Max Planck and the Beginnings of the Quantum Theory

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1. Introduction

On December 14, 1900, MAX PLANCK presented his derivation of the distribution law for black-body radiation to the German Physical Society, and the concept of energy quanta made its first appearance in physics. Considering the enormous consequences which the quantum theory has had, it is astonishing that so little attention has been devoted to detailed study of the reasoning which brought PLANCK to the first radical step of introducing quanta. There are, of course, many descriptions of the origin of the quantum theory in the literature, but almost all of them are historically inaccurate, uncritical, and quite misleading as to both PLANCK'S own work and the context in which it was done. We do have PLANCK'S retrospective accounts *[1]* which give a clear and consistent picture of his own view of the development, and there is also an excellent monograph by ROSENFELD [2], too little known, on the early years of the quantum theory, which presents PLANCK'S work in its proper historical setting.

It seems to me that there are still two critical questions, not unrelated, which must be answered, if we are to understand fully the nature of PLANCK'S decisive step and the extent to which it marked a real break with previous thinking. The first is really an historical question: *Was* PLANCK *aware of the radiation distribution law which* RAYLEIGH *had derived as a necessary consequence of classical physics?* Most authors answer this question in the affirmative and describe PLANCK'S introduction of quanta as his response to the challenge of the "crisis" brought about by the disagreement between classical theory and experimental results and by the internal failure of classical theory as expressed in the "ultraviolet catastrophe". As a matter of fact, there was no such crisis, or perhaps one should say there was no awareness of such a crisis. All of the work on black-body radiation prior to the summer of 1900 was done without benefit of the knowledge of just what classical physics did imply for this problem. It was only in June, 1900 that Lord RAYLEIGH published a two-page note in which the classical distribution law was first derived, and the very serious implications of RAYLEIGH'S paper were not generally realized for quite some time. PLANCK makes no reference to RAYLEIGH'S note in his own papers of 1900 and 1901, nor does he refer to RAYLEIGH in his accounts of the origins of the quantum theory published many years later. It does, however, seem likely that PLANCK knew of RAYLEIGH'S work, but that he attached no more significance to it than he did to several other papers, published at about the same time, in which more or less *ad hoc* attempts were made to find an equation which would describe the experimental results. The possible reasons for PLANCK'S neglect of what now seems to be the critically important contribution made by RAYLEIGH are to be sought in PLANCK'S background, in his way of approaching the radiation problem, and also in the manner in which RAYLEIGH had communicated his results.

The second question which I consider to be critical concerns the method which PLANCK actually used in deriving the distribution law: *In what ways did* PLANCK *depart from* BOLTZMANN'S *methods in his statistical calculation of the entropy using energy quanta?* PLANCK himself, in both his original papers and his later accounts, considered that he was using BOLTZMANN'S approach in a rather straightforward way with the discreteness in energy as the only innovation. ROSENFELD [*3*], however, speaks of PLANCK'S calculation of the entropy as being "pure heresy" from the classical Boltzmann point of view. PLANCK actually did depart from BOLTZMANN'S method in several respects, and it took a number of years for the full implications of his departures to be realized. It has never been pointed out, though, just how much PLANCK was influenced in his derivation by the paper of BOLTZMANN'S which was his principal guide in a realm of ideas which had been quite foreign to him before the autumn of 1900.

The discussion of these two questions is the principal theme of the present paper. This discussion requires a brief restatement of the context and background for PLANCK'S work, and this is provided in the next section. The final section of this paper deals briefly with another problem which deserves further study: Why did almost five years go by before PLANCK'S bold solution of the radiation problem was taken up for further study?

2. Background

In 1897, when PLANCK first turned his attention to the problem of black-body radiation, he was almost forty years old, and his scientific career had been devoted principally to clarifying the meaning of the second law of thermodynamics and to exploring its consequences. What attracted PLANCK'S attention to the radiation problem was the universal character of the distribution law which was required by KIRCHHOFF'S theorem. KIRCHHOFF [*4*], and independently BALFOUR STEWART, had shown that the nature of the radiation in thermal equilibrium in an enclosure, whose walls are kept at a fixed temperature, is completely independent of the properties of any material bodies, including the walls, which are in equilibrium with the radiation. The spectral distribution of the radiation then "represents something absolute, and since I had always regarded the search for the absolute as the loftiest goal of all scientific activity, I eagerly set to work" [*5*].

Several properties of the universal function of temperature and frequency which describes this equilibrium spectral distribution had already been established during the preceding two decades. In order to formulate these, it is convenient to introduce the function in question as $\varrho(\nu, T)$, where $\varrho(\nu, T)\,d\nu$ is the energy per unit volume in thermal radiation, at absolute temperature T, which lies in the frequency interval from ν to $\nu+d\nu$. STEFAN [*6*] had found experimentally in 1879 that the total energy density, integrated over all frequencies, is proportional to the fourth power of the temperature; thus the function $\varrho(\nu, T)$ satisfies the equation

$$\int_0^\infty \varrho(\nu, T)\, d\nu = \sigma T^4, \tag{1}$$

where σ is a constant. This experimental result of STEFAN'S was derived theoretically in 1884 by BOLTZMANN [7], who applied the second law of thermodynamics to radiation, treating it as a gas whose pressure was the radiation pressure of MAXWELL'S electromagnetic theory. In 1893 WIEN [8] drew another conclusion from the second law of thermodynamics which imposed a significant limitation on the energy distribution function $\varrho(\nu, T)$. This displacement law of WIEN'S requires that $\varrho(\nu, T)$ have the form

$$\varrho(\nu, T) = \nu^3 f(\nu/T), \tag{2}$$

where $f(\nu/T)$ can depend on only the ratio of frequency to temperature*.

In addition to the two laws expressed in Eqs. (1) and (2), there was one other important result known to PLANCK when he started his work on the radiation problem. This other result was the distribution law proposed by WIEN [9] in 1896 which gave an explicit form for the function $\varrho(\nu, T)$, or the function $f(\nu/T)$:

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

where α and β are constants. WIEN had given a theoretical argument for the correctness of Eq. (3), but as RAYLEIGH [10] wrote: "Viewed from the theoretical side, the result appears to me to be little more than a conjecture." The important thing about WIEN'S distribution in the late 1890's was not WIEN'S derivation, but rather the fact that it gave an adequate account of all the experimental results on the energy distribution in black-body radiation which were then available. It seemed reasonable to suppose that a fundamental theory of radiation, such as PLANCK proposed to develop, would have to conclude with an adequate grounding for the Wien distribution law, if the theory were to be in accord with experiment.

In the first [11] of a series of five papers which PLANCK presented to the Prussian Academy of Sciences in the years 1897 to 1899, he set forth his program for a theory of radiation. This program arose naturally from his earlier work in thermodynamics, since he took as his goal the finding of a basis in electrodynamics for the irreversible approach of radiation to equilibrium. His idea was that the conservative system consisting of electromagnetic radiation in an enclosure, interacting with a collection of harmonic oscillators, could be shown to approach an equilibrium state, without the need for any assumptions beyond the laws of electromagnetism. For PLANCK, such a demonstration would have completed the understanding of the second law of thermodynamics. PLANCK thought he saw the basic mechanism for the irreversible behavior of the system in the way in which an oscillating dipole emits electromagnetic energy as a spherical wave, changing the character of the radiation incident upon it in an apparently irreversible manner.

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* It is worth noting that the WIEN displacement law implies the STEFAN-BOLTZMANN law, since $\int_0^\infty \varrho(\nu, T)\, d\nu = \int_0^\infty \nu^3 f(\nu/T)\, d\nu = T^4 \int_0^\infty x^3 f(x)\, dx$, and the last integral, so long as it exists, is just a pure number.

PLANCK'S direct advance along this line of thought was promptly stopped by criticism from BOLTZMANN [*12*]. BOLTZMANN, better than anyone else, was in a position to see the flaw in PLANCK'S reasoning since he had concerned himself for many years with the nature of irreversibility, and he knew from rather bitter experience the subtleties and difficulties which blocked an understanding of this elusive concept. Only months earlier he had had to defend and restate his ideas on the essentially statistical origin of irreversibility against an attack launched by ZERMELO, a student of PLANCK. BOLTZMANN'S answers to ZERMELO had apparently still not been grasped by PLANCK since, in this same paper, he had referred approvingly to ZERMELO'S work and questioned the success of the kinetic theory's explanation of irreversibility. This situation certainly did not make BOLTZMANN delay in pointing out to PLANCK that there was nothing in the equations of electromagnetism which excluded processes inverse to those PLANCK had considered, so that the laws of electromagnetism did not, by themselves, determine the irreversible approach of radiation to equilibrium, any more than the laws of mechanics, by themselves, determined the irreversible approach of a gas to equilibrium. Additional assumptions were needed; statistical assumptions about the disordered character of the initial state such as BOLTZMANN had made in the theory of gases. Then, said BOLTZMANN, one could deduce a theorem for radiation which would be analogous to the second law and would play the role of his H-theorem in the kinetic theory of gases. PLANCK eventually, though not immediately, accepted BOLTZMANN'S criticism as sound, and formulated an assumption of "natural radiation" which assured irreversibility, much as BOLTZMANN'S assumption of "molecular chaos" had done in kinetic theory.

In PLANCK'S subsequent investigations, he continued to treat the interaction between radiation and oscillating dipoles. The harmonic oscillators were chosen, not because they were thought to be a realistic model for matter, but rather because KIRCHHOFF'S theorem asserted that the equilibrium radiation distribution was independent of the system with which the radiation interacted, and oscillators were the simplest to treat. One important result of this work was the proof of a theorem [*13*] relating the spectral distribution $\varrho(\nu, T)$ to the average energy $\bar{u}_\nu(T)$ of a harmonic oscillator of frequency ν. This theorem, which was derived by equating the emission and absorption rates of the oscillator at equilibrium, had the form

$$\varrho(\nu, T) = (8\pi\nu^2/c^3)\,\bar{u}_\nu(T), \tag{4}$$

where c is the velocity of light.

It is evident from Eq. (4) that PLANCK needed only to determine $\bar{u}_\nu(T)$, the average energy of a harmonic oscillator at temperature T, in order to have the explicit form for the distribution law. Remarkably enough, although classical statistical mechanics provided a "well-known" and simple answer for $\bar{u}_\nu(T)$ from the equipartition theorem, PLANCK made no use of it, nor did he then or later indicate that he realized its existence. (This point will be discussed again in the following section.) Instead PLANCK took what he later referred to as a "thermodynamic" approach, looking for a suitable relationship between the energy and the entropy of the oscillator, rather than one between the energy and the temperature. This relationship was introduced, in the fifth and final paper [*13*] of the series under discussion, by means of a definition:

$$S = -\frac{u}{\beta\nu}\ln\frac{u}{a e \nu} \tag{5}$$

where S is the entropy of the oscillator, u is its energy [previously called $\bar{u}_\nu(T)$], β and a are constants and e is the base of the natural logarithms. In the original paper, PLANCK did not motivate this definition when he introduced it, but from his discussion later in that paper and also from his later reviews of this work, it seems most likely that he was guided by the form of WIEN'S distribution law, Eq. (3).*

With the entropy of an oscillator defined by Eq. (5), PLANCK could then determine the entropy of the radiation in equilibrium with it and go on to prove that the total entropy was a monotonically increasing function of time, just the property required of the entropy by the second law. That PLANCK could also demonstrate that the equilibrium distribution was the Wien law of Eq. (3) is hardly remarkable, since that result followed inevitably from his choice of the entropy expression given by Eq. (5), as already indicated. PLANCK wrote that he was impressed by the simplicity of the relationship expressed in Eq. (5) and particularly by the fact that $\partial^2 S/\partial u^2$, which entered directly into his calculation, was simply proportional to minus u^{-1}. He was, nevertheless, aware that his choice of a particular expression for entropy as a function of energy determined the resulting distribution law, and he gave arguments which seemed to make that choice uniquely determined by the requirements of consistency with the displacement law and the second law of thermodynamics. His conclusion was expressed in the following sentence [*14*]. "I believe that it must therefore be concluded that the definition given for the entropy of radiation, and also the Wien distribution law for the energy which goes with it, is a necessary consequence of applying the principle of entropy increase to the electromagnetic theory of radiation, and that the limits of validity of this law, should there be any, therefore coincide with those of the second law of thermodynamics. Further experimental test of this law naturally acquires all the greater fundamental interest for this reason."

These arguments and remarks were made in a paper presented to the Academy on May 18, 1899 and were repeated verbatim in PLANCK'S article [*15*] in the *Annalen der Physik* which summarized the series of five Academy papers. The *Annalen* paper was received by the editors on November 7, 1899, and it appeared in print early in 1900. By the time PLANCK corrected the proofs of this paper, the "further experimental tests", which he had called for, were in progress. The results of these tests which had already been published caused him to add a note in proof remarking that experimental deviations from the Wien distribution had been observed. As PLANCK had already indicated, deviations from WIEN'S law created a serious problem indeed from the standpoint of his theory, and PLANCK proceeded to reconsider his arguments in some detail. In a paper

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* From Eqs. (3) and (4) it would follow that $u = (\alpha c^3/8\pi)\,\nu\exp(-\beta\nu/T)$. From this last result, one can solve for $T^{-1} = -\frac{1}{\beta\nu}\ln\left(\frac{8\pi}{\alpha c^3}\frac{u}{\nu}\right)$. But since $T^{-1} = \partial S/\partial u$, one can integrate to obtain S as a function of u in just the form of Eq. (5) with a equal to $\alpha c^3/8\pi$.

received by the editors of the *Annalen* on March 22, 1900, he reported his new considerations. The experimental situation was not clear yet since PASCHEN'S latest measurements supported WIEN'S law, but the work of LUMMER & PRINGSHEIM [*16*], which extended to longer wave lengths, had indicated serious deviations. A new distribution law had actually been proposed by THIESEN [*17*] (independently of LUMMER & PRINGSHEIM'S work) which was constructed to fit the data and at the same time to be consistent with the Stefan-Boltzmann law and the displacement law. PLANCK'S review of the assumptions and reasoning in his former work led him to propose new arguments, this time attempting to derive the form he had previously assumed for the energy-entropy relationship. PLANCK found, however, that in order to satisfy the second law of thermodynamics, *i.e.*, in order to have the entropy increase monotonically in time, it would suffice to have $\partial^2 S/\partial u^2$ be any negative function of the energy u; the specific form $-(g(\nu)/u)$, which was equivalent to WIEN'S law, was not a thermodynamic necessity. Nevertheless, PLANCK concluded that WIEN'S distribution law could still be deduced, if he made a very plausible assumption on the functional dependence of the time derivative of the entropy. Once again he ended his arguments with the Wien distribution, even if they did not have the full weight of thermodynamic reasoning to support them.

By October 1900, however, the experimental picture had changed considerably. The very careful work of RUBENS & KURLBAUM with long waves over a wide range of temperatures had shown beyond any doubt that WIEN'S distribution law was inadequate. These new measurements also indicated clearly that for very long wavelengths the distribution function $\varrho(\nu, T)$ approached a very different form, becoming proportional to the absolute temperature T. PLANCK had been informed [*18*] of these results by RUBENS & KURLBAUM several days before they were reported to the German Physical Society on October 19, 1900, so that he had the opportunity to reflect on the results and to prepare an extended "remark" for the discussion after KURLBAUM delivered the paper [*19*]. This "discussion remark" was devoted to *An Improvement of the Wien Distribution* [*20*], the improvement being a new distribution law, now universally known as the Planck distribution law. The arguments for this new distribution law and the discussion of its immediate results properly belong to the next stage of our discussion.

3. Rayleigh, Planck and Equipartition

PLANCK'S problem was now to determine a distribution law which was consistent both with the positive results of his own work and with the new experimental findings of RUBENS & KURLBAUM. Since the quantity $\partial^2 S/\partial u^2$ had figured prominently in his earlier analysis of how the entropy increased in time, it was natural for PLANCK to center his attention on the form of this function. We have already seen that the negative reciprocal of $\partial^2 S/\partial u^2$ is simply proportional to u when the Wien distribution is valid. The next simplest possibility is to take $\partial^2 S/\partial u^2$, or rather its negative reciprocal, proportional to u^2.. It is easy to see that, when this is done, u, and therefore $\varrho(\nu, T)$, will be proportional to T, just as RUBENS & KURLBAUM had found to be the case in the long wave length limit. The proper limiting forms for low and high frequencies could then be preserved by taking $-(\partial^2 S/\partial u^2)^{-1}$ proportional to $u(\gamma + u)$, where γ is a (frequency dependent) constant. On these grounds, of simplicity and proper behavior in the limit, PLANCK proposed the distribution law

$$\varrho(\nu, T) = \frac{A\,\nu^3}{\exp(B\,\nu/T) - 1}, \tag{6}$$

where A and B are constants. This is the law which follows from the assumption just mentioned for $\partial^2 S/\partial u^2$, where the frequency dependence is fixed by the displacement law together with Eq. (4).*

The adequacy of PLANCK'S proposed distribution law was confirmed immediately. As PLANCK described it later [*21*], "The very next morning I received a visit from my colleague RUBENS. He came to tell me that after the conclusion of the meeting, he had that very night checked my formula against the results of his measurements and found a satisfactory concordance at every point ... Later measurements, too, confirmed my radiation formula again and again—the finer the methods of measurement used, the more accurate the formula was found to be."

Now one of the key points in determining PLANCK'S choice of the distribution formula was that it agreed with the experimental results in being proportional to T in the limit of small ν. PLANCK'S formula was not the first in the literature to show this property, and he referred in a footnote to an empirical formula proposed by LUMMER & JAHNKE [*22*] which had the same property. He did not, however, refer to another paper in which a distribution law proportional to T for long wave lengths was not only proposed but was also related to the basic ideas of statistical mechanics: the paper by Lord RAYLEIGH [*10*].

RAYLEIGH had published a short note in the June, 1900 issue of the *Philosophical Magazine* under the title "*Remarks upon the Law of Complete Radiation*". In two pages, he had shown that if the equipartition theorem of statistical mechanics could be applied to "the modes of aetherial vibration", then the distribution law for black-body radiation is uniquely determined to have a form radically different from that of the Wien distribution. RAYLEIGH was well aware of the conditional nature of this conclusion saying, "The question is one to be settled by experiment; but in the meantime I venture to suggest a modification of [the Wien distribution], which appears to me more probable *a priori*. Speculation upon this subject is hampered by the difficulties which attend the Boltzmann-Maxwell doctrine of the partition of energy. According to this doctrine, every mode of vibration should be alike favoured; and although for some reason not yet explained, the doctrine fails in general, it seems possible that it may apply to the graver modes."

RAYLEIGH'S method for arriving at the radiation distribution law was essentially different from PLANCK'S. His argument concerned itself directly with the radiation and did not need to refer to a material system with which it was in equilibrium. The number of standing waves or allowed modes of electromagnetic

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* Taking $\partial^2 S/\partial u^2$ proportional to $-[u(\gamma+u)]^{-1}$, one can integrate to find $\partial S/\partial u$ as a function of u. This quantity, $\partial S/\partial u$, is, however, equal to T^{-1} from the second law so that one easily obtains u in the form $d_1[\exp(d_2/T) - 1]^{-1}$, where d_1 and d_2 are (frequency dependent) constants. Using Eq. (4), it follows that $\varrho(\nu, T) = (8\pi\, d_1/c^3)\,\nu^2\,[\exp(d_2/T) - 1]^{-1}$, so that d_1 and d_2 must both be proportional to ν in order to satisfy the displacement law; *i.e.*, Eq. (6) must hold.

vibration of the enclosure, whose frequencies lie in the interval from ν to $\nu + d\nu$, is proportional to $\nu^2\, d\nu$, by reasoning which was practically second nature of the author of *The Theory of Sound*. According to "the Boltzmann-Maxwell doctrine", *i.e.*, the equipartition theorem, the average energy of every one of these modes, regardless of its frequency, would be proportional to T at thermal equilibrium, with a universal proportionality constant. It follows at once that the distribution function $\varrho(\nu, T)$ must have the form,

$$\varrho(\nu, T) \propto \nu^2\, T. \tag{7}$$

As RAYLEIGH remarked, this is in accord with the displacement law.

Although RAYLEIGH did not trouble to point it out explicitly in this note, it must have been quite obvious to him that a distribution law of this form could not possibly hold for all frequencies, since it would lead to an infinite concentration of energy at the high frequencies; the integral of $\varrho(\nu, T)$ over frequency would diverge. This undoubtedly accounts both for RAYLEIGH's reference to "the graver modes", and also for the conclusion of his paper. After having obtained the result expressed in Eq. (7), RAYLEIGH added, "If we introduce the exponential factor, the complete expression will be

$$\varrho(\nu, T) \propto \nu^2\, T \exp(-\beta\, \nu/T). \tag{8}$$

Whether [this equation] represents the facts of observation as well as [the Wien distribution] I am not in a position to say. It is to be hoped that the question may soon receive an answer at the hands of the distinguished experimenters who have been occupied with this subject."

This last equation of RAYLEIGH'S, clearly intended as only a guess at how the rigorous result of the classical theory, expressed in Eq. (7), might be modified at higher frequencies, was apparently the only thing in his paper which attracted the notice of those to whom it was addressed. This is evident from the paper [*23*] which RUBENS & KURLBAUM presented to the Prussian Academy on October 25, 1900, less than a week after PLANCK'S new distribution had come to their attention. RUBENS & KURLBAUM made a systematic comparison of their results with five different formulas which had been proposed for the distribution law: those of WIEN [Eq. (3)], PLANCK [Eq. (6)], RAYLEIGH [Eq. (8)] and two others due to THIESEN and to LUMMER & JAHNKE. They concluded that only PLANCK'S formula and that proposed by LUMMER & JAHNKE were in agreement with their results, and they gave their preference to PLANCK'S formula on grounds of simplicity. (The Lummer-Jahnke formula contained ν/T to the power 1.3 in the exponent, where the number 1.3 was chosen solely for fitting the results.)

The point to be stressed is that RUBENS & KURLBAUM discussed RAYLEIGH'S work in the same tone of voice, so to speak, that they used in dealing with strictly *ad hoc* formulas which had no theoretical foundations. They failed to grasp the fundamental importance of the fact that their results did show that ϱ was proportional to T for low frequencies, in complete agreement with RAYLEIGH'S conclusion that equipartition should apply "to the graver modes". When RAYLEIGH'S paper was reprinted in his *Scientific Papers* two years later, he took the opportunity to remark on the proportionality of ϱ to T for low frequencies.

"This is what I intended to emphasize. Very shortly afterwards the anticipation above expressed was confirmed by the important researches of RUBENS & KURLBAUM who operated with exceptionally long waves."

RUBENS & KURLBAUM were not the only ones who missed this central point in RAYLEIGH'S paper, which he had probably not underlined sufficiently. I have already mentioned that PLANCK made no reference to RAYLEIGH in his October, 1900 communication. Nor did he refer to RAYLEIGH in his papers introducing the quantum concept which appeared a few months later. Although it might appear from this lack of reference that PLANCK did not know of RAYLEIGH'S work, as ROSENFELD concludes, I find this a rather unlikely hypothesis. PLANCK had been devoting virtually all of his efforts to the radiation problem for over three years by this time, and he is not likely to have missed something on this subject written by a leading thinker and published in a major journal. Furthermore, we know that RUBENS & KURLBAUM had seen RAYLEIGH'S paper and must have referred to it in preparing their own report during the week after PLANCK proposed his new equation to them. We also know that PLANCK kept in close touch with the experimenters' attempts to fit their results with his and other distribution laws. Finally, in his paper [*24*] of December 14, 1900, PLANCK referred explicitly to the RUBENS & KURLBAUM paper in which RAYLEIGH'S work was quoted. It seems hard to believe, therefore, that PLANCK was not aware of RAYLEIGH'S article.

It is not hard to understand, though, why PLANCK might have missed the significance of RAYLEIGH'S reasoning: everything in PLANCK'S background argues against his having been ready to receive RAYLEIGH'S ideas. RAYLEIGH had formulated his argument in such a way that it would be clear to anyone at home in the writings of BOLTZMANN and MAXWELL. His reference in passing to the difficulties attending the equipartition theorem was intended to suggest the whole bothersome, unsolved problem of the specific heats of gases. RAYLEIGH had himself written on the equipartition problem at some length earlier in the year. PLANCK, however, had been thinking along quite another line. He tells us himself that statistical mechanics had not been at all to his liking. In a passage of his *Scientific Autobiography* concerning the energetics controversy, in which he found himself allied with BOLTZMANN against the dominant school of energeticists headed by OSTWALD, he wrote [*25*], "After all that I have related, in this duel of minds I could play only the part of a second to BOLTZMANN—a second whose services were evidently not appreciated, not even noticed, by him. For BOLTZMANN knew very well that my viewpoint was basically different from his. He was especially annoyed by the fact that I was not only indifferent but to a certain extent even hostile to the atomic theory which was the foundation of his entire research. The reason was that at that time I regarded the principle of the increase of entropy as no less immutably valid than the principle of the conservation of energy itself, whereas BOLTZMANN treated the former merely as a law of probabilities—in other words, as a principle that could admit of exceptions."

PLANCK'S comment on what his attitude toward statistical mechanics was in 1900 is borne out by reference to his writings prior to that date. In all of PLANCK'S work on the meaning and implications of the second law of thermodynamics, he had never used the methods of statistical mechanics, never even referred to

BOLTZMANN's statistical interpretation of the entropy. PLANCK had begun a series of papers [26] *On the Principle of Increasing Entropy* in 1887 by saying explicitly that he wanted to extend the series of conclusions drawn from the second law "taken by itself, *i.e.*, irrespective of definite conceptions about the nature of molecular motions". In a lecture [27] in 1891, PLANCK admitted the existence of kinetic or molecular methods as an alternative to the purely thermodynamic ones which he found so much more to his taste, but he went on to point at once to the disappointments of the molecular approach after its initial successes. "Anyone who studies the works of the two scientists who have probably penetrated most deeply in the analysis of molecular motions, MAXWELL and BOLTZMANN, 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 same attitude toward the molecular approach is displayed in the preface to the first edition (1897) of PLANCK's *Treatise on Thermodynamics* [28] in which he refers to the "insurmountable obstacles" and the "essential difficulties in the mechanical interpretation of the fundamental principles of thermodynamics

I think it is fair to conclude that PLANCK's often expressed distrust of the whole molecular approach of statistical mechanics made it very unlikely that he would see the point of RAYLEIGH's very condensed discussion, or even that he would take it very seriously if he had. As we shall see in the next section, it was probably a very good thing that PLANCK was not constrained in his thinking by the tight classical web which RAYLEIGH had woven.

4. The Introduction of Quanta

"But even if the absolutely precise validity of the radiation formula is taken for granted, so long as it had merely the standing of a law disclosed by a lucky intuition, it could not be expected to possess more than a formal significance. For this reason, on the very day when I formulated this law, I began to devote myself to the task of investing it with a true physical meaning. This quest automatically led me to study the interrelation of entropy and probability—in other words, to pursue the line of thought inaugurated by BOLTZMANN." "After a few weeks of the most strenuous work of mv life, the darkness lifted and an unexpected vista began to appear" [29].

These are the words PLANCK used many years later to describe his efforts from October 19 to December 14, 1900 on which date he presented his results to the German Physical Society in a paper entitled *On the Theory of the Energy Distribution Law in the Normal Spectrum* [24]. During those two months PLANCK had successfully changed the direction of all of his previous thought in recognizing and adopting BOLTZMANN's insight into the relationship between entropy and probability. In addition, he had created a concept which was eventually to change the most basic features of physical theory. These two aspects of what he had done are almost inextricably woven together in both the paper already referred to and in the more complete paper published soon afterwards in the *Annalen der Physik* [30]. We must, nevertheless, try to separate them here if we are to appreciate the innovations which PLANCK made.

PLANCK'S earlier work had shown that only one more key step was necessary for the theory of the radiation spectrum: a sound theoretical determination of the relationship between the energy u and the entropy S of a harmonic oscillator of frequency ν. Once this was known, the average energy of the oscillator could be found, and the distribution function $\varrho(\nu, T)$ would then be fixed with the help of Eq. (4), which relates u and $\varrho(\nu, T)$. (It might be well to re-emphasize the point that harmonic oscillators entered the picture only because PLANCK chose them as the simplest material system which could be in equilibrium with the electromagnetic radiation, availing himself of the freedom given by KIRCHHOFF'S theorem.) PLANCK'S previous attempts at fixing the relationship between S and u on general thermodynamic grounds supplemented by plausibility arguments had failed, as we have seen. He was quite sure that he knew what this relationship had to be (from the work discussed in the last section); if his conjectured distribution law, Eq. (6), were correct, as it seemed to be, then it implied the equation

$$S = \frac{A'}{B}\left[\left(1 + \frac{u}{A'\nu}\right)\ln\left(1 + \frac{u}{A'\nu}\right) - \frac{u}{A'\nu}\ln\frac{u}{A'\nu}\right], \tag{9}$$

where A and B are the constants of Eq. (6), and $A' = Ac^3/8\pi^2$.* In order to establish Eq. (9), new methods were necessary, and as already mentioned, PLANCK found these in BOLTZMANN'S work.

According to BOLTZMANN, the entropy of a system in a given state is proportional to the logarithm of the probability of this state. This probability in turn is to be found as the number of complexions, the number of distinct microscopic arrangements, compatible with the given state. PLANCK'S task then, once this general approach was accepted, was to find a method for determining W, the number of complexions of his set of oscillators. It is sufficient to consider N oscillators, all of frequency ν, whose total energy U_N is then N times the average energy u of one oscillator. Since the entropy is an additive function, S_N will also be N times S, the entropy of one oscillator:

$$U_N = Nu, \tag{10a}$$

$$S_N = NS. \tag{10b}$$

The entropy of the N oscillator system, S_N, is now set equal to a proportionality constant k times the logarithm of W,

$$S_N = k \ln W, \tag{11}$$

where the additive constant which might appear is set equal to zero. PLANCK then made the same assumption that BOLTZMANN had made, that any one complexion of the system is as likely to occur as any other so that W can be obtained by counting the number of complexions. *But*, in order to carry out this counting procedure, it is essential that the energy to be shared among the N oscillators must not be considered as a continuously varying, infinitely divisible quantity. It must instead be treated as consisting of an integral number of finite equal

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* From Eqs. (4) and (6), it follows that $u = A'\nu\,[\exp(B\nu/T) - 1]^{-1}$. The entropy equation is derived by solving this last equation for T^{-1}, which is equal to $\partial S/\partial u$, and then integrating.

parts, if meaningful, finite values for W are to be obtained. PLANCK refers to these as elements of energy ε and writes

$$U_N = P\,\varepsilon, \tag{12}$$

where P is a (large) integer representing the total number of elements of energy.

With this assumption made, it is evident that there is a finite number of complexions equal to the number of ways in which the P elements of energy can be divided up among the N oscillators. This number W is given by combinatorial analysis as

$$W = \frac{(N+P-1)!}{P!\,(N-1)!} \cong \frac{(N+P)^{N+P}}{P^P\,N^N}, \tag{13}$$

where the second, approximate, form comes from dropping the 1 compared to the large numbers N and P and using STIRLING's approximation for the factorials. From Eqs. (11) and (13), the entropy is given by the equation

$$S_N = k\,\{(N+P)\ln(N+P) - P\ln P - N\ln N\}. \tag{14}$$

When P/N is replaced by u/ε, and S_N/N by S, according to Eqs. (10) and (12), the entropy S of one oscillator in terms of its average energy u has the form

$$S = k\left\{\left(1+\frac{u}{\varepsilon}\right)\ln\left(1+\frac{u}{\varepsilon}\right) - \frac{u}{\varepsilon}\ln\frac{u}{\varepsilon}\right\}. \tag{15}$$

At this stage in the argument, the size of the energy elements ε is completely arbitrary. In fact, however, S must depend on the frequency of the oscillators as well as on u in a way prescribed by WIEN's displacement law, and since k is a universal constant, this frequency dependence must come into ε. The displacement law actually requires that the entropy have the form*

$$S = g(u/\nu), \tag{16}$$

so that the energy element ε must be proportional to the frequency of the oscillator,

$$\varepsilon = h\,\nu \tag{17}$$

where h is the second universal natural constant in the theory. The expression for S as a function of u is now fully determined in terms of the constants h and k,

$$S = k\left\{\left(1+\frac{u}{h\nu}\right)\ln\left(1+\frac{u}{h\nu}\right) - \frac{u}{h\nu}\ln\frac{u}{h\nu}\right\}. \tag{18}$$

This result has exactly the same form as Eq. (9), and the distribution law that goes with it must therefore** be

$$\varrho(\nu, T) = \frac{8\pi\nu^2}{c^3}\,\frac{h\nu}{\exp(h\nu/kT) - 1}. \tag{19}$$

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* Eqs. (2) and (4) require that $u = \nu f(\nu/T)$. An equivalent way of writing this result is $T = \nu F(u/\nu)$. Using the fact that $T^{-1} = \partial S/\partial u$, one obtains $\partial S/\partial u = \nu^{-1}[F(u/\nu)]^{-1}$ so that, after integration over u, S is simply a function of u/ν.

** Eq. (19) is just Eq. (6) rewritten with the constants A and B determined by comparison of Eqs. (9) and (18). One can also obtain Eq. (19) directly from Eq. (18) by differentiating the latter with respect to u to introduce the temperature and then applying Eq. (4).

The two constants were numerically determined from experimental results: the total energy density or STEFAN'S constant σ [from Eq. (1)] determines one combination of h and k, and the ratio of frequency to temperature at the maximum of the distribution determines a second combination of h and k. From the experimental values, PLANCK computed h to be 6.55×10^{-27} erg sec and k to be 1.346×10^{-16} erg/K°. But what significance was to be attached to these constants?

In his December 14, 1900 report to the German Physical Society, PLANCK referred to "other relationships" deduced from his theory "which seem to me to be of considerable importance for other fields of physics and also of chemistry". I think there can be little doubt that this was a reference to the far-reaching importance of the two constants he had calculated, and in particular, to the constant k. At the end of this first paper on the quantum theory, PLANCK pointed out that since k is a universal proportionality factor connecting entropy and $\ln W$, it follows from BOLTZMANN'S work on the entropy of a gas that

$$k = R/N_0 \tag{20}$$

where R is the gas constant which appears in the macroscopic equation of state of an ideal gas, and N_0 is AVOGADRO'S number, the number of molecules in a gram mole. Since the value of R was well established, PLANCK'S computation of k meant that he had also determined AVOGADRO'S number. PLANCK'S value for it was 6.175×10^{23} molecules per mole. Other quantities follow directly, such as LOSCHMIDT'S constant, the number of molecules per cubic centimeter of gas at standard conditions, and the mean kinetic energy of a molecule. Less obvious, especially in 1900, was the fact that the elementary unit of electric charge e was now also determined as essentially the ratio of the macroscopic FARADAY constant to AVOGADRO'S number. PLANCK'S value for e was 4.69×10^{-10} esu.

PLANCK thoroughly appreciated the importance of these determinations of the basic natural constants which his theory had made possible. As he said, "All these relationships can lay claim to absolute, not approximate validity, so long as the theory is really correct ... Their test by more direct methods will be a problem (for further research) as important as it is necessary." These words appear at the conclusion of the paper we have been discussing, and when PLANCK rewrote this work a few weeks later for the *Annalen der Physik* [*31*] he separated these considerations on the natural constants from the principal argument concerning the radiation distribution in order to give them the emphasis they well deserved. In his later writings, PLANCK carefully pointed out on several occasions that although k was understandably referred to as BOLTZMANN'S constant, BOLTZMANN had never attached any great significance to it nor had he ever made any estimate of its numerical value.

PLANCK'S values of N_0 and e were by far the best estimates of these basic quantities which had yet appeared in the literature. There had, in fact, been no direct determination of N_0; the only estimates of N_0 available were very indirect ones based on oversimplified models from the kinetic theory of gases. (Estimates of N_0 by these methods were first made by BOLTZMANN'S senior colleague, LOSCHMIDT, in 1865.) It was not until 1908 that PERRIN began his series of experiments which were to give an essentially direct determination of N_0, but one which was less reliable than PLANCK'S. As for e, the natural unit of charge or the charge on the electron, attempts at a direct determination had only just begun in J. J. THOMSON'S laboratory in Cambridge, and there was to be no good measurement until MILLIKAN'S work almost a decade later [*32*]. PERRIN'S report [*33*] to the first Solvay Congress in 1911 gives a vivid picture of the status of these fundamental constants at that time and indirectly indicates why PLANCK laid so much emphasis on this aspect of his theory.

5. Boltzmann, Planck, and Quanta

Let us now go back to PLANCK'S statistical calculation in which energy quanta were introduced. The calculation has been described in the last section pretty much as PLANCK himself presented it. This was a necessary preliminary to a discussion of the question raised in the introduction; how did PLANCK depart from BOLTZMANN'S method? I think that this question can best be handled by comparing PLANCK'S analysis with BOLTZMANN'S own treatment of a closely related problem in the memoir [*34*] to which PLANCK refers repeatedly. This is BOLTZMANN'S great memoir of 1877, *"On the Relation between the Second Law of Thermodynamics and the Theory of Probability"*, in which the statistical interpretation of entropy is set forth at length, separated from the difficulties of the kinetic treatment of the approach to equilibrium. The very first problem which BOLTZMANN treats in this paper, as a simple introduction to his concepts and methods, bears a remarkable resemblance to PLANCK'S own problem [*35*].

BOLTZMANN considers a simple model of a gas consisting of N molecules, in which the energy of each individual molecule can take on only certain discrete values which form an arithmetic progression $0, \varepsilon, 2\varepsilon, \ldots, M\varepsilon$. His comments on this model are revealing. "This fiction does not, to be sure, correspond to any realizable mechanical problem, but it is indeed a problem which is much easier to handle mathematically and which goes over directly into the problem to be solved, if one lets the appropriate quantities become infinite. If this method of treating the problem seems at first sight to be very abstract, it nevertheless is generally the quickest way of getting to one's goal in such problems, and if one considers that everything infinite in nature never has meaning except as a limiting process, one cannot understand the infinite manifold of possible energies for each molecule in any way other than as the limiting case which arises when each molecule can take on more and more possible velocities."

BOLTZMANN then turns his attention to the possible states of this gas model when it is assigned a total energy of $P\varepsilon$, where P is a large integer. Any such state is characterized by the set of integers $w_0, w_1, \ldots, w_M$ which give the number of molecules having energy $0, \varepsilon, \ldots, M\varepsilon$. The w's are subject to the two constraints,

$$\sum_{r=1}^{M} w_r = N \tag{21}$$

and

$$\sum_{r=1}^{M} r\, w_r = P, \tag{22}$$

which express the fixed number of particles and the fixed total energy. Each of the states, characterized by a set of numbers $\{w_r\}$, can be achieved in many ways, which BOLTZMANN refers to as complexions, depending on *which* of the molecules are found with energies $0, \varepsilon, \ldots$. The number of complexions for a given distribution $\{w_r\}$ is readily recognized to be given by the expression

$$W_B = \frac{N!}{w_0!\, w_1! \ldots}. \tag{23}$$

BOLTZMANN makes the basic assumption that any particular complexion (in which, for example, molecule number one has energy 17ε, molecule number two has energy 3ε, *etc.*) is as likely to occur as any other particular complexion. (He makes this assumption plausible by a comparison to the game of lotto, or bingo.) It follows, then, that the probability of occurrence of a state characterized by the set $\{w_r\}$ is equal to W_B for this state divided by $\sum W_B$, where the sum is over all sets $\{w_r\}$ compatible with Eqs. (21) and (22).

Now it is essential in BOLTZMANN'S procedure that he asks for that state, *i.e.*, that set of numbers $\{w_r\}$, for which W_B is a maximum, since it is that most probable state which he will identify with the state of thermodynamic equilibrium. It is not necessary to repeat here the calculation in which W_B is maximized and the $\{w_r\}$ in the equilibrium state are shown to obey the "Boltzmann distribution", *i.e.*, w_r in the equilibrium state is proportional to $\exp(-\beta' r\, \varepsilon)$, where the constant β' is shown to be proportional to T^{-1}. It is important, however, to recall that at an appropriate stage in the calculation BOLTZMANN takes the limit in which ε goes to zero and M goes to infinity in such a way that the molecules can really take on *all* values for their energy. For BOLTZMANN the ε is an artifice which makes the calculation possible (and makes the continuum intelligible!).

We can now compare BOLTZMANN'S procedure with PLANCK'S way of handling his problem. (The formal similarity in the problems has been deliberately stressed by using a common notation.) The first evident difference between the two procedures is in the meaning attached to the quantity W. In BOLTZMANN'S discussion, the quantity W_B, in Eq. (23), is the number of complexions, detailed assignments of the energies of the individual molecules, compatible with a given distribution. It is proportional to the probability of one state $\{w_r\}$ compared to another. PLANCK, on the other hand, never introduces quantities analogous to the $\{w_r\}$. For him the W of Eq. (13) is a probability *by definition:* he has no "model" for understanding this probability in any sense analogous to BOLTZMANN'S. Thus when PLANCK sets $k \ln W$ equal to the entropy, he says [*30*], "In my opinion, this stipulation basically amounts to a definition of the probability W; for we have absolutely no point of departure, in the assumptions which underlie the electromagnetic theory of radiation, for talking about such a probability with a definite meaning."

PLANCK, then, does not find the number of complexions which belong to the most probable state at all. Instead he takes for his W a quantity which is the total number of complexions for *all* sets $\{w_r\}$ which satisfy the constraints of Eqs. (21) and (22). In other words, PLANCK'S W is equal to the quantity BOLTZMANN called $\sum W_B$, and the equivalent of Eq. (13) appears in BOLTZMANN'S memoir when he calculates $\sum W_B$, the normalization factor for his probabilities.

It is natural, though rather pointless, to ask why PLANCK deviated from BOLTZMANN'S procedure at this particular stage. Had he carried on with BOLTZMANN'S method, he would have arrived at exactly the same result for the average energy of an oscillator, namely $\varepsilon/\{\exp(\varepsilon/kT)-1\}$. ROSENFELD [*36*] suggests that PLANCK actually started with Eq. (9) for the entropy of an oscillator required by his conjectured distribution law, and went from that to the corresponding form for S_N, the entropy of N oscillators. If S_N were to be given by an expression of the form $k \ln W$, the form of W was then determined to be something like $(N+P)^{N+P}/N^N P^P$. This last result could then be recognized as a legitimate approximation to $(N+P-1)!/(N-1)!\,P!$, a standard formula of the theory of combinations, which, as we have just seen, actually appeared in the Boltzmann paper to which PLANCK was referring. This rather plausible conjecture is well confirmed by what PLANCK himself says in his *Naturwissenschaften* article [*1* (b)] written in 1943.

There is one other aspect of PLANCK'S combinatorial procedure which deserves a comment here. Some years after PLANCK'S work, when EINSTEIN had driven the theory a long step further by showing that radiation itself could behave as if it consisted of energy quanta, physicists tried to reinterpret PLANCK'S reasoning along this same line. This attempt to consider PLANCK'S energy elements as, in some sense, particles of energy seemed a plausible one, but it was quite inconsistent with the combinatorial treatment which had to be given these "particles" if one were to obtain the Planck distribution law. This was pointed out by EHRENFEST in 1911 [*37*] and again, in more detail, in 1914 [*38*]. (The latter paper is especially noteworthy as it contains the simple and graphic derivation of the basic combinatorial formula, Eq. (13), which is now universally given.) What EHRENFEST showed, in effect, was that "particles" which have to be counted according to Eq. (13) are not independent particles in any ordinary sense. They are, in fact, particles which obey the BOSE-EINSTEIN statistics, but that concept could not be clarified until many years later [*39*].

This first, combinatorial, deviation from BOLTZMANN is less striking than the one we shall now consider. As we have already seen, BOLTZMANN too used "energy elements" ε in order to carry out his combinatorial procedure, but BOLTZMANN was always ready to take the limit $\varepsilon \to 0$, once the discreteness was no longer necessary to the analysis. It is obviously of the very essence of PLANCK'S work that ε could not be allowed to vanish, if the proper distribution law were to be reached. PLANCK apparently did not even consider the possibility of taking this limit. This is undoubtedly related to PLANCK'S apparent unawareness of the equipartition theorem and all it implied, which we have already seen.

This aspect of PLANCK'S work seems to have been recognized first in 1905, and it came out very clearly in the course of an exchange between JEANS and Lord RAYLEIGH in the columns of *Nature*. In the May 18, 1905 issue, RAYLEIGH [*40*] repeated his calculation of five years before (see Sect. 3 above), but this time he took care to include all of the proportionality constants which he had not bothered with earlier. The distribution law he obtained was

$$\varrho(\nu, T) = (8\pi\nu^2/c^3)\,(kT), \tag{24}$$

and, as he pointed out, this is exactly the same as the form that PLANCK'S law, Eq. (19), takes in the limit of low frequencies (*i.e.*, when $h\nu/kT \ll 1$), a limit which PLANCK had not explicitly considered. It followed that the quantity k, and therefore AVOGADRO'S number N_0, could in principle be determined from the experimental value of $\varrho(\nu, T)$ at low frequencies using Eq. (24) without any reference to the Planck distribution itself. RAYLEIGH went on to say, "A critical comparison of the two processes (*i.e.* his own and PLANCK'S) would be of interest, but not having succeeded in following PLANCK'S reasoning, I am unable to undertake it. As applying to all wave lengths, his formula would have the greater value if satisfactorily established. On the other hand, the reasoning which leads to [Eq. (24)] is very simple, and this formula appears to me to be a necessary consequence of the law of equipartition as laid down by BOLTZMANN and MAXWELL. My difficulty is to understand how another process, also based upon BOLTZMANN'S ideas, can lead to a different result."

Actually RAYLEIGH had made an error of a factor of eight in his calculation which was soon pointed out by JEANS. (Eq. (24) is, however, correct, and it is the limiting form of PLANCK'S law.) RAYLEIGH [*41*] readily admitted his error but returned to the same point: "But while the precise agreement of results in the case of very long waves is satisfactory so far as it goes, it does not satisfy the wish expressed in my former letter for a comparison of processes. In the application to waves that are not long, there must be some limitation on the principle of equi-partition."

RAYLEIGH'S repeated request for a critical discussion was finally met, at least in part, by JEANS [*42*] in *Nature* for July 27, 1905. (JEANS was then, and for a number of years thereafter, doing his utmost to account for black-body radiation on strictly classical grounds, preserving the truth of the equi-partition theorem in general, and treating deviations from it as due to the absence of true thermodynamic equilibrium.) JEANS undertook a severe criticism of PLANCK'S arguments on two principal points. These points are just the two we have been discussing, where PLANCK broke with BOLTZMANN. Thus JEANS attacked PLANCK'S use of W as a "probability", pointing out that no population was given from which probabilities could be calculated, and that one could not introduce such a population with an *a priori* probability law consistent with PLANCK'S arguments. JEANS' second point was that PLANCK had no right to refrain from taking the limit in which ε is zero. If this were done, PLANCK'S expression for the average energy of an oscillator would reduce to kT in accord with the equipartition theorem. JEANS recognized that PLANCK had fixed ε as equal to $h\nu$ by the use of WIEN'S displacement law, but he argued that nothing in the displacement law determined the value of h, "whereas statistical mechanics gives us the further information that the true value of h is $h=0$". If by "true" one means in agreement with the equipartition theorem, then JEANS was correct. JEANS erred only in supposing that "the methods of both are in effect the methods of statistical mechanics and of the theorem of equipartition of energy". That was JEANS' method, but it was certainly not PLANCK'S.

The most revealing exposure of the deep chasm which PLANCK had opened between his own ideas and BOLTZMANN'S was made by EHRENFEST [*43*]. He pointed out that PLANCK'S work really re-opened the whole question of the statistical foundation of the second law of thermodynamics, since PLANCK'S energy elements amounted to a radical change in the *a priori* weight function introduced into phase space. BOLTZMANN'S statistical mechanics had been built on the assumption that regions of equal volume in phase space were to be assigned equal *a priori* weights, but if the energy were to be a discrete variable, some new basic assumption would be needed to rebuild the foundations.

6. Conclusion

A revolutionary idea is not always recognized as such, not even by its propounder. PLANCK'S concept of energy quanta went practically unrecognized in the literature of physics for over four years. His radiation formula was accepted as describing the experimental facts in a simple and adequate way, but the theory which he had proposed as a basis for this formula drew no attention until 1905. Although this virtual ignoring of what later came to be recognized as a major advance in physics may seem odd, there are several possible explanations for it. The most obvious is that the theory of radiation was not the center of interest in physics in 1900. I need only mention that X-rays were discovered in 1895, radioactivity in 1896, the electron in 1897, radium in 1898, *etc.*, to remind the reader of the series of exciting discoveries which were being made and which were drawing the attention of a substantial fraction of the best minds in physics.

In addition to the competition of these unparalleled advances, PLANCK'S work suffered from another serious hazard. At just this time, when not only the atom but even its constituent parts were taking the center of the experimental stage, a substantial and influential group of theorists on the continent had set themselves against the whole atomic theory [*44*]. With varying degrees of emphasis, such men as OSTWALD, MACH and DUHEM were denying the significance of the whole program of the kinetic theory of gases and the general atomic, mechanical view of physics which BOLTZMANN had championed. BOLTZMANN carried on a vigorous polemic, particularly against OSTWALD, in the latter 1890's, feeling himself obliged to justify "The Indispensability of Atomism in the Natural Sciences". (PLANCK had joined BOLTZMANN in the attack on the "energetics" school in 1896, despite his own lack of sympathy with BOLTZMANN'S work at that time, pointing out that the "energeticists" misconceived the proper meaning of the second law of thermodynamics.)

The seriousness of the attacks made by OSTWALD and others against the kinetic molecular theory can be measured by the tone of the preface which BOLTZMANN wrote in 1898 for the second volume of his *Gastheorie* [*45*]. "When the first part of this book was printed I had almost completely finished a manuscript of the present second and last part in which the more difficult parts of the subject were not treated. Just at that time [1896] the attacks against the kinetic theory multiplied. I am now convinced that these attacks are based completely on misconceptions and that the role of the kinetic theory in science is far from being played out ... In my opinion it would be a loss to science if the kinetic theory were to fall into temporary oblivion because of the present, dominantly hostile mood, as, for example, the wave theory did because of NEWTON'S authority. I am conscious of how powerless the individual is against the currents of the times. But in order to contribute whatever is within my powers so that when the kinetic theory is taken up once again, not too much will have to be rediscovered, I have also treated the most difficult parts of the kinetic theory in the present volume, those which are most liable to misunderstandings, and I have tried to give as easily intelligible an exposition of these as possible, at least in outline."

Now PLANCK had quite deliberately associated his thinking with BOLTZMANN'S in his papers on quanta at just the time when BOLTZMANN himself was under the dark cloud cast by the school of "energetics". (This gives a touch of poignancy to PLANCK'S remark, "As an offset against much disappointment, I derived much satisfaction from the fact that LUDWIG BOLTZMANN, in a letter acknowledging my paper, gave me to understand that he was interested in, and fundamentally in agreement with, my ideas." [*46*]) There is little doubt that the intentionally Boltzmann-like tone of PLANCK'S papers on quanta contributed to the delay in their recognition, at least on the continent.

In England, as we have already seen, RAYLEIGH and JEANS did some probing into the significance of PLANCK'S work in 1905. It is certainly fair to say, however, that neither RAYLEIGH nor JEANS was sympathetic to the idea of energy quanta nor was either of them interested in developing the idea any further. Such a revolutionary idea could take root and grow only in a mind keen enough to see its implications and bold enough to develop them immediately in a variety of directions. Such a mind was ready, fortunately for science, and in the work of ALBERT EINSTEIN the full significance of PLANCK'S concept began to show itself.

In the first [*47*] of the three great papers which he wrote in the spring of 1905, EINSTEIN pointed out the distribution law which was required by classical physics, the "Rayleigh-Jeans law" (Eq. (24) above) and stressed both its inconsistency with experiment and its internally paradoxical nature, due to the infinite radiation energy which it implies. This was apparently done quite independently of RAYLEIGH'S 1900 paper to which EINSTEIN does not refer and which there is no reason to believe he knew. EINSTEIN also pointed out, as RAYLEIGH did simultaneously in the *Nature* letter discussed in the last section, that PLANCK'S determination of AVOGADRO'S number is really independent of his radiation formula, and that the same result could be found from the classical formula using the experimental results on black-body radiation. All these things, as well as the deep gap between PLANCK'S quanta and classical physics were, as EINSTEIN was to write many years later [*48*], "quite clear to me shortly after the appearance of PLANCK'S fundamental work". In addition to these points, which RAYLEIGH saw too, EINSTEIN showed that the non-classical part of PLANCK'S radiation formula, the Wien limit, so to speak, had a remarkable consequence. It implied, as EINSTEIN demonstrated by a characteristically simple argument, that radiation itself behaved as if it consisted of energy quanta whose magnitude was given by $h\nu$. This went well beyond any conclusion which PLANCK himself had drawn, since PLANCK had quantized only the energy of the material oscillators and not the radiation. EINSTEIN went on to show in a few pages how the photoelectric effect, STOKES' rule for fluorescence, and the photoionization of gases could all be very simply understood by treating light as composed of energy quanta $h\nu$. None of these phenomena had been explicable on the basis of the electromagnetic wave theory of light.

EINSTEIN was well aware that all of this marked the beginning of a new era in physics, and he indicated that awareness by referring to his work in the title of his paper as offering "a heuristic viewpoint". He saw that thoroughgoing changes in the foundations were needed, but even "without having a substitute for classical mechanics, I could nevertheless see to what kind of consequences this law of temperature radiation leads".

The effect of Planck's quantum theory on physics in this period is perhaps best expressed in Einstein's words [*48*]: "It was as if the ground had been pulled out from under one, with no firm foundation to be seen anywhere upon which one could have built."

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