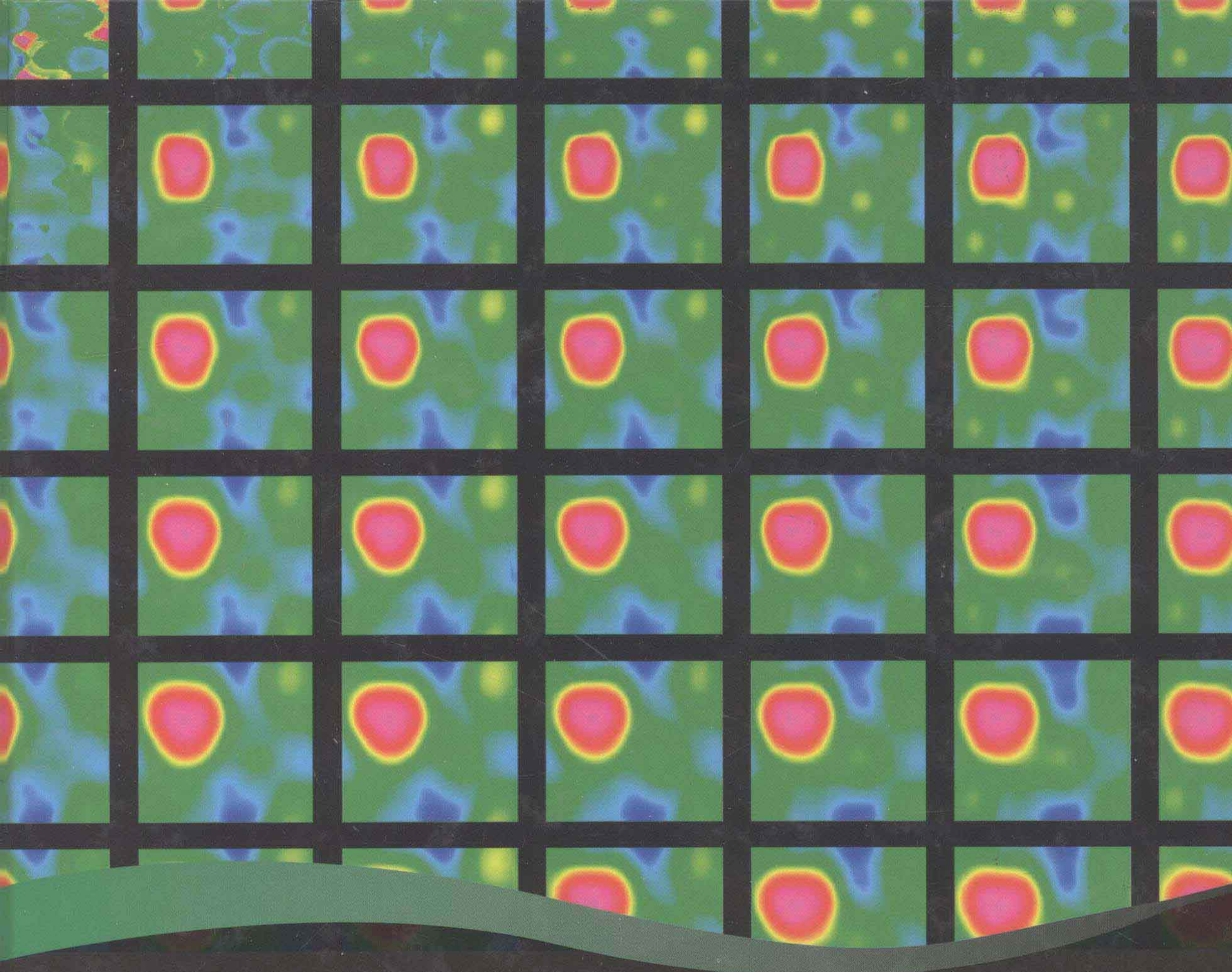

Statistical Mechanics: Theory and Molecular Simulation

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Mark E. Tuckerman
Department of Chemistry, New York University
and Courant Institute of Mathematical Sciences, New York

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To my parents, Jocelyn, and Delancey

Preface

Statistical mechanics is a theoretical framework that aims to predict the observable static and dynamic properties of a many-body system starting from its microscopic constituents and their interactions. Its scope is as broad as the set of "many-body" systems is large: as long as there exists a rule governing the behavior of the fundamental objects that comprise the system, the machinery of statistical mechanics can be applied. Consequently, statistical mechanics has found applications outside of physics, chemistry, and engineering, including biology, social sciences, economics, and applied mathematics. Because it seeks to establish a bridge between the microscopic and macroscopic realms, statistical mechanics often provides a means of rationalizing observed properties of a system in terms of the detailed "modes of motion" of its basic constituents. An example from physical chemistry is the surprisingly high diffusion constant of an excess proton in bulk water, which is a single measurable number. However, this single number belies a strikingly complex dance of hydrogen bond rearrangements and chemical reactions that must occur at the level of individual or small clusters of water molecules in order for this property to emerge. In the physical sciences, the technology of molecular simulation, wherein a system's microscopic interaction rules are implemented numerically on a computer, allow such "mechanisms" to be extracted and, through the machinery of statistical mechanics, predictions of macroscopic observables to be generated. In short, molecular simulation is the computational realization of statistical mechanics. The goal of this book, therefore, is to synthesize these two aspects of statistical mechanics: the underlying theory of the subject, in both its classical and quantum developments, and the practical numerical techniques by which the theory is applied to solve realistic problems.

This book is aimed primarily at graduate students in chemistry or computational biology and graduate or advanced undergraduate students in physics or engineering. These students are increasingly finding themselves engaged in research activities that cross traditional disciplinary lines. Successful outcomes for such projects often hinge on their ability to translate complex phenomena into simple models and develop approaches for solving these models. Because of its broad scope, statistical mechanics plays a fundamental role in this type of work and is an important part of a student's toolbox.

The theoretical part of the book is an extensive elaboration of lecture notes I developed for a graduate-level course in statistical mechanics I give at New York University. These courses are principally attended by graduate and advanced undergraduate students who are planning to engage in research in theoretical and experimental physical chemistry and computational biology. The most difficult question faced by anyone wishing to design a lecture course or a book on statistical mechanics is what to include and what to omit. Because statistical mechanics is an active field of research, it comprises a tremendous body of knowledge, and it is simply impossible to treat the entirety of the subject in a single opus. For this reason, many books with the words "statistical mechanics" in their titles can differ considerably. Here, I have attempted to bring together topics that reflect what I see as the modern landscape of statistical mechanics. The reader will notice from a quick scan of the table of contents that the topics selected are rarely found together in individual textbooks on the subject; these topics include isobaric ensembles, path integrals, classical and quantum time-dependent statistical mechanics, the generalized Langevin equation, the Ising model, and critical phenomena. (The closest such book I have found is also one of my favorites, David Chandler's *Introduction to Modern Statistical Mechanics.*)

The computational part of the book joins synergistically with the theoretical part and is designed to give the reader a solid grounding in the methodology employed to solve problems in statistical mechanics. It is intended neither as a simulation recipe book nor a scientific programmer's guide. Rather, it aims to show how the development of computational algorithms derives from the underlying theory with the hope of enabling readers to understand the methodology-oriented literature and develop new techniques of their own. The focus is on the molecular dynamics and Monte Carlo techniques and the many novel extensions of these methods that have enhanced their applicability to, for example, large biomolecular systems, complex materials, and quantum phenomena. Most of the techniques described are widely available in molecular simulation software packages and are routinely employed in computational investigations. As with the theoretical component, it was necessary to select among the numerous important methodological developments that have appeared since molecular simulation was first introduced. Unfortunately, several important topics had to be omitted due to space constraints, including configuration-bias Monte Carlo, the reference potential spatial warping algorithm, and semi-classical methods for quantum time correlation functions. This omission was not made because I view these methods as less important than those I included. Rather, I consider these to be very powerful but highly advanced methods that, individually, might have a narrower target audience. In fact, these topics were slated to appear in a chapter of their own. However, as the book evolved, I found that nearly 700 pages were needed to lay the foundation I sought.

In organizing the book, I have made several strategic decisions. First, the book is structured such that concepts are first introduced within the framework of classical mechanics followed by their quantum mechanical counterparts. This lies closer perhaps to a physicist's perspective than, for example, that of a chemist, but I find it to be a particularly natural one. Moreover, given how widespread computational studies based on classical mechanics have become compared to analogous quantum investigations (which have considerably higher computational overhead) this progression seems to be both logical and practical. Second, the technical development within each chapter is graduated, with the level of mathematical detail generally increasing from chapter start to chapter end. Thus, the mathematically most complex topics are reserved for the final sections of each chapter. I assume that readers have an understanding of calculus (through calculus of several variables), linear algebra, and ordinary differential equations. This structure hopefully allows readers to maximize what they take away from each chapter while rendering it easier to find a stopping point within each chapter. In short, the book is structured such that even a partial reading of a chapter allows the reader to gain a basic understanding of the subject. It should be noted that I attempted to adhere to this graduated structure only as a general protocol. Where I felt that breaking this progression made logical sense, I have forewarned the reader about the mathematical arguments to follow, and the final result is generally given at the outset. Readers wishing to skip the mathematical details can do so without loss of continuity.

The third decision I have made is to integrate theory and computational methods within each chapter. Thus, for example, the theory of the classical microcanonical ensemble is presented together with a detailed introduction to the molecular dynamics method and how the latter is used to generate a classical microcanonical distribution. The other classical ensembles are presented in a similar fashion as is the Feynman path integral formulation of quantum statistical mechanics. The integration of theory and methodology serves to emphasize the viewpoint that understanding one helps in understanding the other.

Throughout the book, many of the computational methods presented are accompanied by simple numerical examples that demonstrate their performance. These examples range from low-dimensional "toy" problems that can be easily coded up by the reader (some of the exercises in each chapter ask precisely this) to atomic and molecular liquids, aqueous solutions, model polymers, biomolecules, and materials. Not every method presented is accompanied by a numerical example, and in general I have tried not to overwhelm the reader with a plethora of applications requiring detailed explanations of the underlying physics, as this is not the primary aim of the book. Once the basics of the methodology are understood, readers wishing to explore applications particular to their interests in more depth can subsequently refer to the literature.

A word or two should be said about the problem sets at the end of each chapter. Math and science are not spectator sports, and the only way to learn the material is to solve problems. Some of the problems in the book require the reader to think conceptually while others are more mathematical, challenging the reader to work through various derivations. There are also problems that ask the reader to analyze proposed computational algorithms by investigating their capabilities. For readers with some programming background, there are exercises that involve coding up a method for a simple example in order to explore the method's performance on that example, and in some cases, reproduce a figure from the text. These coding exercises are included because one can only truly understand a method by programming it up and trying it out on a simple problem for which long runs can be performed and many different parameter choices can be studied. However, I must emphasize that even if a method works well on a simple problem, it is not guaranteed to work well for realistic systems. Readers should not, therefore, naïvely extrapolate the performance of any method they try on a toy system to high-dimensional complex problems. Finally, in each problem set, some problem are preceded by an asterisk (*). These are problems of a more challenging nature that require deeper thinking or a more in-depth mathematical analysis. All of the problems are designed to strengthen understanding of the basic ideas.

Let me close this preface by acknowledging my teachers, mentors, colleagues, and

coworkers without whom this book would not have been possible. I took my first statistical mechanics courses with Y. R. Shen at the University of California Berkeley and A. M. M. Pruisken at Columbia University. later, I audited the course team-taught by James L. Skinner and Bruce J. Berne, also at Columbia. I was also privileged to have been mentored by Bruce Berne as a graduate student, by Michele Parrinello during a postdoctoral appointment at the IBM Forschungslaboratorium in Rüschlikon, Switzerland, and by Michael L. Klein while I was a National Science Foundation postdoctoral fellow at the University of Pennsylvania. Under the mentorship of these extraordinary individuals, I learned and developed many of the computational methods that are discussed in the book. I must also express my thanks to the National Science Foundation for their continued support of my research over the past decade. Many of the developments presented here were made possible through the grants I received from them. I am deeply grateful to the Alexander von Humboldt Foundation for a Friedrich Wilhelm Bessel Research Award that funded an extended stay in Germany where I was able to work on ideas that influenced many parts of the book. In am equally grateful to my German host and friend Dominik Marx for his support during this stay, for many useful discussions, and for many fruitful collaborations that have helped shaped the book's content. I also wish to acknowledge my long-time collaborator and friend Glenn Martyna for his help in crafting the book in its initial stages and for his critical reading of the first few chapters. I have also received many helpful suggestions from Bruce Berne, Giovanni Ciccotti, Hae-Soo Oh, Michael Shirts, and Dubravko Sabo. I am indebted to the excellent students and postdocs with whom I have worked over the years for their invaluable contributions to several of the techniques presented herein and for all they have taught me. I would also like to acknowledge my former student Kiryn Haslinger Hoffman for her work on the illustrations used in the early chapters. Finally, I owe a tremendous debt of gratitude to my wife Jocelyn Leka whose finely honed skills as an editor were brought to bear on crafting the wording used throughout the book. Editing me took up many hours of her time. Her skills were restricted to the textual parts of the book; she was not charged with the onerous task of editing the equations. Consequently, any errors in the latter are mine and mine alone.

M.E.T.
New York
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Contents

1
Classical mechanics

1.1 Introduction

The first part of this book is devoted to the subject of classical statistical mechanics, the foundation of which are the fundamental laws of classical mechanics as originally stated by Newton. Although the laws of classical mechanics were first postulated to study the motion of planets, stars and other large-scale objects, they turn out to be a surprisingly good approximation at the molecular level (where the true behavior is correctly described by the laws of quantum mechanics). Indeed, an entire computational methodology, known as *molecular dynamics*, is based on the applicability of the laws of classical mechanics to microscopic systems. Molecular dynamics has been remarkably successful in its ability to predict macroscopic thermodynamic and dynamic observables for a wide variety of systems using the rules of classical statistical mechanics to be discussed in the next chapter. Many of these applications address important problems in biology, such as protein and nucleic acid folding, in materials science, such as surface catalysis and functionalization, and structure and dynamics of glasses and their melts, as well as in nanotechnology, such as the behavior of self-assembled monolayers and the formation of molecular devices. Throughout the book, we will be discussing both model and realistic examples of such applications.

In this chapter, we will begin with a discussion of Newton's laws of motion and build up to the more elegant Lagrangian and Hamiltonian formulations of classical mechanics, both of which play fundamental roles in statistical mechanics. The origin of these formulations from the action principle will be discussed. The chapter will conclude with a first look at systems that do not fit into the Hamiltonian/Lagrangian framework and the application of such systems in the description of certain physical situations.

1.2 Newton's laws of motion

In 1687, the English physicist and mathematician Sir Isaac Newton published the *Philosophiae Naturalis Principia Mathematica*, wherein three simple and elegant laws governing the motion of interacting objects are stated. These may be stated briefly as follows:

1. In the absence of external forces, a body will either be at rest or execute motion along a straight line with a constant velocity $\mathbf{v}$.
2. The action of an external force $\mathbf{F}$ on a body produces an acceleration $\mathbf{a}$ equal to the force divided by the mass m of the body:

$$\mathbf{a} = \frac{\mathbf{F}}{m}, \qquad \mathbf{F} = m\mathbf{a}. \tag{1.2.1}$$

3. If body A exerts a force on body B, then body B exerts an equal and opposite force on body A. That is, if $\mathbf{F}_{\rm AB}$ is the force body A exerts on body B, then the force $\mathbf{F}_{\rm BA}$ exerted by body B on body A satisfies

$$\mathbf{F}_{\rm BA} = -\mathbf{F}_{\rm AB}. \tag{1.2.2}$$

In general, two objects can exert attractive or repulsive forces on each other, depending on their relative spatial location, and the precise dependence of the force on the relative location of the objects is specified by a particular *force law*.

Although Newton's interests largely focused on the motion of celestial bodies interacting via gravitational forces, most atoms are massive enough that their motion can be treated reasonably accurately within a classical framework. Hence, the laws of classical mechanics can be approximately applied at the molecular level. Naturally, there are numerous instances in which the classical approximation breaks down, and a proper quantum mechanical treatment is needed. For the present, however, we will assume the approximate validity of classical mechanics at the molecular level and proceed to apply Newton's laws as stated above.

The motion of an object can be described quantitatively by specifying the Cartesian position vector $\mathbf{r}(t)$ of the object in space at any time t. This is tantamount to specifying three functions of time, the components of $\mathbf{r}(t)$,

$$\mathbf{r}(t) = (x(t), y(t), z(t)). \tag{1.2.3}$$

Recognizing that the velocity $\mathbf{v}(t)$ of the object is the first time derivative of the position, $\mathbf{v}(t) = {\rm d}\mathbf{r}/{\rm d}t$, and that the acceleration $\mathbf{a}(t)$ is the first time derivative of the velocity, $\mathbf{a}(t) = {\rm d}\mathbf{v}/{\rm d}t$, the acceleration is easily seen to be the second derivative of position, $\mathbf{a}(t) = {\rm d}^2\mathbf{r}/{\rm d}t^2$. Therefore, Newton's second law, $\mathbf{F} = m\mathbf{a}$, can be expressed as a differential equation

$$m\frac{{\rm d}^2\mathbf{r}}{{\rm d}t^2} = \mathbf{F}. \tag{1.2.4}$$

(Throughout this book, we shall employ the overdot notation for differentiation with respect to time. Thus, $\dot{\mathbf{r}}_i = {\rm d}\mathbf{r}_i/{\rm d}t$ and $\ddot{\mathbf{r}}_i = {\rm d}^2\mathbf{r}_i/{\rm d}t^2$.) Since eqn. (1.2.4) is a second order equation, it is necessary to specify two initial conditions, these being the initial position $\mathbf{r}(0)$ and initial velocity $\mathbf{v}(0)$. The solution of eqn. (1.2.4) subject to these initial conditions uniquely specifies the motion of the object for all time.

The force $\mathbf{F}$ that acts on an object is capable of doing *work* on the object. In order to see how work is computed, consider Fig. 1.1, which shows a force $\mathbf{F}$ acting on a system along a particular path. The work ${\rm d}W$ performed along a short segment ${\rm d}\mathbf{l}$ of the path defined to be

$${\rm d}W = \mathbf{F}\cdot{\rm d}\mathbf{l} = F\cos\theta{\rm d}l. \tag{1.2.5}$$

The total work done on the object by the force between points A and B along the path is obtained by integrating over the path from A to B: