Statistical Mechanics: Theory and Molecular Simulation

Classical statistical mechanics was developed in the latter part of the nineteenth century by Maxwell, Boltzmann, and Gibbs. Their approach was to represent macroscopic states of systems as distributions of classical phase space points (consisting of momenta and positions of molecules), in such a way as to be consistent with any external macroscopic thermodynamic constraints imposed on the system. With the advent of quantum mechanics in the 1920s, statistical mechanics was quickly reformulated in terms distributions of the system among accessible discrete quantum states. The quantum mechanical approach is conceptually simpler, mathematically more compact, and has gained prominence in most statistically mechanics textbooks written after that time.

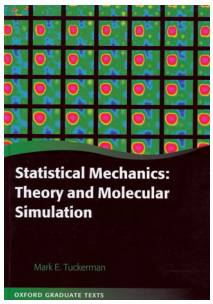
As the use of classical molecular dynamics and Monte Carlo simulation methods are becoming widespread, familiarity with classical statistical mechanical methods has again become important. In classical molecular simulation methods, molecular velocities and positions are manipulated with the classical Newtonian laws of motion, and the results of system-wide properties are interpreted in terms of classical statistical mechanical principles. The textbook, *Statistical Mechanics: Theory and Molecular Simulation* provides a modern treatment to classical and quantum statistical mechanics, with an eye towards applications of the principles to molecular simulation methods.

The emphasis of the book is on the statistical mechanics principles, and although some methods are discussed in detail, is perhaps not an introductory text on molecular simulation methods. The book is mathematically rigorous and targeted towards graduate students of chemistry and physics. Chemistry students with a good introductory course in quantum mechanics/quantum chemistry should have sufficient background to follow the arguments in the book. Although knowledge of quantum mechanics is not formally needed for the first part of the text book, and indeed Chapter 9 gives a brief summary of quantum mechanical principles, familiarity with quantum mechanics will greatly enhance the comprehension of the classical mechanics chapters. Some of the classical mechanical arguments are motivated by the quantum mechanical analogs and studied alone may seem somewhat puzzling to the reader. For example, in Chapter 3, the time-evolution operator approach is introduced for integrating the classical equations of motion. This chapter will be very clear to those familiar with the time-dependent Schrödinger equation. The Verlet algorithms and multiple time scale algorithms are derived as specific examples of the time-evolution operator approach.

A very useful aspect of the book to beginning practitioners is that it covers many modern simulation methods (some from among the author's own impressive research contributions) that are not easily found with this level of detail in other textbooks, thus providing systematic background material and consistent notation required for understanding these topics. These methods include the reference system propagator algorithm (RESPA, Chapter 3), Nosé–Hoover chains (Chapter 4), replica exchange and transition path sampling methods (Chapter 7), Jarzynski's inequality (Chapter 8), Free energy methods (metadynamics, umbrella sampling, Chapter 8), and Feynman path integral methods (an excellent introduction for which is given in Chapter 12).

The first eight chapters give an introduction to classical statistical methods. The first chapter gives a detailed introduction to classical mechanics methods, with an emphasis on the Lagrangian formulation. A pedagogical aspect of the text is that specialized classical mechanical techniques needed for molecular simulations are introduced along with basic theory of mechanics and statistical mechanics. For example, Euler angle and quaternion methods for rigid body motion are introduced in the first chapter along with other applications of the Lagrangian formulation. The foundations of statistical mechanics, the microcanonical, canonical, isobaric, and grand canonical ensemble formulations are discussed in Chapters 2 to 6. Nosé-based thermostats and Andersen/Parrinello–Rahman barostat methods for molecular simulations are incorporated naturally in these chapters. The method of Lagrange multipliers are not directly used in deriving the expression for the partition functions, which provides an alternative pathway to the expressions for the partition function from that which appears in many texts. Chapter 7 covers Monte Carlo methods and follows naturally from the ensemble methods of the previous chapters. An emphasis is on specialized techniques that utilize the Monte Carlo method's capability for sampling high energy states. Chapter 8 discusses modern methods for calculating the thermodynamic free energy associated with physical and chemical processes using molecular simulation methodology.

Quantum mechanics and quantum statistical mechanics are introduced from Chapter 9 onwards. Some quantum mechanical principles are discussed in Chapter 9. Given the sophistication of the treatment of classical mechanics in previous chapters of the book, some of the quantum mechanical concepts introduced in this chapter may seem elementary (for example the forms of the harmonic



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oscillator wave-functions). However, this chapter provides a good review of the notation used in later chapters. Chapter 10 describes the formulation of equilibrium ensembles in quantum mechanical language with an emphasis on the density matrix to describe the state of the system. The consequences of the quantum mechanical description on the statistical mechanics of the ideal gas are discussed in Chapter 11 which covers the Fermi and Bose ideal gases in detail.

Chapter 12 which discusses Feyman path integral methods can be one of the most useful chapters of the book. This chapter discusses how classical molecular simulation methods can be implemented within a quantum mechanical framework to compute estimates of quantum behaviors of systems.

Chapters 13 through 16 cover some chosen specialized topics. Classical and quantum mechanical time-dependent statistical mechanics are introduced in Chapters 14 and 15 with the emphasis on classical linear response theory (Green–Kubo relations and transport coefficients), quantum mechanical time-dependent perturbation theory (spectroscopic applications), and quantum linear response theory. Chapter 15 introduces the Langevin equation and its generalization. These methods introduce stoichastic perturbations in the mechanical system as a means of modeling the effect of the surroundings of the system under study. Critical phenomena and statistical mechanical study of phase transitions are presented in Chapter 16. The Ising model is used to illustrate the principles involved. Each chapter in the text is followed by a problem set. These are mostly conceptual and most require considerable thought to solve.

To summarize, the book will be most useful to those with some introductory and practical knowledge of quantum mechanics, statistical mechanics, and molecular dynamics/Monte Carlo principles. Some standard methods used in molecular dynamics codes (such as the Verlet or leap-frog algorithms, Ewald summation methods, neighbor lists) are discussed briefly, whereas more fundamental methods are discussed in detail. Some traditional statistical mechanics topics such as the applications of statistical mechanics to molecular spectroscopy (translation, rotational, vibrational partition functions), force fields, and grand canonical Monte Carlo simulations of adsorption isotherms for non-ideal gases may not be covered, but these are often widely available in other textbooks and monographs. The mathematical reasoning in the text is often sophisticated but clearly presented. At places, the presentation can be streamlined without loss of clarity by reducing some of the algebraic steps shown without loss of clarity.

Those interested in molecular simulation method development or obtaining a deeper understanding of these techniques and their scope, will find reading this text rewarding and enjoyable.

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