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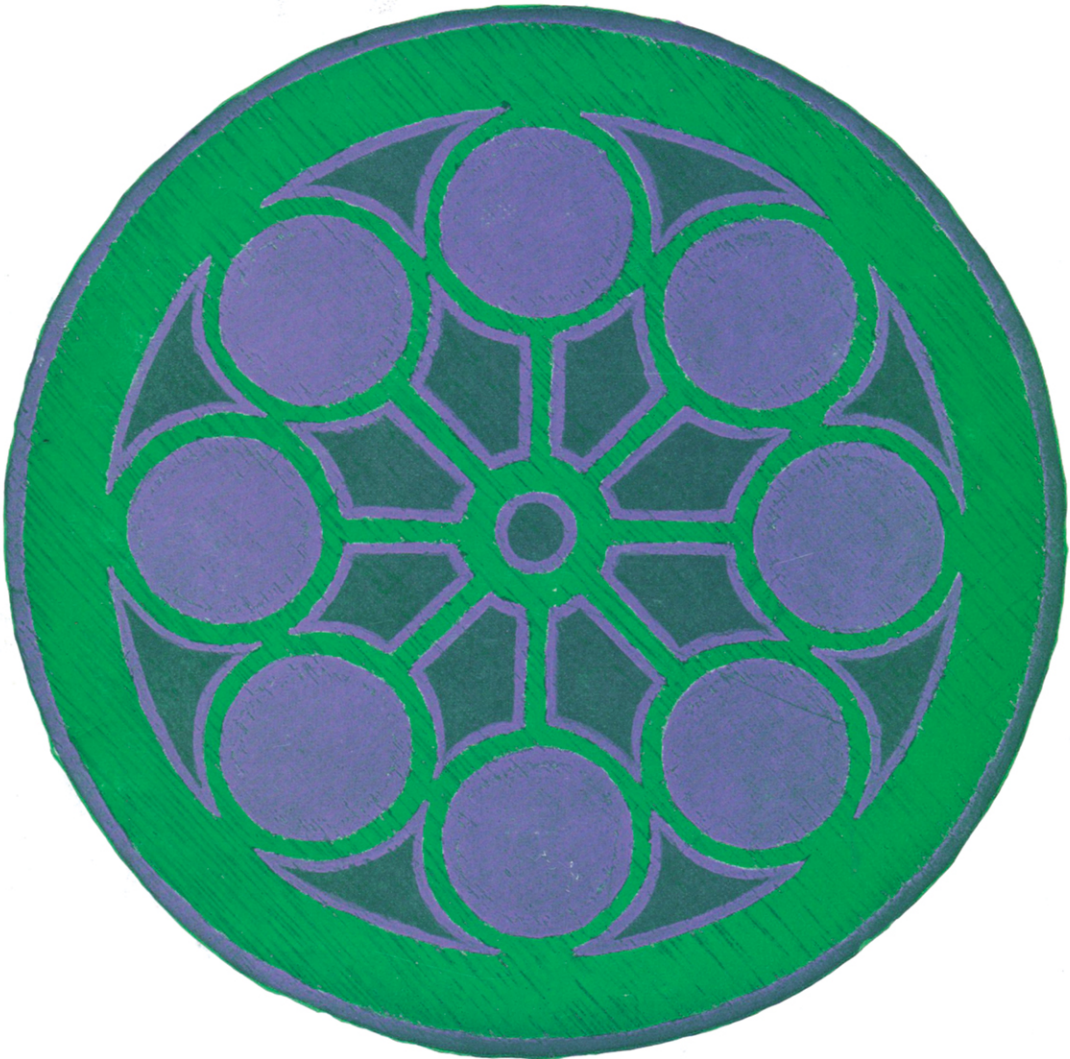
Volume 3

**The Chapman–Enskog solution
of the transport equation for
moderately dense gases**

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Volume 3

*The Chapman–Enskog solution of the
transport equation for moderately dense gases*

S. G. BRUSH



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To Nicholas

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Preface

THIS book was originally prepared as the third volume of the sequence on *Kinetic Theory* in the Selected Readings in Physics series, edited by Dr. D. ter Haar. However, because of its size and the more technical nature of the contents, a somewhat different format seemed advisable. Most of the works translated or reprinted here (in Part 2) will be useful primarily to graduate students and others undertaking research in kinetic theory, though it is hoped that Part 1 and Chapman's lecture reprinted at the end of Part 2 will be of more general interest.

It may seem strange that a collection of papers, most of which were published about 50 years ago, should be considered useful to modern theorists, while at the same time the advances of more recent years are only briefly summarized. The explanation is simple: at the present time there are half a dozen competing groups who disagree on notation, methodology, and judgment as to what problems are most worth solving; expositions of their respective viewpoints are easily available in a number of recent publications, and there would be no point in trying to select one for reprinting here. Perhaps the only thing generally agreed by most modern researchers in kinetic theory is that the achievement of Hilbert, Chapman, and Enskog in the period 1912–22 amounted to a milestone in the modern development of the subject, showing that systematic mathematical work was both necessary and fruitful, and pointing out the path to be followed by subsequent workers.

Up to now the usual introduction to the subject (at least for English-language students) has been Chapman and Cowling's monograph, *The Mathematical Theory of Non-uniform Gases*, which includes an exposition of Enskog's theory. This has been supplemented more recently by the Hirschfelder–Curtiss–Bird treatise on the *Molecular Theory of Gases and Liquids*, emphasizing practical applications, and by Harold Grad's article "Principles of the kinetic theory of gases" in the *Handbuch der Physik*, on the mathematical aspects. It is no criticism of those three excellent works to suggest that something is still to be gained by reading some of the earlier publications which they summarize and elaborate. In particular, there has long been a need for English translations of Enskog's 1917 dissertation and his 1922 paper on dense gases, and even the original German-language versions are not available in most libraries.

A brief explanation of the scope of the book is in order. The Chapman–Enskog theory was originally intended to apply to ordinary gases at densities within an order of magnitude of that corresponding to atmospheric pressure and room temperature. The molecular model for which most calculations were done was spherically symmetric with short-range repulsive force, with or without intermediate-range attractive forces, but without any long-range forces of the type involved in electrically charged systems. Moreover, it was

assumed that classical mechanics could be used once the molecular model was specified. In modern research, however, the term "kinetic theory of gases" includes a number of generalizations: to rarefied gases (of interest especially in aerodynamics); to systems of charged particles (plasma physics); to quantum mechanical systems (especially at very low temperatures); to more complicated molecular models representing polyatomic molecules, perhaps with internal structure; to mixtures; and to dense gases and liquids. The first three of these involve assumptions or methods basically different from those of Chapman and Enskog (though the Chapman-Enskog approach may still have some utility) and are not considered in this book. We restrict ourselves to *monatomic* gases since this is a reasonably self-contained subject; another volume at least would be required to deal with all the special problems involved in the theory of polyatomic gases. We include some reference to research on diffusion and thermal diffusion in mixtures, but we have ignored most other work on mixtures. Finally, we do include the extension of the theory to dense gases, and, indeed, this is the one area of modern research to which the Chapman-Enskog theory now seems most relevant.

Acknowledgments. The author is especially indebted to Prof. J. R. Dorfman, Prof. J. V. Sengers, and Prof. C. Truesdell, who spent considerable time in discussing various technical points concerning the modern kinetic theory of gases and in correcting errors in an earlier draft of the manuscript. For further valuable information and criticism the author wishes to thank Prof. E. G. D. Cohen, Prof. C. A. Coulson, Dr. A. F. Devonshire, Dr. H. E. DeWitt, Dr. D. Gass, Prof. M. S. Green, Dr. D. ter Haar, Prof. K. Kawasaki, Prof. E. A. Mason, Prof. S. Rice, Dr. B. Robertson, Prof. J. S. Rowlinson, Prof. R. J. Swenson, Dr. M. G. Velarde, Dr. J. Weinstock, Prof. D. R. Willis, and Prof. R. Zwanzig. The preparation of this book was supported by the U. S. National Science Foundation, research grant GS-2475, and in part by the Clark Fund of Harvard University.

PART 1

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CHAPTER I

The Work of Hilbert, Chapman, and Enskog

AT THE beginning of the 20th century the statistical–molecular viewpoint seemed to have been largely abandoned by scientists. Despite Boltzmann’s valiant defense of atomism and the statistical interpretation of irreversibility,¹ the more sophisticated and articulate scientists had succeeded in undermining the confidence in mechanical models that had been prevalent during the third quarter of the 19th century.² Even though the average scientist probably still believed in a molecular reality lying beneath the appearances with which he dealt, fashion favored the positivistic, phenomenological approach.

Of course there were exceptions; and while Boltzmann seemed to be almost the only practitioner of statistical physics in Germany and Austria, he could find followers in other countries. His visit to England in 1894 stimulated a lively discussion on the equipartition theorem and related problems, although Lord Kelvin continued to insist that the dynamical theory of heat had not yet emerged from under its 19th-century cloud.³ In Holland an active group of physicists and physical chemists led by J. D. van der Waals was pursuing new experimental knowledge on the equilibrium states of fluids, and integrating this knowledge with molecular theory;⁴ and H. A. Lorentz was applying Boltzmann’s kinetic theory to sound propagation and to the behavior of electrons in metals.⁵ When Boltzmann traveled to the St. Louis Exposition to speak at the Congress of Arts and Science in 1904, he took notice of the recently published *Statistical Mechanics* of J. Willard Gibbs, perhaps foreseeing that this elegant American version of his theories was better adapted for survival in the 20th century than his own somewhat cumbersome

¹ L. Boltzmann, *The Monist* **11**, 226, **12**, 65 (1901); papers translated in S. G. Brush, *Kinetic Theory*, vol. 2, Pergamon Press, 1966; René Dugas, *La Théorie Physique au sens de Boltzmann*, Editions du Griffon, Neuchatel-Suisse, 1959.

² See S. G. Brush, *Graduate Journal* **7**, 477 (1967) and works cited in the translator’s notes of Boltzmann’s *Lectures on Gas Theory*, University of California Press, Berkeley, 1964, pp. 23–24, 215. The idea of a mechanical basis being desirable for all physical explanation was also undermined by the attempts of Abraham and others to develop an electrodynamic theory of mass; see Max Jammer, *Concepts of Mass*, Harvard University Press, Cambridge, 1961, chapter 11. A good survey of the situation in 1900 is given in two articles by H.R. Post, *Phys. Educ.* **3**, 225, 307 (1968).

³ See the letters of Boltzmann, Bryan, Burbury, and Fitzgerald published in *Nature*, **51** and **52** (1894–5); Kelvin, *Phil. Mag.* [6] **2**, 1 (1901), based on a lecture at the Royal Institution, April 27, 1900.

⁴ See S. G. Brush, *Amer. J. Phys.* **29**, 593 (1961); J. R. Partington, *An Advanced Treatise on Physical Chemistry*, vol. 1, Longmans, London, 1949, pp. 568–579, 604–606, 640–645, 658–703.

⁵ Lorentz (1880, 1904, 1909) [see the Bibliography for details of major works, which are cited only by author’s name and year of publication in the text and notes].

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approach.⁶ And even in France, the home of positivism, the great Poincaré was beginning to look with more favor on kinetic theory, and Marcel Brillouin and Paul Langevin were trying to interpret and improve the works of Maxwell and Boltzmann.⁷

But the restoration of kinetic theory to a prominent position in physical research after 1905 was a result of other developments apparently unrelated to those mentioned above: the Einstein–Smoluchowski theory of Brownian movement, verified experimentally by Perrin;⁸ and the quantum theory of electromagnetic radiation, initiated by Max Planck.⁹ Boltzmann was only dimly aware of the significance of these unexpected applications of his methods before he committed suicide in 1906.¹⁰

The impact of the Brownian movement experiments, fortuitously combined with experiments on electrons, was immediate and dramatic: Einstein's theory was published in 1905. Perrin began his experiments the following year, and by 1910 the body of opinion hostile to the statistical–molecular viewpoint had dissolved; even Ostwald, one of the most prominent skeptics, had to admit that atoms really exist.¹¹ The role of statistical considerations in quantum theory was already recognized by this time, and was to become even more important. Ironically it was Max Planck, one of the skeptics of the 1880's and 1890's, and at that time a firm believer in the absolute validity of the second law of thermodynamics, who first applied Boltzmann's statistical theory of entropy to black-body radiation.¹² This theory became increasingly popular as it became associated with other early triumphs of quantum theory such as the Einstein–Debye theory of specific heats of solids, the Nernst heat theorem, and the Sackur–Tetrode theory of chemical reactions. (The latter finally provided a definite answer to the question. How does one define “probability” in Boltzmann's formula relating entropy to probability? The size of the “cell in phase space,” previously indeterminate, was now shown to be determined by Planck's constant.)

The central role of kinetic theory in the development of modern physics, especially quantum theory, is indicated by the fact that important international meetings such as the

⁶ L. Boltzmann, *Congress of Arts and Science, Universal Exposition, St. Louis, 1904*, ed. H. J. Rogers, vol. I, Houghton, Mifflin & Co., Boston, 1905, p. 591.

⁷ M. Brillouin (1900, 1902); Langevin (1905).

⁸ See S. G. Brush, *Arch. Hist. Exact Sciences* **5**, 1 (1968).

⁹ See D. ter Haar, *The Old Quantum Theory*, Pergamon Press, 1967; M. J. Klein, *Arch. Hist. Exact Sciences* **1**, 459 (1962).

¹⁰ According to Lise Meitner, Boltzmann in his lectures in Vienna from 1902 to 1906 never mentioned Planck's quantum theory or Einstein's explanation of the photoelectric effect and Brownian motion; see *Advancement of Science* **20**, no. 88, p. 39 (1964), also *Bull. Atomic Scientists*, Nov. 1964, p. 2. However, Max Planck, in his *Scientific Autobiography*, recalls that he told Boltzmann that the quantum theory was based on Boltzmann's statistical theories. (See Max Planck, *Scientific Autobiography and other papers*, Philosophical Library, New York, 1949, pp. 33, 41.)

¹¹ W. Ostwald, *Grundriss der allgemeinen Chemie*, Engelmann, Leipzig, 4, Aufl. 1909, quoted by Brush, *op. cit.* (note 8). See also T. Levi-Civita, *Scientia* **11**, 275 (1912).

¹² For remarks illustrating Planck's skepticism, see *Ann. Phys.* [3] **15**, 446 (1882), **19**, 358 (1883), and *Scientific Autobiography*, pp. 29–33. He probably had to become familiar with the mathematical apparatus of kinetic theory in the process of editing Kirchhoff's lectures on heat for publication; this involved him in a minor dispute with Boltzmann on the proof of the *H*-theorem [*Ann. Phys.* [3] **53**, 955 (1894), **55**, 220, 223 (1895)]. Even before Planck had adopted his statistical theory of radiation, he used a logarithmic entropy formula to prove, in effect, an *H*-theorem for radiation, in a manner very similar to Boltzmann's proof for gases; see Planck's *Physikalische Abhandlungen und Vorträge*, Vieweg, Braunschweig, 1958, Bd. I, pp. 585–589.