INTRODUCTION TO MODERN STATISTICAL MECHANICS

David Chandler

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David Chandler
University of California, Berkeley

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Preface

This book presents the material I use in my lectures on elementary statistical mechanics, a one-semester course I have taught at the University of Illinois and at the University of Pennsylvania. Students enter this course with some knowledge of thermodynamics, the Boltzmann distribution law, and simple quantum mechanics, usually acquired from undergraduate physical chemistry or modern physics at the level of Moore's *Physical Chemistry*. The purpose of my lectures is not only to give the students a deeper understanding of thermodynamics and the principles of equilibrium statistical mechanics, but also to introduce them to the modern topics of Monte Carlo sampling, the renormalization group theory, and the fluctuation-dissipation theorem. The ideas surrounding these topics have revolutionized the subject of statistical mechanics, and it is largely due to them that the practitioners of statistical mechanics now play a significant role in the current research and discoveries of fields ranging from molecular biology to material science and engineering, to chemical structure and dynamics, and even to high energy particle physics. Thus, in my opinion, no serious student of the natural sciences is properly educated without some understanding of these modern topics and concepts such as "order parameters" and "correlation functions." It is also my opinion and experience that these topics and concepts can and should be covered in a one-semester introductory course.

To cover this material at an introductory level, I make frequent use of simplified models. In this way, I can keep the mathematics relatively simple yet still describe many of the sophisticated ideas in the field. I refrain from treating advanced theoretical techniques (e.g., diagrammatic and field theoretic methods) even though these are among my favorite topics for research. I also treat only briefly the traditional statistical thermodynamics subjects of ideal gases and gas phase chemical equilibria. In the former case, this book should provide necessary background for the interested student to pursue advanced courses or readings in many-body theory. In the latter case, since there are already so many excellent texts devoted to these topics, it is wastefully redundant to spend much time on them here. Furthermore, these subjects have now become rather standard in the materials presented in undergraduate physical chemistry courses.

I have adopted a particular sequence of topics that perhaps deserves some comment. The first two chapters are devoted entirely to macroscopic thermodynamics, and microscopic statistical principles do not appear until Chapter 3. In Chapter 1, I review elementary thermodynamics and introduce Legendre transforms, and in Chapter 2, I develop the concepts of phase equilibria and stability. I use this strategy because the techniques and language introduced here greatly add to the swiftness with which the principles of statistical mechanics can be understood and applied. Another approach could begin with the first half of Chapter 3 where the second law appears as the direct consequence of the statistical assumption that macroscopic equilibrium is the state of greatest randomness. Then the thermodynamics in Chapters 1 and 2 could be combined with the associated material in the latter half of Chapter 3 and in Chapters 4 and 5. The different ensembles and the role of fluctuations are treated in Chapter 3. Chapters 4 and 5 refer to my discussions of the statistical mechanics of non-interacting ideal systems and phase transformations, respectively.

The treatment of phase transitions in Chapter 5 focuses on the Ising model. Within the context of that model, I discuss both mean field approximations and the renormalization group theory. In the latter case, I know of no other introductory text presenting a self-contained picture of this important subject. Yet, as I learned from Humphrey Maris and Leo Kadanoff's pedagogical article,* it is possible to teach this material at an elementary level and bring the students to the point where they can perform renormalization group calculations for problem set exercises.

Chapter 6 presents another very important subject not treated in other texts of this level—the Monte Carlo method. Here, I again use the Ising model as a concrete basis for discussion. The two-dimensional case illustrates the behavior of fluctuations in a system

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* H. J. Maris and L. J. Kadanoff, *Am. J. Phys.* **46**, 652 (1978).

which, if large enough, could exhibit true phase equilibria and interfacial phenomena. The one-dimensional case serves to illustrate principles of quantum Monte Carlo. The Metropolis algorithm is described, and programs are provided for the student to experiment with a microcomputer and explore the power and limitations of the method.

In Chapter 7, we consider the equilibrium statistical mechanics of classical fluids. In chemistry, this is a very important topic since it provides the basis for understanding solvation. Some of the topics, such as the Maxwell-Boltzmann velocity distribution, are rather standard. But others are less so. In particular, definitions and descriptions of pair correlation functions for both simple and molecular fluids are presented, the connection between these functions and X-ray scattering cross sections is derived, and their relationship to chemical equilibria in solutions is discussed. Finally, an illustration of Monte Carlo for a two-dimensional classical fluid of hard disks is presented which the student can run on a microcomputer.

The last chapter concerns dynamics—relaxation and molecular motion in macroscopic systems that are close to or at equilibrium. In particular, I discuss time correlation functions, the fluctuation-dissipation theorem and its consequences for understanding chemical kinetics, self-diffusion, absorption, and friction. Once again, in the context of modern science, these are very important and basic topics. But in terms of teaching the principles of non-equilibrium statistical mechanics, the subject has too often been considered as an advanced or special topic. I am not sure why this is the case. A glance at Chapter 8 shows that one may derive the principal results such as the fluctuation-dissipation theorem with only a few lines of algebra, and without recourse to sophisticated mathematical methods (e.g., propagators, projectors, and complex variables).

In all the chapters, I assume the reader has mastered the mathematical methods of a typical three-semester undergraduate calculus course. With that training, the student may find some of the mathematics challenging yet manageable. In this context, the most difficult portion of the book is Chapters 3 and 4 where the concepts of probability statistics are first encountered. But since the material in these chapters is rather standard, even students with a weak background but access to a library have been able to rise to the occasion. Students who have taken the course based on this text have been advanced undergraduates or beginning graduates majoring in biochemistry, chemistry, chemical engineering, or physics. They usually master the material well enough to answer most of the numerous Exercise questions. These Exercises form an integral part of the book, reinforcing and testing every subject, and in some cases my only coverage of certain topics is found in the Exercises.

After their study of this book, I do hope a significant number of students will pursue more advanced treatments of the subjects than those I present here. For that reason, I have purposely peppered the text with comments and questions to spur the students' curiosity and perhaps send them to the library for more reading. The Bibliography at the end of each chapter suggests places for the students to start this reading. In this sense, this book serves as both an introduction and a guide to a discipline too broad and powerful for any one text to adequately describe.

In creating this book, I have benefited from the help of many people. John Wheeler has given his time unstintingly to help weed out logical errors and points of confusion. Encouragement and advice from Attila Szabo are greatly appreciated. I am also grateful to John Light for his helpful review of an earlier version of the text. Several students and my wife, Elaine, wrote and tested the computer programs included in the book. Elaine provided a great deal of advice on the content of the book as well. Finally, I am indebted to Evelyn Carlier and Sandy Smith, respectively, for their expert manuscript preparations of the first and final versions of the text.

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D. C.

Contents

INTRODUCTION TO MODERN STATISTICAL MECHANICS

CHAPTER 1

Thermodynamics, Fundamentals

Statistical mechanics is the theory with which we analyze the behavior of natural or spontaneous fluctuations. It is the ubiquitous presence of fluctuations that makes observations interesting and worthwhile. Indeed, without such random processes, liquids would not boil, the sky would not scatter light, indeed every dynamic process in life would cease. It is also true that it is the very nature of these fluctuations that continuously drives all things toward ever-increasing chaos and the eventual demise of any structure. (Fortunately, the time scales for these eventualities are often very long, and the destruction of the world around us by natural fluctuations is not something worth worrying about.) Statistical mechanics and its macroscopic counterpart, thermodynamics, form the mathematical theory with which we can understand the magnitudes and time scales of these fluctuations, and the concomitant stability or instability of structures that spontaneous fluctuations inevitably destroy.

The presence of fluctuations is a consequence of the complexity of the systems we observe. Macroscopic systems are composed of many particles—so many particles that it is impossible to completely control or specify the system to an extent that would perfectly prescribe the evolution of the system in a deterministic fashion. Ignorance, therefore, is a law of nature for many particle systems, and this ignorance leads us to a statistical description of observations and the admittance of ever-present fluctuations.

Even those observed macroscopic properties we conceive of as being static are irrevocably tied to the statistical laws governing dynamical fluctuations. As an illustration, consider a dilute gas that obeys the ideal gas equation of state: $pV = nRT$ (p is pressure, V is the volume of the container, n is the number of moles, T is temperature, and R is the gas constant). In Chapter 3, we will show that this equation is equivalent to a formula for the mean square density fluctuations in the gas. The equation can be regarded entirely as a consequence of a particular class of statistics (in this case, the absence of correlations between density fluctuations occurring at different points in space), and need not be associated with any details of the molecular species in the system. Further, if these (uncorrelated) density fluctuations ceased to exist, the pressure would also vanish.

As we will see later in Chapter 8, we can also consider the correlation or influence of a fluctuation occurring at one instant with those occurring at other points in time, and these considerations will tell us about the process of relaxation or equilibration from nonequilibrium or unstable states of materials. But before we venture deeply into this subject of characterizing fluctuations, it is useful to begin by considering what is meant by "equilibrium" and the energetics associated with removing macroscopic systems from equilibrium. This is the subject of thermodynamics. While many readers of this book may be somewhat familiar with this subject, we take this point as our beginning because of its central importance to statistical mechanics. As we will discuss in Chapter 3, the reversible work or energetics associated with spontaneous fluctuations determines the likelihood of their occurrence. In fact, the celebrated second law of thermodynamics can be phrased as the statement that at equilibrium, all fluctuations consistent with the same energetics are equally likely. Before discussing the second law, however, we need to review the first law and some definitions too.

1.1 First Law of Thermodynamics and Equilibrium

The first law is concerned with the *internal energy*. The quantity, to which we give the symbol E, is defined as the total energy of the system. We postulate that it obeys two properties. First, internal energy is *extensive*. That means it is additive. For example, consider the composite system pictured in Fig. 1.1. By saying that the internal energy is extensive, we mean

$$E = E_1 + E_2.$$

Due to this additivity, extensive properties depend linearly on the size of the system. In other words, if we double the size of the system keeping other things fixed, the energy of the system will double.

The second postulated property is that we assume energy is

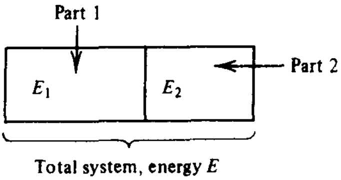

Fig. 1.1. Composite system.

conserved. This means that if the energy of a system changes, it must be as a result of doing something to the system—that is, allowing some form of energy to flow into or out of the system. One thing we can do is perform mechanical work. What else is there? Empirically we know that the energy of a system can be changed by doing work on the system, or by allowing heat to flow into the system. Therefore, we write as a definition of *heat*:

$$\boxed{dE = \text{đ}Q + \text{đ}W.}$$

This equation is usually referred to as the first law. In it, $\text{đ}W$ is the differential work done *on* the system (manipulating mechanical constraints), and $\text{đ}Q$ is the differential heat flow into the system. The work term has the general form

$$\text{đ}W = \mathbf{f} \cdot d\mathbf{X},$$

where $\mathbf{f}$ is the applied "force," and $\mathbf{X}$ stands for a mechanical extensive variable. A familiar example is

$$\text{đ}W = -p_{\text{ext}}\, dV,$$

where V is the volume of a bulk system, and p_{ext} is the external pressure. As another example,

$$\text{đ}W = f\, dL,$$

where here f is the tension applied to a rubber band and L is the length of that rubber band. In general, there are many mechanical extensive variables, and their changes involve work. The abbreviated vector notation, $\mathbf{f} \cdot d\mathbf{X}$, is used to indicate all the associated work terms, $f_1\, dX_1 + f_2\, dX_2 + \cdots$.

The definition of heat is really not complete, however, unless we postulate a means to control it. *Adiabatic walls* are the constraints that prohibit the passage of heat into the system. Provided that one state, say A, of the system can be reached from another, call it B, by some mechanical process while the system is enclosed by an adiabatic wall, it is then possible to measure the energy difference, $E_A - E_B$, by determining the work required to pass between these states by an adiabatic process.

In this remark on the measurability of energy, we are assuming that there is an experimental means for characterizing the "state" of a system.

Another important point to keep in mind is that work and heat are forms of energy *transfer*. Once energy is transferred ($\text{đ}W$ or $\text{đ}Q$) it is indistinguishable from energy that might have been transferred differently. Although $\text{đ}W + \text{đ}Q = dE$, and there is a quantity E, there are no quantities W and Q. Hence $\text{đ}W$ and $\text{đ}Q$ are *inexact differentials,* and the strokes in $\text{đ}W$ and $\text{đ}Q$ are used to indicate this fact.

Exercise 1.1 List a few familiar examples of the two types of energy flow (e.g., two ways to melt ice—stirring or sitting in the sun).

Experimentally we know that isolated systems tend to evolve spontaneously toward simple terminal states. These states are called *equilibrium states.* By "simple" we mean that *macroscopically* they can be characterized by a small number of variables. In particular, the equilibrium state of a system is completely characterized macroscopically by specifying E and $\mathbf{X}$. For a system in which the relevant mechanical extensive variables are the volume and the numbers of molecules, the variables that characterize the system are

$$E,\ \underset{\substack{\uparrow\\ \text{volume}}}{V},\ n_1,\ \ldots,\ \underset{\substack{\uparrow\\ \text{number of moles of}\\ \text{species } j}}{n_j},\ \ldots,\ n_r \leftarrow r \text{ components.}$$

If an electric field is applied, the total dipole of the system must be added to the list of relevant variables. (By the way, in the case of electric and magnetic fields, care is required in the development of an *extensive* electrical and magnetic energy. Can you think of the source of the difficulty? [*Hint*: Think about the spatial range of interactions between dipoles.])

Incidentally, in a completely deductive development of macroscopic thermodynamics, one should distinguish between the composition variables $n_1, n_2, \ldots, n_r$ and the mechanical extensive variables such as the volume, V. We choose to ignore the distinction in this text because one can, by use of semipermeable membranes, electrochemical cells, or phase equilibria, design experiments (real or thought) in which transfer of moles and mixing occurs with the

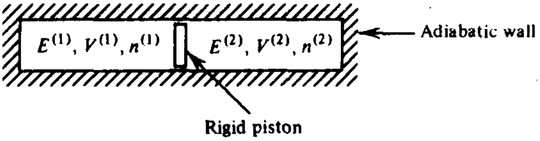

Fig. 1.2. An illustrative system.

consumption or production of work. This observation can be used to verify that composition variables play a mathematically equivalent role to the standard mechanical extensive variables. See Exercise 1.5 below.

The complete list of relevant variables is sometimes a difficult experimental issue. But whatever the list is, the most important feature of the macroscopic equilibrium state is that it is characterized by a very small number of variables, small compared to the overwhelming number of mechanical degrees of freedom that are necessary to describe in general an arbitrary non-equilibrium state of a macroscopic many particle system.

Virtually no system of physical interest is rigorously in equilibrium. However, many are in a metastable equilibrium that usually can be treated with equilibrium thermodynamics. Generally, if in the course of observing the system, it appears that the system is independent of time, independent of history, and there are no flows of energy or matter, then the system can be treated as one which is at equilibrium, and the properties of the system can be characterized by $E, V, n_1, \dots, n_r$ alone. Ultimately, however, one is never sure that the equilibrium characterization is truly correct, and one relies on the internal consistency of equilibrium thermodynamics as a guide to the correctness of this description. An internal inconsistency is the signature of *non*-equilibrium behavior or the need for additional macroscopic variables and not a failure of thermodynamics.

What can thermodynamics tell us about these equilibrium states? Consider a system in equilibrium state I formed by placing certain constraints on the system. One (or more) of these constraints can be removed or changed and the system will evolve to a new terminal state II. The determination of state II can be viewed as the basic task of thermodynamics.

As examples, consider the system pictured in Fig. 1.2, and imagine the following possible changes:

1. Let piston move around.
2. Punch holes in piston (perhaps permeable only to one species).