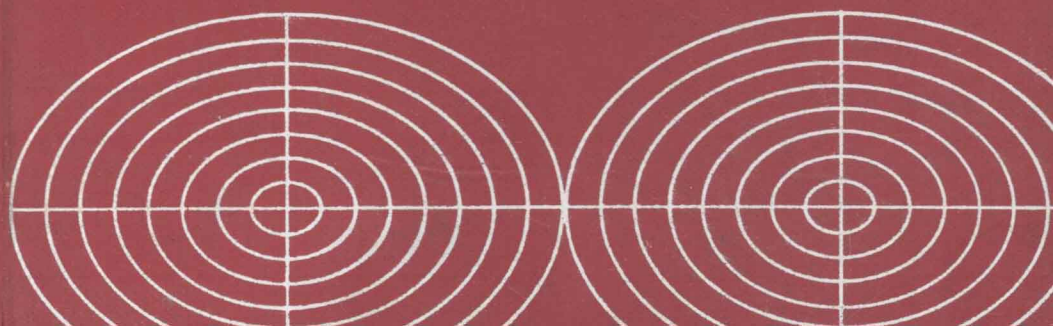# Elements
of
Thermostatistics

D. ter Haar

Second Edition

ELEMENTS
OF
THERMOSTATISTICS

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Second Edition

ELEMENTS

OF

THERMOSTATISTICS

TO

MY

WIFE

PREFACE TO THE SECOND EDITION

More than thirteen years have elapsed since the manuscript of the first edition was completed. For some time it has been clear that a second edition was needed. In the last fifteen years statistical mechanics has developed at an enormous pace, and a textbook on statistical mechanics should take these developments into account. When I started to contemplate what changes should be made, it soon became clear that, if the book were to cover even approximately the same ground as the first edition did, it would have to be greatly expanded. It was then decided to split the book into two parts, the first volume covering the basic theory; a second volume, advanced theory. As a result, the present volume is now probably more suitable as a textbook for advanced undergraduate courses than the first edition was. To improve its usefulness a variety of problems has been included. I am greatly indebted to R. Kubo and the North Holland Publishing Company for permission to incorporate some of the problems from Kubo's *Statistical Mechanics* and to the Oxford University Press for permission to incorporate problems from Oxford University Examination Papers. To some extent I have adopted Kubo's philosophy in that I feel that, to get the greatest advantage from the present volume, the student should work through most of the problems and so learn the subject by practicing it. A number of topics—especially in the theory of metals and semiconductors, which were treated in the text of the first edition, have now been relegated to the problems section, partly to give the student experience in using statistical methods and partly to make room for other topics.

I should like to express my thanks to the many readers, users, and reviewers who have given me the benefit of their comments and criticism. In many cases I have followed their advice, and I have found that the reactions of my own students especially have been invaluable in finding out obscure passages that needed clarification.

I have finally had the strength of my convictions and have used Kramers' terminology "Thermostatistics" in the title of the second edition.

A comparison between the first edition and the second edition will show that the present volume contains Chapters I to IV of the first edition as Chapters 1 to 4; Chapters V and VI of the first edition make up the present

Chapter 5, while Chapter VII becomes Chapter 6. Parts of Chapter IX of the first edition are incorporated in Chapter 4 and in a problem at the end of Chapter 5; Chapter X and XI of the old edition have been nearly completely incorporated in various problems; and some topics of Chapter XIII have also been incorporated in problems. A few sections of the first appendix have been put either in problems or in Chapters 5 and 6; Appendix II has become Chapter 8; Appendix III, Chapter 9; Appendix IV, Section 4.5; and Appendix VI, Chapter 7. The various parts of the mathematical appendix have been inserted at the appropriate spots in the earlier chapters. The main new topics covered in this book are the Saha equilibrium (Section 6.9), the Kramers-Casimir discussion of the third law (Section 9.2), fluctuations (Sections 7.1 and 7.2), and a more extensive discussion of the density matrix. A fair amount of new material is also to be found in the problems sections. Readers will probably also notice that the notation has been changed considerably to bring it in line with present-day practice.

Once again I appeal to readers and reviewers to let me have the benefit of their detailed criticism.

D. t. H.

Magdalen College, Oxford
May 1966

PREFACE TO THE FIRST EDITION

It is usual for an author to explain in a preface the reasons for writing the particular book which he is presenting to the public, to state who are the readers whom he has in mind for the book, to sketch the history of the writing of the book, and, last but not least, to express his thanks to all people who have been of assistance during the completion of the book.

The reason for writing another textbook on statistical mechanics was the feeling that there should be a textbook which combined in not too large a volume an outline of the main elements of statistical mechanics, starting from the Maxwell distribution and ending with quantum mechanical grand ensembles, with an account of a number of successful applications of these elements. Almost all existing textbooks stress only one or the other of these two aspects. It is hoped that readers will point out to me how far my own attempt has been successful, and I should at this point like to express the hope that reviewers will let me have the benefit of their detailed criticism.

The book is meant to be a textbook and is thus primarily intended for students. I have had in mind graduate students. This means that it should be used as a text for graduate lectures in the United States or for postgraduate lectures in the United Kingdom. It will probably be too advanced as a textbook for honors courses in British universities, although parts of it might be used as such and have been used as such by me. It is hoped that the book can also be used as a research tool and that it is possible to see from the applications how the theory might be applied to other subjects. For that reason I have tried to give as complete a bibliography as was feasible in the framework of a textbook. As the manuscript of the book was essentially completed at the beginning of 1952, references to papers published in 1951 or 1952 will not be complete.

A first rough outline of the book was sketched during the last war-winter in Leiden. A number of students were deprived of the regular lecture courses because Leiden University was closed by the occupying authorities, and the outline of the present book served as a substitute for the regular statistical mechanics course. The manuscript then rested until I wrote the first draft of Parts A and B at Purdue University during 1947–1948. There was another

interval until 1950, when I came to St. Andrews, where the manuscript in its present form was started and finished.

It is a pleasant task to thank the many physicists who have given me their advice on parts of the manuscript. My thanks are especially due to Professors F. J. Belinfante, H. M. James, K. Lark-Horovitz, H. Margenau, R. E. Peierls, and F. E. Simon, who have helped me with their criticism and advice. If the approach is sometimes not very clear and if my English has sometimes a distinct foreign flavor, it cannot be blamed on Professor F. Y. Poynton, who has tried to make Parts A and B as far as possible easy reading for students, or on Professors E. S. Akeley and J. F. Allen, who have tried to weed out of the text all barbarisms. I should like to express to them my warmest gratitude. Finally I should like to express my great indebtedness to Professor H. A. Kramers. Anybody who is familiar with his lectures on statistical mechanics will immediately see how much this book owes to him. It is far from a platitude to say that it would never have been written but for Professor Kramers. Not only did he give me an outline of the contents of Parts A and B; in discussions and in lectures he has taught me the fundamental ideas of the subject. I can therefore with some justification claim that the method of treatment in Parts A and B goes straight back to Boltzmann, via Kramers and Ehrenfest. Large parts of the book are, indeed, nearly wholly based on a series of lectures given by Professor Kramers in Leiden during 1944–1945.

In conclusion, I should like to express my thanks to Professor K. Lark-Horovitz and Miss A. Scudder for their help in editing the manuscript.

D. t. H.

Department of Natural Philosophy
St. Andrews
January, 1954

INTRODUCTION

Thermostatistics, to use the term coined by Kramers for statistical mechanics, is a subject that can be fruitfully studied only if a great number of other subjects in physics are well understood. It has thus been assumed that the reader is well acquainted with classical mechanics, quantum theory, thermodynamics, and calculus. As an indication of the standard assumed, we give the following, rather arbitrary, list of textbooks.

GENERAL THEORETICAL PHYSICS

R. M. Eisberg, *Fundamentals of Modern Physics*, New York, 1961.
G. Joos, *Theoretical Physics*, New York, 1944.
R. B. Leighton, *Modern Physics*, New York, 1959.

CLASSICAL MECHANICS

D. ter Haar, *Elements of Hamiltonian Mechanics*, Amsterdam, 1961.
L. D. Landau and E. M. Lifshitz, *Mechanics*, Oxford, 1960.

QUANTUM THEORY

A. S. Davydov, *Quantum Mechanics*, Oxford, 1965.
H. A. Kramers, *Quantum Mechanics*, Amsterdam, 1957.
A. Messiah, *Quantum Mechanics*, Amsterdam, 1960.

THERMODYNAMICS

D. ter Haar and H. Wergeland, *Elements of Thermodynamics*, Reading, Mass., 1966.
L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Oxford, 1958.

MATHEMATICAL PHYSICS

E. T. Whittaker and G. N. Watson, *Modern Analysis*, Cambridge, 1927.
H. and B. S. Jeffreys, *Mathematical Physics*, Cambridge, 1946.

Many subjects that belong to statistical mechanics have not been treated in the present book. From among the large number of textbooks now available we mention the following ones as treating topics not to be found

in the present textbook or—more often—as treating the various topics in a different manner. We wish to emphasize that this list is at least as arbitrary as the list of books given above.

J. de Boer and G. E. Uhlenbeck (eds.), *Studies in Statistical Mechanics*, Amsterdam, Vol I, 1962 (continuing series).

R. H. Fowler, *Statistical Mechanics*, Cambridge, 1936.

R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge, 1939.

J. W. Gibbs, *Elementary Principles in Statistical Mechanics*, New Haven, 1902.

T. L. Hill, *Statistical Mechanics*, New York, 1956.

K. Huang, *Statistical Mechanics*, New York, 1963.

C. Kittel, *Elementary Statistical Physics*, New York, 1958.

L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Oxford, 1958.

D. K. C. MacDonald, *Introductory Statistical Mechanics for Physicists*, New York, 1963.

J. E. and M. G. Mayer, *Statistical Mechanics*, New York, 1940.

A. Münster, *Statistische Thermodynamik*, Berlin, 1956.

G. S. Rushbrooke, *Introduction to Statistical Mechanics*, Oxford, 1949.

E. Schrödinger, *Statistical Thermodynamics*, Cambridge, 1948.

R. C. Tolman, *Statistical Mechanics*, Oxford, 1938.

G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics*, Providence, R. I., 1963.

We further refer to the monographs and papers mentioned at the end of each chapter.

Sections printed in small type indicate arguments that can be omitted on first reading or that are slightly more advanced or complicated than the rest of the text. The decimal system is used to number the equations. The number before the decimal point refers to the chapter and the first decimal number (or in the case of Chapter 5, the first two decimal numbers) to the section. Figures are numbered consecutively within each chapter. The first occurrence of a symbol is given in the glossary at the back of the book.

CONTENTS

CHAPTER 1/   THE MAXWELL DISTRIBUTION

CHAPTER 2/   THE MAXWELL-BOLTZMANN DISTRIBUTION

I

The Maxwell
Distribution

1.1 THE MAXWELL DISTRIBUTION

Equilibrium statistical mechanics, or "thermostatistics," to use a term coined by Kramers,* is that branch of physics which attempts to derive the equilibrium or thermal properties of matter in bulk, and of radiation, from the properties of the constituent particles. Such an atomistic interpretation of the thermal properties of matter was first attempted in the kinetic theory of gases, developed in the nineteenth century by Clausius, Maxwell, and Boltzmann. In this theory it was shown how such phenomenological concepts as

* H. A. Kramers, *Nuovo cimento*, **6** Suppl., 158 (1949).

temperature and entropy could be interpreted in terms of the *average* properties of the particles that were the constituent parts of the systems under consideration. Kinetic theory could be applied as long as one could either completely neglect the interactions between the particles or could neglect them to a first approximation, taking them into account in second approximation. Such an approach leads, for instance, to the van der Waals law of an imperfect gas, as we shall see in Section 1.3 of this chapter. In most physical systems, however, this approach is much too simplified, and one needs to have recourse to more sophisticated methods of averaging.

This more sophisticated approach is statistical mechanics proper, a term coined by J. W. Gibbs in 1901 for that branch of rational mechanics which deals statistically with systems consisting of large numbers of constituents. In the first four chapters we shall consider systems of independent particles, a subject which really is part of kinetic theory, while in later chapters we shall consider statistical mechanics proper. The reason for using statistical methods to treat physical systems is partly because they are so complicated that they present us with "well-nigh unsurmountable mathematical difficulties"* if we try to solve their equations of motion exactly; and partly because, even if we could solve these equations of motion exactly, we have only incomplete experimental data from which we can obtain the boundary conditions for the equations of motion.

In the present chapter we shall confine ourselves to the simplest possible system: a monatomic gas, that is, a system of point particles, enclosed in a vessel of volume V. We shall assume that there are no external forces acting upon the gas apart from the forces which the walls of the vessel will exert on the gas and which in fact will keep the gas within the vessel. We introduce Cartesian coordinates x, y, and z to describe the system; the position of the ith particle is thus determined by its three position coordinates x_i, y_i, and z_i, or by the vector $\mathbf{r}_i$.† We denote by u, v, and w the x, y, and z components of a velocity $\mathbf{c}$, and u_i, v_i, and w_i are thus the components of the velocity $\mathbf{c}_i$, of the ith particle. Once the positions and velocities of all the atoms are given, the microscopic behavior of the system is completely determined, provided the interatomic forces and the forces exerted by the walls on the atoms are known. If N be the number of atoms in the system, we need $6N$ quantities, for instance, x_i, y_i, z_i, u_i, v_i, w_i ($i = 1$ to N) to determine the microscopic behavior. However, usually we are interested only in a few combinations of these $6N$ quantities that will determine the macroscopic behavior of the system. We mentioned a moment ago that the exact knowledge of all $6N$ coordinates and velocities is outside the experimental possibilities, while the computation of their values from the equations of motion is outside our mathematical powers. As N is usually an extremely large number — of the order of 10^{19}

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* H. A. Kramers, *ibid.*
† Vectors are denoted by boldface type.

for one cm³ of a gas at NTP—we can use this fact and apply statistical methods in the safe knowledge that, because of the extremely large number of degrees of freedom, fluctuations will in general be small.

Let us for the moment neglect first of all the influence of the wall, and secondly possible fluctuations. In that case the number of atoms in a unit volume of the gas will be independent of the position of that unit volume in the gas. If we denote the number of atoms per unit volume by n, we have

$$n = \frac{N}{V}.$$
(1.101)

Let us denote by

$$f(u,v,w)\ du\ dv\ dw$$

the number of atoms per unit volume the velocity components of which lie in the specified intervals $(u,u+du)$, $(v,v+dv)$, and $(w,w+dw)$. The function $f(u,v,w)$ will be called the *distribution function*. It determines the fraction of atoms with velocities within given intervals. This fraction is obtained by dividing $f(u,v,w)\ du\ dv\ dw$ by n.

We shall call the Cartesian three-dimensional space in which we can plot the x, y, and z components of the velocities *velocity space*, and the point (u,v,w) in velocity space will be called the *representative point* of an atom with velocity components u, v, and w.

From the definition of $f(u,v,w)$ it follows that it satisfies the equation of *normalization*

$$\int_{-\infty}^{+\infty} du \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dw f(u,v,w) = n.$$
(1.102)

In the present chapter we shall assume that $f(u,v,w)$ is not only independent of x, y, and z, but also does not depend explicitly on the time t.

Let A be a quantity that is a function of the velocity components of an atom, but which does not explicitly depend on either x, y, and z or t. As an example we may give the kinetic energy of an atom. We can now ask for the *average value*, $\bar{A}$, of $A(u,v,w)$ where the average is taken over all the atoms of the gas and where the average value is equivalent to the arithmetic mean, that is, defined by the equation

$$\bar{A} = \frac{1}{n} \iiint_{-\infty}^{+\infty} du\ dv\ dw A(u,v,w) f(u,v,w).$$
(1.103)

Neither A nor f depends on x, y, z, or t, so that $\bar{A}$ will also be independent of x, y, z, and t.