



# Statistical Mechanics

THIRD EDITION

统计力学 第3版

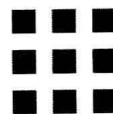
R. K. Pathria & Paul D. Beale



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## Third Edition

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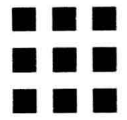
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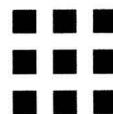
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# **Statistical Mechanics**

Third Edition



# Preface to the Third Edition

The second edition of *Statistical Mechanics* was published in 1996. The new material added at that time focused on phase transitions, critical phenomena, and the renormalization group — topics that had undergone vast transformations during the years following the publication of the first edition in 1972. In 2009, R. K. Pathria (R.K.P.) and the publishers agreed it was time for a third edition to incorporate the important changes that had occurred in the field since the publication of the second edition and invited Paul B. Beale (P.D.B.) to join as coauthor. The two authors agreed on the scope of the additions and changes and P.D.B. wrote the first draft of the new sections except for Appendix F which was written by R.K.P. Both authors worked very closely together editing the drafts and finalizing this third edition.

The new topics added to this edition are:

- *Bose–Einstein condensation and degenerate Fermi gas behavior in ultracold atomic gases:* Sections 7.2, 8.4, 11.2.A, and 11.9. The creation of Bose–Einstein condensates in ultracold gases during the 1990s and in degenerate Fermi gases during the 2000s led to a revolution in atomic, molecular, and optical physics, and provided a valuable link to the quantum behavior of condensed matter systems. Several of P.D.B.’s friends and colleagues in physics and JILA at the University of Colorado have been leaders in this exciting new field.
- *Finite-size scaling behavior of Bose–Einstein condensates:* Appendix F. We develop an analytical theory for the behavior of Bose–Einstein condensates in a finite system, which provides a rigorous justification for singling out the ground state in the calculation of the properties of the Bose–Einstein condensate.
- *Thermodynamics of the early universe:* Chapter 9. The sequence of thermodynamic transitions that the universe went through shortly after the Big Bang left behind mileposts that astrophysicists have exploited to look back into the universe’s earliest moments. Major advances in astronomy over the past 20 years have provided a vast body of observational data about the early evolution of the universe. These include the Hubble Space Telescope’s deep space measurements of the expansion of the universe, the Cosmic Background Explorer’s precise measurements of the temperature of the cosmic microwave background, and the Wilkinson Microwave Anisotropy Probe’s mapping of the angular variations in the cosmic microwave background. These data sets have led to precise determinations of the age of the universe, its composition and early evolution. Coincidentally, P.D.B.’s faculty office is located in the tower named after George Gamow, a member of the faculty at the University of Colorado in the 1950s and 1960s and a leader in the theory of nucleosynthesis in the early universe.
- *Chemical equilibrium:* Section 6.6. Chemical potentials determine the conditions necessary for chemical equilibrium. This is an important topic in its own right, but also plays a critical role in our discussion of the thermodynamics of the early universe in Chapter 9.



- *Monte Carlo and molecular dynamics simulations*: Chapter 16. Computer simulations have become an important tool in modern statistical mechanics. We provide here a brief introduction to Monte Carlo and molecular dynamics techniques and algorithms.
- *Correlation functions and scattering*: Section 10.7. Correlation functions are central to the understanding of thermodynamic phases, phase transitions, and critical phenomena. The differences between thermodynamic phases are often most conspicuous in the behavior of correlation functions and the closely related static structure factors. We have collected discussions from the second edition into one place and added new material.
- *Fluctuation–dissipation theorem and the dynamical structure factor*: Sections 15.3.A., 15.6.A, and 15.6.B. The fluctuation–dissipation theorem describes the relation between natural equilibrium thermodynamic fluctuations in a system and the response of the system to small disturbances from equilibrium, and it is one of the cornerstones of nonequilibrium statistical mechanics. We have expanded the discussion of the fluctuation–dissipation theorem to include a derivation of the key results from linear response theory, a discussion of the dynamical structure factor, and analysis of the Brownian motion of harmonic oscillators that provides useful practical examples.
- *Phase equilibrium and the Clausius–Clapeyron equation*: Sections 4.6 and 4.7. Much of the text is devoted to using statistical mechanics methods to determine the properties of thermodynamic phases and phase transitions. This brief overview of phase equilibrium and the structure of phase diagrams lays the groundwork for later discussions.
- *Exact solutions of one-dimensional fluid models*: Section 13.1. One-dimensional fluid models with short-range interactions do not exhibit phase transitions but they do display short-range correlations and other behaviors typical of dense fluids.
- *Exact solution of the two-dimensional Ising model on a finite lattice*: Section 13.4.A. This solution entails an exact counting of the microstates of the microcanonical ensemble and provides analytical results for the energy distribution, internal energy, and heat capacity of the system. This solution also describes the finite-size scaling behavior of the Ising model near the transition point and provides an exact framework that can be used to test Monte Carlo methods.
- *Summary of thermodynamic assemblies and associated statistical ensembles*: Appendix H. We provide a summary of thermodynamic relations and their connections to statistical mechanical ensembles. Most of this information can be found elsewhere in the text, but we thought it would be helpful to provide a rundown of these important connections in one place.
- *Pseudorandom number generators*: Appendix I. Pseudorandom number generators are indispensable in computer simulations. We provide simple algorithms for generating uniform and Gaussian pseudorandom numbers and discuss their properties.
- *Dozens of new homework problems*.

The remainder of the text is largely unchanged.

The completion of this task has left us indebted to many a friend and colleague. R.K.P. has already expressed his indebtedness to a good number of people on two previous occasions — in 1972 and in 1996 — so, at this time, he will simply reiterate the many words of gratitude he has already written. In addition though, he would like to thank Paul Beale for his willingness to be a partner in this project and for his diligence in carrying out the task at hand both arduously and meticulously.

On his part, P.D.B. would like to thank his friends at the University of Colorado at Boulder for the many conversations he has had with them over the years about research and pedagogy of statistical mechanics, especially Noel Clark, Tom DeGrand, John Price, Chuck Rogers, Mike

Dubson, and Leo Radzihovsky. He would also like to thank the faculty of the Department of Physics for according him the honor of serving as the chair of this outstanding department.

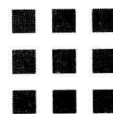
Special thanks are also due to many friends and colleagues who have read sections of the manuscript and have offered many valuable suggestions and corrections, especially Tom DeGrand, Michael Shull, David Nesbitt, Jamie Nagle, Matt Glaser, Murray Holland, Leo Radzihovsky, Victor Gurarie, Edmond Meyer, Matthew Grau, Andrew Sisler, Michael Foss-Feig, Allan Franklin, Shantha deAlwis, Dmitri Reznik, and Eric Cornell.

P.D.B. would like to take this opportunity to extend his thanks and best wishes to Professor Michael E. Fisher whose graduate statistical mechanics course at Cornell introduced him to this elegant field. He would also like to express his gratitude to Raj Pathria for inviting him to be part of this project, and for the fun and engaging discussions they have had during the preparation of this new edition. Raj's thoughtful counsel always proved to be valuable in improving the text.

P.D.B.'s greatest thanks go to Matthew, Melanie, and Erika for their love and support.

*R.K.P.*

*P.D.B.*



## Preface to the Second Edition

The first edition of this book was prepared over the years 1966 to 1970 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 toward correcting that deficiency.

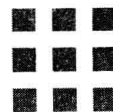
Despite the aforementioned shortcoming, the first edition of this book has continued to be popular over the last 20 years or so. I, therefore, decided not to tinker with it unnecessarily. Nevertheless, to make room for the new material, I had to remove some sections from the present text which, I felt, 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 more than 60 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 benefited 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 to 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 heartfelt 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.

*R.K.P.*





# 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 (1964–1965), the University of Alberta (1965–1967), the University of Waterloo (1969–1971), and the University of Windsor (1970–1971). 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 to 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 to 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 a historical introduction to the subject which stands separate from the main text. I trust the readers, especially the instructors, will find it of interest.

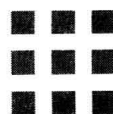
For those who wish to continue their study of statistical mechanics beyond the confines of this book, a fairly extensive bibliography is included. It contains a variety of references — old as well as new, experimental as well as theoretical, technical as well as pedagogical. I hope that this will make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

*R.K.P.*



# Historical Introduction

Statistical mechanics is a formalism that 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, and so on. Furthermore, the formalism of statistical mechanics enables us to investigate the *nonequilibrium* 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, and so on, the real work on this subject 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, therefore, be computed by considering the dynamical influence of the 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 was 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.<sup>1</sup>

Joule was the first to show that the pressure  $P$  was directly proportional to the square of the molecular speed  $c$ , which he had initially assumed to be the same for all molecules. Krönig (1856) went a step further. Introducing the “quasistatistical” assumption that, *at any time  $t$* ,

<sup>1</sup>As is well known, this “correction” was correctly evaluated, much later, by van der Waals (1873) who showed that, for large  $V$ ,  $b$  is *four times* the “actual” volume of the molecules; see Problem 1.4.

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; so 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 argument 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 equation (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.<sup>2</sup> 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 Clausius as the “principal founder of the kinetic theory of gases,” while Gibbs, in his Clausius obituary notice, called him the “father of statistical mechanics.”<sup>3</sup>

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 farther than his predecessors by deriving his famous law of the “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 skilfully used, leads to the same results as one gets from the more fundamental equation due to Boltzmann.<sup>4</sup>

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 1868–1871 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  $\varepsilon$  denotes the *total* energy of a molecule. These investigations also led to the *equipartition theorem*. Boltzmann further showed that, just

<sup>2</sup>For an excellent review of this and related topics, see Ehrenfest and Ehrenfest (1912).

<sup>3</sup>For further details, refer to Montroll (1963) where an account is also given of the pioneering work of Waterston (1846, 1892).

<sup>4</sup>This equivalence has been demonstrated in Guggenheim (1960) where the coefficients of viscosity, thermal conductivity, and diffusion of a gas of hard spheres have been calculated on the basis of Maxwell’s transport equation.

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, will ultimately go over to a Maxwell-Boltzmann distribution. In 1876 Boltzmann derived his famous transport equation, which, in the hands of Chapman and Enskog (1916–1917), has proved to be an extremely powerful tool for investigating macroscopic properties of systems in nonequilibrium 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 (1876–1877) 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 *quasiperiodic* 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, unfortunately, could not convince his opponents of the correctness of his viewpoint. At the same time, the energeticians, led by Mach and Ostwald, were criticizing the very (molecular) basis of the kinetic theory,<sup>5</sup> while Kelvin was emphasizing the “nineteenth-century clouds hovering over the dynamical theory of light and heat.”<sup>6</sup>

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

*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 on to the development of the more sophisticated approach known as the *ensemble theory*, which may in fact be regarded as the statistical mechanics proper.<sup>9</sup> In this approach, the dynamical state of a

<sup>5</sup>These critics were silenced by Einstein whose work on the Brownian motion (1905b) established atomic theory *once and for all*.

<sup>6</sup>The first of these clouds was concerned with the mysteries of the “aether,” and was dispelled by the theory of relativity. The second was concerned with the inadequacy of the “equipartition theorem,” and was dispelled by the quantum theory.

<sup>7</sup>Some people attribute Boltzmann's suicide on September 5, 1906 to this cause.

<sup>8</sup>Quotation from Montroll (1963).

<sup>9</sup>For a review of the historical development of kinetic theory leading to statistical mechanics, see Brush (1957, 1958, 1961a,b, 1965–1966).



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 an infinitely large number of “mental copies” thereof; that is, an *ensemble* of similar systems under identical physical constraints (though, at any time  $t$ , the various systems in the ensemble would differ widely in respect of their dynamical states). In the phase space, then, one has a swarm of infinitely many  $G$ -points (which, at any time  $t$ , are widely dispersed and, with time, move along their respective trajectories). The fiction of a host of infinitely many, identical but independent, systems allows one to replace certain dubious assumptions of the kinetic theory of gases by readily acceptable statements of statistical mechanics. The explicit formulation of these statements was first given by Maxwell (1879) who on this occasion used the word “statistico-mechanical” to describe the study of ensembles (of gaseous systems) — though, eight years earlier, Boltzmann (1871) had already worked with essentially the same kind of ensembles.

The most important quantity in the ensemble theory is the *density function*,  $\rho(q_i, p_i; t)$ , of the  $G$ -points in the phase space; a stationary distribution ( $\partial\rho/\partial t = 0$ ) characterizes a *stationary ensemble*, which in turn represents a system *in equilibrium*. Maxwell and Boltzmann confined their study to ensembles for which the function  $\rho$  depended solely on the energy  $E$  of the system. This included the special case of *ergodic* systems, which were so defined that “the undisturbed motion of such a system, if pursued for an unlimited time, would ultimately traverse (the neighborhood of) each and every phase point compatible with the *fixed* value  $E$  of the energy.” Consequently, the *ensemble average*,  $\langle f \rangle$ , of a physical quantity  $f$ , taken at *any* given time  $t$ , would be the same as the *long-time average*,  $\bar{f}$ , pertaining to *any* given member of the ensemble. Now,  $\bar{f}$  is the value we expect to obtain for the quantity in question when we make an appropriate measurement on the system; the result of this measurement should, therefore, agree with the theoretical estimate  $\langle f \rangle$ . We thus acquire a recipe to bring about a direct contact between theory and experiment. At the same time, we lay down a rational basis for a microscopic theory of matter as an alternative to the empirical approach of thermodynamics!

A significant advance in this direction was made by Gibbs who, with his *Elementary Principles of Statistical Mechanics* (1902), turned ensemble theory into a most efficient tool for the theorist. He emphasized the use of “generalized” ensembles and developed schemes which, in principle, enabled one to compute a complete set of thermodynamic quantities of a given system from purely mechanical properties of its microscopic constituents.<sup>10</sup> In its methods and results, the work of Gibbs turned out to be much more general than any preceding treatment of the subject; it applied to any physical system that met the simple-minded requirements that (i) it was mechanical in structure and (ii) it obeyed Lagrange’s and Hamilton’s equations of motion. In this respect, Gibbs’s work may be considered to have accomplished for thermodynamics as much as Maxwell’s had accomplished for electrodynamics.

These developments almost coincided with the great revolution that Planck’s work of 1900 brought into physics. As is well known, Planck’s *quantum hypothesis* successfully resolved the essential mysteries of the black-body radiation — a subject where the three best-established disciplines of the nineteenth century, namely mechanics, electrodynamics, and thermodynamics, were all focused. At the same time, it uncovered both the strengths and the weaknesses of these disciplines. It would have been surprising if statistical mechanics, which linked thermodynamics with mechanics, could have escaped the repercussions of this revolution.

<sup>10</sup>In much the same way as Gibbs, but quite independently of him, Einstein (1902, 1903) also developed the theory of ensembles.



The subsequent work of Einstein (1905a) on the photoelectric effect and of Compton (1923a,b) on the scattering of x-rays established, so to say, the “existence” of the *quantum of radiation*, or the *photon* as we now call it.<sup>11</sup> It was then natural for someone to derive Planck’s radiation formula by treating black-body radiation as a *gas of photons* in the same way as Maxwell had derived his law of distribution of molecular speeds for a gas of conventional molecules. But, then, does a gas of photons differ so radically from a gas of conventional molecules that the two laws of distribution should be so different from one another?

The answer to this question was provided by the manner in which Planck’s formula was derived by Bose. In his historic paper of 1924, Bose treated black-body radiation as a gas of photons; however, instead of considering the allocation of the “individual” photons to the various energy states of the system, he fixed his attention on the number of states that contained “a particular number” of photons. Einstein, who seems to have translated Bose’s paper into German from an English manuscript sent to him by the author, at once recognized the importance of this approach and added the following note to his translation: “Bose’s derivation of Planck’s formula is in my opinion an important step forward. The method employed here would also yield the quantum theory of an ideal gas, which I propose to demonstrate elsewhere.”

Implicit in Bose’s approach was the fact that in the case of photons what really mattered was “the set of numbers of photons in various energy states of the system” and not the specification as to “which photon was in which state”; in other words, photons were *mutually indistinguishable*. Einstein argued that what Bose had implied for photons should be true for material particles as well (for the property of indistinguishability arose essentially from the wave character of these entities and, according to de Broglie, material particles also possessed that character).<sup>12</sup> In two papers, which appeared soon after, Einstein (1924, 1925) applied Bose’s method to the study of an ideal gas and thereby developed what we now call *Bose–Einstein statistics*. In the second of these papers, the fundamental difference between the new statistics and the classical *Maxwell–Boltzmann* statistics comes out so transparently in terms of the indistinguishability of the molecules.<sup>13</sup> In the same paper, Einstein discovered the phenomenon of *Bose–Einstein condensation* which, 13 years later, was adopted by London (1938a,b) as the basis for a microscopic understanding of the curious properties of liquid He<sup>4</sup> at low temperatures.

Following the enunciation of Pauli’s exclusion principle (1925), Fermi (1926) showed that certain physical systems would obey a different kind of statistics, namely the *Fermi–Dirac statistics*, in which not more than one particle could occupy the same energy state ( $n_i = 0, 1$ ). It seems important to mention here that Bose’s method of 1924 leads to the Fermi–Dirac distribution as well, provided that one limits the occupancy of an energy state to *at most* one particle.<sup>14</sup>

<sup>11</sup>Strictly speaking, it might be somewhat misleading to cite Einstein’s work on the photoelectric effect as a proof of the existence of photons. In fact, many of the effects (including the photoelectric effect), for which it seems necessary to invoke photons, can be explained away on the basis of a wave theory of radiation. The only phenomena for which photons seem indispensable are the ones involving *fluctuations*, such as the Hanbury Brown–Twiss effect or the Lamb shift. For the relevance of fluctuations to the problem of radiation, see ter Haar (1967, 1968).

<sup>12</sup>Of course, in the case of material particles, the total number  $N$  (of the particles) will also have to be conserved; this had not to be done in the case of photons. For details, see Section 6.1.

<sup>13</sup>It is here that one encounters the *correct* method of counting “the number of distinct ways in which  $g_i$  energy states can accommodate  $n_i$  particles,” depending on whether the particles are (i) distinguishable or (ii) indistinguishable. The occupancy of the individual states was, in each case, *unrestricted*, that is,  $n_i = 0, 1, 2, \dots$

<sup>14</sup>Dirac, who was the first to investigate the connection between statistics and wave mechanics, showed, in 1926, that the wave functions describing a system of identical particles obeying Bose–Einstein (or Fermi–Dirac) statistics must be symmetric (or antisymmetric) with respect to an interchange of two particles.

Soon after its appearance, the Fermi–Dirac statistics were applied by Fowler (1926) to discuss the equilibrium states of white dwarf stars and by Pauli (1927) to explain the weak, temperature-independent paramagnetism of alkali metals; in each case, one had to deal with a “highly degenerate” gas of electrons that obey Fermi–Dirac statistics. In the wake of this, Sommerfeld produced his monumental work of 1928 that not only put the electron theory of metals on a physically secure foundation but also gave it a fresh start in the right direction. Thus, Sommerfeld could explain practically all the major properties of metals that arose from conduction electrons and, in each case, obtained results that showed much better agreement with experiment than the ones following from the classical theories of Riecke (1898), Drude (1900), and Lorentz (1904–1905). Around the same time, Thomas (1927) and Fermi (1928) investigated the electron distribution in heavier atoms and obtained theoretical estimates for the relevant binding energies; these investigations led to the development of the so-called *Thomas–Fermi model* of the atom, which was later extended so that it could be applied to molecules, solids, and nuclei as well.<sup>15</sup>

Thus, the whole structure of statistical mechanics was overhauled by the introduction of the concept of indistinguishability of (identical) particles.<sup>16</sup> The statistical aspect of the problem, which was already there in view of the large number of particles present, was now augmented by another statistical aspect that arose from the probabilistic nature of the wave mechanical description. One had, therefore, to carry out a *two-fold* averaging of the dynamical variables over the states of the given system in order to obtain the relevant expectation values. That sort of a situation was bound to necessitate a reformulation of the ensemble theory itself, which was carried out step by step. First, Landau (1927) and von Neumann (1927) introduced the so-called *density matrix*, which was the quantum-mechanical analogue of the *density function* of the classical phase space; this was elaborated, both from statistical and quantum-mechanical points of view, by Dirac (1929–1931). Guided by the classical ensemble theory, these authors considered both *microcanonical* and *canonical* ensembles; the introduction of *grand canonical* ensembles in quantum statistics was made by Pauli (1927).<sup>17</sup>

The important question as to which particles would obey Bose–Einstein statistics and which Fermi–Dirac remained theoretically unsettled until Belinfante (1939) and Pauli (1940) discovered the vital connection between spin and statistics.<sup>18</sup> It turns out that those particles whose spin is an integral multiple of  $\hbar$  obey Bose–Einstein statistics while those whose spin is a half-odd integral multiple of  $\hbar$  obey Fermi–Dirac statistics. To date, no third category of particles has been discovered.

Apart from the foregoing milestones, several notable contributions toward the development of statistical mechanics have been made from time to time; however, most of those contributions were concerned with the development or perfection of mathematical techniques that make application of the basic formalism to actual physical problems more fruitful. A review of these developments is out of place here; they will be discussed at their appropriate place in the text.

<sup>15</sup>For an excellent review of this model, see March (1957).

<sup>16</sup>Of course, in many a situation where the wave nature of the particles is not so important, classical statistics continue to apply.

<sup>17</sup>A detailed treatment of this development has been given by Kramers (1938).

<sup>18</sup>See also Lüders and Zumino (1958).

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