

BLACK-BODY THEORY
AND THE
QUANTUM DISCONTINUITY
1894-1912

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With a new Afterword

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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,

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

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,

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

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,

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

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 became 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 formula⁹

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

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 $\lambda_m T = \text{Constant}$. Since the two laws were in other respects clearly

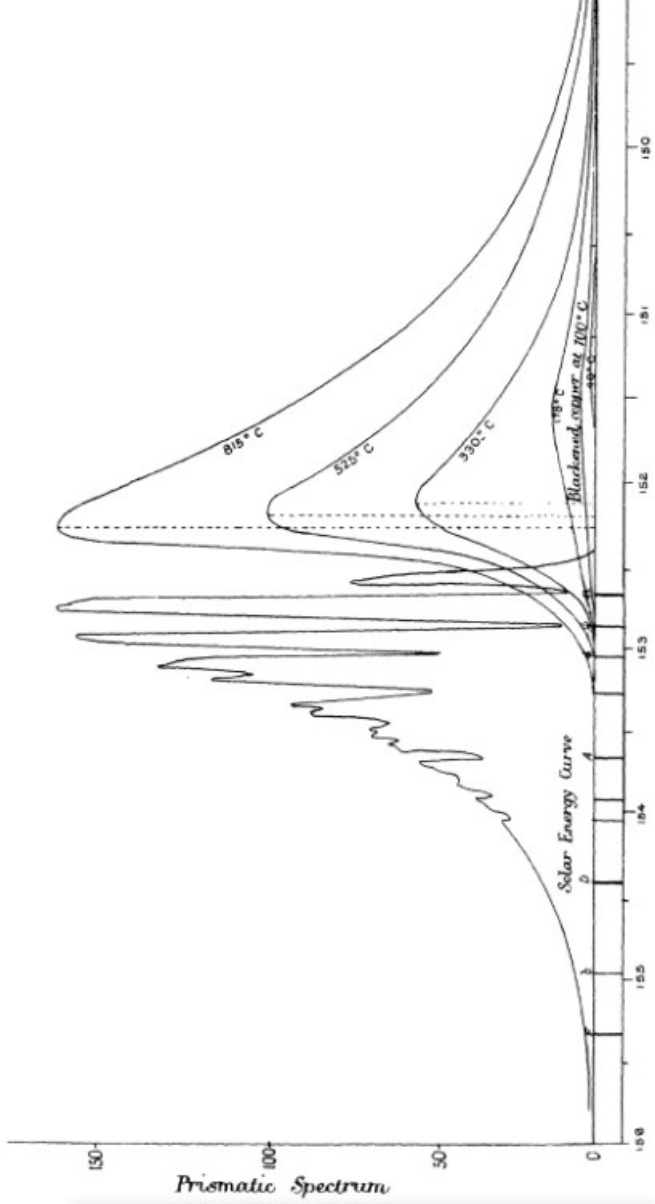


Figure 1. A set of Langley's curves comparing radiant energy from the sun with that from an experimental radiator of blackened copper. The horizontal axis is the length of the prismatic spectrum measured on an arbitrary linear scale.

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,

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

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

$$\oint \frac{dQ}{T} \leq 0, \quad (3)$$

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:

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

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

$$S' - S \geq 0, \quad (5)$$

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.²⁷¹ 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 energy³¹ 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 $\frac{2}{3}pV = \frac{1}{2}nmv^2$, 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 print³⁹ 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

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

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

was therefore likely to continue "to point the direction in which research should move One ought to use all available means," he continued, "to develop the final [*letzten*] consequences of the mechanical viewpoint for all areas of physics, chemistry, and so on."⁴⁸ A letter to be examined below suggests that Planck began his black-body research in response to that directive.

Towards the atomic or molecular articulation of mechanics, Planck's attitude was more equivocal. For the most part, however, it is well represented by remarks he made at the start of his *Habilitationsschrift*, the second dissertation which, in 1880, licensed him to teach at Munich. To study equilibria between isotropic materials, Planck began, one needs a knowledge of the forces at work in the interior of bodies. Such forces depend, he pointed out, "not only on the relative position of the smallest particles of the body but also on their temperature." The special value of thermodynamics, he then emphasized, is that it provides a means to investigate the temperature dependence of these forces between particles "without its being necessary to introduce special assumptions about the molecular constitution of the body."⁴⁹ Here, as in many passages in his subsequent work, Planck appears simply to have taken atoms and molecules for granted.⁵⁰ He urged, however, that the physicist make minimal use of special hypotheses about their structure and about the forces between them.

Applied to research on gas theory, that viewpoint suggests, not that such research is wrong in principle, but rather that it is an error in strategy. One of Planck's rare published statements on the subject, read to the Physics and Chemistry Sections of the annual *Naturforscherversammlung* in 1891, makes the point explicit:

Anyone who has studied the works of Maxwell and Boltzmann—the two scientists who have penetrated most deeply into the analysis of molecular motion—will scarcely be able to escape the impression that the remarkable physical insight and mathematical skill exhibited in conquering these problems is inadequately rewarded by the fruitfulness of the results gained. A remarkable situation has very recently reinforced this evaluation. The far-reaching analogy between the behavior of matter in dilute solutions and in perfect gases was not discovered by kinetic theory. On the contrary, kinetic theory, even after the event, has had to overcome great difficulties in accounting for this behavior, so that it cannot, at least in the near future, be expected to contribute to further progress with this problem.^{51†}

Three years after those remarks were made, Boltzmann would open his criticism of Kirchhoff's *Lectures* by attributing to their editor, Planck, the view that efforts devoted to gas theory were a waste of time and

1871 in a series of "Textbooks of science adapted for the use of artisans and students in the public and science schools," the book appeared in German translations in both 1877 and 1878. Planck's reference is to the two-page section "Limitations of the Second Law of Thermodynamics," the first place where the statistical nature of the second law was pointed out. That law, Maxwell said,

is undoubtedly true as long as we can deal with bodies only in mass, and have no power of perceiving or handling the separate molecules of which they are made up. But if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is at present impossible for us. For we have seen that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower ones to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics.⁵⁴

The special "being" able to make heat flow from a colder to a warmer body is, of course, the one since known as "Maxwell's demon."⁵⁵

In England, Maxwell's view of the second law was quickly accepted. Thomson developed it somewhat further in 1874; soon after that P. G. Tait (1831–1901) included it in the second edition of his widely used *Sketch of Thermodynamics*⁵⁶; and Maxwell then gave it further currency in a long review of Tait's book published in *Nature* at the beginning of 1878. "The truth of the second law," Maxwell wrote, "is therefore a statistical, not a mathematical, truth, for it depends upon the fact that the bodies we deal with consist of millions of molecules. . . . Hence, the second law of thermodynamics is continuously being violated, and that to a considerable extent, in any small group of molecules belonging to a real body."⁵⁷ Thereafter the problem of the second law disappeared from British gas theory for almost twenty years.

On the Continent, attitudes were far more varied. At one extreme were the energeticists, who rejected atomism, mechanics, and the independence of the second law. At the other were Clausius and Boltzmann, who conceded that the second law was only macroscopic but who continued, as though dissatisfied by that conclusion, to display great interest in mechanical systems that showed non-statistical

analogies to that law.⁵⁸ Neither of those positions was satisfying to Planck, who believed in mechanics and thought the second law absolute like the first. Recollecting the years before the turn of the century, he later wrote: "At that time, I thought the principle of entropy increase was valid without exception, like the principle of energy conservation, while for [Maxwell and] Boltzmann this principle was only a law of probability and thus subject to exceptions."⁵⁹ While he held that position, Planck could not have accepted the statistical approach.

But why should he have held it, at least for so long? By the 1880s no one else is known to have viewed the status of the second law as Planck did. Nor was there apparent reason to do so, for until 1896 no one even suggested that the "exceptions" to which that law was subject might conceivably be observable or have physical consequences.⁶⁰ Clausius dismissed Tait's claim that Maxwell had disproved his version of the second law with the words:

The excess kinetic energy which may at a given moment pass from a colder to a warmer body by virtue of an accidental deviation from the [molecules'] average behavior is a magnitude of the same order as the mass of a single molecule compared with the masses directly accessible to our senses. Magnitudes of that order are, however, negligible for considerations relevant to the second law.⁶¹

Why could not Planck have taken a similar position? Is it possible that his autobiographical recollection did not quite catch the essentials of his objection to the probabilistic approach?

No conclusive answer is possible, but a plausible one relates directly to the reformulation of the second law that Planck worked out in his doctoral thesis and subsequent publications: all isolated physical systems move irreversibly from states of lower to states of higher entropy. In the thesis itself that strong a generalization is not yet fully explicit. There Planck introduces the term "natural" for processes to which the inequality sign in equation (5) applies; if the equality sign holds instead, the processes are called "neutral." The terminology itself suggests that neutral processes are an idealization, but in his thesis Planck never quite said so.⁶² Three years later, however, the terminological implication had become both explicit and central:

There is in nature a function (for which we can retain Clausius's designation entropy) that is perpetually increasing, in the sense that the sum of the entropies of all bodies participating in any process is larger at the end than at the beginning. The entropy is thus to be recognized as completely determined by the state of a body (*i.e., the totality of the positions and velocities of all its parts*) . . . Those processes for which the entropy is the same in the initial and final state, for example directly reversible

processes, form a limiting case. These sorts of processes do not really occur, however, but are to be regarded as an idealization.⁶³

That passage makes irreversibility the core of the second law, and the italicized phrase suggests that the relevant irreversibility is microscopic. No one but Planck had taken such a position. The energeticists did not believe in atoms or recognize the distinction between reversible and irreversible change. Clausius, who did, had nevertheless developed thermodynamics in terms of reversible processes, introducing irreversible ones as a special case. In both versions of his *Mechanical Theory of Heat*, the second law first appears in the third chapter as $\oint dQ/T = 0$, and that form of the law is thereafter applied to a variety of physical problems. Only in the tenth chapter does Clausius turn to "Processes which are not reversible" and provide a "Completion of the mathematical expression of the second law" by writing $\oint dQ/T \leq 0$.⁶⁴ At that point only three more chapters remain in his book.

For Planck, then, a mechanical explanation of the second law had to be an explanation of irreversibility, preferably microscopic, and this he felt the statistical approach had failed to provide. Maxwell, though his treatment was suggestive, had not even touched on the general problem. Both Thomson and Boltzmann had gone farther, arguing that the final state of an irreversible process is more probable than its initial state.⁶⁵ Boltzmann had even given reasons to suppose that the entropy of a state is proportional to the logarithm of its probability. How and when Planck first heard of this approach is unclear (he may not have known Thomson's paper at all), but he was entirely dissatisfied with it when he did. That emerges clearly from a long letter that he wrote in the spring of 1897, at which time his black-body research was under way.

The letter requires a brief introduction. During 1895 Planck's young Berlin Assistant Ernst Zermelo (1871–1923) developed what has since been known as the recurrence paradox. Applying a mathematical theorem published by Poincaré five years before, Zermelo argued that no mechanical proof of the second law is possible, because any mechanical system left to itself must ultimately return to a configuration arbitrarily close to the one from which it began. "Hence," Zermelo wrote, "in such a system *irreversible processes are impossible* since (aside from singular initial states) no single-valued continuous function of the state variables, such as entropy, can continuously increase; if there is a finite increase, then there must be a corresponding decrease when the initial state recurs."⁶⁶

Boltzmann's reply emphasized that the second law was not simply mechanical but also statistical, and the argument continued to the end of 1896. Early in the following year Planck commented on it in a letter to his friend Leo Graetz (1856-1941). The problem of reconciling the second law with mechanics is, he wrote, "the most important with which theoretical physics is currently concerned." Then he continued:

On the main point I side with Zermelo, in that I think it altogether hopeless to [attempt to] derive the speed of irreversible processes—e.g., viscosity or heat conduction in gases—in a really rigorous way from contemporary gas theory. Since Boltzmann himself admits that even the *direction* in which viscosity and heat conduction act can be derived only from considerations of probability, how can it happen that under all conditions the *magnitude* of these effects has an entirely determinate value. Probability calculus can serve, if nothing is known in advance, to determine the most probable state. But it cannot serve, if an improbable [initial] state is given, to compute the following [state]. That is determined not by probability but by mechanics. To maintain that change in nature always proceeds from [states of] lower to higher probability would be totally without foundation.

Here the question is not whether the second law admits exceptions, but a more fundamental one: can probability alone determine the direction in which a system develops? Planck's negative answer to that question appears to have provided his primary reason for rejecting statistical versions of the second law.

Shortly after challenging the proposition that nature must proceed towards more probable states, Planck's letter returned to the problem of irreversibility:

Zermelo, however, goes farther [than I], and I think that incorrect. He believes that the second law, considered as a law of nature, is incompatible with any mechanical view of nature. The problem becomes essentially different, however, if one considers continuous matter instead of discrete mass-points like the molecules of gas theory. I believe and hope that a strict mechanical significance can be found for the second law along this path, but the problem is obviously extremely difficult and requires time.

Planck's hope is the one he had expressed in 1881, but its relation to his research had meanwhile changed. His effort to retrieve irreversibility from continuum mechanics had, in fact, begun more than two years before. Another passage in his letter suggests the spirit of the undertaking:

I see only one way to reach a definitive conclusion about the question. One must embrace one of the two positions [mechanics or statistics] in advance and see how far one can proceed towards the light or towards

the absurd. That task will certainly be easier and more promising if one assumes the second law to be strictly valid (something which certainly cannot be shown from the kinetic theory of gases in its present form) rather than having recourse to hypotheses about the [improbable] initial state of the world simply to *save* gas theory That is to renounce any deeper insight.⁶⁷

When Planck wrote those sentences, the first reports of his black-body research had already begun to appear. Their content will shortly concern us, but the first developed public statement of their objective belongs here. The passage that follows is the opening section of a paper Planck read to the Prussian Academy of Sciences in early February 1897. It introduces the first installment of a series, "On Irreversible Radiation Processes," which was to occupy him until the summer of 1899.

The principle of energy conservation requires that all natural occurrences be analyzable ultimately into so-called conservative effects like, for example, those which take place in the motion of a system of mutually attracting or repelling material points, or also in completely elastic media, or with electromagnetic waves in insulators. Non-conservative forces, on the other hand—like friction, inelastic impact, galvanic resistance—are not elementary in nature since they do not independently satisfy the energy principle. Therefore, in a complete system of physics, they must be reduced to the former [i.e., to conservative effects, all of them apparently reversible].

On the other hand, the principle of the increase of entropy teaches that all changes in nature proceed in one direction. When, for example, a system is isolated from its environment, then, after a longer or shorter time, an equilibrium or stationary state must set in, one from which the system does not depart under any circumstances while external conditions remain the same.

From this opposition arises the fundamental task of theoretical physics, the reduction of unidirectional change to conservative effects.⁶⁸

That "fundamental task" was what had brought Planck to the black-body problem. After an intervening paragraph outlining the failure of earlier attempts to solve it, Planck allowed his audience a glimpse at the grounds for his hopes:

I believe I must recognize as a unidirectional process made up of entirely conservative effects the influence of a frictionless or resistanceless vibrating resonator on the wave which excites it Any such resonator is excited by absorbing energy from the vibration which falls upon it and is damped by radiating energy. The radiated energy is, however, generally not of the same sort as the absorbed, so that the vibrations of the resonator alter the character of the electromagnetic waves propagated in its vicinity. It can be shown that these alterations are unidirectional in various respects and that they have an equilibrating [*ausgleichende*] tendency.⁶⁹

In the absence of one or more resonators, Planck pointed out, no such equilibration would occur. Electrical waves would be governed by Maxwell's equations alone, and they, like the equations of mechanics, are invariant when the direction of time is changed. But a resonator, Planck insisted, would alter the field, for example by absorbing energy from an incident plane wave and re-emitting it in the form of a spherical wave. In addition, because its amplitude changes only slowly with that of the field, a resonator will gradually eliminate fluctuations in the intensity of the radiation incident upon it. Finally, because it has a finite response range due to radiation damping, a resonator will interact through the field with resonators at neighboring frequencies, and that interaction will alter the distribution of radiation "color" or wavelength, as molecular collisions alter the distribution of molecular velocities. Analysis of the last of these equilibrating tendencies should, Planck pointed out, permit "important conclusions about the distribution of radiant energy in the stationary state,"⁷⁰ i.e., about the form of Kirchhoff's universal function.

Planck on the continuum and electromagnetism

The preceding pages have brought Planck step by step to the black-body problem, but an obvious question remains. Why should Planck have supposed that resorting to the continuum would permit a mechanical or quasi-mechanical explanation of irreversibility and thus allow "the reduction of unidirectional processes to conservative effects"? That question, in turn, needs to be discussed twice, once for the years immediately following the completion of Planck's thesis, when he was apparently aware only that Maxwell's demon could upset the second law, and again for the 1890s, when he focused on irreversibility and turned his attention to the electromagnetic field. For neither period are complete answers possible, partly from lack of relevant information about Planck and partly because late nineteenth-century attitudes towards mechanics, the continuum, and the electromagnetic field have been too little studied.⁷¹ But some relevant considerations can be isolated, and examining them will supply information also needed elsewhere about the state of electromagnetic theory at the time Planck's black-body work was done.

When Planck in 1882 announced his avowedly premature belief that atomic theory, despite its great success, would ultimately have to be abandoned in favor of the assumption of continuous matter, he is likely to have had something like the following in mind. In a continuum,

which Planck may have conceived as studded with massy bits, motion in neighboring regions is strictly correlated. When the hole guarded by Maxwell's demon is open, regions on opposite sides of it are neighbors and move together. Energy may be transmitted through the hole nonetheless, but only from regions of more, to regions of less violent motion. Planck, who was a fine musician and often used acoustical analogies in his work, may from the start have thought of the resonant response of a stretched string coupled by a spring or other continuous medium to a driving source.⁷²

Though it must remain speculative, that suggestion is indirectly reinforced by Helmholtz's views on the status of continuum mechanics. During 1877 Planck had heard Helmholtz lecture on the subject, and his student notes refer to an important and presently relevant distinction still discussed, many years later, in the published form of the lectures. There, Helmholtz began by reminding readers of his earlier treatment of particle mechanics. "We were then conscious," he wrote, "that that picture was only one of the observation-simplifying abstractions the consequences of which can represent the facts in certain areas of experience with adequate completeness and brevity." Elastic phenomena, Helmholtz went on, cannot be developed in their full generality by a theory that posits a particulate representation of matter. To treat elasticity, he concluded, "we will instead make use of the *opposite limiting conception* of the constitution of matter, namely the one in which matter continuously fills the occupied space."⁷³ Neither here nor elsewhere in his discussion is there a suggestion that one "picture" fits reality while the other is merely a convenient idealization. Rather the two are polar abstractions, useful in different realms of experience. Other cases, Helmholtz suggests, may require a compromise between the two, for example the theory of optical dispersion, a problem closely related to the one Planck would pose about resonators.⁷⁴

That attitude is one that Planck, who believed in mechanics but was wary of models, would have found congenial. The distinction to which his notes on Helmholtz's lectures refer was intended to articulate and reinforce it. Particle mechanics, Helmholtz pointed out, recognizes two sorts of motion. One is the "ordered motion" in which all particles participate together (his example is the movement of a swarm of midges). The other is "disordered motion," the independent movements which the particles (or midges) carry out within the space their aggregate occupies. For Helmholtz the distinguishing feature of continuum mechanics was the prohibition of disordered motion.⁷⁵ With it

vanished, however, the function for which Maxwell had conceived his demon.

Considerations of this sort were almost certainly still in Planck's mind when he took up black radiation in 1894, but their context had meanwhile changed. Now his problem was to demonstrate that irreversibility could characterize a system governed by conservative forces. In elaborating a solution, furthermore, he turned from the equations of mechanics to those governing the electromagnetic field. For Planck at this time, however, that second step was not a large one. He had chosen the black-body problem because his primary specialty, thermodynamics, was of unquestioned relevance to it. As a result, he was required to proceed from the field equations, which had been central to the thermodynamic arguments with which he was concerned. But in 1895 and again in 1897 he insisted that his method of demonstrating irreversibility could be applied equally well to the mechanical vibrations of acoustic resonators in a continuous medium of air.⁷⁶

Quite possibly Planck thought the electromagnetic formulation the more fundamental: acoustic resonators cannot function in a vacuum⁷⁷; for air, unlike the electromagnetic ether, there was a satisfactory particulate representation. But, during the early years of his research on the black-body problem, electromagnetic theory was for Planck a special sort of continuum mechanics, and his previous hopes for the continuum therefore applied to it unchanged. Only after 1897 did references to an equivalent acoustic proof of irreversibility disappear from his writings, and only at the end of 1900 did his papers begin to suggest that the transition from Newton's to Maxwell's equations might involve fundamentals. Both for Planck and for others, that was an important change of view, but it played no apparent role in Planck's thought until after the twentieth century had begun.

Though not the only viewpoint current, the close association of electromagnetism and mechanics was still widespread through the middle 1890s. Maxwell's own work provided clear precedent. In his *Treatise on Electricity and Magnetism*, published in 1873, the route to equations governing the field began with a series of Lagrangians in which the positions of circuits and the values of the currents in them served as generalized coordinates. Though the structure of the medium in which both currents and circuits moved remained unspecified, Maxwell continued to expect that it would be possible to work backwards from these mechanical equations governing the macroscopic variables to the hidden motions of unseen masses. Meanwhile, he conceived both

the variables and the equations governing them as mechanical, and he repeatedly resorted to mechanical analogy in developing the equations and in clarifying their effects.⁷⁸ Very similar attitudes toward the mechanical basis of electromagnetism can be found in the relevant writings of Helmholtz, Boltzmann, and Hertz. Even H. A. Lorentz (1853–1928), soon to be known for his pioneering attempts to derive mechanics from electromagnetism, treated the field as a dynamical system in the first version of his electron theory, published in 1892.⁷⁹ The same conceptual continuum bridging mechanical and electromagnetic theories is a frequent feature of technical research papers in the 1880s and 1890s, the theory of optical dispersion supplying a particularly clear and apposite example. Until the late 1880s dispersion theory was primarily based on the laws of mechanics, thereafter increasingly on the laws of electromagnetic theory. But many of the same equations appeared in both modes of treatment; people engaged in one could borrow freely results achieved by the other; there was little sense of conceptual division between the two.⁸⁰

Subject to further investigation, the preceding remarks on continuum mechanics must supply the context in which Planck's initially surprising references to that subject are to be viewed. In addition, they may explain Planck's early belief that continuum mechanics would defeat Maxwell's demon. But they provide no clue at all to his conviction that irreversibility could be derived from consideration of purely conservative effects. How could Planck, who recognized that the equations governing the field in an empty reflecting cavity were time-reversible, have supposed that the insertion of a resonator could generate unidirectional effects? Part of the answer has already been given. Planck's intuition plausibly suggested that the resonator's equilibrating effects—e.g., the conversion of a plane wave, traveling in a single direction, to a spherical wave, traveling in all—could not be reversed. But by 1896 Planck had another more concrete reason for faith in his research program. It depends on the state of electromagnetic theory in the 1890s, and considering it will bring us quickly to Planck's first black-body papers and to his earliest significant contribution to the theory of the electromagnetic field.

Until the development of Lorentz's electron theory during the 1890s, none of the main formulations of Maxwell's theory provided an account of the interaction between the field quantities (ether displacements) and matter.⁸¹ Maxwell and many of his main successors, including Hertz, denied the existence of isolated electric charges and thus of charged

material particles on which the field might have acted directly. Electric current did, of course, figure in the field equations, but ordinarily as an additional field quantity, another sort of ether-polarization, not as charge in motion. All three field quantities—electric, magnetic, and current—existed and satisfied Maxwell's equations both in free space and in the interior of bodies, their values in different media being related by appropriate proportionality constants and boundary conditions. While he conceived electromagnetism in this way, Planck's "resistanceless vibrating resonator" could not have been the charge-bearing mechanical vibrator which, as a bound electron, it was later to become. Instead, it was a tiny oscillating current, and thus a field quantity. The techniques appropriate to its study were a microscopic version of those Hertz had applied to the tuned circuits and dipoles with which, a few years earlier, he had generated and detected electromagnetic waves.

These differences are consequential. If Planck had analyzed Hertz's tuned circuits with twentieth-century field equations, in which isolated charges figure and in which current is represented as charge in motion, he would have recognized immediately that the equations relevant to the resonator problem are fully time reversible, like those for the field in free space. As it was, however, Planck followed Hertz in representing a physical resonator by means of boundary conditions on a surface exterior to it. Under those circumstances, reversibility was a characteristic to be investigated, not one to be discovered at a glance. Planck's first two black-body papers laid the groundwork for its exploration, and what emerged in the second of them was the first theoretical expression for what is now called radiation damping. When a small term representing that damping was introduced into the differential equation for a resonator, the equation ceased to be reversible in time, precisely the sort of effect on which Planck's hopes for the continuum depended. His treatment involved approximations, of course, and their elimination would have restored reversibility, not to his resonator equation, which is still in use, but to the equations for resonator plus field. But Planck was not to know that for a number of years, by which time it was inconsequential. He had long since abandoned hope that irreversible processes might be generated by conservative effects alone.

Detailed examination of the two papers in which Planck established the properties of his damped resonators would require a longer excursion into turn-of-the-century electromagnetic theory than is appropriate to the central concerns of this book. A brief sketch will, however, give

body to what has just been said and simultaneously prepare for what is to come. Both papers open by underlining the conceptual novelty of the situation Planck is about to explore. For him its essential feature is the notion of "conservative damping."⁸² Resonators are to be resistanceless if electric, frictionless if acoustic. They may, that is, lose energy only by radiation, so that total energy is retained in a directly mechanical form. In actual radiative processes, Planck concedes, there is also "consumptive damping," which converts vibratory energy to heat by friction or electrical resistance. But these consumptive effects may be minimized in practice, and they must be eliminated from theory to achieve "the reduction of unidirectional change to conservative effects."⁸³

Planck's first paper, presented to the Prussian Academy in the spring of 1895, considers the case of a resonator in equilibrium with an incident field. Modeling his treatment explicitly on a paper Hertz had published six years before,⁸⁴ Planck first produced a free-space solution of Maxwell's equations in the form of a spherical wave train expanding with velocity c and wavelength λ from the origin of coordinates where the resonator is located. Assuming the resonator capable only of linear oscillations, Planck restricted attention to expanding waves symmetric about its axis. The field thus specified is the one emitted by the resonator (more accurately, the "resonator" is defined as the localized oscillating current that permits the field equations to be satisfied at the origin by the specified field), and it is fully determined by two constants, one fixing amplitude, the other phase. In his next paper and thereafter Planck would refer to it as the "secondary" field.

Planck then introduced a primary radiation from which the resonator might receive energy. For simplicity, it was restricted to a train of plane waves polarized parallel to the resonator's axis and with wavelength equal to that of the secondary radiation, and its nature was therefore also specified by a pair of constants fixing amplitude and phase. Adding the two fields together, Planck was able to compute the net energy flux through a small spherical surface about the origin. For equilibrium, that flux was required to be zero: the resonator at equilibrium emits as much energy as it absorbs. Assuming that the resonance was maximum, so that the two phase constants were equal, Planck was able finally to compute the ratio at equilibrium of the amplitude factors of the secondary and primary radiation. It proved to be dependent only on wavelength, not at all on the particular structure of the resonator. The latter would, Planck had shown, affect the

field only very near the origin, and he had integrated over a surface farther out.

That is just the sort of result Planck had been looking for. After pointing out, near the end of his paper, that his methods apply equally to acoustic vibrations in air, he continued:

Neither acoustical nor narrowly electrical problems have, however, motivated the preceding investigation. Rather, it was stimulated by the question of stationary radiation processes within a mechanical medium at rest at a constant temperature and surrounded by bodies with the same temperature.

Referring to his computation of the ratio of emission to absorption, he then went on:

Kirchhoff's law for the proportionality of the emission and absorption capacities is an unmistakable consequence of this behavior. For the computation of vibration amplitudes one need not consider the detailed structure of the emitting particle; it suffices if the dimensions of the center of vibration are small compared with the wavelength.⁸⁵

That result is Planck's first contribution to black-body theory, but its content is small and limited by numerous special hypotheses, particularly the restrictions to equilibrium and to a primary field at precisely the resonator's frequency. Within a year, however, Planck presented the Academy with a second paper in which the first restriction was dropped and the second relaxed. In that paper the primary and secondary fields were treated much as before except that their amplitudes were permitted to vary. In addition, the net energy flux through the small test sphere was allowed to depart slightly from zero so that the accumulated energy within the sphere might slowly change. Lacking information about the resonator's structure, Planck simply assumed that his computation would be unaffected if he extrapolated the dipole field outside of the sphere to its interior. The energy U of the dipole producing that field was known to be

$$U = \frac{1}{2}Kf^2 + \frac{1}{2}Lf^2, \quad (7)$$

where f is dipole moment, and K and L are resonator-dependent constants. Since any net flux across the sphere must appear within it as a change in dipole energy, Planck was able finally to combine his previous flux computation with equation (7) to produce a differential equation for the resonator itself. It proved to be

$$Kf + L\dot{f} - \frac{2}{3c^3}\ddot{f} = E, \quad (8a)$$

where E is the electric field in the direction of the resonator axis due to the primary radiation.

Planck quickly pointed out that a resonator governed by equation (8a) has a natural period τ_0 and a logarithmic damping constant σ given by

$$\tau_0 = 2\pi \sqrt{\frac{L}{K}}, \quad \text{and} \quad \sigma = \frac{2\pi}{3c^3} \sqrt{\frac{K}{L^3}}. \quad (9)$$

Rewritten in terms of those parameters, the condition that resonator energy respond slowly to variations in the external field becomes $\sigma \ll 1$. For a resonator which satisfies that condition, Planck further showed that his first resonator equation is equivalent to

$$Kf + \frac{2K}{3c^3L} \dot{f} + L\ddot{f} = E, \quad (8b)$$

a form he subsequently used interchangeably with equation (8a). Both displayed the characteristic likely to have concerned him most. The radiation-damping term—third on the left in (8a), second on the left in (8b)—changes sign on time reversal, the other terms remaining the same. That result is a probable source of Planck's confidence that he was en route to a proof of irreversibility.

Planck did not make that point, however, presumably because he did not yet have such a proof. His resonators were imaginary entities of unspecified structure. Recourse to them in black-body theory was licensed only by Kirchhoff's law, which made the black-body field independent of cavity material. Both theoretically and experimentally, the black-body problem was about fields, not resonators, and it was therefore to fields that Planck had now to extend his work. The series of papers "On Irreversible Radiation Processes," of which the opening paragraphs were reproduced above, undertook that task, and its pursuit is the subject of Chapter III.

Before turning to Planck's work on irreversible changes in the electromagnetic field, however, a long detour is essential. Through most of the year 1897, Planck continued to believe that he could prove irreversibility directly, without the aid of any statistical or other special hypotheses. That proof had been his initial objective in taking up the black-body problem at all. But by the spring of 1898 he had recognized that that goal could not possibly be achieved, and the concepts deployed in his subsequent papers came more and more to resemble those developed by Boltzmann for gas theory. Some aspects of that resemblance

may have been the result of independent discovery, but they cannot all be accounted for in that way. An understanding of selected aspects of Boltzmann's thought is therefore prerequisite to the study of Planck's development after 1897, especially because part of what Planck found in Boltzmann has been lost from view during the subsequent development of statistical mechanics.