

## SELECTED READINGS IN PHYSICS

There is a tendency nowadays for undergraduates to learn their physics completely from textbooks, not becoming acquainted with the original literature and therefore not realising how the subject grew and developed. The purpose of the series in which this volume is published is to present a set of reasonably priced books which give, for a particular subject, or a particular physicist, reprints of those papers which record the development of new ideas, preceded by a careful introduction which places the papers in the context of present-day physics.

### KINETIC THEORY

#### VOLUME 2 IRREVERSIBLE PROCESSES

This book, like volume 1, is intended to aid the teaching of physics from a historical viewpoint. The papers are mostly of a more technical character, reflecting the further development of the kinetic theory after 1865. The two long papers by Maxwell and Boltzmann contain detailed discussions of the foundations of the theory of transport processes in gases, including the original derivation of Boltzmann's transport equation and the "H-theorem". The transport coefficients are calculated exactly for the special case of particles interacting with inverse fifth-power forces. These papers still provide the starting point for modern research in the subject; more recent work has amplified but not superseded them.

The famous controversy about irreversibility and the direction of time is contained in the other papers by William Thomson, Boltzmann, Poincaré, and Zermelo. Most of these papers can be understood by readers without a mathematical background, and they are still of great significance for the history and philosophy of science.

The papers by Boltzmann, Poincaré, and Zermelo are here published in English for the first time.

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# KINETIC THEORY

Volume 2 IRREVERSIBLE PROCESSES

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by

S. G. BRUSH



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SELECTED READINGS IN PHYSICS

*General Editor:* D. TER HAAR

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## KINETIC THEORY

Volume 2: Irreversible Processes

**Volume 1. The Nature of Gases and of Heat**

**Volume 2. Irreversible Processes**



*To Denise*

## Preface

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THIS is the second volume of a collection of fundamental papers on the kinetic theory of gases; it includes the two papers by Maxwell and Boltzmann in which the basic equations for transport processes in gases are formulated, together with the first derivation of Boltzmann's "*H*-theorem" and a sample of the later discussion of this theorem and the problem of irreversibility.

Whereas in Volume 1 of this series we restricted ourselves to reprinting short papers of a relatively elementary character, or gave only extracts from longer works, the present volume is almost entirely occupied by two rather long and detailed memoirs, one of which is published here in English for the first time. It is hoped that serious students of physics (at the advanced undergraduate or beginning postgraduate level) will benefit by a close study of these works. Although some of the results of Maxwell's and Boltzmann's investigations have been incorporated into modern textbooks, the derivations are usually presented in a very condensed form. Boltzmann's exposition goes to the opposite extreme and is perhaps unduly elaborate and repetitious; nevertheless one can acquire a deeper understanding of the subject if he is willing to spend the time to follow through the details of the derivations (as is indicated by the continued and deserved popularity of Tolman's monumental book, *The Principles of Statistical Mechanics*). It may be noted that Maxwell's theory, which for many years was considered somewhat irrelevant to physics because of its reliance on an artificial molecular model, is now recognized to be of great value in the mathematical treatment of transport phenomena; the Maxwellian inverse fifth-power force law provides an idealized limiting case that plays the same role in transport theory as the ideal gas does in the study of equilibrium thermodynamic properties.

For readers who wish to acquire a bird's-eye view of the subject without making an intensive study of the technical parts, we recommend the following: Introduction; Selection 1, first 7 pages and last 10 pages; Selection 2, first 5 pages; sections immediately following equations (16) and (25), and the discussion of entropy in the last 3 pages; Selection 3, first 5 pages; all of Selection 6; all of Selection 10.

### **Addendum to Volume 1**

After the first volume of this series was prepared, historical research was published which showed that the relation between pressure and volume of a gas, commonly known as Boyle's Law, should be credited to Henry Power as well as to Towneley and Boyle. See C. Webster, *Nature* **197**, 226 (1963), *Arch. Hist. Exact Sci.* **2**, 441 (1965), and I. B. Cohen, *Nature* **204**, 618 (1964).





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## *Part 1*





## Introduction

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THE works reprinted in the first volume of this series were concerned with establishing the fundamental nature of heat and of gases. By about 1865 this question seemed to have been definitely settled by the general adoption of thermodynamics and the kinetic theory of gases. Scientists could now turn their attention to working out the detailed consequences of these theories and comparing them with experiments.

Knowing the empirical laws relating pressure, volume, and temperature, many scientists had discovered for themselves the kinetic explanation based on the collisions of molecules with the walls of the container. The ideal gas laws could be deduced by assuming that the space occupied by the molecules themselves is negligible compared to that total volume of the gas; it was only a natural extension of the theory to try to explain deviations from the ideal gas laws by dropping this assumption, although it was not until 1873 that J. D. van der Waals found the most fruitful mathematical formulation of this extension. But accurate experimental data on viscosity, heat conductivity, and diffusion were not available until well after 1850, and the first kinetic theorists had to make their calculations of these properties without the advantage of knowing the answer beforehand. Moreover, the type of assumption that one makes about short-range intermolecular forces determines the first approximation to the transport coefficients, whereas it comes in only in the second approximation to the equilibrium properties. Of course, such circumstances made it all the more convincing when experiments confirmed the theoretical predictions; for example, Maxwell's discovery that the viscosity of a gas is independent of density (Selection 10, Vol. 1) was very important in establishing the kinetic theory.

One may distinguish two types of irreversible process: in the first, there is a continuous flow of mass, momentum, or energy resulting from variations in concentration, velocity, and temperature imposed externally; in the second, a gas that is initially in a non-equilibrium state spontaneously moves toward equilibrium in the absence of external interference. (The two types are, of course, intimately related, as shown by Maxwell's theory of relaxation processes (Selection 1) and by modern work on the "fluctuation-dissipation theorem"—transport coefficients can be expressed in terms of the relaxation of fluctuations, and conversely.)

Following the introduction of the "mean-free-path" concept by Clausius in 1858 (Vol. 1, Selection 9) and Maxwell's theory of transport processes based on it (Vol. 1, Selection 10) there was a large amount of theoretical work by such scientists as O. E. Meyer, J. Stefan, P. G. Tait, G. Jäger, and J. H. Jeans.<sup>†</sup> This work was devoted to refining the mean-free-path theory and applying it to various phenomena. Maxwell himself realized almost immediately that the mean-free-path method was inadequate as a foundation for kinetic theory, even though it might be useful for rough approximations, and while he revised his own original treatment of diffusion and heat conduction he did not publish any further works based on this method.<sup>‡</sup> Instead he developed the much more accurate technique based on transfer equations, described in Selection 1.

Maxwell's transfer equations provide a method for computing the rate of transport of any quantity such as mass, momentum, and energy which can be defined in terms of molecular properties, consistently with the macroscopic equations such as the Navier-Stokes equation of hydrodynamics. However, the actual calculation of transport coefficients depends in general on a knowledge of

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<sup>†</sup> See the works by Boltzmann (1896-8), Brush (1962), Jeans (1925) Kennard (1938) and Loeb (1934), cited in the Bibliography.

<sup>‡</sup> For diffusion theory, see Furry (1948). It is hoped that Maxwell's manuscripts on heat conduction and other topics in kinetic theory will be published shortly.

the velocity-distribution function, which is no longer assumed to be the same as the equilibrium Maxwell distribution; yet there is no direct way to compute this function. It was not until 1916 that Sydney Chapman worked out a systematic method for calculating the velocity-distribution function and all the transport coefficients of gases by means of the transfer equations. However, Maxwell discovered that in one special case, when the force between the molecules varies inversely as the fifth power of the distance, the distribution function enters the equations in such a way that one can calculate the transport coefficients without knowing it. In this case it turns out that the viscosity coefficient is directly proportional to the temperature, whereas in the case of hard spheres it is proportional to the square root of the temperature. Maxwell's own measurements of the viscosity of air, which he had been carrying out at about the same time, led him to believe that the former result is in agreement with experiment.† The inverse fifth-power force, which is an exactly soluble case for purely mathematical reasons, therefore seemed to be at the same time a good model for real gases, and Maxwell adopted it provisionally as the basis for his later work.‡

### Boltzmann

Ludwig Boltzmann (1844–1906), whose writings occupy the major part of this volume, was born and educated in Vienna, and taught there most of his life. He is best known for his work on the kinetic theory of gases and statistical mechanics. His equation for the velocity-distribution function of molecules (first derived in the work reprinted here as Selection 2) has been used extensively to study transport properties such as viscosity, thermal conductivity, and diffusion. Boltzmann's equation is actually equivalent to

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† J. C. Maxwell, *Phil. Trans. Roy. Soc. London* **156**, 249 (1866).

‡ J. C. Maxwell, *Trans. Cambridge Phil. Soc.* **12**, 547 (1879); see also Boltzmann (1896), Chapter III. The later work of Chapman and Enskog showed that thermal diffusion, which takes place in systems of molecules with any general force law, happens to be absent in the special case of inverse fourth-power forces.



Maxwell's set of transfer equations, and its solution presents exactly the same difficulties. Just as Chapman solved Maxwell's equations, so did David Enskog (1917) solve Boltzmann's equation in the general case, and the Maxwell-Boltzmann-Chapman-Enskog theory constitutes the completion of the classical kinetic theory of low-density gases. The basic theory has remained essentially unchanged since 1917; with appropriate modifications, it forms the basis for many modern theories of liquids, solids, plasmas, and neutron transport.

Though Boltzmann himself did not obtain the complete solution to his equation for the distribution function, he did deduce from it one important consequence, which later† came to be known as the *H*-theorem (see the last part of the first section of Selection 2). The *H*-theorem attempts to explain the irreversibility of natural processes by showing how molecular collisions tend to increase entropy; any initial distribution of molecular positions and velocities will almost certainly evolve into an equilibrium state, in which the velocities are distributed according to Maxwell's law.

The Maxwell velocity distribution law was also generalized by Boltzmann so as to apply to physical systems in which interatomic forces and external fields must be taken into account.‡ The so-called Boltzmann factor,  $e^{-E/kT}$ , which gives the relative probability of a configuration of energy  $E$  at a temperature  $T$ , provides the basis for all calculations of the equilibrium properties of matter from the molecular viewpoint. Boltzmann further showed that the entropy of a system in any physical state may be calculated from its probability by counting the number of molecular configurations corresponding to that state.§ This result, and the

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† Boltzmann himself originally used the letter  $E$ , and did not change to  $H$  until 1895; the first use of  $H$  for this quantity was apparently by S. H. Burbury, *Phil. Mag.* **30**, 301 (1890). A rumour has circulated among modern physicists that  $H$  was intended to be a capital eta, the letter eta having been used for entropy by Gibbs and other writers [see S. Chapman, *Nature* **139**, 931 (1937)]. This can hardly be true if in fact the usage was originated by Burbury, since he makes no such suggestion in his paper.

‡ L. Boltzmann, *Wien. Ber.* **58**, 517 (1868).

§ L. Boltzmann, *Wien. Ber.* **76**, 373 (1877).