# STATISTICAL MECHANICS

From First Principles to Macroscopic Phenomena

Based on the author's graduate course taught over many years in several physics departments, this book takes a "reductionist" view of statistical mechanics, while describing the main ideas and methods underlying its applications. It implicitly assumes that the physics of complex systems as observed is connected to fundamental physical laws represented at the molecular level by Newtonian mechanics or quantum mechanics. Organized into three parts, the first section describes the fundamental principles of equilibrium statistical mechanics. The next section describes applications to phases of increasing density and order: gases, liquids and solids; it also treats phase transitions. The final section deals with dynamics, including a careful account of hydrodynamic theories and linear response theory.

This original approach to statistical mechanics is suitable for a 1-year graduate course for physicists, chemists, and chemical engineers. Problems are included following each chapter, with solutions to selected problems provided.

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# Preface

This book is based on a course which I have taught over many years to graduate students in several physics departments. Students have been mainly candidates for physics degrees but have included a scattering of people from other departments including chemical engineering, materials science and chemistry. I take a "reductionist" view, that implicitly assumes that the basic program of physics of complex systems is to connect observed phenomena to fundamental physical laws as represented at the molecular level by Newtonian mechanics or quantum mechanics. While this program has historically motivated workers in statistical physics for more than a century, it is no longer universally regarded as central by all distinguished users of statistical mechanics[1,2] some of whom emphasize the phenomenological role of statistical methods in organizing data at macroscopic length and time scales with only qualitative, and often only passing, reference to the underlying microscopic physics. While some very useful methods and insights have resulted from such approaches, they generally tend to have little quantitative predictive power. Further, the recent advances in first principles quantum mechanical methods have put the program of predictive quantitative methods based on first principles within reach for a broader range of systems. Thus a text which emphasizes connections to these first principles can be useful.

The level here is similar to that of popular books such as those by Landau and Lifshitz,[3] Huang[4] and Reichl.[5] The aim is to provide a basic understanding of the fundamentals and some pivotal applications in the brief space of a year. With regard to fundamentals, I have sought to present a clear, coherent point of view which is correct without oversimplifying or avoiding mention of aspects which are incompletely understood. This differs from many other books, which often either give the fundamentals extremely short shrift, on the one hand, or, on the other, expend more mathematical and scholarly attention on them than is appropriate in a one year graduate course. The chapters on fundamentals begin with a description of equilibrium for classical systems followed by a similar description for quantum

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mechanical systems. The derivation of the equilibrium aspects of thermodynamics is then presented followed by a discussion of the semiclassical limit.

In the second part, I progress through equilibrium applications to successively more dense states of matter: ideal classical gases, ideal quantum gases, imperfect classical gases (cluster expansions), classical liquids (including molecular dynamics) and some aspects of solids. A detailed discussion of solids is avoided because, at many institutions, solid state physics is a separate graduate course. However, because magnetic models have played such a central role in statistical mechanics, they are not neglected here. Finally, in this second part, having touched on the main states of matter, I devote a chapter to phase transitions: thermodynamics, classification and the renormalization group.

The third part is devoted to dynamics. This consists first of a long chapter on the derivation of the equations of hydrodynamics. In this chapter, the fluctuation–dissipation theorem then appears in the form of relations of transport coefficients to dynamic correlation functions. The second chapter of the last part treats stochastic models of dynamics and dynamical aspects of critical phenomena.

There are problems in each chapter. Solutions are provided for many of them in an appendix. Many of the problems require some numerical work. Sample codes are provided in some of the solutions (in Fortran) but, in most cases, it is advisable for students to work out their own solutions which means writing their own codes. Unfortunately, the students I have encountered recently are still often surprised to be asked to do this but there is really no substitute for it if one wants a thorough mastery of simulation aspects of the subject.

I have interacted with a great many people and sources during the evolution of this work. For this reason acknowledging them all is difficult and I apologise in advance if I overlook someone. My tutelage in statistical mechanics began with a course by Allan Kaufman in Berkeley in the 1960s. With regard to statistical mechanics I have profited especially from interactions with Michael Gillan, Gregory Wannier (some personally but mainly from his book), Mike Thorpe, Aneesur Rahman, Bert Halperin, Gene Mazenko, Hisao Nakanishi, Nigel Goldenfeld and David Chandler. Obviously none of these people are responsible for any mistakes you may find, but they may be given some credit for some of the good stuff. I am also grateful to the many classes that were subjected to these materials, in rather unpolished form in the early days, and who taught me a lot. Finally I thank all my Ph.D. students and postdocs (more than 30 in all) through the years for being good company and colleagues and for stimulating me in many ways.

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Minneapolis
July 2005

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