somewhere between 90°C and 20°C. The fact that systems spontaneously relax to equilibrium is one of the most important concepts in thermodynamics. Of the many different kinds of soft materials you will come across, most are usually found in their equilibrium state. Once in equilibrium, a system will tend to stay that way.

A similar concept can be applied to mixing liquids, but the idea of equilibrium between two or more populations of molecules in a liquid requires us to go one step further. In addition to their thermal equilibration, the molecules in a two-component liquid can diffuse around each other, plus they may also interact (by attraction or repulsion). Such interactions can result in the spontaneous formation of stable structures as the different molecules arrange themselves favorably. Take for example, the addition of cold milk to a hot cup of tea. In the cup, the milk is in good thermal contact with the tea, and the two liquids come to thermal equilibrium. The two liquids will also mix gradually (by diffusion or stirring) until both tea and milk are uniformly distributed. Milk, however, is not a simple solution, but actually an aqueous suspension of tiny fat droplets, surrounded by stabilizing proteins. In equilibrium, the fat molecules do not disperse throughout the tea (fat molecules should separate from water), instead, they tend to stay with the proteins, and under the right conditions these stabilized droplets suspend with a uniform distribution throughout the tea. This simple example highlights the fact that there are often fascinating structures underlying apparently simple systems. Throughout this book you will read about many examples of complicated mixed systems, including detergent molecules in water, polymer gels containing a solvent, and particles in suspension in a liquid phase. In most cases, the different populations of molecules are in thermal and chemical equilibrium, so when left for a long time at the same temperature and pressure, the material will not vary in macroscopic structure. Consider that the equilibrium state of a system may not be the most uniform, but in fact can have a complex microstructure.

In addition to materials in equilibrium, there are many examples of systems that, while maintaining a steady state, are in fact, not in equilibrium. Some materials exist in what we call a metastable state, i.e., they are trapped out of equilibrium in a local energy well. Instead of reaching their lowest energy state, they have stabilized in an intermediate structure. There are many different examples of this behavior in polymer or colloidal systems where the constituent particles or molecules can become entangled or jammed. Active systems represent another class of out-of-equilibrium materials. In contrast to equilibrium systems, active fluids and systems of active particles consume energy from the environment. They often exhibit self-generated internal flows and behaviors such as swarming and clustering. Examples of active matter can be seen in self-propelled colloids and ATP-driven biological assembles. We will take a look at an example of an active phase later on in Chapter 7.

1.2.2 PHASE TRANSITIONS

A phase is an equilibrium state of matter with a distinct structure that does not vary in time. This structure can be described by the average molecular arrangement of the component molecules. For example, ice and liquid water are two different phases of the same material, but oil and water can be two different compositional phases in a mixture. In a two-phase system, there will be a clear boundary between the two states of matter. We can map the presence of different phases in a pure or mixed material using a phase diagram. The phase diagram shows the equilibrium conditions under which certain phases occur (i.e., temperature, pressure, composition, etc.); we revisit this idea in more detail in

Section 1.6.

We are most familiar with the three standard phases of matter: the solid, liquid, and gaseous states (Figure 1.2); however, the idea of a phase can be much broader. In fact, there are many different states of matter that can be defined inbetween the solid and gas phases, and we will learn about a number of them in this book. Soft materials often exhibit complex phase behavior with many different phases possible under different conditions (i.e., temperature, composition, pressure, etc.). Understanding the structure and properties of these phases and how we can move between them is at the heart of soft matter science.

At a phase transition, a material will suddenly transform from one state to another; for example, a melting crystalline solid will go from a regular lattice structure to a disordered fluid. This transformation may have an energy associated with it, and we can define the *heat of transformation Q*:

$$Q = Lm \tag{1.1}$$

where L is a constant associated with the particular transition and material, and m is the mass of the material. For example, the latent heat of vaporization L_v for water is 2260 kJ/kg at a temperature of 100°C. This is the amount of heat measured in kilojoules released from vaporizing 1 kg of liquid water. The latent heat of fusion L_f is the amount of heat needed to melt 1 kg of ice. Latent heat represents the stored energy in the lower-temperature phase released on heating the material to a temperature above the phase transition point; Table 1.1 shows some values for common materials. At a phase transition, this latent heat is equal to the change in the *enthalpy* of the system (ΔH).
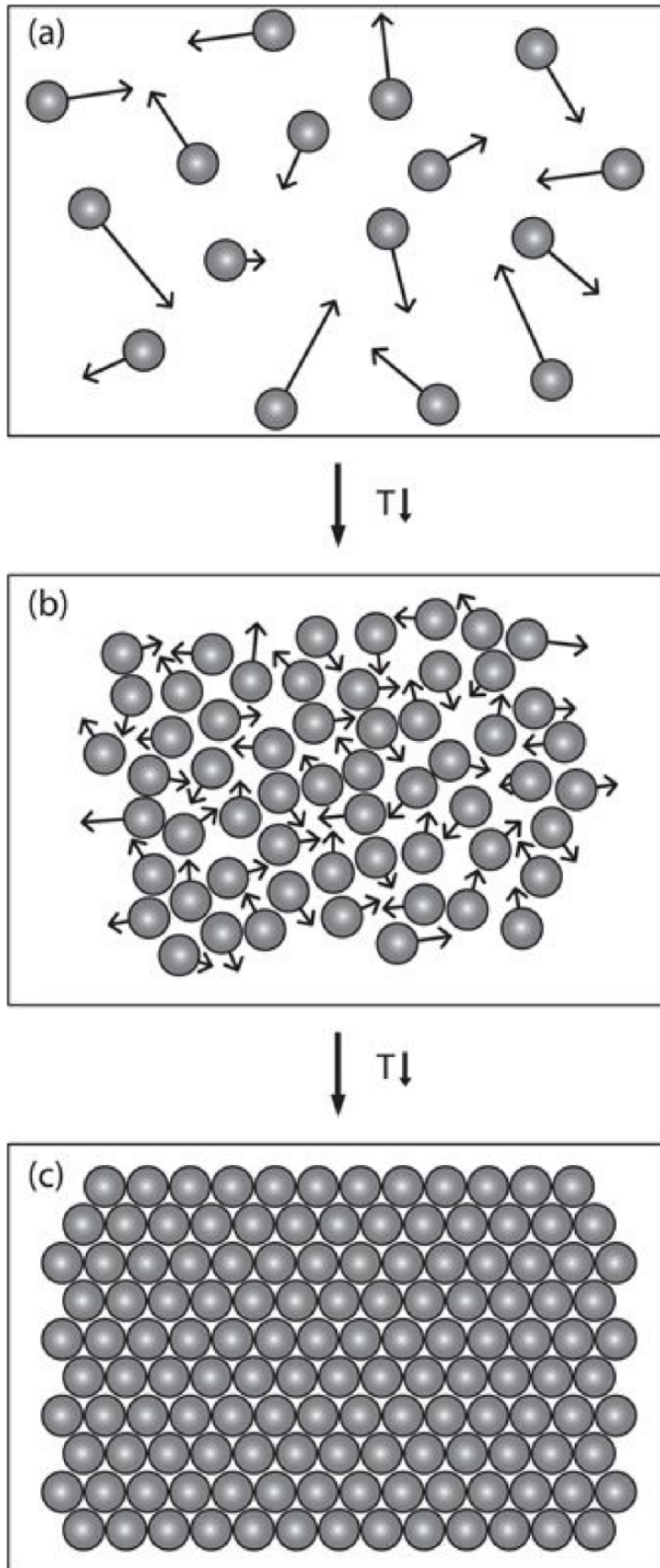
FIGURE 1.2 The three most well-known phases of matter—(a) gas, (b) liquid, and (c) solid—shown as spheres in a box. The material undergoes two phase changes as the temperature (T) is decreased. Each sphere represents an individual molecule or atom in the system, and the arrows indicate molecular velocity vectors. In the case of the solid, atoms in the lattice will vibrate, but they cannot move independently from their lattice positions, so no arrows are shown.

TABLE 1.1

Latent Heat of Fusion L_f and Vaporization L_v for Some Common Materials

Material	L_f (kJ/kg)	L_v (kJ/kg)
Water	334	2,260
Ethanol	109	879
Gold	63.7	1,645
Carbon dioxide	571	205
Copper	209	4,730
Mercury	11.4	295
Silicon	1790	12,800

Note: Notice how these values compare to kT at room temperature.

Phase transitions in a material can be classified as *first order* and continuous (second order). At a first-order phase transition, we will observe a discontinuity of some physical property representative of the degree of order in the system. For example, this could be material density or a calculated measure of order in the material (i.e., an order parameter). If we measure this parameter across the phase boundary, there will be a step, or discontinuity, at the transition point. An example of a typical first-order phase transition is ice melting. At the transition point, the density of the material abruptly changes as we go from ice to liquid water. First-order transitions also have a measurable latent heat. Some phase transitions can be described as "weakly first order." In this case, the enthalpy change associated with that transition is very small. This is often true of phase transitions in soft matter systems. As a result, the enthalpy change may be difficult to measure, making the phase change difficult to detect by thermal properties alone.

Second-order phase transitions do not have an associated latent heat, and their density along with other important order parameters varies continuously across the phase boundary.

1.2.3 SOLIDS, LIQUIDS, AND GASES

When discussing how materials behave in response to a temperature change, we should be familiar with the concept of their "phase." Usually, this means whether the material is a solid, a liquid, or a gas, and a brief review of these basic states will help us to understand many concepts in soft materials. A gas model, such as the ideal gas can be used to describe dilute systems with minimal inter-particle interactions. However, in the denser liquid state, inter-particle interactions become important, and we will describe their effects in the following sections.

(a)   (b)

FIGURE 1.3 Examples of different solids, (a) amethyst, a crystalline solid and (b) glassy amber, an amorphous solid.

Solids can be either crystalline or amorphous (Figure 1.3), but in both cases the atoms that form the solid are very close together. The material is difficult to deform and has a well-defined shape. On heating, some increase in the volume may occur, but this change is small in comparison to the overall size of the object. Crystalline solids are highly regular in structure, have long-range order, and can be characterized by a unit cell, the smallest possible repeat unit in the crystal. Metals, salts, and precious stones are examples of crystalline solids.

There are also many amorphous solids around us, in fact probably more than there are crystalline solids. Most of the amorphous solids that you will see are plastics and glasses. These materials do not have a long-range regular structure: The molecules that make them up are organized randomly, "frozen" into that arrangement as the material was cooled during the manufacturing process.

In a liquid, the molecules are not frozen into a set position, but are free to move throughout the material. Liquids are relatively dense and incompressible compared to the gas phase; therefore, intermolecular forces play an important role in the properties of the liquid. Intermolecular forces are extremely important in soft materials and are discussed later in this chapter. The liquid state is the most relevant of the three basic phases of matter, and many of the materials and phases we will discuss have fluid-like properties. Another definition of soft materials is that they are "structured fluids": The material may flow or exhibit diffusion properties in common with simple liquids, but there is some degree of ordering that can be measured in its molecular arrangement.

1.2.4 THE IDEAL GAS

In the gaseous phase, we can usually think about the molecules being on average very far apart from each other and moving very quickly. The behavior of a gas can be described using the *ideal gas model*. In an ideal gas, we assume that:

1. The molecules (or atoms) in the gas are very small point masses and therefore do not take up any volume
2. Intermolecular forces are negligible

This successful model for dilute gases works very well for systems that are far from a phase transition and not under high pressure. That is, for the model to work, we make sure that the molecules are not, on average, sufficiently close to each other to experience any significant intermolecular forces, or that their physical size needs to be taken into account when describing their behavior.

The speeds of the molecules in an ideal gas are distributed over a wide range of values. At a given instant in time, if you were to take a snapshot of the gas, measure the instantaneous speed of every molecule, and plot the results as a histogram, you would obtain a Maxwell-Boltzmann distribution of speeds. Some examples of this distribution function at different temperatures are shown in Figure 1.4; higher temperatures lead to a greater proportion of molecules moving with high velocities, although there are always significant numbers of slow-moving molecules in any system as a result of the random collisions they undergo.
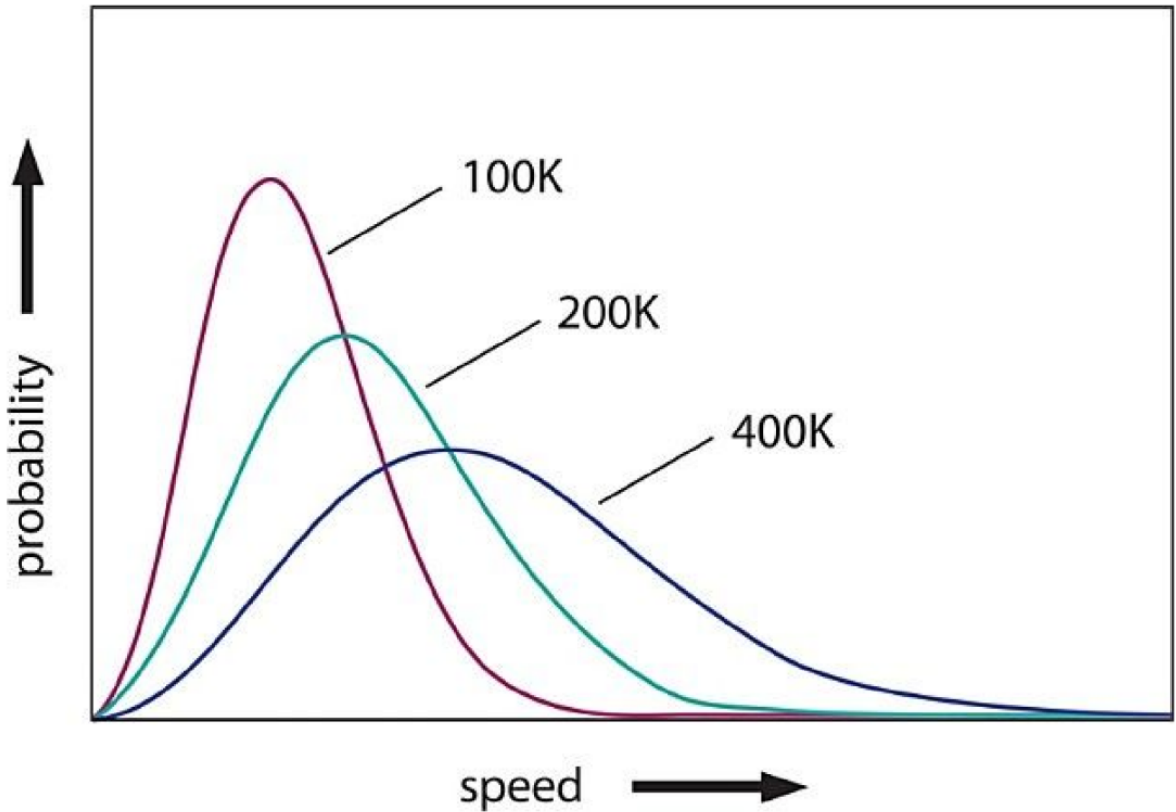
FIGURE 1.4 The Maxwell-Boltzmann distribution for different temperature gases. At three different temperatures, the plot represents the probability of a gas molecule in the system having a particular speed.

The average kinetic energy *KE* of a molecule in a monoatomic ideal gas is given by:

$$KE_{av} = \tfrac{3}{2} k_B T \qquad (1.2)$$

½ *KT* for each translational degree of freedom (*x*, *y*, and *z*).

So for a single molecule of mass *m* we can use:

$$\tfrac{1}{2} m v^{-2} = \tfrac{3}{2} k_B T \qquad (1.3)$$

and thus obtain an equation for the root mean square (rms) velocity of a molecule in the gas:

$$v_{rms} = \sqrt{\tfrac{3 k_B T}{m}} \qquad (1.4)$$

This value for the rms velocity falls close to the peak of the curve in Figure 1.4, although the value is always slightly shifted to the right of the peak due to the asymmetry of the curve. The exact shape of this curve is given by the following equation:

$$D(v) = \left(\tfrac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-mv^2/2k_B T} \qquad (1.5)$$

where *D(v)* is the probability distribution for molecular speed in the gas. At high temperatures, this curve dies away exponentially. A simple derivation for this formula can be found in the popular thermodynamics textbook, *An Introduction to Thermal Physics* by Daniel V. Schroder.[2]

The macroscopic properties of the ideal gas can be described very well in terms of pressure *P*, temperature *T*, and volume *V* using the *ideal gas equation*.

$$PV = nRT \qquad (1.6)$$

This useful and well-known equation relates these parameters using the ideal gas constant (*R* = 8.314

J/K · mol) for *n* moles of gas.

Although the ideal gas is not a good model for soft matter—which is much more condensed than a gas of course—it is an important to think about, as it helps us to gain intuition when thinking about molecular motions in fluid systems and intermolecular interactions. Soft materials are usually condensed fluid phases, in which excluded volume and intermolecular interactions play a very important role. They are also very temperature-sensitive and thermal molecular motions contribute significantly to their macroscopic properties.

1.3   PHASE DIAGRAMS

Materials can change their phase as a function of a variety of different thermodynamic variables, such as temperature, pressure, volume, or concentration in a mixture. A diagram of this phase behavior, or "phase diagram," can be constructed by plotting the parameter ranges over which different phases occur. The simplest form of the phase diagram plots the position of the phases as a function of just two parameters, such as the pressure/temperature phase diagram for water shown in Figure 1.5; however, it is also common to see graphical representations of three or even four different parameters on the same diagram. We can refer to the boundaries of phase existence in terms of thermodynamic parameters as the phase's position in "phase space." If a material system exhibits several different phases, then the phase diagram can become quite complicated.
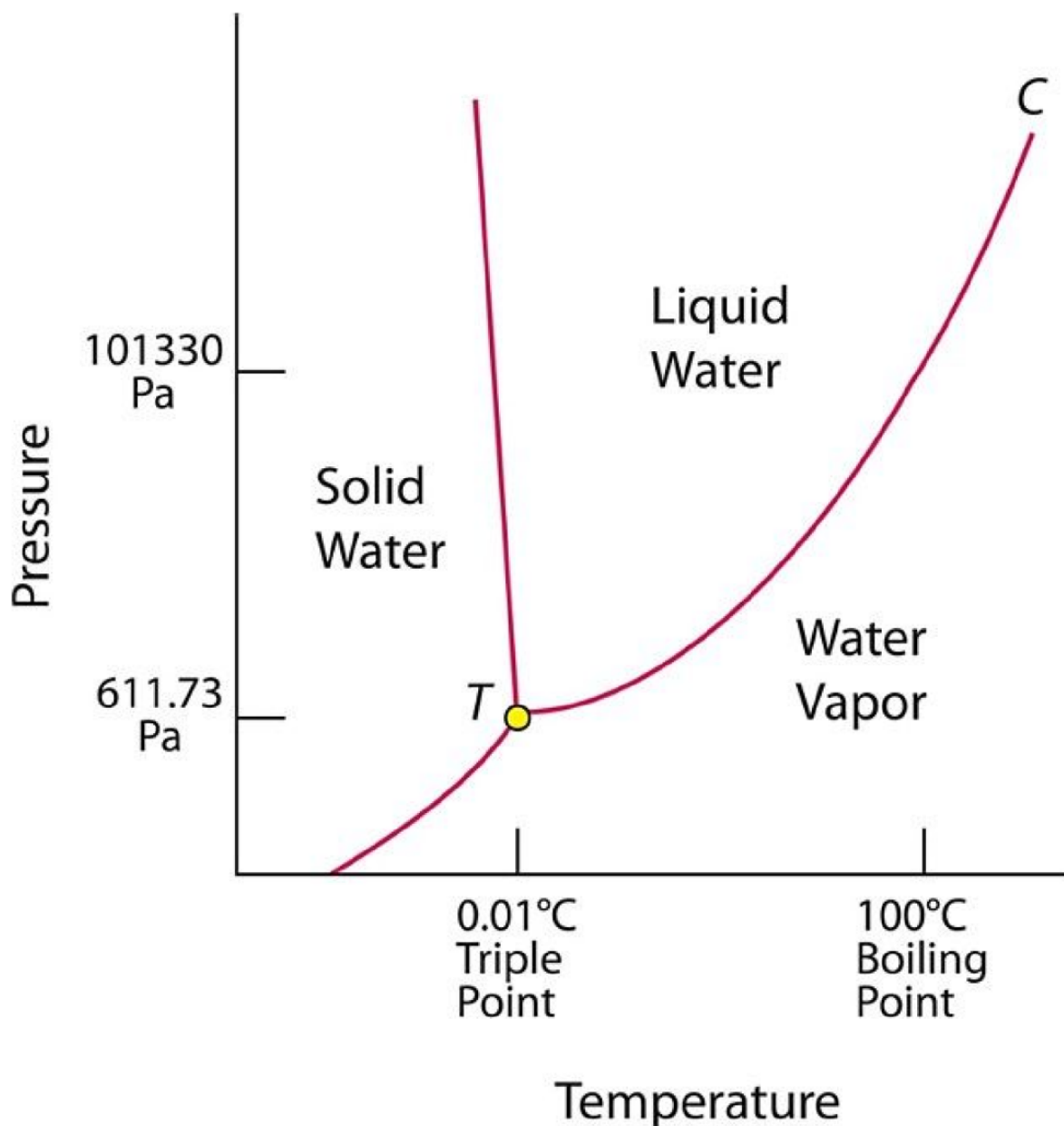
FIGURE 1.5 The pressure/temperature phase diagram for water indicating the triple point at point *T* and a critical point at *C*. The phase boundaries are indicated by the solid red lines.

Looking at the phase diagram for water, we can identify some interesting points. The solid red lines represent boundaries between the different phases, and as a reference point, the boiling point of water at atmospheric pressure (101,330 Pa or 1 atm at sea level), is indicated. As we can see from the diagram in Figure 1.5, the temperature at which water boils can vary significantly with a change in pressure; even relatively small changes in pressure can give a noticeable difference, and this effect can be easily tested in real life. At high altitude, food takes longer to cook because water boils at a lower temperature at lower pressures; in fact, in the "mile-high" city of Denver, Colorado, the air pressure is so reduced that water boils at close to 95°C.

Point *T* in Figure 1.5 marks the meeting point of the three different phase boundaries and is known as the *triple point*. The triple point occurs at a unique temperature, volume, and pressure for a material, and at this point all three phases (solid, liquid, and gas) may coexist. The triple point of water is particularly important as it provides the definition of the Kelvin (K), the SI unit of thermodynamic temperature. In 1954, the General Conference on Weights and Measures (*Conférence Générale des Poids et Mesures*,

GCPM), an international organization responsible for the SI system of measures, defined the Kelvin unit as "the fraction 1/273.16 of the thermodynamic temperature of the triple point of water."[3]

At point *C*, we can note another interesting feature of the diagram. The line that defines the transition between liquid and gas is discontinuous and ends at this point. This is a *critical point*. Below the critical point, the phase transition is discontinuous, with an associated latent heat (first order), but above this line there is no defined phase transition from liquid to gas, and the density of the material varies continuously.

THE CLAUSIUS-CLAPEYRON EQUATION

The lines on a phase diagram represent the boundaries between thermodynamically stable phases, and close to these lines it takes just a very small change in temperature or pressure (some other parameter) to go from one phase to another.

Let us consider the well-known Pressure-Temperature phase diagram for water shown in Figure 1.5. Water in the liquid phase will have a Gibbs free energy G_l, and in the gas phase, a Gibbs free energy of G_g.

If we define a point that lies on the phase boundary between the liquid and gas phases, then at that point,

$$Gl = Gg \qquad (1.7)$$

This is true at any point on the phase boundary line. To move a small distance along the line, we change the temperature by dT and the pressure by dP; thus,

$$dGl = dGg \qquad (1.8)$$

Now, the Gibbs free energy is defined as

$$G = U - TS + PV \qquad (1.9)$$

Where S represents entropy using the first law of thermodynamics, $U = Q - W$ at our phase boundary, where U is the internal energy of the materials, Q represents heat flow and W is work we can write (see if you can make this step):

$$-SldT + VldP = -SgdT + VgdP \qquad (1.10)$$

This equation can then be rearranged to:

$$dPdT = Sg - Sl Vg - Vl \qquad (1.11)$$

Since we know that the heat required for the transition $\Delta Q = T\Delta S$ is equal to the latent heat L, this equation is rewritten as:

$$dPdT = LT \Delta Vl \qquad (1.12)$$

This result is the *Clausius-Clapeyron equation* and describes the shapes of the phase boundary lines on a pressure temperature (*PT*) phase diagram. In particular, this expression is useful for calculating the vapor pressures of different materials (for either evaporation or sublimation).

1.4 DIFFUSION AND RANDOM WALKS

Add a few drops of ink to a glass of water without stirring and you soon observe how the ink gradually spreads through the water, moving from areas of high concentration to areas of lower concentration. This mass transport process can be summarized by Fick's law:

$$J = -Ddcdx \qquad (1.13)$$

where *J* is the molecule flux (or number of molecules passing through a unit area per unit time). *D* is a constant, the diffusion coefficient, and *c* is the molecular number density. Therefore, dc/dx represents a molecular concentration gradient.

Diffusion is quite well known in solutions and gases, but also takes place in soft materials, for example, colloidal particles suspended in a liquid. Large particles, when placed in a fluid-like medium, will diffuse through the solution as a result of random thermal motions by the liquid molecules. The larger particles dispersed in the medium are subject to a phenomenon known as *Brownian motion*. We alluded to this phenomenon when discussing the thermal motion of particles. In a system comparable to the ideal gas, all particles in a system at a temperature *T* move randomly with a distribution of speeds. The speed distribution is represented by the Maxwell-Boltzmann distribution (Figure 1.4), and the

average speed is related to the particle mass m. When a large particle or molecule is placed into a fluid comprised of smaller particles, many collisions between the different-size particles take place. All of the particles in the system are subject to random forces as a result of these collisions. The smaller particles move around rapidly and collide often with the larger particles, and this random bombardment results in a net force on the larger particle that will vary in direction with time. The overall average net force on a particle will be zero measured over a long time; however, at any specific time the random nature of the collisions will cause the particle to experience a fluctuating force. The large particle will accelerate in response to that changing force and move through the medium with a Brownian motion. Occasionally, the random force can be large, resulting in a significant jump in the particle's trajectory.

This kind of motion was first studied by a Scottish scientist, Robert Brown, in 1828. Brown was a botanist and observed the phenomenon as he looked at pollen grains on the surface of water. He noticed a random spontaneous motion of the grains and investigated the effect with a variety of small particles. It was not until the later nineteenth century, however, that this phenomenon was related to research being carried out on the kinetic theory of gases and the ideal gas. In fact, it was Einstein who published the definitive paper on the link between the statistical movement of particles and the macroscopic Brownian motion effect.[4] Interestingly, the idea was not generally accepted at the time because concepts of atoms and molecules were still in their infancy.

The motion of the Brownian particle can be described as a *random walk* because the particle appears to move disjointedly in random directions (Figure 1.6). An estimate for the 3D diffusion of a particle in solution can therefore be made using the following equation:

$$\lambda = (6Dt)1/2 \qquad (1.14)$$

where λ represents the characteristic displacement of the particle at time t, and D is the diffusion coefficient. λ gives a measure of the size of the space explored by the particle in its random path after a certain time, or the average size of a random walk over time, t. This formula can be used to describe the diffusion of particles or molecules in a fluid over time. In real systems, the shape of the large particle is a factor in the diffusion rate, and at the length scales applicable to some soft materials, viscous drag on the particle becomes important.
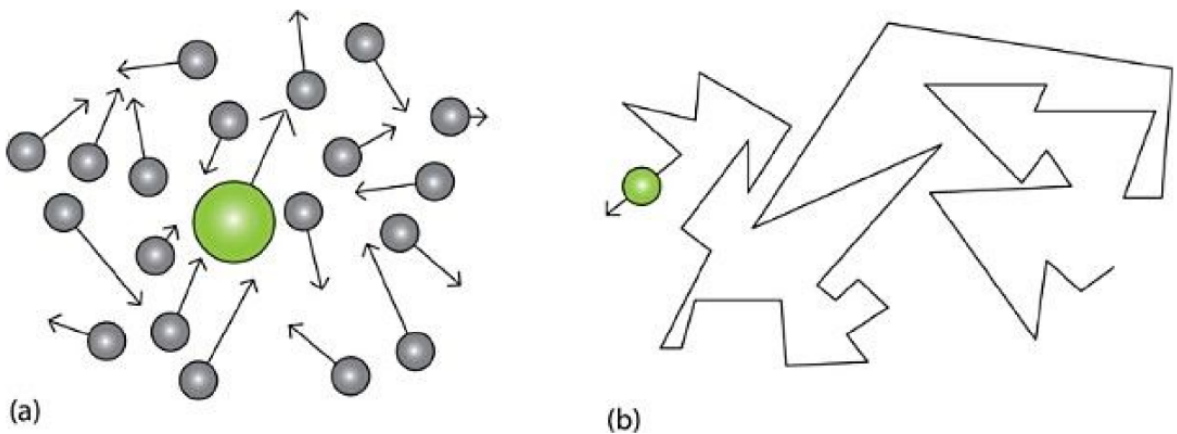
FIGURE 1.6 (a) Small particles bombard a larger (green) particle randomly, giving it a net motion. (b) If we watch the motion of the green particle over time, it can be described as taking a random walk.

The *Stokes-Einstein equation* that follows provides us with the diffusion coefficient for a spherical particle suspended in a liquid by taking into account the drag force on the particle:

$$D = kBT6\pi \eta r \qquad (1.15)$$

Here, η is the viscosity of the medium, and r is the effective radius of the particle or molecule. As we

will see in Chapter 6, the Brownian motion described here is applicable not only to spherical colloidal particles in solution, but also to the configuration of a polymer chain. These arguments relate the diffusion process to the kinetics of an ideal gas, so do not take into account intermolecular interactions. Additional attractive or repulsive forces within a fluid can have a significant effect on diffusion rates in soft materials.

FICK'S FIRST LAW AND THE DIFFUSION CONSTANT

Fick's first law describes the diffusion rate of molecules in a concentration gradient.

Let us define a plane of area, A, in a concentration gradient. Particles are more concentrated on one side of the plane. The particles move randomly and can pass through the plane from x to $x + \Delta x$. And back in 1D. The number of particles on the left side of the plane is $N(x)$ and on the right, $N(x + \Delta x)$.

Since the particles move randomly back and forth on both sides, there is a 50% probability that a particle on either side will cross the volume in time, τ, therefore the net flow of particles to the right is equal to,

$$\Delta N = -\frac{1}{2}[N(x + \Delta x) - N(x)] \tag{1.16}$$

This gives us a flux, J of molecules crossing the plane in time τ as,

$$J = -\frac{1}{2}[N(x + \Delta x) - N(x)]\Delta\tau \tag{1.17}$$

If we let the particle concentration, $c(x) = N(x)A\Delta x$, then we can rewrite as,

$$J = -\frac{\Delta x^2}{2\tau}[c(x + \Delta x) - c(x)]\Delta x \tag{1.18}$$

Then, by defining, D, the diffusion constant as,

$$D = \frac{\Delta x^2}{2\tau} \tag{1.19}$$

We obtain Fick's first law,

$$J = -D\frac{dc(x)}{dx} \tag{1.20}$$

and see that the diffusion rate is proportional to the concentration gradient and the diffusion constant. Incidentally, then we can write the useful relation for 1D,

$$\Delta x = 2D\tau \tag{1.21}$$

where Δx represents a characteristic diffusion length over which a particle is expected to travel in time, τ. This can be expanded to two- and three-dimensional diffusion, adding the additional degrees of freedom and defining λ as the characteristic diffusion length, so $\lambda_{2D} = 4D\tau$ and $\lambda_{3D} = 6D\tau$.

QUESTIONS

Soft Materials and their Characteristics

1. Soft materials can be described as having a "large response function"; they deform readily under external stimuli. Look around you and identify some soft materials. How many of the materials around you are crystalline solids?
2. Give some examples of non-Newtonian fluids in everyday life. Would you consider these materials "soft matter"? Explain your answer.

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3. Which of these materials can be considered an equilibrium phase of matter? (a) a pile of sand, (b) a diamond, (c) milk, and (d) a stretched elastic band.
4. What is the physical significance of the negative slope of the ice/liquid water phase boundary on the water pressure/temperature phase diagram?
5. The pressure/temperature phase diagram for water shows that increasing pressure can melt ice. A commonly stated example of this effect is that the pressure on the blade of an ice skate melts a layer of ice beneath the skate, allowing the skater to glide smoothly. Do you think this idea is true? Use the Clausius-Clapeyron equation to investigate. What other factors could contribute to smooth skating?

6. A pollen grain on the surface of a lake appears to move around in a random, jerky motion. Can you explain this observed phenomenon to a high school student?

7. A droplet containing a concentrated solution of protein molecules is deposited at one end of a narrow microfluidic channel, 3 mm long, containing water. Assuming that the sole mechanism for molecular transport is diffusion, calculate the average time it will take for the proteins to reach the other end of the channel. You can assume that the protein molecules are 5 nm in diameter to estimate the diffusion constant, D.

8. Fick's 1st law gives us the rate of diffusion in a steady state system with a fixed concentration gradient, but does not take into account the time dependent variation in that concentration gradient. Fick's 2nd law takes the variation of concentration over time into account. Can you derive this equation using a similar approach to that used to derive Fick's first law?

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2}$$

9. In an ideal gas, the distribution of molecular speeds is given by the Maxwell distribution function,

$$D(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi v^2 e^{-mv^2/2k_B T}$$

where m is the molecular mass, T is the temperature, k is the Boltzmann constant, and v is the molecular speed. Use this equation to derive a simple expression for the most likely speed in the gas. Why does this differ from the rms speed?

10. The van der Waals equation of state,

$$\left(P + \frac{aN^2}{V^2}\right)(V - nb) = nRT,$$

relaxes the assumptions of the ideal gas model by allowing for particle volume and inter-particle interactions. In this equation, P is the pressure, V is the volume, n is the number of moles, and R is the ideal gas constant. Two coefficients are introduced: the Van der Waals coefficients a and b. Constant a provides a correction for intermolecular forces and b corrects for finite molecular size (i.e., two particles cannot be in the same place at the same time). Notice how the equation reverts to the ideal gas equation when these constants are zero.

In an aqueous suspension of 1 μm radius particles, there are 10^8 particles/cm^3. Calculate the volume fraction occupied by the particles (the excluded volume). Compare your answer using He atoms and 10 μm radius particles. How does excluded volume fraction scale with particle radius?

11. Using the Clausius-Clapeyron equation, estimate the boiling point of water on top of Mount Everest.

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Self-assembly and Structure in Soft Matter

LEARNING OBJECTIVES

1. Become familiar with the concept of self-assembly and structure in soft materials
2. Review basic physical concepts important in soft structure formation including intermolecular forces
3. Learn about fractals and other ways to describe amorphous structures
4. Introduce the mechanical properties of soft materials

2.1   SELF-ASSEMBLY

The term *self-assembly* has become ubiquitous in materials science over the past few decades, particularly in the field of soft matter and in related fields at the convergence of soft and hard materials. It is important for us to understand this concept, as it will be used frequently throughout the book. Self-assembly can be described as spontaneous molecular ordering resulting from the balance between entropic and intermolecular forces in a material. A self-assembled system or state is one that forms without external mechanical manipulation of the components. Instead, the elements of the material (molecules, particles, etc.) are subject to forces between these elements and thereby spontaneously adopt a particular configuration, or structure by coming to either an equilibrium or locally stable state.

Visualize a system composed of particles moving freely in a fluid at room temperature. The particles are attracted to each other; but, Brownian motion at room temperature keeps the particles constantly moving randomly. Here, we can see that there is competition between the attractive interaction—driving particle clustering, and the disordering effects of the thermal environment. This delicate balance determines the equilibrium structure of the material at a particular temperature. If the temperature is too high, thermal motions will prevent the particles from condensing into a solid structure of clustered particles; however, if the temperature is low, thermal motions will not be large enough to overcome the attractive potential, and the particles will stick together. This simple idea can be expanded to systems with many complicated interparticle interaction forces. The interplay between intermolecular forces (attractive or repulsive), and thermal motion drives the self-assembly of an enormous range of soft structures and phases, many of which are described in this book.

Self-assembly into a soft phase is most likely to occur if the material is in a fluid-like or semifluid-like state because for ordering to arise out of random fluctuations, the molecules need to be able to move around and try out different arrangements. It is statistically possible for the constituent molecules in a material to have any possible configuration, however unlikely, but the final structure is determined by the most likely and therefore energetically favorable molecular arrangement. Figure 2.1 shows two interesting examples of self-assembly in action: the spontaneous folding of a complex protein structure and the formation of a liquid crystal phase.

The term *self-assembly* is also often applied to the deposition of thin films on surfaces (for example, self-assembled monolayers, [SAMs]) in the field of nanoscience. The formation of self-assembled films

can involve a variety of interactions, such as electrostatics, van der Waals forces, or even a chemical bond. Such non-crystalline molecular films should also fall under the umbrella of soft matter as they are weakly or unordered systems. They are, however, not equilibrium thermodynamic phases.

(a)
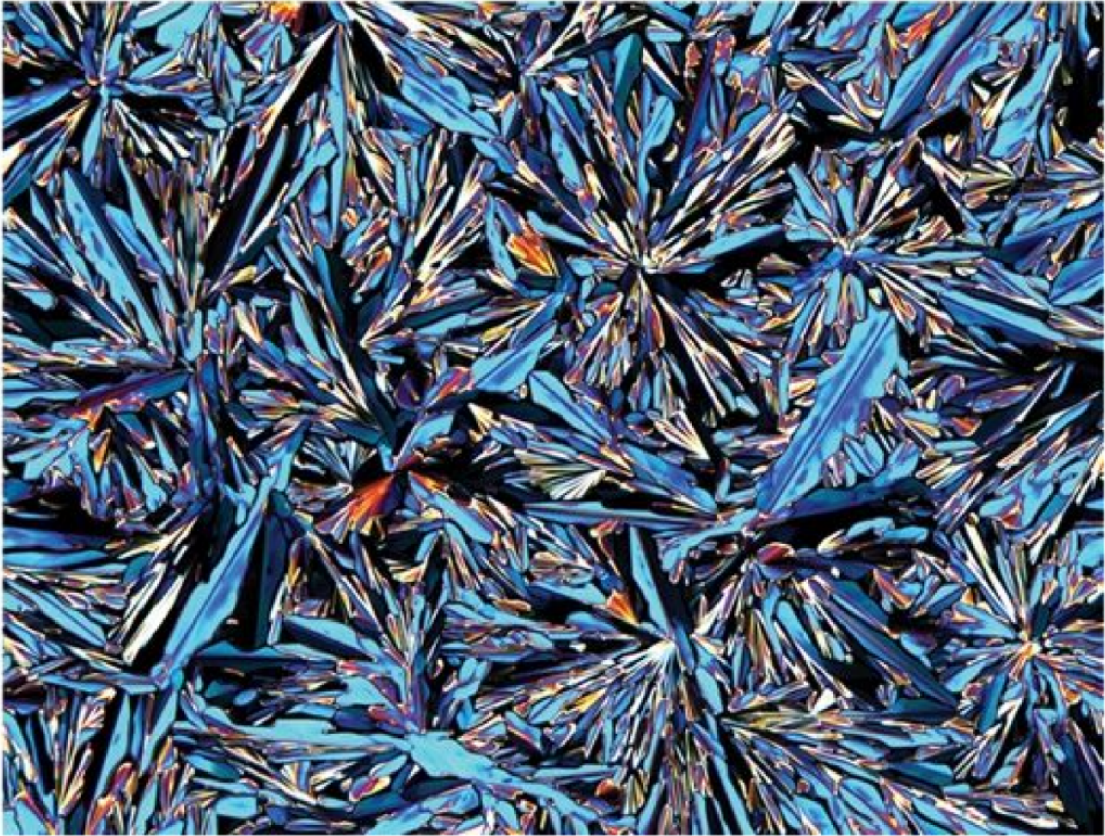
(b)

FIGURE 2.1 Two examples of self-assembly in action: (a) A ribbon diagram of the magnesium membrane transporter protein CorA (rendered using Pymol from Protein Data Bank file 2lUB). Proteins composed of a long amino acid chain assemble into a highly specific shape through chain–chain interactions. (b) Polarized microscopy image of the liquid crystal B1 phase in which banana-shaped molecules pack together to form a columnar liquid crystal phase with a characteristic defect texture.

   To think about self-assembly in this way, we can compare two different methods for depositing a molecular pattern on a surface. First, I could coat a substrate with positively charged ions in a particular pattern, then immerse the substrate in a solution containing a negatively charged polymer. The negatively charged polymer molecules move randomly in the solution until they encounter a positively charged area on the substrate, and stick. In this way, the polymer self-assembles into a patterned coating on the substrate by electrostatic attraction. Figure 2.2 shows an example of a polymer self-assembly formed in this way. An alternate strategy would be to directly paint (by some clever method) the charged polymer onto the surface in the required pattern. This second method does not involve self-assembly as the coating is directed mechanically and not by thermal fluctuations and intermolecular forces. As you can imagine, self-assembly can be a very attractive way to obtain interesting two- and three-dimensional structures with little effort—if the molecules do what you want them to do!