BLACK–BODY THEORY

AND THE

QUANTUM DISCONTINUITY

1894-1912

Thomas S. Kuhn

With a new Afterword

THE UNIVERSITY OF CHICAGO PRESS
Chicago & London

The University of Chicago Press, Chicago 60637
The University of Chicago Press, Ltd., London

 Published 1978
University of Chicago Press Edition 1987
Printed in the United States of America

96 95 94 93 5 4 3

Reprinted by arrangement with
Oxford University Press.

Library of Congress Cataloging-in-Publication Data

Kuhn, Thomas S.
Black-body theory and the quantum discontinuity, 1894–1912.

Reprint. Originally published: Oxford, Oxfordshire : Clarendon Press ; New York : Oxford University Press, 1978. With a new afterword.
Bibliography: p.
Includes index.
1. Black-Body radiation—History. 2. Quantum theory—History. I. Title.
[QC484.K83 1987] 530.1'2 86–30833
ISBN 0–226–45800–8 (pbk.)

For
Sarah, Liza, and Nat,
my teachers in discontinuity

PREFACE

This book is the outcome of a project I had not intended to undertake. An account of its genesis may therefore suggest the volume's purpose and simultaneously provide some clues to the nature of historical research. Early in 1972 a change in professional circumstances enabled me to begin detailed study of the history of quantum theory, a topic with which I had long been concerned but one of which my knowledge was for the most part superficial. At that time I intended to presuppose the first stage of the development of quantum concepts, for it had been much studied by extremely competent scholars.[1] Rather than begin at the beginning, as this volume does, I planned to prepare a monograph on the development of quantum conditions, a central theme in the evolution of the so-called old quantum theory and one which could provide a strategic overview of the development of that theory as a whole. Only against the background provided by that overview, I thought, could the emergence of matrix mechanics, wave mechanics, and electron spin during 1925 and 1926 be understood.

In a general way I was aware of the structure of the developments I wished to explore, and I also knew the climactic episodes with which my story would close: the inventions, during 1922 and 1923, of Landé's vector model of the atom and of Bohr's model of the periodic table. Nevertheless, I lacked one detail prerequisite to the start of focused research. I did not know when physicists first began to look for quantum conditions, when they first asked about the nature of the restrictions placed by the quantum on the motion of systems more general than Planck's one-dimensional harmonic oscillator. That question, I was aware, had been much discussed at the first Solvay Congress late in 1911, but I did not know when or how it had initially arisen, and I could not therefore tell where the story I wished to relate should begin. Neither the printed proceedings of the Congress nor the abundant secondary literature on the first decade of the development of quantum concepts provided clues.

After numerous weeks of fruitless search for an answer, I determined to attempt a less direct approach: I would work my way chronologically through Planck's relevant papers, readily accessible in his collected scientific works. Planck might not, of course, be the person who first conceived the need for generalized quantum conditions, but his first mention of that need would localize my problem in time and very probably, through context and accompanying citations, in space as well. As always at the beginning of a major research project, the time available seemed ample, and I did not therefore begin my search by reading Planck's famous quantum papers of 1900 and 1901, papers I had read many times before and thought I understood. Instead, I started with his earlier work on black-body theory, the first product of which had been published in 1895.

That reading program had, for me, an extraordinary result. Having assimilated Planck's classical black-body theory, I could no longer read his first quantum papers as I and others had regularly read them before.[2] They were not, I now saw, a fresh start, an attempt to supply an entire new theory. Rather they aimed to fill a previously recognized gap in the derivation of Planck's older theory, and they did not at all require that the latter be set aside. In particular, the arguments in Planck's first quantum papers did not, as I now read them, seem to place any restrictions on the energy of the hypothetical resonators that their author had introduced to equilibrate the distribution of energy in the black-body radiation field. Planck's resonators, I concluded, absorbed and emitted energy continuously at a rate governed precisely by Maxwell's equations. His theory was still classical.

Shortly afterwards I discovered that that same classical viewpoint was also developed, but far more clearly, in the first edition of Planck's well-known *Lectures on the Theory of Thermal Radiation*, delivered in the winter of 1905–06 and published late in the following spring. Even in the middle of 1906, neither restrictions on classically permissible energy nor discontinuities in the processes of emission or absorption were to be found in Planck's work. Those are, however, the central conceptual novelties we have come to associate with the quantum, and they have invariably been attributed to Planck and located in his work at the end of 1900. Only after studying the extended treatment of Planck's theory in the *Lectures* of 1906 was I quite able to believe that I was now reading his first quantum papers correctly and that they did not posit or imply the quantum discontinuity.

At that point, early in the summer of 1972, I temporarily suspended my attempt to locate the start of the search for quantum conditions. Instead, I began work on an article embodying my new reading of Planck. Gradually and against my will, that article became a book, partly because I found that understanding Planck's early black-body theories demanded an acquaintance with previously unexplored aspects of Boltzmann's statistical treatment of irreversibility and partly because I came to realize that I must explain how discontinuity had entered physics if it had not, as previously thought, come from Planck. Numerous revisions later, this book results.

In its final form the manuscript is divided into three parts, the last a brief epilogue. Part One is the story I had originally intended to tell in an article, but much extended, especially at the start, to provide the background material appropriate to a book. Chapter I opens with a sketch of the black-body problem, describes the development of Planck's research before he took that problem up, and explores the ways in which his earlier concern with the foundations of thermodynamics both motivated and shaped his approach to thermal radiation. It concludes with a sketch of the earliest stage of Planck's black-body research, culminating in 1896 with his presentation of differential equations for a radiation-damped resonator.

Chapter II is a long but essential digression on the development of Boltzmann's statistical treatment of irreversibility, which proved critically important to the route followed by Planck's research from the beginning of 1898. Chapter III, which describes the development of Planck's black-body theory from 1896 through 1899, presents the first of two distinct stages in his assimilation of Boltzmann's statistical approach. The second emerges in Chapter IV, which considers the direction taken by Planck's research during 1900 and 1901, years in which he invented his famous black-body distribution law and then provided the first two derivations for it. Chapter V, which concludes Part One, considers how Planck and his first readers understood his revised theory during the years from 1900 to 1906.

The four following chapters, which constitute Part Two, trace the emergence and assimilation of the concept of a discontinuous physics. Chapters VI and VII deal primarily with the work of Ehrenfest and Einstein, the two physicists who first recognized that Planck's black-body law could not be derived without restricting resonator energy to integral multiples of $h\nu$ or some equivalent non-classical step. Their demonstrations, both published in 1906, had little apparent impact, but the next, presented by Lorentz in 1908, is the presumptive cause of a rapid change in the attitude, at least of German physicists, towards the quantum. Chapter VIII considers the circumstances that led Lorentz to embrace the discontinuous version of Planck's black-body theory and describes the way in which other recognized experts on radiation—most notably Wien, Planck himself, and probably James Jeans—followed Lorentz's lead during 1909 and 1910. By the end of the latter year most of the theorists who had studied the black-body problem in depth were convinced that it demanded the introduction of discontinuity.

As that conviction was established, the black-body problem lost its central role in the development of quantum concepts, for it offered no clues to the source and nature of discontinuity. Further progress would depend on the investigation of other areas proposed for the quantum's application, and by the beginning of 1911 there had been many of these, though only one that was beginning to be taken seriously. That situation is the one described in Chapter IX, which sketches the development of other proposed quantum applications in the course of a survey of the state of the quantum in 1911 and 1912. Among other things, it suggests that during the first of these years, leadership in the investigation of the quantum very suddenly passed from the black-body problem to the previously neglected topic of specific heats at low temperatures. One by-product of that transfer was a far larger audience for the quantum, which was soon internationally known. Another provides the answer to the question from which my reluctant search of the black-body literature began. Because it transformed the locus of discontinuity from Planck's resonators to massive atoms and molecules, the specific heat problem is the primary source of the search for quantum conditions. The question of how to apply the quantum to multi-dimensional mechanical problems was not raised publicly until 1911, but it was then raised repeatedly and in a variety of forms.

That survey of the state of the quantum concludes Part Two, and a brief epilogue, constituting Part Three, closes this volume. Its subject is the so-called second theory of black-body radiation, developed by Planck during 1911–12 and definitively formulated in the second edition of his *Lectures*, which differs decisively from the first. Usually interpreted as a retreat towards classical theory and a sign of its author's conservatism, the second theory proves to be the first in which Planck found a place for discontinuity of any sort. Localizing discontinuity in what he later called "the physical structure of phase space," it was also a serious piece of physics, one that influenced a number of contemporaries, including Niels Bohr, and which was briefly a serious contender

in the growing field of competing non-classical formulations of the interaction between radiation and matter. Because it simultaneously returns attention to the themes of Part One and illustrates the state of the quantum early in the second decade of this century, the second theory provides an appropriate ending for this volume. The black-body problem would not, for some years, carry physical theory further.

Though my own close involvement with the black-body problem began only in the spring of 1972, my concern with the development of the quantum theory is a decade older. It originated in my association during the years 1961–64 with Sources for History of Quantum Physics, an archival project that sought, both by interviewing participants and by making copies of original manuscripts, to preserve records on which future studies of the development of the subject might be based.[3] Because still living physicists were the primary object of that enterprise's attention, very few of the records it succeeded in preserving are directly relevant to the years dealt with in this volume. The project, however, also sought to locate relevant manuscripts already on deposit in European libraries. Virtually all the manuscript materials referred to below were located in the course of that library survey; in its absence, many of them would doubtless be unknown to me.

Equally important, though far less tangible, work on the project supplied much of the overview of the quantum theory's development which has set the concerns and guided the selection of materials for this volume. Though a historian may not work backwards from the end project of the development to be explored, he can scarcely work at all without a preliminary sketch of the terrain. I have been particularly fortunate in mine, for it was a cooperative project to which my principal assistants, John L. Heilbron and Paul L. Forman, made major contributions as did some of the physicists to whom the project introduced us. Footnotes will record the debts I can still detail, but will not thereby begin to suggest the extent of what I owe them.

More recent debts have been accumulated during the long course of this volume's preparation. Hans Kangro and Martin Klein have provided the basic previous accounts from which much of my work departs, in both senses of the word. Just because we have differed at key points of interpretation, I am especially grateful for their generosity in hearing and criticizing my views at an early stage of their development. Later, as my manuscript took shape, a number of colleagues in history of science offered significant suggestions about all or parts of it. John Heilbron, Russell McCormmach, Noel Swerdlow, John Stachel, and

Spencer Weart responded to one or another version of the whole. Jed Buchwald, Stephen Brush, Paul Forman, and Daniel Siegel criticized drafts of one or more chapters. For guidance through or around occasionally recondite problems of physical theory, I am indebted to discussions with John Bahcall, Freeman Dyson, Edward Frieman, and John Hopfield. Finally, three of my students or former students—Robert Bernstein, Bruce Wheaton, and Norton Wise—have studied the manuscript with care in the course of checking footnotes, quotations, translations, and bibliographical citations. Their critical contributions have gone well beyond the significant minutiae assigned to them, and Robert Bernstein has also taken responsibility for the index. All these people have helped me clarify my text and avoid errors of both commission and omission. Nevertheless, the canonical disclaimer is more than usually appropriate in this case: for residual problems in the present text, I alone am responsible.

Anyone engaged in work of this sort makes a nuisance of himself to librarians. I must specially acknowledge the patience and good cheer with which my depredations have been borne by the staffs of the Mathematics and Natural Science Library at the Institute for Advanced Study and the Mathematics-Physics Library at Princeton University. Much of the manuscript material upon which my narrative depends is deposited on microfilm in the Library of the American Philosophical Society, and I am grateful to Murphy Smith and his staff for making copies easily available to me. Other essential help with manuscripts has been provided by Dr. Tilo Brandis of the Staatsbibliothek Preussicher Kulturbesitz and his staff, by Dr. A. Opitz of the Deutsches Museum, and by E. van Laar of the Algemeen Rijksarchief at The Hague. For permission to reproduce materials which the custodians of these collections have made available to me, I am most grateful to: Frau Gerda Föppl, on behalf of the Wien heirs; Professor T. H. Von Laue; Dr. Otto Nathan, for the Einstein estate; Frau Dr. Nelly Planck; and Fru Pia de Hevesey. Dr. van Laar of the Algemeen Rijksarchief and Mrs. M. Fournier of the Museum Boorhaave have also transmitted authorization on behalf of their respective institutions.

To Helen Dukas, who has done so much to assemble and preserve the Einstein archive at the Institute for Advanced Study, I owe a special debt. Not only has she been a generous guide to the rich collection over which she presides, but, exposed by proximity to my repeated importunities, she has been a constant help on questions of German

orthography and idiom. Other help of the same sort has from time to time been provided by my colleagues Albert Hirschman and Michael Mahoney as well as by occasional German visitors to the Institute for Advanced Study. And, at a time of great need, Victor Lange deciphered for me some key phrases in Gabelsberger shorthand scattered through the Ehrenfest research notebooks discussed in Chapter VI.

Work on this volume was begun during a one-semester leave from Princeton University, supported in part by the University and in part by the National Science Foundation under Grant S-1265.[4] The effectiveness of my work, then and since, has also been much enhanced by an association with the Institute for Advanced Study, first as a visitor and more recently as a part-time member. In the latter capacity my work was for two years supported in part by the National Endowment for the Humanities under Grant H-5426 and for another three by the National Science Foundation under Grants GS 42905x and SOC 74-13309. To all of these institutions, as well as to the patient secretarial staff of the School of Social Science at the Institute for Advanced Study, I am very deeply in debt. In arrangements for publication and for the book's final form, I have had much valued assistance from the staff of the Oxford University Press, especially Leona Capeless, who has provided the perceptive and firm, but nonetheless flexible and understanding, editorial criticism that I had previously concluded could not exist. Both in detail and tone the manuscript has greatly benefitted from her intervention.

My most extended and least tangible debt is to the members of my family. They bore patiently and usually cheerfully the dislocations of home and school life caused by my involvement with the archival project that first interested me in the history of quantum physics. Since its close, they have tolerated the preoccupations and inattentions which, in my case at least, seem the usual concomitant of scholarly effort. Sometimes they must have wondered whether the flame is worth the candle, but they have been supportive nonetheless. For that and a great deal else, I thank them.

Princeton, N.J.
September 1977

T.S.K.

NOTE TO THE PAPERBACK EDITION

The prospect of a new edition of *Black-Body Theory* gives me great pleasure. Paperback publication will make the book accessible to a wider and more casual audience than is likely to come to terms with the hardcover version. Republication also makes possible the inclusion within a single binding both of the original text and of a retrospective article about it, the latter reprinted here as an afterword. Prepared six years after the book's original publication, that afterword has multiple purposes. For those requiring guidance through the technical complexities of the text, it supplies a summary of the book's major points and of some reasons to take them seriously. In addition, it considerably clarifies the description, in chapter IV, of Planck's derivation of the black-body law and of the connection between my account of that derivation and the book's main thesis. Third, the afterword discusses a topic on which the book itself remains scrupulously silent: the relationship between the historical enterprise illustrated by this volume and the more abstract view of scientific development presented, especially, in *The Structure of Scientific Revolutions*. Understanding that relationship, it suggests, may also help in understanding aspects of the book's initial reception. I am most grateful to the editors of *Historical Studies in the Physical Sciences* for permission to reprint the article here, to the University of Chicago Press for their willingness to include it, and to the Oxford University Press for permitting this reissue of the book.

Boston, Mass.
November, 1986

T.S.K.

CONTENTS

PART ONE. PLANCK'S BLACK-BODY THEORY, 1894–1906: THE CLASSICAL PHASE

I. PLANCK'S ROUTE TO THE BLACK-BODY PROBLEM . . 3
The Black-Body Problem 3
Planck and Thermodynamics 11
Planck and the Kinetic Theory of Gases 18
Planck on the Continuum and Electromagnetism 29

II. PLANCK'S STATISTICAL HERITAGE: BOLTZMANN ON IRREVERSIBILITY 38
Boltzmann's H-Theorem 39
The First Interpretation of the H-Theorem 42
Loschmidt's Paradox and the Combinatorial Definition of Entropy . 46
The Conflation of "Molecular" and "Molar" 54
Molecular Disorder 60
Epilogue: Molecular Disorder and the Combinatorial Definition after 1896 67

III. PLANCK AND THE ELECTROMAGNETIC H-THEOREM, 1897–1899 72
Cavity Radiation without Statistics 73
The Entry of Statistics and Natural Radiation 76
Planck's "Fundamental Equation" 82
Entropy and Irreversibility in the Field 84

IV. PLANCK'S DISTRIBUTION LAW AND ITS DERIVATIONS, 1900–1901 92
Planck's Uniqueness Theorem and the New Distribution Law . . 92
Recourse to Combinatorials 97
Deriving the Distribution Law 102
The New Status of the Radiation Constants 110

V. THE FOUNDATIONS OF PLANCK'S RADIATION THEORY, 1901–1906 114
The Continuity of Planck's Theory, 1894–1906 115
Natural Radiation and Equiprobable States 120

Energy Elements and Energy Discontinuity . . . 125
The Quantum of Action and Its Presumptive Source . . . 130
Planck's Early Readers, 1900–1906 . . . 134

PART TWO. THE EMERGENCE OF THE QUANTUM DISCONTINUITY, 1905–1912

VI. DISMANTLING PLANCK'S BLACK-BODY THEORY: EHRENFEST, RAYLEIGH, AND JEANS. . . . 143
The Origin of the Rayleigh–Jeans Law, 1900–1905 . . . 144
Ehrenfest's Theory of Quasi-Entropies . . . 152
The Impotence of Resonators . . . 158
Complexion Theory and the Rayleigh–Jeans Law . . . 167

VII. A NEW ROUTE TO BLACK-BODY THEORY: EINSTEIN, 1902–1909 . . . 170
Einstein on Statistical Thermodynamics, 1902–1903 . . . 171
Fluctuation Phenomena and Black-Body Theory, 1904–1905 . . . 176
Einstein on Planck, 1906–1909 . . . 182

VIII. CONVERTS TO DISCONTINUITY, 1906–1910 . . . 188
Lorentz's Rome Lecture and Its Aftermath . . . 189
Planck on Discontinuity, 1908–1910 . . . 196
The Consolidation of Expert Opinion: Wien and Jeans . . . 202

IX. BLACK-BODY THEORY AND THE STATE OF THE QUANTUM, 1911–1912 . . . 206
The Decline of Black-Body Theory . . . 207
The Emergence of Specific Heats . . . 210
Quanta and the Structure of Radiation . . . 220
The Quantum and Atomic Structure . . . 226
The State of the Quantum . . . 228

PART THREE. EPILOGUE

X. PLANCK'S NEW RADIATION THEORY. . . . 235
Planck's "Second Theory" . . . 235
Revising the *Lectures*. . . . 240
Some Uses of the Second Theory . . . 244
The Fate of the Second Theory. . . . 252

NOTES . . . 255
BIBLIOGRAPHY . . . 323
AFTERWORD: Revisiting Planck . . . 349
INDEX . . . 371

BLACK-BODY THEORY
AND THE
QUANTUM DISCONTINUITY
1894–1912

Part One

PLANCK'S BLACK-BODY THEORY, 1894–1906: THE CLASSICAL PHASE

I

PLANCK'S ROUTE TO THE BLACK-BODY PROBLEM

Between late 1894 and the end of 1900 three lines of nineteenth-century scientific research were associated in novel ways by the work of the established German physicist Max Planck (1858–1947). An unexpected product of their interaction was the quantum theory, which, during the next three decades, transformed the classical physical theories from which it had developed. Part One of this volume describes the conception and gestation of that new theory during the years before 1906, a period in which Planck worked alone; Part Two considers its birth and early development from 1906 to 1912, when others reformulated the theory with a success sufficient to ensure its survival; Part Three, an epilogue, returns briefly to Planck in order to examine his initial constructive response to their apparently revolutionary reformulation. This opening chapter describes the problem to which Planck turned in the mid-1890s, discusses the concerns that led him to it, and examines the first stage of the research that followed.

The black-body problem

The research topic that led Planck to the quantum is the so-called black-body problem, usually known at the time as the problem of black radiation.[1] If a cavity with perfectly absorbing (i.e., black) walls is maintained at a fixed temperature T, its interior will be filled with radiant energy of all wavelengths. If that radiation is in equilibrium, both within the cavity and with its walls, then the rate at which energy is radiated across any surface or unit area is independent of the position and orientation of that surface. Under those circumstances, the energy flux reaching an infinitesimal surface $d\sigma$ from an infinitesimal cone of solid angle $d\Omega$ may be written $K \cos\theta \, d\Omega \, d\sigma$, where K is the intensity of the radiation and θ is the angle between the normal to $d\sigma$ and the axis of the cone $d\Omega$. Since radiation at a variety of wavelengths contributes to the total flux, the intensity may be more precisely specified by a distribution function K_λ such that K is given by $\int_0^\infty K_\lambda \, d\lambda$ and $K_\lambda \, d\lambda$ is the intensity due to radiation with wavelength between λ and $\lambda + d\lambda$. Determining and explaining the form of K_λ are the central components of the black-body problem, which originated in the work of Gustav Kirchhoff (1824–87).

During the winter of 1859–60 Kirchhoff announced the following theorem.[2] Let $d\sigma$ be an element of the interior surface of the wall of an arbitrary cavity, not necessarily black, and let $a_\lambda(T)$ be the fraction of the incident energy with wavelength between λ and $\lambda + d\lambda$ absorbed by that element when the cavity is maintained at temperature T. The rate at which energy in that range is absorbed by $d\sigma$ is then $\pi a_\lambda K_\lambda \, d\sigma$, the factor π being introduced by integration over $d\Omega$. Similarly, let $\pi e_\lambda(T) \, d\sigma$ be the rate at which energy in the same range is radiated into the cavity from $d\sigma$. Obviously, for equilibrium, total emission and absorption must be equal, or $\int_0^\infty a_\lambda K_\lambda \, d\lambda = \int_0^\infty e_\lambda \, d\lambda$. Kirchhoff was able to show, by considering a cavity with different materials in different walls, that the equality of emitted and absorbed energy must also apply separately to each infinitesimal wave-length range, i.e., that $a_\lambda K_\lambda = e_\lambda$. In addition, he demonstrated that, since K_λ is constant throughout the cavity, the ratio of e_λ to a_λ must be the same for all materials, however differently those materials may emit and absorb. Those results constitute Kirchhoff's radiation law:

$$\frac{e_\lambda}{a_\lambda} = K_\lambda(T),$$

where the intensity distribution K_λ is a universal function, dependent only on temperature and wavelength, not on the size or shape of the cavity or on the material of its walls. For a cavity with black walls, $a_\lambda = 1$ everywhere, and $e_\lambda = K_\lambda$. The radiation emitted by a black body is therefore identical, in its intensity distribution, to the equilibrium radiation contained in a cavity of any material for which $a_\lambda \neq 0$ at all wavelengths. The cavity may even have perfectly reflecting walls ($a_\lambda = 0$) provided that it somewhere contains a speck of dust which will, by absorption and re-emission, permit an initially arbitrary distribution of energy to approach equilibrium.

Beginning late in 1894, Planck undertook to explain that remarkable uniformity and, a few years later, to derive the form of the universal function $K_\lambda(T)$. By then, however, two other striking regularities of black radiation had been discovered, and these, especially the second, supplied essential background for his research. When Kirchhoff wrote on cavity radiation just after mid-century, he assumed only that radiant energy was propagated in waves, like light; little else could be taken for granted about it. Thirty years later, especially after Heinrich Hertz (1857–94) demonstrated the existence of electric waves in 1888, both visible and thermal radiation were increasingly assumed to be electromagnetic, with properties governed by Maxwell's equations. Consequences of those equations were first applied to black-body radiation in 1884 by the Austrian Ludwig Boltzmann (1844–1906). Then, in 1893, the year before Planck began his work on black radiation, Boltzmann's results were decisively extended by Wilhelm Wien (1864–1928), a recently licensed docent at the University of Berlin.

Boltzmann's initial objective was to show that recognition of the existence of radiation pressure could eliminate an apparent conflict between the second law of thermodynamics and the behavior of the recently invented radiometer.[3] Its pursuit led him to a powerful formulation of radiation thermodynamics. For equilibrium, the net flux of energy across the surface of any volume in a cavity's interior must be zero, a condition which Boltzmann showed could be satisfied only if the density u of radiant energy were related to its intensity K by the equation $u = 4\pi K/c$, with c the velocity of propagation. (The equation applies also to the distribution functions for energy density and intensity; u_λ must therefore, like K_λ, be a universal function of wavelength and temperature, and u must be a function of temperature alone.) It had previously been shown, in addition, that a plane wave perpendicularly incident on a reflecting or perfectly conducting surface exerts a pressure p equal to its energy density,[4] so that for isotropic radiation $p = u/3$. Taken together, these relations permit the direct application of thermodynamics to black radiation.

Let the radiation be confined in a cylinder of volume V closed by a reflecting piston. If radiation pressure does work, increasing the cylinder's volume by δV, then heat δQ must be added to maintain the temperature constant. By the first law of thermodynamics,

$$\delta Q = \delta U + p\,\delta V = \delta(uV) + \tfrac{1}{3}u\,\delta V = V\frac{\partial u}{\partial T}\,\delta T + \left(V\frac{\partial u}{\partial V} + \tfrac{4}{3}u\right)\delta V.$$

The expansion δV also changes the entropy of radiation S by an amount $\delta S = \delta Q/T$, where T is measured from absolute zero. By the second law of thermodynamics, δS must be an exact differential, so that $\partial^2 S/\partial V\,\partial T = \partial^2 S/\partial T\,\partial V$. Since u is a function only of T by Kirchhoff's law, straightforward manipulation yields the equations $du/dT = 4u/T$ and

$$u = \sigma T^4,$$

where σ is a universal constant. That relation between the energy density of black radiation and the cavity temperature had been proposed in 1879 by Josef Stefan (1835–93) as a likely extrapolation from preliminary experiments.[5] In the literature on black-body theory it is generally known as the Stefan-Boltzmann law.

That law is of no present importance, but the techniques developed in obtaining it are. Less than a decade after they were made public, Wien used them to derive a fundamental property of the distribution functions u_λ and K_λ.[6] Like Boltzmann, he dealt with radiation in a cylinder closed by a piston, but both his cylinder and piston were perfectly reflecting so that an arbitrary initial distribution of energy would be preserved unless the piston were moved. If the cavity volume were increased adiabatically, however, two effects would combine to alter the distribution. First, the energy in each wavelength range would be reduced as the corresponding radiation did work in moving the piston. Second, the wavelength of any radiation reflected from the moving piston would be increased by the Doppler effect, which would thus transfer the corresponding energy from one wavelength range to another.

Calling on the second law of thermodynamics, Wien showed that, if the radiation were initially at equilibrium with the cavity at a particular temperature, it would remain in equilibrium as the piston moved and the temperature rose or fell. (By introducing a suitably chosen radiation filter he was able to demonstrate that a departure from equilibrium would permit the direct conversion of heat to work.) Next, by a quantitative analysis of the redistribution of energy due to the Doppler effect and to work done by the piston, Wien showed how to compute the final distribution of energy from the initial one for a given intervening change in the cavity's volume. In the case of an equilibrium distribution, recourse to the Stefan-Boltzmann law enabled him also to specify the temperature corresponding to both the initial and final states. If the distribution function u_λ were known at one temperature, Wien could compute its form at any other.

Wien's result is called the displacement law because it shows how the curve for u_λ is displaced as the temperature of the cavity changes. In modern notation it takes the following simple form,

$$u_\lambda = \frac{4\pi}{c} K_\lambda = \lambda^{-5}\phi(\lambda T), \qquad (1a)$$

where ϕ is an arbitrary function of a single variable. When, in consequence of Planck's work, frequency replaced wavelength as the standard independent variable, the displacement law assumed the more familiar form,

$$u_\nu = \frac{4\pi}{c} K_\nu = \nu^{-3}\phi(\nu/T), \qquad (1b)$$

where u_ν and K_ν are, respectively, the energy density and intensity in the frequency range ν to $\nu + d\nu$. With ϕ unspecified the distribution law remained unknown, but Wien's result provided an important clue to its pursuit. What required specification had become a function of a single variable, no longer of two.

Physicists able to follow Wien's argument and to accept its premises presumably found his result persuasive. During the first decade of this century the displacement law rapidly become a standard tool. But it could scarcely have had that status at the time of its announcement in 1893. Arguments from the second law were not everywhere well understood; Maxwell's equations were only beginning to be widely known and used; the radiation from hot bodies was primarily the province of experimentalists, and their results were still preliminary in numerous respects. Postponing until later in this chapter consideration of the status of thermodynamics and electromagnetic theory in the 1890s, let us look briefly at the state of experimentation relevant to the distribution law.[7]

Suggestive observations date from William Herschel's discovery of the sun's infrared spectrum at the beginning of the nineteenth century, and they include measurements reported by J. H. J. Müller in 1858, John Tyndall in 1865, and A. P. P. Crova in 1880. But these experiments, like all those made before the mid-1880s, examined the spectra of only a few sources (the sun, gas flames, glowing filaments), all very hot and with temperatures only vaguely known. Measurements drawn from them provided little information in the infrared region and were, in any case, of questionable relevance to the properties of equilibrium radiation because the sources of radiation were not necessarily black. The first experiments which began to supply the sort of information needed to fix K_λ were those reported in 1886 by the American astronomer S. P. Langley (1834–1906). His objective was to determine the effect on solar radiation of its absorption and re-emission from the relatively cool surface of a planet.

Langley's radiator was copper, coated with lampblack, and he investigated the continuous spectrum to which it gave rise at a series of controlled temperatures below 1000 °C. At such temperatures, the detectable emission spectrum is confined to the infrared. To explore it, Langley improved the thermocouple, invented the bolometer, and skillfully calibrated a rock-salt prism for infrared wavelengths up to about 5 μ. Figure 1 reproduces one set of the curves which he obtained.[8] Qualitatively, they conform closely to all subsequent measurements, displaying temperature-dependent intensity maxima from which each curve declines asymptotically to zero with both increasing and decreasing wavelength. But their significance is primarily qualitative: only the three highest temperature curves have maxima in the region where Langley could establish reliable wavelengths. Published barely eight years before Planck took up the black-body problem, Langley's experiments are the mere beginning of the work on which the development and evaluation of quantitative black-body laws would depend.

It was, however, an important beginning, since it stimulated both experimentalists and theoreticians (doubtless including Wien) to pursue the determination of Kirchhoff's universal function. In 1887 the Russian W. A. Michelson (1860–1927) combined the Stefan–Boltzmann law with a speculative statistical hypothesis about the mechanism of emission to derive the radiation formula[9]

$$K_\lambda = b\lambda^{-6}T^{3/2}\,e^{-a/\lambda^2 T},$$

with a and b disposable constants. That equation, he showed, reproduced all the qualitative characteristics of Langley's experimental curves. But quantitatively it was not very satisfactory, a fact soon emphasized by H. F. Weber (1843–1912) of the Zurich Technische Hochschule, a physicist currently engaged in measuring the emission spectrum from carbon filament lamps.[10] After criticizing the theoretical basis of Michelson's derivation (including its reliance on the Stefan–Boltzmann law), Weber proposed an alternate formula based on his own and other experiments. His candidate for the Kirchhoff function required three disposable constants and took the form

$$K_\lambda = b\lambda^{-2}\,e^{hT-(a/\lambda^2T^2)}.$$

When Wien, five years later, published the displacement law, his only reference to experiment was through Weber's law. Like his own law, Wien pointed out, Weber's required that the wavelength λ_m at which the intensity function reached its maximum be governed by the equation $\lambda_m T$ = Constant. Since the two laws were in other respects clearly

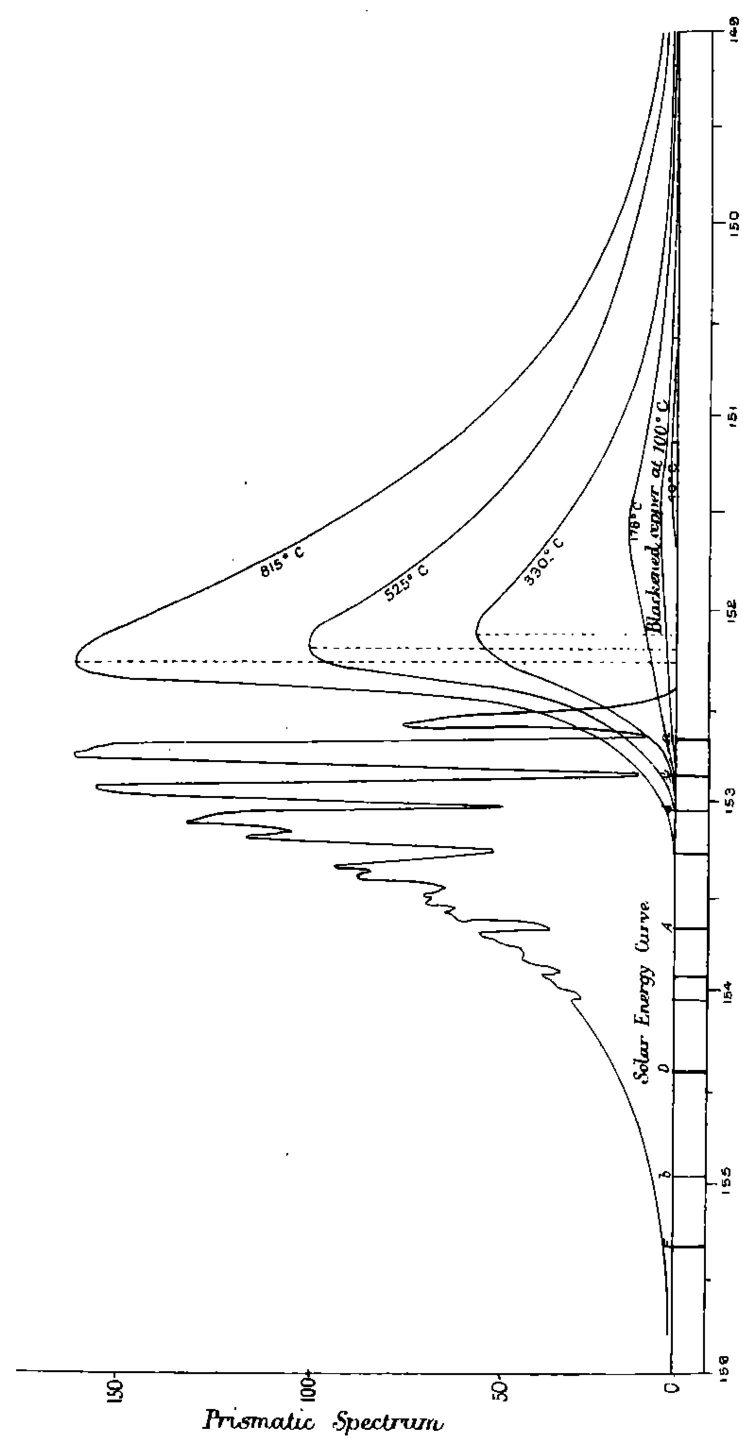

Figure 1. A set of Langley's curves comparing radiant energy from the sun with that from an experimental radiator of blackened copper. The horizontal axis is the length of the prismatic spectrum measured on an arbitrary linear scale.

incompatible, Wien's invocation of Weber's formula highlights the very limited authority of experiments on black radiation in 1893.

Three years later the situation had changed notably. Following the publication of Langley's work, a number of young experimentalists had set out to improve the sensitivity of bolometric measurements and to increase the range and precision of wavelength determinations in the infrared. One of them was Friedrich Paschen (1865–1947), then an Assistant at the Technische Hochschule in Hannover and at the beginning of what was to prove a distinguished career in spectroscopy. Paschen applied his improved instruments to the search for Kirchhoff's function with striking success. In 1895 he reported that the wavelength λ_m is, to a close approximation, inversely proportional to absolute temperature, thus providing direct evidence for the displacement law. Then, in the following year, an extension of his measurements led him to propose a new and especially simple form for the distribution function

$$K_\lambda = b\lambda^{-\gamma} e^{-a/\lambda T}.$$

Paschen's values for the constants were necessarily tentative, but γ appeared to lie in the range 5 to 6 with a mean value of 5.66.[11]

Paschen's radiation formula was first published, with his permission, in a paper by Wien, who had learned of it through correspondence and had at once seen its relation to a highly speculative derivation of his own, one he had previously refrained from publishing. A heated gas, Wien pointed out, can serve as the source of black radiation. In such a gas the number of molecules with velocities in the range between v and $v + dv$ is, by Maxwell's distribution law, proportional to $v^2 \exp(-v^2/\alpha^2)$ with α^2 proportional to the gas temperature T. If, in addition, one makes the far from natural assumption that both the wavelength and the intensity of the radiation from a given molecule are functions only of that molecule's velocity, then the distribution of radiation from the gas must take the form $K_\lambda = F(\lambda) \exp[-f(\lambda)/T]$. In that expression both F and f are unknown functions, derivable from the also unknown relations between wavelength and velocity, on the one hand, and between intensity and velocity, on the other. To specify them further, Wien noted that his formula would conform with the Stefan–Boltzmann and the displacement law only if $F = b\lambda^{-5}$ and $f = a/\lambda$. The result is the famous Wien distribution law,

$$K_\lambda = b\lambda^{-5} e^{-a/\lambda T}, \qquad (2)$$

a formula differing from Paschen's only in that it specifies the value of

the constant γ. Unless $\gamma = 5$, Wien pointed out, Paschen's law is irreconcilable with the Stefan-Boltzmann law, itself an apparently unproblematic consequence of thermodynamics.[12]

As a product of theory, the Wien distribution law had, of course, little authority until Planck rederived it by a very different route in 1899. The hypothesis that both wavelength and intensity are functions only of the translational velocity of the emitting molecules was at best ad hoc. But the law was nevertheless unlikely to be merely wrong. It did conform to the requirement of the displacement law, and that law was derivable without resort to ad hoc hypotheses. Probably more important, it very closely resembled the law that Paschen had adduced from the best experiments made to date. A reduction in γ by less than 15 percent would make the two coincide. Further experiments might well bring about that reduction. Very soon they did.

By January 1899, Paschen's own investigations were directed to checking Wien's form of the law, and he soon reported that the value of γ declined from 6.4 to 5.2 as the emitter was changed from reflecting platinum to highly absorbent carbon. In February of the same year, Otto Lummer (1860–1925) and Ernst Pringsheim (1859–1917) provided fuller confirmation of Wien's form, using, for the first time, an experimental black cavity within which radiation could reach equilibrium before its intensity was measured. Other experts on infrared technique, including both Ferdinand Kurlbaum (1857–1927) and Heinrich Rubens (1865–1922), provided additional support, and Planck—still in 1899—supplied a magistral derivation from first principles.[13] Whatever the status of its derivation, Wien's law had triumphed. In the event, of course, that triumph was extremely brief. Early in 1900 the application of new long-wavelength infrared techniques to the newly deployed experimental cavities disclosed the law's limitation, with decisive effects on the subsequent development of physics. But that is another chapter, to be considered at an appropriate point below. No such outcome could have been foreseen when Planck's black-body research began or when, in 1899, it reached its first, apparently satisfactory, conclusion.

Planck and thermodynamics

Despite its brevity, the preceding sketch of the black-body problem discloses the three fields that were to interact consequentially within Planck's work. Two are obvious: thermodynamics and electromagnetic theory. The third, statistical mechanics, is the source of the Maxwell distribution to which both Michelson and Wien appealed when deriving their proposed distribution laws. Before 1900 Planck had made important contributions to all three, but they occupied very different places in his thought. Thermodynamics had been his first love, and his work in it was well known before he first turned, at age thirty-six, to electromagnetism. For him the latter's role was initially instrumental: Maxwell's equations provided conceptual tools with which to solve thermodynamic problems, particularly the problem of black radiation. Statistical techniques entered Planck's research later still and against much resistance. Though their appearance marks the first step on his path to immortality, Planck's resort to them was at the time an admission of failure. The remainder of this chapter will consider Planck's background in thermodynamics, his hopes for electromagnetic theory, and the beginning of his attempts to apply that theory to cavity radiation. In the process, his reasons for resisting statistics will be encountered as well.

Thermodynamics, as an abstract quantitative theory of the role of heat in macroscopic physical processes, was a relative novelty when Planck first encountered it in the 1870s. Its historical roots are traceable to the gas and steam-engine theories of the first third of the nineteenth century, but its formulation required a series of experimental and conceptual innovations that cluster at mid-century.[14] During the 1840s numerous thermal, chemical, electrical, and mechanical effects were recognized as qualitatively interconvertible without quantitative gain or loss. The generalization that captured those results was soon to be known as the law of conservation of energy, and it surpassed all earlier physical principles in the range of its concrete applications. Once conceptually assimilated, furthermore, it seemed so nearly inevitable that it was sometimes accorded a priori status. Indeed, the theorem that every cause must be quantitatively equivalent to its effect, else the universe will run down, had played a role in several of its initial enunciations.[15]

Conservation of energy is the first law of thermodynamics, and the second followed quickly, though by no means straightforwardly. In 1824 a young French engineer, Sadi Carnot (1796–1832), had derived a consequential set of theorems concerning heat engines from the assumption that heat is a special caloric fluid which does work as it passes from a higher to a lower temperature reservoir. Virtually unknown for more than a decade after its publication, Carnot's theory was revived, extended, and successfully applied to significant new problems in the 1840s, just as the law of energy conservation was

gaining currency. Since Carnot's theory in its original formulation required that heat be conserved, the two were incompatible. But the disturbing conflict was resolved in 1850–51 when Rudolph Clausius (1822–88) and William Thomson (1824–1907) independently developed a new way of deriving Carnot's theorems. For that purpose they required a new physical principle, later usually known as the impossibility of perpetual motion of the second kind. Clausius gave it in the form: heat cannot of itself pass from a colder to a warmer body, the rest of the universe remaining unchanged. Thomson's formulation was equivalent: it is impossible to construct an engine that will raise a weight simply by cooling a heat reservoir. Those were the first statements of the second law of thermodynamics.[16]

Because these statements supply an observational basis for the second law, one of them, or an equivalent, still often appears early in books on thermodynamics. But as statements about what cannot occur in nature, their positive physical import is by no means transparent, and they are therefore rapidly displaced by some more perspicuous formulation, one that can be applied directly to a variety of physical situations. That sort of formulation was first systematically developed by Clausius in a series of papers which appeared between 1854 and 1865. All but the last were collected with supplementary commentary in the first edition of his *Mechanical Theory of Heat*, published in 1864 when Planck was a young schoolboy at Kiel. Republished in English in 1867 and in French in 1868, that book was the first monograph on thermodynamics, and many physicists learned the subject from it.[17] Its second edition, furthermore, was the field's first text. In its new preface, Clausius pointed out that, "The mechanical theory of heat in its present state of development already constitutes a wide-ranging and independent subject of study." He had therefore, he continued, reworked the contents of his papers so that the new edition of his book "would form a coherent developing whole and thus take the form of a textbook."[18] That version of Clausius's thermodynamics was published in 1876, and Planck was among the first to put it to its intended use.[19] Its formative influence on his career was great. Early in 1879 he submitted to the University of Munich a doctoral thesis based on Clausius's work but recommending a fundamental reformulation of his approach. As one might expect, Planck's subsequent research was the first to be affected by that recommendation.

Before examining Planck's reformulation of thermodynamics, let us look briefly at the route on which he had encountered Clausius's version.[20]

Born at Kiel in 1858, Planck was educated primarily in Munich, where his father assumed the University's chair of civil law in 1867. Very little science of any sort was included in his Gymnasium curriculum, but he did acquire some bits of physics from a much-admired mathematics teacher, and they impressed him deeply. In later life he particularly emphasized the impact—"like a sacred commandment"—of the conservation of energy. It was, he wrote, the first law he had learned "which possessed absolute validity, independent of man."[21†] Whether or not a product of hindsight, that memory of an early concern with laws of the greatest possible depth and generality indicates what particularly attracted him to thermodynamics.

For three years, beginning in the fall of 1874, Planck studied physics at the University of Munich, where he encountered the mechanical theory of heat though probably not the developed second law.[22] Next he spent a year at Berlin, where he attended the courses of Helmholtz and Kirchhoff. Both, he wrote in his *Scientific Autobiography*, attracted him greatly as men; in addition, his exposure to them and the Berlin circle "greatly expanded [his] scientific horizons." But, Planck continued,

> I must acknowledge that I gained little from the lectures.... Therefore, I could only still my need for continuing scientific education by reading works which interested me, and those naturally were ones relating to the energy principle. In this way I came upon the papers of Rudolph Clausius, whose clarity of expression and thought made a powerful impression. With growing enthusiasm I worked my way deeply into them. What I particularly admired was the exact formulation of the two laws of thermodynamics and the pioneering demonstration [*erstmalige Durchführung*] of the sharp separation between them. Previously, as a consequence of the material theory of heat, the opinion had been current that the transmission of heat from a higher to a lower temperature was like the sinking of a weight from a higher to a lower altitude, and this erroneous view was not easily suppressed.[23]

That encounter with Clausius determined Planck's choice of subject for a doctoral thesis, and the ideas he developed there helped to shape his approach to the black-body problem fifteen years later. An examination of what Clausius had done and of how Planck's approach to thermodynamics differed will show what was involved.

In 1850, as previously noted, Clausius had modified the foundations of Carnot's theory to reconcile it with energy conservation. The way in

† This sign (†) is attached to occasional notes to indicate that they contain substantive additions to or qualifications of the text, not simply citations and bibliographical discussion.

which he thereafter built on that modified foundation was, however, very much like Carnot's own. In particular, the primary thermodynamic systems considered by Clausius were always, like the idealized cylinder and piston imagined by Carnot, in thermal and mechanical interaction with their environment. In addition, all Clausius's formulations of the second law were statements about the behavior of such systems when carried through a closed cycle. In 1854 he gave the second law the form

$$\oint \frac{dQ}{T} \leq 0, \tag{3}$$

where the equality sign applies only if the cycle is reversible, and where dQ is the quantity of heat absorbed by the system from its environment and T the absolute temperature at which that heat is absorbed.[24]

Clausius, of course, quickly went farther. His later papers considered the value of $\int dQ/T$ over open paths. In 1865 he introduced both the symbol S and the name entropy for the value of that integral:

$$S_1 = S_0 + \int_0^1 \frac{dQ}{T}, \tag{4}$$

where the path from configuration 0 to configuration 1 must be reversible.[25] Applying the second law, equation (3), to that definition, he demonstrated that entropy must be a single-valued function of a system's configuration or state. Finally, from that property together with the first law in its standard thermodynamic form, he showed how to pass quickly to many of the now-familiar partial differential relations governing the macroscopic variables which characterize physical systems. But equation (3) or a close equivalent continued, for him, to represent the second law.[26]

Approaching his subject in the late 1870s, Planck found his starting point in Clausius rather than Carnot: it was equation (4), which defines entropy as a single-valued function of the state variables of a specified system. How, Planck asked, would entropy change with time as the corresponding system developed *by itself*, in thermal and mechanical isolation from its environment? The early pages of his thesis presented his answer in the form

$$S' - S \geq 0, \tag{5}$$

where S' is the entropy at a later time, S at an earlier.

That equation was Planck's version of the second law. Though recognizing its mathematical equivalence to Clausius's form, equation (3), Planck nevertheless insisted that it was conceptually clearer, more general, and more fundamental.[27†] Just as the first law governed the behavior of energy over time, so the second governed that of entropy. More important, by catching the parallel between the two absolute laws from which thermodynamics derived, the new formulation highlighted their decisive difference. The total energy of an isolated system must remain constant over time; its entropy can only increase or, in the ideal limiting case, remain constant. Equation (5) prohibited not simply the spontaneous passage of heat from a lower to a higher temperature but any process which would decrease the entropy of an isolated system. Viewed in this way, the second law rapidly became for Planck "The Principle of the Increase of Entropy."[28] Its function, emphasized by Planck in the opening paragraph of his doctoral thesis, was to determine the direction in which natural processes develop "so that a return of the world to a previously occupied state is impossible."[29]

Planck's reformulation of the second law has a presumptive bearing on the subsequent development of thermodynamics, but its significance here is more restricted. In its new form the law was especially well adapted to the study of equilibrium and the approach of a closed system to it. Planck made the point himself late in a paper published three years after the appearance of his thesis. Its title was "Evaporation, Melting and Sublimation," and its main text developed several significant thermodynamic theorems. Then, its concluding section began:

> All the previously enumerated theorems are strict consequences of a single proposition: that stable equilibrium corresponds to the maximum of entropy. That proposition, in turn, follows from the more general one that in every natural process the sum of the entropies of all participating bodies is increased. Applied to thermal phenomena this law is the most general expression of the second law of the mechanical theory of heat as I have [elsewhere] shown in detail.[30]

Black radiation is, however, a case of thermal equilibrium, and the preceding passage suggests how Planck would later approach it. If an arbitrary initial distribution of energy is injected into an insulated cavity, then the distribution will move towards equilibrium as energy is absorbed and re-emitted by any bits of black material the cavity contains. The approach to thermal equilibrium is irreversible, and entropy must therefore increase until equilibrium is achieved. If one had a formula for the entropy of radiation as a function of the field variables, then the black-body distribution function would be the one that maximized the total entropy of the radiation in the cavity. That is the approach Planck would begin to explore late in 1894, reaching a first conclusion in 1899. Clausius's formulation of the second law offered no equally apparent point of entry.

Planck is not likely, however, to have had the black-body problem in mind when he defended his thesis in 1879. During the fifteen years that followed, his published research continued much as it had begun. Many of his papers as well as a small book on conservation of energy[31] were intended to extend and clarify the foundations of thermodynamics, a field still widely misunderstood, especially by a prominent group of anti-mechanists known as the energeticists. Accepting the first law of thermodynamics as the fundamental principle of science, they hoped to reduce both matter and force to mere manifestations of energy. Discarding the distinction between reversible and irreversible processes, they believed they could derive a totally general version of the second law from the first.[32] Planck was referring to them when he later wrote of the difficulties in suppressing the view "that the transmission of heat from a higher to a lower temperature was like the sinking of a weight from a higher to a lower altitude."[33] Other early papers published by Planck dealt with applications of thermodynamics, initially to physical problems including saturation, change-of-phase, and equilibrium. Then, between 1887 and 1894, he turned increasingly to the exciting new field of physical chemistry just being opened by the pioneering research papers of Arrhenius and van't Hoff. Planck later emphasized, apparently with much justice, how little attention had been paid to at least the more basic aspects of his thermodynamic theory.[34] But that theory or its applications, more likely the latter, were sufficiently significant and well known to justify his appointment in 1885 to a special chair of mathematical physics at Kiel and then, in 1889, to the University of Berlin as Kirchhoff's successor.[35]

The move to Berlin brought Planck back, of course, not only to the center of German physics but more obviously to what would shortly become the world center for theoretical and experimental research on black radiation. Wien, Lummer, Pringsheim, Rubens, and Kurlbaum all worked there, either at the University, the Technische Hochschule, or the Physikalisch-Technische Reichsanstalt in nearby Charlottenburg. In such a setting Planck's turn from physical chemistry to radiation theory is not surprising. By the mid-1890s a physicist in Berlin could scarcely be unaware that Kirchhoff, Boltzmann, and Wien had firmly established the applicability of thermodynamic argument to radiation.

What Planck had begun to do by applying thermodynamics to chemistry, he could now reasonably expect to achieve for radiation theory as well. Actually, as the following pages will show, the program on which he embarked in 1894 had a far more ambitious goal, but he might never have pursued it if research on the black-body problem had not offered by-products of a more familiar sort.

Planck and the kinetic theory of gases

Planck's larger objective in taking up the black-body problem was to reconcile the second law with mechanics. By the mid-1890s, problems in the relation between the two were widely recognized and, in England, much discussed. But Planck had been aware of difficulties long before and, in 1881, had suggested the direction from which he expected their solution to emerge. In retrospect his suggestion seems extraordinarily implausible, but it is nevertheless the one that motivated his turn to black radiation thirteen years later. A first step in recovering its original cogency requires a digression on the early developmental stages of the kinetic theory of gases.

The belief that heat was the motion of material particles had dominated seventeenth-century science and had never thereafter been lost from view, not even during the thirty years, roughly 1790 to 1820, when most physicists subscribed to the caloric theory. But transforming the mode-of-motion viewpoint into a quantitative theory of significant scope depended on the development of a model of material aggregates to which mathematics could be easily applied. Ultimately, gas models proved to have the requisite simplicity, but not until the end of the eighteenth century. Previously, gases had been thought to be a distinct chemical species. (Before the eighteenth century air was its only member.) Their particles, which were usually conceived as space-filling, could only rotate or vibrate in place.[36†] Gas models thus presented would-be kinetic theorists with all the complexities still characteristic of liquids and solids. That situation changed only after Lavoisier's new chemistry had persuaded scientists that gases were simply a particular physical state of substances which could also exist in the solid and liquid form. Once it was recognized that steam, for example, was a gas like any other, easily imagined estimates showed that its molecules could occupy only a minuscule fraction of the volume filled by the gas. Initially, the newly empty space was thought to be filled with caloric fluid, a view which nicely accounted for the

uniform properties of gases. After 1820, however, as the belief in caloric declined, gas models in which molecules traveled for some distance in straight lines between collisions were first conceived.[37]

Models of that sort proved quite persuasive after the recognition at mid-century of the interconvertibility of heat and work, and more of them then began to appear. The first to attract much attention, however, was contained in a pair of papers published by Clausius in 1857 and 1858.[38] He had been working on them for some time, refraining from publication so that their speculative micromechanics would not, by association, interfere with the reception and understanding of his purely thermodynamic work, and his papers are particularly rich in accomplishment and suggestiveness as a result of the delay. The first paper opened by showing that, if gas pressure is due to the mechanical impact of molecules on the container's walls, then $\frac{3}{2}pV = \frac{1}{2}nmv^2$, where p is pressure, V volume, and n the number of gas molecules, each with mass m and speed v. Comparing that result with the Boyle-Charles law, Clausius pointed out that absolute temperature must be proportional to the translational kinetic energy of a molecule.

That result had been derived several times before, but Clausius's papers quickly carried it farther. The first includes, for example, the earliest distinction in print[39] between the translatory motion of molecules, on the one hand, and their rotational and vibrational motion, on the other. It also suggests that the ratio of total kinetic energy to translatory energy must be fixed for a given gas, and it relates that ratio to the ratio of the specific heats at constant pressure and constant volume. The second paper introduces the concepts of mean free path and sphere of molecular action, and it applies them to explaining the observed slow rate of gaseous diffusion. Systematic development of the kinetic theory of gases dates from these papers, the second of which was published in the year Planck was born.

Clausius's papers quickly captured the interest of James Clerk Maxwell (1831–79), whose first contribution to kinetic theory was published in 1860.[40] That paper extended and improved Clausius's results in several significant respects, the most important being the application of statistical concepts to the distribution of molecular velocities in a gas. Clausius had known that those velocities varied greatly, both from molecule to molecule and, for an individual molecule, from time to time, but for purposes of computation he had used a fixed speed v. Adapting a standard argument from error theory,[41] Maxwell argued that the fraction of molecules with speeds between v and $v + dv$ must be given by

$$\frac{4}{\alpha^3\sqrt{\pi}} v^2 e^{-(v^2/\alpha^2)} dv, \tag{6}$$

where α is a constant easily shown to equal $\frac{2}{3}$ the mean value of v. The foundations of the argument by which Maxwell first arrived at that distribution law were subject to criticism, but he presented a much improved derivation in 1867,[42] and there have been numerous others since. Two of them, both due to Boltzmann, had an important influence on the development of Planck's black-body theory and will therefore be central topics in the next chapter.

From the start, the distribution law opened new avenues to Maxwell. He used it to show, for example, that a mixture of two gases could be in equilibrium only if the individual molecules of each had the same mean translational energy. Since two gases in equilibrium also have the same temperature, the results that Clausius had gained by comparing kinetic theory with the gas laws could be made more precise: absolute temperature is proportional to mean translational energy per molecule, the proportionality constant being independent of the gas; equal volumes of two gases at the same temperature and pressure must, as a consequence, contain the same number of molecules. Elsewhere in his 1860 paper Maxwell improved Clausius's computation of the mean free path and applied the result to the theory of viscosity, a quantity he was startled to find independent of pressure. Finally, after considering additional problems concerning diffusion and heat conduction, Maxwell treated the general question of equilibrium between complex molecules, concluding that the mean translational and rotational energies per molecule must be the same. Together with his result for mixed gases, this conclusion foreshadowed the equipartition theorem, a general result which both he and Boltzmann later derived. Very nearly the full range of problems that would occupy kinetic theorists for a generation had emerged by 1860.

Two related aspects of that problem-constellation require special emphasis, for both are relevant to the way in which statistical considerations entered research on the black-body problem, and both changed rapidly soon after that entry had occurred. First, until after 1900 the research subject of the men who applied statistics and molecular mechanics to the study of heat was gas theory, not statistical mechanics. From Watson's *Treatise on the Kinetic Theory of Gases*

(1876), through Boltzmann's *Lectures on Gas Theory* (1896, 1898), to Jeans's *Dynamical Theory of Gases* (1904), the former phrase was regularly selected to describe their work.[43] Second, because the object of gas theory was to explain the observable behavior of gases (specific heats, viscosity, thermal conductivity, etc.), very few of its practitioners were significantly concerned with thermodynamics. Very occasionally a discussion of gas theory would point out that, when the Maxwell distribution obtains, dQ/T is an exact differential.[44] There were also, as will shortly appear, a few isolated discussions of the statistical basis of the second law. But only Boltzmann attempted to develop a statistical theory of entropy, and that aspect of his work was entirely ignored by other gas theorists until after Planck took it up at the end of 1900. In short, the set of concerns now covered by the phrase "statistical mechanics" or "statistical thermodynamics" scarcely existed during the nineteenth century. They appear first during 1902 in a famous book by J. Willard Gibbs (1839–1903) and in an almost forgotten article by Albert Einstein (1879–1955).[45†] With the rapid assimilation of those works, statistical physics became a different field, one unavailable to Planck when his attitude towards the relation between mechanics and the second law was formed.

Though he probably did not follow its technical development closely, Planck knew at least the main lines of gas theory. Clausius, whom he admired, continued a significant contributor to the field. After Clausius's death in 1888, Planck helped to prepare his *Kinetic Theory of Gases* for the press.[46] Shortly after that he was sole editor for the posthumous publication of Kirchhoff's *Lectures on the Theory of Heat*,[47] a task which involved him deeply enough with gas theory to produce a significant confrontation with Boltzmann. Together with other evidence to be examined below, that confrontation suggests that, until the last years of the century, Planck's knowledge of Boltzmann's own gas-theory papers was spotty, but he was surely aware of their existence and probably of their main lines. Though he had no great interest in gas theory, Planck did not find it repulsive. His attitude thus differed markedly from that of the energeticists and other anti-mechanists of the day.

Planck was, in the first place, a convinced if undogmatic believer in mechanics or the mechanical world view. It did not, he thought, yet display either the generality or the virtually incontestable empirical base that characterized thermodynamics. But, as he wrote in 1887, its evolution had been marked by a long series of striking successes, and it