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Planck, Entropy, and Quanta, 1901–1906

I

If there is a single concept that unifies the long and fruitful scientific career of Max Planck, it is the concept of entropy. From the Munich dissertation which he wrote at the age of twenty-one, right through to the papers he wrote during his late seventies, the Second Law of Thermodynamics and the associated idea of entropy were always central in his thought. Although much of his work can be viewed as an extended series of variations on what he called his pet theme ("Lieblingsthema"), the theme itself was radically altered in 1900. In that year Planck introduced, in his theory of the black-body radiation spectrum, the idea which immortalized his name, the idea of energy quanta. This idea grew directly from Planck's years of study of the way in which the second law of thermodynamics applied to the behavior of radiation.[1] But despite its connections with his work on entropy during the previous twenty years, it was the very success of his theory of radiation that forced Planck to make a thorough revision of his ideas on entropy.

Before 1900 Planck had resolutely followed the single line of pure thermodynamics in his work, avoiding the difficulties that surrounded the path of kinetic theory. He was willing to grant that the attempts to expose the molecular basis of macroscopic behavior offered the hope of more fundamental insight into nature; but he expressed his doubts, on more than one occasion, that these attempts to dig deeper than the laws of thermodynamics could meet with real success in the foreseeable future. At no point in any of the forty or so papers that he wrote prior to 1900 did Planck use, or even refer to, the relationship that Ludwig Boltzmann had discovered between entropy and the probability of molecular configurations. (The muse of entropy was as dear to Boltzmann's heart as to Planck's, but how different she appeared to her two admirers!) As Planck wrote many years later, referring to his work in 1900: "I had not cared about the connection between entropy and probability myself until that time; there was nothing tempting about it for me because every probabilistic law admits exceptions, and at that time I attributed universal validity to the second law of thermodynamics."[2] And yet, within two years after his first paper on quanta, Planck had not only accepted Boltzmann's statistical interpretation of entropy as a useful idea, but had begun to build it into the very basis of his own thought.

Planck's introduction of quanta constituted, then, only half of the revolutionary change in his thinking that began in 1900; the other half was his acceptance of the statistical interpretation of entropy. Naturally enough, it took time for the implications of both changes to be fully absorbed into his physical outlook. This absorption occurred during the years between 1900 and 1906, from the time Planck first constructed his successful theory of the radiation spectrum, in those "few weeks of the most strenuous work of my life," to the appearance of his book, *Lectures on the Theory of Heat Radiation.*[3] The changes in Planck's views on both entropy and the quantum theory have never been traced before, so far as I know.[4] Planck himself makes no mention of these years in any of his retrospective accounts of the discovery of quanta, and even so perceptive a student of the period as Rosenfeld has written: "In fact, and it is a phenomenon often recorded, Planck does not go all the way to the end of the new trail which he opened. At first he stops, seeks a diversion in works of quite another kind; when he returns to the question five years later, it is still not to go forward, but rather to retrace, in a series of masterly lectures, the entire route already traversed."[5] This statement hardly does justice to the increase in insight and change in viewpoint that Planck had reached by 1906. While Planck did not develop the quantum theory along radically new lines in the manner of Albert Einstein, his understanding of the basic questions that his work had posed, was markedly deeper in 1906 than it had been in 1900. This is hardly surprising, since, as Planck reported in 1911, he had been struggling incessantly from the beginning to push the theory further, even though his efforts had not been successful.[6] But it was precisely his increasingly surer grasp of the statistical interpretation of entropy and the second law of thermodynamics which clearly shows in his deeper insight into the problems of the quantum theory.

II

In the preface to his *Treatise on Thermodynamics,*[7] written in April, 1897, Planck contrasted the possible methods of developing the subject. Of the kinetic theory, which attempts to express all thermodynamic concepts and laws in terms of molecular motions, he wrote that it "penetrates deepest into the nature of the processes considered, and, were it possible to carry it out exactly, would be characterized as the most perfect." But, he went on to say, "Obstacles, at present insurmountable, seem to stand in the way of its further progress. These are due not only to the highly complicated mathematical treatment, but principally to essential difficulties, not to be discussed here, in the mechanical interpretation of the fundamental principles of thermodynamics." In view of these obstacles, Planck thought that the most fruitful method to follow, the one corresponding best to the present state of the science, was one which, "keeping aloof from definite assumptions as to its nature, starts direct from a few very general empirical facts, mainly the two fundamental principles of thermodynamics" and proceeds "by pure logical reasoning," i.e., the method of pure thermodynamics.

These characteristic remarks, fully in keeping with Planck's thermodynamic researches during the previous two decades, take on a more explicit meaning, however, when read in conjunction with a paper that he had published only two months before the treatise was written.[8] This paper was the first in what was to become an extended series of studies of irreversible radiation processes that would eventually lead into the quantum theory. In the introduction, Planck formulated the problem that he viewed as basic: to demonstrate that the electromagnetic radiation in an enclosure would evolve irreversibly into an equilibrium state as a result of its interactions with a collection of charged harmonic oscillators. Such a demonstration, wrote Planck, would be the first proof that a conservative system could actually exhibit the irreversible behavior required by the second law of thermodynamics. If such a proof could be carried out, it should also lead to a determination of the energy spectrum of black-body radiation, that is, to a full determination of the properties of the equilibrium state, and it was known from Kirchoff's work that this energy spectrum was a function of universal significance.

Planck pointed out that the kinetic theory of gases had undertaken to solve just such a problem in another domain: to prove that the molecules of a gas would approach a unique equilibrium state as a result of their collisions, the approach being monotonic as required by the second law. The corresponding equilibrium state would be characterized by the Maxwell-Boltzmann velocity distribution. Planck expressed his doubts that Boltzmann's famous H-theorem had actually solved this problem. By citing Zermelo's criticisms of Boltzmann's reasoning, Planck implied his feeling that Boltzmann's work was marred by the need for a statistical hypothesis in addition to the basic dynamical equations. (These criticisms made by E. Zermelo, who was Planck's student, surely represent the "essential difficulties" in the kinetic interpretation of the second law to which Planck referred in the preface to his *Thermodynamics* quoted above.) Planck hoped that his own program could be carried out without the need for any statistical hypotheses, and that irreversibility could be deduced by purely electrodynamic arguments.

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These hopes were soon dashed when Boltzmann himself showed that the equations of electrodynamics could no more produce irreversibility in the system of oscillators and radiation than the equations of mechanics could in the case of a gas.[9] Planck saw the force of Boltzmann's criticism and in November 1899, when he rewrote his work as a single monograph for the *Annalen der Physik*, he incorporated this criticism into his presentation.[10] By this time, Planck had developed the statistical hypothesis whose necessity had been pointed out by Boltzmann. Several pages of the lengthy introduction to the *Annalen* paper deal in detail with the parallelism between Planck's statistical hypothesis of "natural radiation" and Boltzmann's hypothesis of "molecular chaos" in the theory of gases. Both hypotheses were necessary, Planck admitted, to bridge the gap in their respective theories between the reversible equations of motion and the irreversible macroscopic behavior demanded by the second law. This admission clearly marked the first step which Planck had taken in the direction of Boltzmann's ideas, but it was still only the first step.

As we have seen, Planck was searching for a derivation of the spectral distribution of black-body radiation.[11] This distribution is defined as the function $\rho(\nu, T)$, where $\rho(\nu, T)\,d\nu$ is the energy per unit volume of the equilibrium radiation in an enclosure at temperature T, which lies in the frequency interval between ν and $\nu + d\nu$. Planck knew that this function must satisfy the Wien displacement law, a rigorous result which requires that $\rho(\nu, T)$ have the form,

$$\rho(\nu, T) = \nu^3 f(\nu/T), \tag{1}$$

where $f(\nu/T)$ is a function only of the ratio of frequency to temperature. By taking advantage of the universality of the function ρ, Planck had proved that ρ must be related to the average energy $u_\nu(T)$ of an oscillator of frequency ν with which the radiation is in equilibrium through the equation

$$\rho(\nu, T) = (8\pi\nu^2/c^3)\, u_\nu(T), \tag{2}$$

where c is the velocity of light. Planck's one remaining task was to determine the average energy of such an oscillator as a function of temperature. His earlier work in thermodynamics led him to prefer an alternate formulation in which he had to determine the entropy of the oscillator as a function of its energy.

It must be mentioned at this point, that Wien had proposed an explicit form for $\rho(\nu, T)$ several years earlier,[12] on the basis of a not very convincing theoretical argument. According to Wein, $\rho(\nu, T)$ should have the form

$$\rho(\nu, T) = \alpha\, \nu^3 \exp\,(-\,\beta\, \nu/T), \tag{3}$$

where α and β are constants. The important point is that Wien's distribution law was in good agreement with the available experimental results at the time Planck was writing. Planck must have been especially gratified when his reasoning led to the Wien distribution and seemed to give this empirically verified equation the certainty of the laws of thermodynamics. What Planck had done was to define a form for the entropy-energy relationship of an oscillator which, he showed, was the only form compatible with the second law. New experimental results, obtained in the spring of 1900, produced a very serious problem for Planck, when they indicated that the Wien distribution simply was inadequate at the longer wavelengths. Planck reexamined his reasoning[13] and decided that there was a flaw in it: his entropy-energy relation for an oscillator was really not uniquely fixed by the second law. Nevertheless, Planck offered other arguments for the correctness of his entropy equation and therefore for the validity of the Wien distribution.

By October 1900 new steps were clearly necessary. Rubens and Kurlbaum had made careful measurements of the energy

spectrum in the long wavelength region. Wien's law had failed there, and Planck immediately proposed an improved distribution law which did fit the experimental data over the entire frequency spectrum.[14] This law, announced by Planck in a discussion remark after Kurlbaum's paper to the German Physical Society, had the form

$$\rho(\nu,T) = \frac{\alpha\, \nu^3}{\exp\,(\beta\nu/T) - 1}. \tag{4}$$

Having found what proved to be the correct form for the distribution law, Planck now faced the harder problem of "investing it with a true physical meaning." For Planck this still meant finding and justifying that entropy-energy relationship for a harmonic oscillator which would lead to his distribution law. It was this problem that Planck solved by breaking with his own past and adopting Boltzmann's statistical approach to entropy, and, at the same time, by breaking with the entire past of physics and treating the energy as a discrete variable, rather than as a continuously varying quantity. Planck described his reasoning briefly in a paper[15] before the German Physical Society on December 14, 1900, and again, at greater length, in the paper he sent off to the *Annalen* a few weeks later.[16] In the latter paper, after discussing the inadequacy of his earlier attempts to find the entropy of an oscillator as a function of its energy, Planck wrote: "Another condition must therefore be introduced which allows the calculation of the entropy, and in order to accomplish this a closer investigation into the meaning of the entropy concept is necessary." He made it quite clear how this closer investigation would proceed as he went on to write, "Entropy specifies disorder," a phrase new to Planck's writings. In the earlier version of the paper he was even more explicit: "Since the entropy of an oscillator is specified by the nature of the simultaneous distribution of energy over many oscillators, I conjectured that it would have to be possible to calculate this quantity by introducing probabilistic considerations, whose importance for the

Entropy
of an
Oscillator

second law of thermodynamics was first revealed by L. Boltzmann."

It is significant that Planck viewed his new procedure as merely an extension of the hypothesis of "natural radiation" which he had already introduced. Certainly both were moves in the direction of Boltzmann's ideas, but there was a real difference which was pointed out a few years later by Ehrenfest.[17] Planck's hypothesis of "natural radiation" was the analogue of Boltzmann's hypothesis of "molecular chaos," and it formed a necessary step in a program which paralleled Boltzmann's H-theorem. That is to say, it was part of Planck's original attempt to follow the kinetics of the evolution of the state of the radiation into thermal equilibrium, as Boltzmann's *kinetic* method had done for gases. Planck's new procedure, however, which started with Boltzmann's basic relationship between the entropy S of a state and its probability W,

$$S = k \ln W, \tag{5}$$

√13 was the analogue of the *statistical* or *combinatorial* method, which Boltzmann had used to give an *independent* derivation of the state of thermodynamic equilibrium as the most probable state. Planck gave no indication that he recognized the distinction at this stage of his work and, in fact, he did not even follow Boltzmann's statistical method very closely. Planck considered equation (5) as "fundamentally a definition of the probability" and he did not calculate the equilibrium distribution by maximizing W at all.

III

In his later years Planck remarked on several occasions that, although the proportionality constant *k* which relates entropy

and probability, was, understandably, known as Boltzmann's constant, Boltzmann himself never attached any significance to it and never attempted to estimate its numerical value. Planck, on the other hand, grasped the importance of this constant immediately and laid heavy emphasis on its universality. Boltzmann's constant is one of the two basic physical constants that Planck made use of when he carried out the theoretical derivation of his distribution law, equation (4). The other was, of course, the constant *h*, which bears Planck's name and which determines the magnitude of the energy quanta ϵ for an oscillator of frequency ν through the equation,

$$\epsilon = h\nu. \tag{6}$$

Expressed in terms of these two constants and the velocity of light, the distribution law has the form

$$\rho(\nu,T) = \left(\frac{8\pi\nu^2}{c^3}\right)\left(\frac{h\nu}{\exp\,(h\nu/kT) - 1}\right), \tag{7}$$

where the second factor represents the average energy of the oscillator according to equation (2). The constants *h* and *k* were determined by Planck from measurements of the radiation spectrum.

Planck related the constant *k*, which entered his calculations through equation (5), to other physical quantities by the following argument. Boltzmann had shown that the entropy S_G of a monatomic gas in a given state was related to the probability of that state W_G by the equation

$$S_G = (R/N_0)\ \ln W_G. \tag{8}$$

In this equation R is the gas constant and N_0 is the ratio of the mass of a mole to the mass of an atom, that is, the number of atoms per mole, or Avogadro's number. But if one considers a system composed of a gas together with a collection of oscillators and electromagnetic radiation, the same universal rela-

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tionship must hold between the entropy of the composite system and the probability of the state of the composite system. Since the two parts, gas and oscillators plus radiation, are quite independent of one another, the probability of the joint state is the product of the probabilities of the individual states. It follows then that the proportionality factors k and R/N_0 must be just two different ways of writing the same thing,

$$k = R/N_0. \tag{9}$$

Since the gas constant R was well known and Planck had just evaluated k, this equation fixed the value of Avogadro's number N_0. This meant that the mass of a single atom was also determined, with a precision that went far beyond any of the rough estimates available for this quantity in 1900. And, as Planck pointed out, the quantum of electricity (the charge on a singly charged ion or an electron) was also determined as the ratio of Faraday's constant to Avogadro's number, also with a precision not to be attained by direct measurements for almost a decade.

Planck set great store by these results of his theory. He referred to them in his original communication as "additional relationships which seem to me to be of considerable importance for other fields of physics and for chemistry," whose testing "by more direct methods will be a problem for further investigation as important as it is necessary." When Planck rewrote his theory for the *Annalen der Physik*, he separated off the calculations of the basic constants, which we have just described, and wrote them up as a separate paper to stress their importance. He repeated this discussion once more, this time at much greater length, in a paper he wrote during the summer of 1902 which was published as part of a Festschrift for the Dutch scientist, Johannes Bosscha.[18]

This Bosscha Festschrift article is especially interesting, since in it Planck took the opportunity of stating in some detail his current ideas on entropy. Planck had evidently been reflecting on the relationship between Boltzmann's ideas and his own previous work in thermodynamics. He saw an important methodological connection between them which, in a sense, smoothed his own transition from a purely thermodynamic view of entropy to the probabilistic interpretation of this concept. The key point in Planck's reasoning was expressed in the following passage. "One of the most important methods of probing more deeply into the special properties of physical and chemical processes by theoretical means depends on a certain extension or generalization of the conditions which we consider to be characteristic for the state of a material system. According to this interpretation, those states which are really accessible to observation and measurement represent only very special cases, distinguished by particular properties, among the many more numerous and much more general states which are in themselves just as possible in nature, but which are not observable, or not easily observable."

Planck described the successive generalizations of the concept of the state of a system, beginning with the "theoretical," "labile," or unstable states that were used in the discussion of the isotherms and equation of state of fluids by Maxwell, van der Waals, and others. Another class of unobservable states had been used in the study of chemical reactions in gases, where it proved convenient to consider states in which a dissociation reaction, for example, had proceeded to any arbitrary desired degree. Planck had studied such states and, in his work on the theory of solutions, had introduced states even further removed from observation. In order to fix the entropy of the solution, he had found it valuable to imagine the whole system heated to the point where it became an ideal gas.

Up to this point, Planck's description paralleled exactly one he had given eleven years earlier in a lecture on new developments in thermodynamics.[19] In that lecture, however, he had prefaced his discussion by an expression of disappointment at the results of the kinetic theory. "Anyone who studies the works of Maxwell and Boltzmann, the two scientists who have probably penetrated most deeply in the analysis of molecular motions, will not be able to resist the impression that the admirable display of physical ingenuity and mathematical cleverness shown in overcoming these problems is not in suitable proportion to the fruitfulness of the results achieved." This time he went on in a very different vein, and I shall quote at some length to indicate how profoundly he had altered his views. Planck is still discussing the generalization of the concept of the state of a system.

"The kinetic theory of gases goes still further in the designated direction. . . . According to the kinetic theory, the state of a definite quantity of a monatomic gas, enclosed in a definite volume, is not yet defined when its total kinetic energy is given; this requires a full knowledge of the position and velocity distributions of the atoms, that is, a knowledge of the number of atoms whose coordinates and velocity components lie between any specified pairs of limits. In the observable stationary state, there is, to be sure, only one definite spatial distribution, the uniform one, and one definite velocity distribution, the Maxwell distribution; but, in general, one can assume a completely arbitrary distribution law for both the spatial and velocity distributions, and only when this distribution law is given can one consider the state of the gas as completely definite. Each such arbitrarily given state corresponds to a definite entropy, and the maximum of the entropy yields the conditions for the stationary state, according to the second law of thermodynamics. In order to find the stationary state it is therefore essential to know the general expression for the entropy of the gas in any state. Now, as Boltzmann has shown, there is a simple theorem which permits one to calculate the entropy for any arbitrary given state of the gas, that is, for any arbitrary given law for the distribution of molecular positions and velocities, and which is therefore to be considered as fundamentally an extension of the definition of entropy beyond the domain of pure thermodynamics into that of the kinetic theory of gases."

N.B

Further along in this same article, after repeating Boltzmann's calculation of the entropy of a gas, Planck commented on the value of the probabilistic interpretation of the entropy.

"The magnitude of the entropy acquires a particularly intuitive meaning if one introduces the idea of probability. Since the number of different possible complexions which correspond to a definite state specifies the probability of this state, one can say in general that the entropy of the gas in any state is a measure for the probability of this state, and that the stationary state is distinguished by the maximum value of the probability."

Planck had indeed been converted to Boltzmann's way of looking at entropy. He developed his views further in a paper written, appropriately enough, for the Boltzmann-Festschrift in 1903.[20] This time Planck actually championed Boltzmann's views on entropy against those of Gibbs whose *Elementary Principles in Statistical Mechanics* had appeared the previous year. Although Planck was, relatively speaking, a novice in statistical mechanics, his twenty years of close familiarity with entropy in thermodynamics enabled him to see directly into the advantages that Boltzmann's entropy definition possessed in comparison to the various definitions that Gibbs had introduced. The principal advantage was closely related to the train of thought in the paper we have just discussed: Planck saw Boltzmann's entropy definition as giving a natural extension of the thermodynamic definition to all nonequilibrium states. Since Planck, like his master, Clausius, found the full meaning of the second law in its explanation of irreversibility through the increase of entropy, it was just this feature of Boltzmann's work that appealed most to him. Despite the apparent generality of Gibbs' definitions that could, in principle, apply even to a system of few degrees of freedom, and despite the fact that all three of Gibbs' definitions gave results in agreement with Boltzmann's for a gas in equilibrium, Planck was not satisfied with them: their generality, at first sight so attractive, was bought at the price of a restriction of their physical meaning. And so, Planck concluded, "Boltzmann's definition of entropy proves itself to be the most relevant and the most productive, among all those known up to now, for irreversible processes, which first give the entropy

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its true meaning and which alone supply the key to the full understanding of thermal equilibrium."

IV

NB Planck regarded "the search for the absolute" as "the loftiest goal of all scientific activity," and, despite his earlier negative attitude, came to look upon Boltzmann's statistical explanation of the second law of thermodynamics as a great stride forward in this search. He developed this theme at some length in an address that he delivered to the science students at the University of Leyden in 1908.[21] In this lecture Planck tried to show the unity of the world picture developed by the physicist, a unity underlying the diversity of phenomena and independent of the accidents of the history of science. He made it clear to his audience that he was fundamentally opposed to the positivism of Ernst Mach and his school and that he saw the future goal of science as the development of a unified theoretical structure, which would truly represent the essential structure of the natural world.

The central sections of Planck's lecture were devoted to the development of the second law of thermodynamics, viewed as a progressive freeing of this law, and its attendant concept of entropy, from their peculiarly anthropomorphic origins. Planck stressed the point that the second law provided a particularly useful and interesting example of his thesis just because this law had not yet put aside all traces of the "egg shell" from NB which it had emerged. In all of the earliest formulations of the second law, the essential feature of the law seemed to be the impossibility of certain kinds of processes, for example, the complete conversion of heat into work in a cyclic process. Early attempts to express the work "lost" when heat flowed from a higher to a lower temperature did not lead to a unique

answer because, as Planck put it, "this formulation of the question was too anthropomorphically colored"; it was put from a standpoint which was "too economically interested." NB What was really involved was the "preference" that nature had for some states rather than others: processes whose final state was less preferred than the initial state were absolutely impossible.

The general measure of this preference for one state rather than another was discovered by Clausius in the concept of entropy. The entropy of a state provided a quantitative measure of nature's preference for this state. The division of processes into those that increase entropy, and so will always occur in nature and cannot be reversed, and those that do not change entropy and can therefore occur, at least ideally, in either direction, marked a more fundamental classification than any based on mechanical or electrical properties, or any other NB apparent differences in processes. And yet, as Planck remarked, this classification itself needed a deeper foundation, since it still rested on the possibilities of experiments, that is, on whether or not an experiment could be carried out to reverse a particular process. The value of the entropy itself, according to Clausius' definition, depended upon the possibility of carrying out an idealized reversible process, and as thermodynamics developed, these idealized processes, with their semipermeable membranes and arbitrarily controllable chemical reactions and other purely conceptual equipment, became so far fetched that it was indeed remarkable that they led to sound results, confirmed by real experiments.

Since, however, the results deduced from these idealized reversible processes made no reference to the processes themselves, but related measurable quantities only, it was difficult, remarked Planck, to suppress the thought that perhaps the essence of the principle of increasing entropy really had not yet been grasped. NB Perhaps it had to be detached from its original connections with the impossibility of "perpetual motion of the second kind," even as the principle of conservation of energy had been detached from the law of the impossibility of perpetual motion. "The completion of this step, the emancipation of the entropy concept from considerations of human experimental abilities and the consequent elevation of the second law into a real Principle, is the scientific life work of Ludwig Boltzmann. It consists, briefly speaking, in the general reduction of the concept of entropy to that of probability. The meaning of the words I used above, as a makeshift, 'the preference of nature for a certain state,' is simultaneously explained in this way. Nature prefers more probable states to less probable states precisely by carrying out only those transitions which are in the direction of greater probability. . . . The calculation of a definite value for the probability of every state of a system is made possible by the introduction of the atomic theory and statistical methods. . . . By means of this interpretation, in one stroke, the second law of thermodynamics is removed from its isolated position, the mystery in the preference of nature for certain states vanishes, and the entropy principle, as a well-founded theorem of probability theory, is connected with the introduction of atomism in the physical picture of the world."

With these words Planck paid even more homage to the central role of Boltzmann's ideas in physics than perhaps Boltzmann himself would have done. He made only one reservation in his otherwise complete acceptance of the statistical world view, trying to hold fast to his idea of the absolute validity of the second law. Boltzmann had left a place—an essential place—in his statistical derivation of the law of increasing entropy, for the occurrence of processes which proceed in the direction inverse to that usually observed. According to Planck, these improbable, entropy-decreasing processes must be excluded, since a world that permits the spontaneous unmixing of gases, for example, is surely no longer our world. Such processes were to be excluded by a general hypothesis of molecular chaos, that is, along the lines of the one Boltzmann himself had used or the one Planck had introduced into his radiation theory. It is remarkable that Planck apparently failed to realize that the improbable processes, which he thought must be excluded from physical theory, had already taken an

important place in Albert Einstein's theory of the Brownian motion. Despite his announced acceptance of the statistical outlook, Planck still could not square a truly statistical view with his deepest convictions on the nature of scientific law. His one reservation would really have drawn the teeth from a probabilistic approach.

Even this last reservation was dropped within a few years, and in two separate publications[22] which appeared in 1914, (Planck emphasized the truly statistical aspect of the second law and its final validation by the appearance of just those improbable processes that he had wanted to exclude. It was apparently the Brownian motion, or rather the strikingly successful explanation of this natural example of perpetual motion by Einstein and Smoluchowski, that convinced Planck of the reality of fluctuation phenomena) even as it convinced Wilhelm Ostwald of the reality of atoms.

V

One thing that Planck learned from his studies of statistical mechanics in the years following 1900 was a proper appreciation for Rayleigh's little note, *Remarks upon the Law of Complete Radiation.*[23] This two-page article (published in June 1900, just a few months before Planck's own radiation law) pointed out the inevitable outcome of applying classical statistical mechanics to the radiation problem. Neither Planck nor his experimental colleagues, Rubens and Kurlbaum, had taken Rayleigh's paper very seriously in the fall of 1900. Rayleigh's proposed distribution law was compared with the experimental data and found to be in disagreement with it, except for long wavelengths. It was then dismissed—along with several other laws which had been proposed on a strictly ad hoc basis. Planck made no specific reference to Rayleigh's work in his own papers of 1900 and 1901, though he must have been acquainted with it—at least through the papers of Rubens and Kurlbaum—and there is no indication that he recognized its basic importance at that time.

During the following five years, Rayleigh's classical radiation theory suffered the same neglect as Planck's radical break with classical ideas. But, by 1906, when Planck published his *Lectures on the Theory of Heat Radiation,* he had seen the point of Rayleigh's compressed and somewhat cryptic remarks. After deriving his own distribution law [equation (7) as stated previously] in his *Lectures,* Planck proceeded to examine its limiting behavior for very large and very small values of the ratio $(h\nu/kT)$.[24] In the limit where $(h\nu/kT)$ is large the Planck law reduces to the Wien distribution [equation (3)] as Planck had known from the beginning and had pointed out at the time he introduced his law. Planck had never previously considered the other limit, however. When $(h\nu/kT)$ is very small compared to one, the Planck law reduces to the equation,

$$\rho(\nu, T) = (8\pi\nu^2/c^3)\ (kT). \qquad (10)$$

Planck remarked that this result had the same form that Rayleigh had derived by very different methods in 1900. It meant that the average energy of a linear oscillator of frequency ν, $u_\nu(T)$ had the universal value required by the equipartition theorem,

$$u_\nu(T) = kT, \qquad (11)$$

as one can see from equation (2). In the light of the discussion given earlier in this paper it is no surprise that Planck had never even mentioned the equipartition theorem in his works prior to 1906.

Planck was now fully aware of the significance of the equipartition theorem, however, and discussed it for gases as well as for radiation in his *Lectures.* He also presented Lord Rayleigh's own method of deriving the distribution law expressed in equation (10). (Although Rayleigh had only sketched the method very briefly in 1900, it had been elaborated on by both Rayleigh and Jeans in papers published in 1905.[25]) In Rayleigh's approach to the radiation problem, neither Planck's harmonic oscillators nor any other material system were ever introduced, but attention was fixed directly on the standing waves (or normal modes) of the radiation in a cavity. The first factor in equation (2) or (10) $(8\pi\nu^2/c^3)$ then appears as the number of modes per unit frequency interval at frequency ν. The second factor $u_\nu(T)$ is the average energy associated with such a mode. The equipartition theorem left no alternative in the choice of $u_\nu(T)$: it had to be set equal to kT, as in equation (11), leading to the Rayleigh distribution.

Planck also included a new way of looking at the underlying assumption of his radiation theory in the *Lectures.*[26] After repeating the arguments he had previously used, in which he counted the number of ways a given number of energy units could be shared among the oscillators, he analyzed the problem afresh in terms of the phase space of an oscillator. The curve representing the locus of phase points of constant energy E is an ellipse, described by the equation,

$$(p^2/2m) + 2\pi^2\nu^2 mq^2 = E, \qquad (12)$$

where m is the mass of the oscillator, ν is its frequency, q is its coordinate, and p is its momentum. The area enclosed by such an ellipse is (E/ν). The elementary cells (or the regions of equal probability corresponding to energy intervals ΔE) are the elliptical rings of area $(\Delta E/\nu)$. In Planck's theory these cells must have areas equal to his new constant h, which then fixes the area of a phase cell for oscillators of all frequencies. As Planck put it, the condition that phase cells of a fixed definite size, h, are introduced is characteristic for his whole theory. If h could be taken to be infinitely small the theory would reduce to the classical case and produce the Rayleigh distribution law.

NB

This Rayleigh distribution suffers from an inherent difficulty that makes it totally unacceptable as a solution to the radiation problem: It implies an infinite amount of energy associated with the high frequency nodes. [For the integral of $\rho(\nu, T)$ with respect to frequency over all frequencies, $\int_0^\infty \rho(\nu, T)\,d\nu$, represents the total energy per unit volume in a cavity containing black-body radiation and equation (10) leads to an integral which evidently diverges.] Although Rayleigh must have been aware of this difficulty in 1900, his original note contained no explicit mention of it. However, he did remark that his use of the equipartition theorem and, consequently, also the distribution law of equation (10) should at least apply to "the graver modes." He also went so far as to suggest an exponential convergence factor, which would lead to an integrable form for $\rho(\nu, T)$, although it had no theoretical basis at all.

Planck had already overcome this difficulty in the classical distribution law in 1900 without even recognizing its existence. His attack on the problem had led him directly to the distribution law given in equation (7) which automatically avoids divergence problems. When he came to the Rayleigh distribution, then, it was only the perfectly legitimate—and correct—low frequency limit of his own law. Precisely because he had not based his arguments on the equipartition theorem and had not been conditioned early to a constraining respect for the central importance of this theorem in classical statistical mechanics, Planck was in a position to see just what was involved in its use here.

By 1905 Jeans had begun the series of attempts he made over the next few years to avoid the necessity for quanta by treating the black-body radiation as being in a nonequilibrium state.[27] Jeans, in other words, was willing to sacrifice the concept of equilibrium in order to preserve the classical mechanics and the equipartition theorem which it entailed. Planck's criticism of Jeans' viewpoint in his *Lectures* is worth repeating here, as an indication of the certainty he felt in his own views. "I am therefore of the opinion that the difficulty under discussion is brought about only by an unjustified application of the equipartition theorem to all independent variables describing the state. In point of fact, the validity of this theorem requires the assumption that the distribution over all possible states, with given total energy, is an ergodic one, or briefly speaking, that the probability that the state of the system lies in a definite little cell (in phase space) is simply proportional to the volume of this cell no matter how small the latter is chosen to be. This hypothesis is, however, not fulfilled in the case of black-body radiation; for the elementary regions, or cells, may not be chosen to be arbitrarily small, but their volume is finite, determined by the value of the elementary quantum of action h. Only if one could assume that the quantum of action h were infinitely small, would one arrive at the equipartition theorem. In fact, as h becomes infinitely small the general distribution law [equation (7) here] goes over into the special one [equation (10) in this article]. . . . Then the energies of all oscillators would be equal, corresponding to the equipartition theorem, which in general is not the case."

Ergodicity
and
separability

The difficulty in classical physics which manifested itself in the impossible distribution law first derived by Rayleigh, had been recognized quite independently by Einstein, in the first of his great trio of papers published in the summer of 1905.[28] Without knowing of Rayleigh's work, Einstein had derived a result equivalent to equation (10) and had seen its devastating implications. He had gone on to develop his revolutionary concept of light quanta and used it as a "heuristic" guide to the understanding of such otherwise unintelligible phenomena as the photoelectric effect. There is a remarkable footnote in Planck's *Lectures*,[29] at the point where he is discussing the equipartition theorem as applied to radiation, in which Planck comments briefly on Einstein's paper. Planck only remarked that the difficulty in the theory of radiation that Einstein had raised (that is, the difficulty we have been discussing) arose because Einstein had taken the equipartition law as valid for all modes, whereas in Planck's theory it held only for the long wavelengths. What is extraordinary about this footnote is first, that Planck apparently did not see—as Einstein had—the inevitability of the equipartition theorem within the framework of classical physics, and second, that Planck made absolutely no mention of Einstein's new ideas.

On the other hand, if we read Einstein's paper—and do so without the benefit of our accepted idea that Einstein was building on Planck's work of 1901, we are surprised to discover that Einstein made no real use of that work at all. The only reference he made to Planck's 1901 paper on quanta was to point out that Planck's deduction of Boltzmann's constant *k*, and the other natural constants, could just as well have been done from the classical distribution [equation (10)], together with the experimental measurements on black-body radiation. (This same remark was made by Rayleigh[30] and by Lorentz,[31] earlier but less completely. All of Einstein's startling new conclusions were drawn from the limiting form of the distribution law for high frequencies, the Wien distribution [equation (2)], which was well established experimentally in its own domain. As a matter of fact, Einstein's work on quanta was not tied directly to Planck's until his second paper on the subject, in 1906.[32] In this latter paper he even remarked, referring to his 1905 work, "At that time it seemed to me as if Planck's theory of radiation formed an antithesis to my work in a certain respect." Only Einstein's new arguments, contained in his 1906 paper, had shown him that Planck's radiation theory made *implicit* use of Einstein's light quantum hypothesis. Planck, however, did not accept Einstein's interpretation of his radiation theory and subsequently devoted considerable effort to trying to avoid Einstein's overly revolutionary ideas. But this discussion belongs to a period later than the one we are considering here.

VI

The concept of energy quanta that Planck introduced to the world in 1900 has taken the central role in the physical science

of the twentieth century. Planck's constant *h* is involved in the structure of matter and radiation in a particularly intimate way. Planck himself emphasized the essential importance of this constant from the very beginning when, in his first report to the German Physical Society, he described his derivation of the radiation distribution as based primarily on the introduction of two new natural constants *h* and *k*. As we have already seen, Planck was immediately able to give his second constant *k* (Boltzmann's constant) a direct physical interpretation and to use it for remarkably accurate calculations of Avogadro's number, the mass of an atom, and the electronic charge. Although he could not interpret *h* so directly, Planck had no doubt that when such an interpretation could be made it would indeed be a significant one. He called attention to the central position of *h* in the theory in several places in his *Lectures*. "There can be no doubt whatsoever that the constant *h* plays a definite role in the basic vibrational processes in emission; our theories up to now do not, however, provide any foothold for an investigation of this role from the electrodynamic side. And yet the thermodynamics of radiation will not have come to a fully satisfactory conclusion until the constant *h* is perceived in its full, universal meaning."[33]

Planck also pointed out that his constant *h*, along with the velocity of light and the universal gravitational constant, could be used to form a truly natural system of units—one "independent of all particular bodies or substances," whose meaning would necessarily be identical "for all times and for all cultures, including extraterrestrial and extrahuman ones," and which "would retain their meaning so long as the laws of gravitation, of the propagation of light in vacuum, and the two laws of thermodynamics remain valid."[34]

Planck stated that his element of action *h* had to acquire a direct electrodynamic meaning, though "the nature of this meaning still remains an open question." He closed his book by pointing to the need of a future elaboration of the theory in which the emission and absorption of radiation could be understood in detail. Such a theory, he concluded, "must in any case bring a more detailed explanation for the physical meaning of the universal element of action *h*, a meaning which is certainly not inferior to that of the basic unit of electric charge."[35]

Footnotes

1. I have given an extended discussion of Planck's original introduction of the quantum theory with full bibliography in another paper: M. J. Klein, Archive for History of the Exact Sciences, **1** (1962), p. 459.

2. M. Planck, Naturwissenschaften, **31** (1943), p. 153. This article is reprinted in Max Planck, *Physikalische Abhandlungen und Vorträge*, (Braunschweig: 1958) Vol. III, p. 264. This collection will be referred to throughout as Phys. Abh.

3. M. Planck, *Vorlesungen über die Theorie der Wärmestrahlung* (Leipzig: 1906).

4. See, however, the article by K. A. G. Mendelssohn in *A Physics Anthology*, ed. N. Clarke (London: 1960), p. 62.

5. L. Rosenfeld, Osiris, **2** (1936), pp. 149–196.

6. M. Planck, Verhandl. deut. physik. Ges. **13** (1911), p. 138; Phys. Abh. Vol. II, p. 249.

7. M. Planck, *Treatise on Thermodynamics* (Reprint of English translation of Seventh German Edition, New York: 1945), p. VII.

8. M. Planck, S.-B. Preuss. Akad. Wiss. (1897), p. 57; Phys. Abh. Vol. I, p. 493.

9. L. Boltzmann, S.-B. Preuss. Akad. Wiss. (1897), pp. 660, 1016.

10. M. Planck, Ann. Phys. **1** (1900), p. 69; Phys. Abh. Vol. I, pp. 614.

11. See references 1, 4, and 5, as well as Planck's own accounts, Phys. Abh. Vol. III, pp. 121, 255, 374. The last of these is also available in M. Planck, *Scientific Autobiography* (English translation, New York: 1949).

12. W. Wien, Wied. Annalen, **58** (1896), p. 662.

13. M. Planck, Ann. Phys. **1** (1900), p. 719; Phys. Abh. Vol. I, p. 668.

14. M. Planck, Verhandl. deut. physik. Ges. **2** (1900), p. 202; Phys. Abh. Vol. I, p. 687.

15. M. Planck, Verhandl. deut. physik. Ges. **2** (1900), p. 237; Phys. Abh. Vol. I, p. 698.

16. M. Planck, Ann. Phys. **4** (1901), p. 553; Phys. Abh. Vol. I, p. 717.

17. P. Ehrenfest, Wien. Ber. (Math.-naturw. Klasse) **114** (1905), p. 1301 and Physik. Z. **7** (1906), p. 528; reprinted in Paul Ehrenfest, *Collected Scientific Papers*, ed. M. J. Klein (Amsterdam: 1959), pp. 88, 120.

18. M. Planck, Ann. Phys. **9** (1902), p. 629; Phys. Abh. Vol. I, p. 731. Also published in Arch. Néerl. (1901), p. 55.

19. M. Planck, Z. physik Chem. 8 (1891), p. 647; Phys. Abh. Vol. I, p. 372.

20. M. Planck, in Boltzmann-Festschrift (Leipzig: 1904), p. 113. Phys. Abh. Vol. II, p. 79. See also the discussion in R. Dugas, *La Théorie Physique au sens de Boltzmann* (Neuchâtel: 1959), Chap. III, (Troisième Partie).

21. M. Planck, Physik. Z. **10** (1909), p. 62; Phys. Abh. Vol. III, p. 6.

22. M. Planck, Phys. Abh. Vol. III, pp. 77, 102.

23. Lord Rayleigh, Phil. Mag. **49** (1900), p. 539; reprinted in Lord Rayleigh, *Scientific Papers* (Cambridge: 1903), Vol. IV, p. 483.

24. See reference 2, pp. 158–160.

25. See reference 2, pp. 172–177. The articles by Rayleigh and Jeans are to be found in Nature, **72** (1905), pp. 54, 243, 293. Also see J. H. Jeans, Phil. Mag. **10** (1905), p. 91.

26. See reference 2, pp. 154–156.

27. J. H. Jeans, Proc. Roy. Soc. **A76** (1905), pp. 296, 545.

28. A. Einstein, Ann. Phys. **17** (1905), p. 132.

29. See reference 2, footnote to p. 160.

30. Lord Rayleigh, Nature, **72** (1905), p. 54.

31. H. A. Lorentz, Proc. Acad. Amsterdam, **5** (1903), p. 666; reprinted in H. A. Lorentz: *Collected Papers* (The Hague: 1936), Vol. III, p. 155.

32. A. Einstein, Ann. Phys. **20** (1906), p. 199.

33. See reference 2, p. 154.

34. See reference 2, pp. 163–165.

35. See reference 2, p. 221.