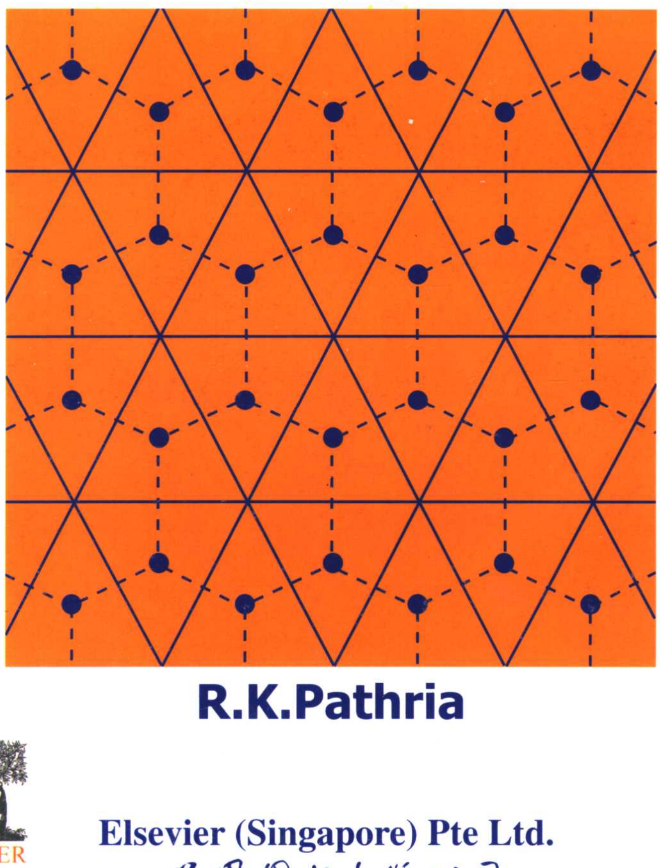
Statistical Mechanics

SECOND EDITION

统计力学

第 2 版



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SECOND EDITION

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BUTTERWORTH HEINEMANN

OXFORD AUCKLAND BOSTON JOHANNESBURG MELBOURNE NEW DELHI

Crash Course! Anatomy, 1st edition

Ameerally

ISBN: 0-7234-2195-2

Authorized English language reprint edition published by the Proprietor.

Reprint ISBN: 981-4095-20-6

Elsevier (Singapore) Pte Ltd.

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STATISTICAL MECHANICS

PREFACE TO THE SECOND EDITION

THE first edition of this book was prepared over the years 1966–70 when the subject of phase transitions was undergoing a complete overhaul. The concepts of scaling and universality had just taken root but the renormalization group approach, which converted these concepts into a calculational tool, was still obscure. Not surprisingly, my text of that time could not do justice to these emerging developments. Over the intervening years I have felt increasingly conscious of this rather serious deficiency in the text; so when the time came to prepare a new edition, my major effort went towards correcting that deficiency.

Despite the aforementioned shortcoming, the first edition of this book has continued to be popular over the last twenty years or so. I, therefore, decided not to tinker with it unnecessarily. Nevertheless, to make room for the new material, I had to remove some sections from the present text which, I felt, were not being used by the readers as much as the rest of the book was. This may turn out to be a disappointment to some individuals but I trust they will understand the logic behind it and, if need be, will go back to a copy of the first edition for reference. I, on my part, hope that a good majority of the users will not be inconvenienced by these deletions. As for the material retained, I have confined myself to making only editorial changes. The subject of phase transitions and critical phenomena, which has been my main focus of revision, has been treated in three new chapters that provide a respectable coverage of the subject and essentially bring the book up to date. These chapters, along with a collection of over sixty homework problems, will, I believe, enhance the usefulness of the book for both students and instructors.

The completion of this task has left me indebted to many. First of all, as mentioned in the Preface to the first edition, I owe a considerable debt to those who have written on this subject before and from whose writings I have benefitted greatly. It is difficult to thank them all individually; the bibliography at the end of the book is an obvious tribute to them. As for definitive help, I am most grateful to Dr Surjit Singh who advised me expertly and assisted me generously in the selection of the material that comprises Chapters 11–13 of the new text; without his help, the final product might not have been as coherent as it now appears to be. On the technical side, I am very thankful to Mrs Debbie Guenther who typed the manuscript with exceptional skill and proof-read it with extreme care; her task was clearly an arduous one but she performed it with good cheer — for which I admire her greatly.

Finally, I wish to express my heart-felt appreciation for my wife who let me devote myself fully to this task over a rather long period of time and waited for its completion ungrudgingly.

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PREFACE TO THE FIRST EDITION

THIS book has arisen out of the notes of lectures that I gave to the graduate students at the McMaster University (1964–5), the University of Alberta (1965–7), the University of Waterloo (1969–71) and the University of Windsor (1970–1). While the subject matter, in its finer details, has changed considerably during the preparation of the manuscript, the style of presentation remains the same as followed in these lectures.

Statistical mechanics is an indispensable tool for studying physical properties of matter "in bulk" on the basis of the dynamical behavior of its "microscopic" constituents. Founded on the well-laid principles of *mathematical statistics* on one hand and *hamiltonian mechanics* on the other, the formalism of statistical mechanics has proved to be of immense value to the physics of the last 100 years. In view of the universality of its appeal, a basic knowledge of this subject is considered essential for every student of physics, irrespective of the area(s) in which he/she may be planning to specialize. To provide this knowledge, in a manner that brings out the essence of the subject with due rigor but without undue pain, is the main purpose of this work.

The fact that *the dynamics of a physical system is represented by a set of quantum states* and the assertion that *the thermodynamics of the system is determined by the multiplicity of these states* constitute the basis of our treatment. The fundamental connection between the microscopic and the macroscopic descriptions of a system is uncovered by investigating the conditions for equilibrium between two physical systems in thermodynamic contact. This is best accomplished by working in the spirit of the quantum theory right from the beginning; the entropy and other thermodynamic variables of the system then follow in a most natural manner. After the formalism is developed, one may (if the situation permits) go over to the limit of the classical statistics. This message may not be new, but here I have tried to follow it as far as is reasonably possible in a textbook. In doing so, an attempt has been made to keep the level of presentation fairly uniform so that the reader does not encounter fluctuations of too wild a character.

This text is confined to the study of the *equilibrium states* of physical systems and is intended to be used for a *graduate course* in statistical mechanics. Within these bounds, the coverage is fairly wide and provides enough material for tailoring a good two-semester course. The final choice always rests with the individual instructor; I, for one, regard Chapters 1–9 (*minus* a few sections from these chapters *plus* a few sections from Chapter 13) as the "essential part" of such a course. The contents of Chapters 10–12 are relatively advanced (not necessarily difficult); the choice of material out of these chapters will depend entirely on the taste of the instructor. To facilitate the understanding of the subject, the text has been illustrated with a large number of graphs; to assess the understanding, a large number of problems have been included. I hope these features are found useful.

I feel that one of the most essential aspects of teaching is to arouse the curiosity of the students in their subject, and one of the most effective ways of doing this is to discuss with them (in a reasonable measure, of course) the circumstances that led to the emergence of the subject. One would, therefore, like to stop occasionally to reflect upon the manner in which the various developments really came about; at the same time, one may not like the flow of the text to be hampered by the discontinuities arising from an intermittent addition of historical material. Accordingly, I decided to include in this account an Historical Introduction to the subject which stands separate from the main text. I trust the readers, especially the instructors, will find it of interest.

For those who wish to continue their study of statistical mechanics beyond the confines of this book, a fairly extensive bibliography is included. It contains a variety of references — old as well as new, experimental as well as theoretical, technical as well as pedagogical. I hope that this will make the book useful for a wider readership.

The completion of this task has left me indebted to many. Like most authors, I owe considerable debt to those who have written on the subject before. The bibliography at the end of the book is the most obvious tribute to them; nevertheless, I would like to mention, in particular, the works of the Ehrenfests, Fowler, Guggenheim, Schrödinger, Rushbrooke, ter Haar, Hill, Landau and Lifshitz, Huang, and Kubo, which have been my constant reference for several years and have influenced my understanding of the subject in a variety of ways. As for the preparation of the text, I am indebted to Robert Teshima who drew most of the graphs and checked most of the problems, to Ravindar Bansal, Vishwa Mittar and Surjit Singh who went through the entire manuscript and made several suggestions that helped me unkink the exposition at a number of points, to Mary Annetts who typed the manuscript with exceptional patience, diligence and care, and to Fred Hetzel, Jim Briante and Larry Kry who provided technical help during the preparation of the final version.

As this work progressed I felt increasingly gratified towards Professors F. C. Auluck and D. S. Kothari of the University of Delhi with whom I started my career and who initiated me into the study of this subject, and towards Professor R. C. Majumdar who took keen interest in my work on this and every other project that I have undertaken from time to time. I am grateful to Dr D. ter Haar of the University of Oxford who, as the general editor of this series, gave valuable advice on various aspects of the preparation of the manuscript and made several useful suggestions towards the improvement of the text. I am thankful to Professors J.W. Leech, J. Grindlay and A.D. Singh Nagi of the University of Waterloo for their interest and hospitality that went a long way in making this task a pleasant one.

The final tribute must go to my wife whose cooperation and understanding, at all stages of this project and against all odds, have been simply overwhelming.

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CONTENTS

HISTORICAL INTRODUCTION

STATISTICAL mechanics is a formalism which aims at explaining the physical properties of matter *in bulk* on the basis of the dynamical behavior of its *microscopic* constituents. The scope of the formalism is almost as unlimited as the very range of the natural phenomena, for in principle it is applicable to matter in any state whatsoever. It has, in fact, been applied, with considerable success, to the study of matter in the solid state, the liquid state or the gaseous state, matter composed of several phases and/or several components, matter under extreme conditions of density and temperature, matter in equilibrium with radiation (as, for example, in astrophysics), matter in the form of a biological specimen, etc. Furthermore, the formalism of statistical mechanics enables us to investigate the *non-equilibrium* states of matter as well as the *equilibrium* states; indeed, these investigations help us to understand the manner in which a physical system that happens to be "out of equilibrium" at a given time t approaches a "state of equilibrium" as time passes.

In contrast with the present status of its development, the success of its applications and the breadth of its scope, the beginnings of statistical mechanics were rather modest. Barring certain primitive references, such as those of Gassendi, Hooke, etc., the real work started with the contemplations of Bernoulli (1738), Herapath (1821) and Joule (1851) who, in their own individual ways, attempted to lay a foundation for the so-called *kinetic theory of gases*—a discipline that finally turned out to be the forerunner of statistical mechanics. The pioneering work of these investigators established the fact that the pressure of a gas arose from the motion of its molecules and could be computed by considering the dynamical influence of molecular bombardment on the walls of the container. Thus, Bernoulli and Herapath could show that, if temperature remained constant, the pressure P of an ordinary gas was inversely proportional to the volume V of the container (Boyle's law), and that it was essentially independent of the shape of the container. This, of course, involved the explicit assumption that, *at a given temperature* T, the (mean) speed of the molecules is independent of both pressure and volume. Bernoulli even attempted to determine the (first-order) correction to this law, arising from the *finite* size of the molecules, and showed that the volume V appearing in the statement of the law should be replaced by $(V - b)$, where b is the "actual" volume of the molecules.[1] Joule was the first to show that the pressure P is directly proportional to the square of the molecular speed c, which he had assumed to be the same for all molecules. Krönig (1856) went a step further. Introducing the "quasi-statistical" assumption that, *at any time* t, one-sixth of the molecules could be assumed to be flying in each of the six "independent" directions, namely $+x$, $-x$, $+y$, $-y$, $+z$

and $-z$, he derived the equation

$$P = \frac{1}{3} n m c^2, \quad (1)$$

where n is the number density of the molecules and m the molecular mass. Krönig, too, assumed the molecular speed c to be the same for all molecules; from (1), he inferred that the kinetic energy of the molecules should be directly proportional to the absolute temperature of the gas.

Krönig justified his method in these words: "The path of each molecule must be so irregular that it will defy all attempts at calculation. However, according to the laws of probability, one could assume a completely regular motion in place of a completely irregular one!" It must, however, be noted that it is only because of the special form of the summations appearing in the calculation of the pressure that Krönig's model leads to the same result as the one following from more refined models. In other problems, such as the ones involving diffusion, viscosity or heat conduction, this is no longer the case.

It was at this stage that Clausius entered the field. First of all, in 1857, he derived the ideal-gas law under assumptions far less stringent than Krönig's. He discarded both leading assumptions of Krönig and showed that eqn. (1) was still true; of course, c^2 now became the *mean square speed* of the molecules. In a later paper (1859), Clausius introduced the concept of the *mean free path* and thus became the first to analyze transport phenomena. It was in these studies that he introduced the famous "Stosszahlansatz"–the hypothesis on the number of collisions (among the molecules)–which, later on, played a prominent role in the monumental work of Boltzmann.[2] With Clausius, the introduction of the microscopic and statistical points of view into the physical theory was definitive, rather than speculative. Accordingly, Maxwell, in a popular article entitled "Molecules", written for the *Encyclopedia Britannica*, referred to him as the "principal founder of the kinetic theory of gases", while Gibbs, in his Clausius obituary notice, called him the "father of statistical mechanics".[3]

The work of Clausius attracted Maxwell to the field. He made his first appearance with the memoir "Illustrations in the dynamical theory of gases" (1860), in which he went much further than his predecessors by deriving his famous law of "distribution of molecular speeds". Maxwell's derivation was based on elementary principles of probability and was clearly inspired by the Gaussian law of "distribution of random errors". A derivation based on the requirement that "the equilibrium distribution of molecular speeds, once acquired, should remain invariant under molecular collisions" appeared in 1867. This led Maxwell to establish what is known as *Maxwell's transport equation* which, if skillfully used, leads to the same results as one gets from the more fundamental equation due to Boltzmann.[4]

Maxwell's contributions to the subject diminished considerably after his appointment, in 1871, as the Cavendish Professor at Cambridge. By that time Boltzmann had already made his first strides. In the period 1868–71 he generalized Maxwell's distribution law to polyatomic gases, also taking into account the presence of external forces, if any; this gave rise to the famous *Boltzmann factor* $\exp(-\beta\varepsilon)$, where ε denotes the *total* energy of a molecule. These investigations also led to the *equipartition theorem*. Boltzmann further showed that, just like the original distribution of Maxwell, the generalized distribution (which we now call the *Maxwell–Boltzmann distribution*) is stationary with respect to molecular collisions. In 1872 came the celebrated *H-theorem* which provided a molecular basis for the natural tendency of physical systems to approach, and stay in, a state of equilibrium. This established a connection between the microscopic approach (which characterizes statistical mechanics) and the phenomenological approach (which characterized thermodynamics) much more transparently than ever before; it also provided a direct method for computing the entropy of a given physical system from purely microscopic considerations. As a corollary to the H-theorem, Boltzmann showed that the Maxwell–Boltzmann distribution is the *only* distribution that stays invariant under molecular collisions and that any other distribution, under the influence of molecular collisions, ultimately goes over to a Maxwell–Boltzmann distribution. In 1876 Boltzmann derived his famous transport equation which, in the hands of Chapman and Enskog (1916–17), has proved to be an extremely powerful tool for investigating macroscopic properties of systems in non-equilibrium states.

Things, however, proved quite harsh for Boltzmann. His H-theorem, and the consequent *irreversible* behavior of physical systems, came under heavy attack, mainly from Loschmidt (1876–77) and Zermelo (1896). While Loschmidt wondered how the consequences of this theorem could be reconciled with the reversible character of the basic equations of motion of the molecules, Zermelo wondered how these consequences could be made to fit with the *quasi-periodic* behavior of closed systems (which arose in view of the so-called Poincaré cycles). Boltzmann defended himself against these attacks with all his might but could not convince his opponents of the correctness of his work. At the same time, the energeticists, led by Mach and Ostwald, were criticizing the very (molecular) basis of the kinetic theory,[5] while Kelvin was emphasizing the "nineteenth-century clouds hovering over the dynamical theory of light and heat".[6]

All this left Boltzmann in a state of despair and induced in him a persecution complex.[7] He wrote in the introduction to the second volume of his treatise *Vorlesungen über Gastheorie* (1898):[8]

> I am convinced that the attacks (on the kinetic theory) rest on misunderstandings and that the role of the kinetic theory is not yet played out. In my opinion it would be a blow to science if contemporary opposition were to cause kinetic theory to sink into the oblivion which was the fate suffered by the wave theory of light through the authority of Newton. I am aware of the weakness of one individual against the prevailing currents of opinion. In order to insure that not too much will have to be rediscovered when people return to the study of kinetic theory I will present the most difficult and misunderstood parts of the subject in as clear a manner as I can.

We shall not dwell any further on the kinetic theory; we would rather move onto the development of the more sophisticated approach known as the *ensemble theory*, which may in fact be regarded as the statistical mechanics proper.[9] In this approach, the dynamical state of a given system, as characterized by the generalized coordinates q_i and the generalized momenta p_i, is represented by a *phase point* $G(q_i, p_i)$ in a *phase space* of appropriate dimensionality. The evolution of the dynamical state in time is depicted by the *trajectory* of the G-point in the phase space, the "geometry" of the trajectory being governed by the equations of motion of the system and by the nature of the physical constraints imposed on it. To develop an appropriate formalism, one considers the given system along with