Thermodynamics and Quanta in Planck's Work

Planck's search for a deeper understanding of the second law of thermodynamics led him to a strange and unexpected result—the concept of energy quanta. His conservative attitude toward this revolutionary discovery expressed itself in his attempts to reconcile the quantum with classical electrodynamics.

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by Martin J. Klein

IN JANUARY 1910 Max Planck sent a paper to *Annalen dar Physik* on the theory of black-body radiation.[1] It was his first paper on this subject since the epoch-making work in which he had introduced the concept of energy quanta almost a decade earlier. Planck had no new results to report, but he felt that it was time he expressed his views on what had been going on in the intervening years. Not that there was so very much to discuss: neither the problems of radiation nor Planck's startling idea that energy could sometimes vary only in discrete steps had yet seriously caught the attention of most of his colleagues. Planck himself, of course, had thought a great deal about these things, as he remarked in a letter to Walther Nernst a few months later:[2] "I can say without exaggeration that for ten years, without interruption, nothing in physics has so stimulated me, agitated me, and excited me as these quanta of action." But his approach to the problems did not coincide with those of the relatively few others who had concerned themselves with the theory of radiation, and Planck wanted to point out the path that he considered most sensible and most promising for future success.

In his paper, Planck arranged the current views on radiation into a spectrum, placing his own in the solid central position. The extreme right wing, represented by James Jeans, was still trying to maintain the soundness of Hamilton's equations and the equipartition theorem. The fact that the equipartition theorem could not account for the existence of the equilibrium distribution of black-body radiation, much less for its observed form, had to be explained, according to Jeans, by the absence of true thermodynamic equilibrium in the radiation. At the opposite end of the spectrum of opinion were the radicals who interpreted the failure of the equipartition theorem as a sign that nineteenth-century physics, for all its great successes, now needed sweeping changes. The most daring of their proposals suggested that radiation be considered as a collection of independent particles of energy—light quanta—rather than as continuous electromagnetic waves. This position was advanced most forcefully by Albert Einstein, who supported it with a variety of arguments, drawing upon his un-

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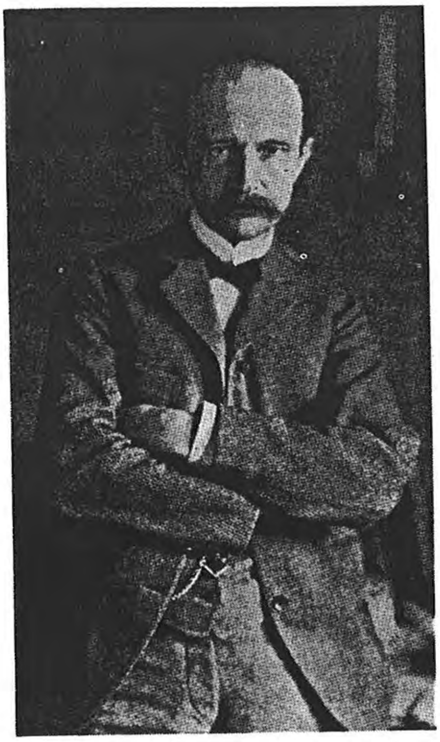

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matched insight into statistical mechanics.

Planck could not accept either of these extreme viewpoints. Jeans' attempts to salvage the equipartition theorem left him unconvinced. Something in classical physics had to be given up. To that extent he could agree with the radicals, but only to that extent. For he was concerned that they wanted to throw out too much. He would not grant the cogency of the arguments for a new corpuscular theory of light, even though Einstein claimed that his light quanta were a *necessary* consequence of the observed form of the black-body radiation law. Planck was not ready to give up the whole development from Huygens to Maxwell and Hertz which had established the electromagnetic wave theory of light, "all those achievements which belong to the proudest successes of physics, of all science," for the sake of what he called a few highly controversial arguments.

He was, however, ready to sacrifice the equations of mechanics, and stated his assurance that Hamilton's equations could no longer be taken as generally valid. In that way the equipartition theorem and its unfortunate consequences could be avoided. Planck was sure of something else: The discontinuity expressed by his quantum of action was real and would have to be reckoned with. He foresaw a future theory that would somehow reconcile the existence of the quantum of action with electrodynamics, but in the meantime he advocated caution: "One should proceed as conservatively as possible in introducing the quantum of action into the theory, making only those changes in existing theory that have proved to be absolutely necessary."

Planck's stand amounted to this: He had no doubts about the fundamental importance of the quantum of action itself, but he saw no need for a real quantum *theory* of radiation and matter of the kind that already seemed inevitable to Einstein. I think that this statement of Planck's views helps one to understand his work during the next few years, in which he seemed to retreat steadily from his own radical step in 1900. I shall discuss some of this work later on in this paper, but I want first to go back and try to point out the way in which the development of Planck's ideas had led him to adopt this attitude towards the quantum and the quantum theory.

Second law as absolute

In his later years Planck often expressed his deep conviction that "the search for the absolute" was "the loftiest goal of all scientific activity."[3] The context of his remarks clearly indicated that he saw the two laws of thermodynamics as a prototype of that "loftiest goal." For Planck had formed himself as a physicist by his self-study of the writings of Rudolf Clausius, that lucid but rather argumentative man who first distinguished and formulated the two laws of thermodynamics, and it was thermodynamics as seen by Clausius that set the pattern of Planck's scientific career. He devoted the first fifteen years or so of that career to clarifying, expounding and applying the second law of thermodynamics and especially the concept of irreversibility. Planck's solid and successful work in this field did not bring him all the satisfaction he might properly have expected. One reason was that he learned, too late, that some of his results had been anticipated a few years earlier in the memoirs of Willard Gibbs. More disturbing was the rise of a powerful school of thought, the "Energeticists," led by Wilhelm Ostwald and Georg Helm, which rejected the clear distinctions made by Clausius, and offered a new master-theory that would have replaced the elegant mathematical structure of thermodynamics by a confused and inconsistent tangle.[4] Planck later described his failure to persuade the Energeticists of the errors of their ways as "one of the most painful experiences of my entire scientific life."

As a disciple of Clausius, Planck looked upon the second law of thermodynamics as having absolute validity: Processes in which the total entropy decreased were to be strictly excluded from the natural world. He did not care to follow Clausius in pursuing "the nature of motion which we call heat," or in searching for a mechanical explanation of the second law of thermodynamics.[5] And he most certainly did not follow Ludwig Boltzmann in his reformulation of the second law of thermodynamics as a statistical law. Boltzmann's statistical mechanics made the increase of entropy into a highly probable rather than an absolutely certain feature of natural processes, and this was not in keeping with Planck's own commitments. The statistical interpretation of entropy is conspicuously absent from the papers Planck wrote in the early 1890's under such titles as "General Remarks on Modern Developments in the Theory of Heat"[6] and "The Essence of the Second Law of Thermodynamics."[7]

One should not think, however, that Planck was content to keep thermodynamics a completely independent subject, separate from the rest of physics. He preferred the rigorous arguments of pure thermodynamics to the difficult but approximate treatment of molecular models in kinetic theory, but he also felt strongly the need to relate the irreversibility described by the second law to the other fundamental laws governing the basic conservative processes. He rejected Boltzmann's approach because it rested on statistical assumptions, and Planck wanted to avoid these. He hoped that the principle of increasing entropy could be preserved intact as a rigorous theorem in some more comprehensive and more fundamental theory.

Second law and Wien distribution

In March 1895 Planck presented a paper to the Academy of Sciences at Berlin that seemed to represent a basic shift in his interests.[8] He had just put aside his usual thermodynamic concerns to discuss the problem of the resonant scattering of plane electromagnetic waves by an oscillating dipole of dimensions small compared to the wave length. A careful reader would have noticed, however, that at the end of the paper Planck admitted that this study was only undertaken as a preliminary to tackling the problem of black-body radiation. The scattering process offered a way of understanding how the equilibrium state of the radiation in an enclosure at fixed temperature could be maintained. The thermodynamics of radiation was the underlying problem, and Planck's attention may have been drawn to it by Wien's paper of 1894 which presented the displacement law.[9]

The following February Planck had further results to report to the Academy.[10] He had extended his studies to the radiation damping of his charged oscillators, and he was impressed by the difference between radiation damping and damping by means of the ordinary resistance of the oscillator. Radiation damping was a completely conservative mechanism that did not require one to invoke the transformation of energy into heat, or to supply another characteristic constant of the oscillator in order to describe its damping. Planck thought this could have far-reaching implications for this fundamental question of irreversibility and the second law. As he put it, "The study of conservative damping seems to me to be of great importance, since it opens up the prospect of a possible general explanation of irreversible processes by means of conservative forces—a problem that confronts research in theoretical physics more urgently every day."

One year later, in February 1897, he communicated the first of what would become a series of five papers, extending over a period of more than two years, on irreversible phenomena

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in radiation.[11] The extended introduction itself indicated that Planck was planning a major work. He began by asserting that no one had yet successfully explained how a system governed by conservative interactions could proceed irreversibly to a final state of thermodynamic equilibrium. He explicitly discounted Boltzmann's H-theorem as an unsuccessful attempt in this direction, citing the criticisms recently raised by E. Zermelo, Planck's own student, against Boltzmann's analysis.[12] Planck then announced his own program for deriving the second law of thermodynamics for a system consisting of radiation and charged oscillators in an enclosure with reflecting walls. He would introduce no damping other than radiation damping, but would take the basic mechanism for irreversibility to be the alteration of the form of an electromagnetic wave by the scattering process—its apparently irreversible conversion from incident plane to outgoing spherical wave. The ultimate goal of this program would be the explanation of irreversibility for conservative systems and, as a valuable by-product, the determination of the spectral distribution of black-body radiation.

Planck had high hopes: His goal was precisely right for a disciple of Clausius. It would have been a splendid conclusion to his work in thermodynamics, and it would have put an end, once and for all, to claims that the second law was merely a matter of probability. How was Planck to know that he was headed in a very different direction, that he had started on what he would later call "the long and multiply twisted path" to the quantum theory?[13]

There was, unfortunately, a fundamental flaw in Planck's proposal and it was promptly pointed out by Boltzmann.[14] The equations of electrodynamics could not produce a monotonic approach to equilibrium any more than the equations of mechanics, both needed to be supplemented by appropriate statistical assumptions. Nothing in the equations of electrodynamics would, for example, forbid the inverse of Planck's scattering process. (It is reasonable to suppose that Boltzmann was, at the least, not deterred from pointing out this error by Planck's negative comments on his own work. Planck's support of Zermelo did not help matters either, since Boltzmann had found Zermelo's criticism particularly irksome; Boltzmann commented that Zermelo's paper showed that if, after a quarter of a century, his work had still not been understood, at least it had finally been noticed in Germany!)[15]

Planck finally granted that a statistical assumption was necessary, and introduced what he called the hypothesis of "natural radiation,"[16] the appropriate analogue of Boltzmann's hypothesis of "molecular chaos," the hypothesis underlying the H-theorem.[17] With the help of this hypothesis Planck was able to complete his program, in a sense, and he reported his

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work in the last paper of the series in June 1899.[18] He proved first that the spectral distribution of the equilibrium radiation at temperature T, $\rho(\nu,T)$ (the energy per minute frequency interval at ν in a unit volume), was related to the average energy, $E(\nu,T)$, of an oscillator of frequency ν by the equation,

$$\rho(\nu,T) = (8\pi\nu^2/c^3)\ E(\nu,T) \qquad (1)$$

This average energy could be determined once he fixed the dependence of the entropy S of the oscillator on its energy E, but he had no independent method for determining the function $S(E)$. He knew, however, that the spectral distribution had to satisfy Wien's displacement law,

$$\rho(\nu,T) = \nu^3 f(\nu/T) \qquad (2)$$

where f is a function of the ratio (ν/T) only, and that Wien had proposed a particular form of the distribution that accounted for all available experimental measurements.[19] Wien's distribution had the form,

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

and, with the help of equation 1 and the thermodynamic definition of the temperature, this would fix the form of the entropy function $S(E)$.

Planck proceeded to *define* $S(E)$ by

$$S(E) = -(E/\beta\nu)\ \{\ln E/a\nu) - 1\} \qquad (4)$$

the form fixed by equation 3, where $a = (\alpha c^3/8\pi)$. He convinced himself that this definition was the only possible one in the sense that if and only if the entropy had this form could he prove that the total entropy of the system increased monotonically to an equilibrium value. This is what I meant when I said that Planck completed his program "in a sense." He had shifted his ground so that he actually *used* the second law to fix the entropy function and thereby the spectral distribution of the black-body radiation.

Planck formulated his result in these words: "I believe that it must therefore be concluded that the definition given for the entropy of radiation, and also the Wien distribution law for radiation that goes with it, are necessary consequences of applying the principle of entropy increase to the electromagnetic theory of radiation, and that the limits of this law, should there be any, therefore coincide with those of the second law of thermodynamics. For this reason further experimental tests of this law naturally acquires so much the more interest."

The absolute system of units

This last statement is remarkable enough in the clear light of our hindsight, especially since this paper was also published, with only minor revisions, in the *Annalen der Physik* early in 1900, only months before the introduction of the quantum.[20] But Planck ended his paper with an even more remarkable section. His expression for the entropy of an oscillator (4) contained two constants, a and β, which also appear in the Wien distribution law, two universal constants as Planck called them when he introduced them. He evaluated these constants numerically from the available experimental data on black-body radiation and found for β the value 0.4818×10^{-10} sec °K and for a the value 6.885×10^{-27} erg sec. Planck observed that these two constants together with the velocity of light c and the gravitational constant G could be used to define new units of mass, length, time and temperature and that these units properly deserved the title of "natural units".

All systems of units previously employed owed their origins to the accidents of human life on this earth, wrote Planck. The usual units of length and time derived from the size of the earth and the period of its orbit, those of mass and temperature from the special properties of water, the earth's most characteristic feature. Even the standardization of length using some spectral line would be quite as arbitrary, as anthropomorphic, since the particular line, say the sodium D line, would be chosen to suit the convenience of the physicist. The new units that he was proposing would be truly "independent of particular bodies or substances, would necessarily retain their significance for all times and for all cultures, including extraterrestrial and non-human ones," and therefore deserved the name of "natural units." That they were of awkward sizes (10^{-33} cm, 10^{-42} sec. etc) was obviously of no importance. "These quantities preserve their natural significance so long as the laws of gravitation and the propagation of light in vacuum, and the two laws of thermodynamics retain their validity."[21]

I have referred earlier to Planck's conviction that the search for the ab-

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solute was the physicist's proper goal. The universal constants as well as the most general physical laws belonged to that category of the absolute for him. As he put it in an essay written in his ninetieth year, "The endeavor to discover [the absolute constants] and to trace all physical and chemical processes back to them is the very thing that may be called the ultimate goal of scientific research and study."[22] He had obviously felt the same way half a century earlier.

It will not have escaped your notice that the constant he called *a* in 1899 was soon to be renamed and reinterpreted. The "further experimental tests" that Planck had called for were promptly made, and as the measurements were extended to longer wavelengths it became apparent to Planck that either the second law of thermodynamics did not have universal validity or there was an error in his arguments.[23] For the Wien distribution law could not represent the new data in the infrared. I do not have space here to recount in detail the exciting events of 1900, but by October Planck was ready to offer a new distribution law which did account for the experimental results obtained by his colleagues Rubens and Kurlbaum, as well as for all subsequent results on the black-body radiation spectrum.[24] The new law had the now familiar form,

$$\rho(\nu,T) = \alpha\nu^3[\exp(\beta\nu/T) - 1]^{-1} \quad (5)$$

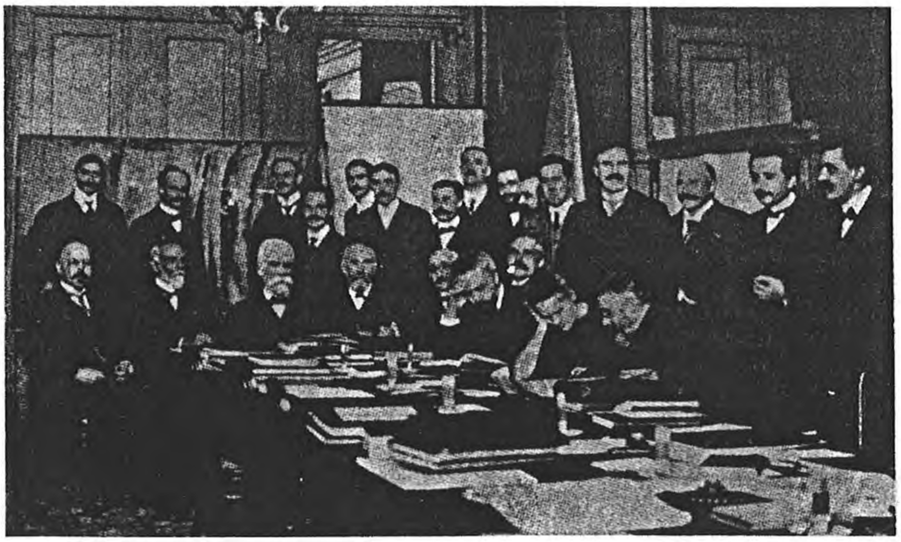
Planck's earlier analysis of the way that entropy increased with time had suggested this as the next simplest possibility after Wien's law. The problem was to create a suitable theoretical foundation for the new distribution law.

Planck had to take a difficult and probably painful step. He had to put aside his opposition to statistical mechanics and his years of occasional controversy with Boltzmann and try to adapt Boltzmann's methods to his problem.[25] All other resources had failed him. The crux of the matter was still the energy-entropy relation for an oscillator; perhaps Boltzmann's equation for the entropy in terms of the number of complexions could fix this one missing relationship. Planck had the great advantage of knowing what the answer had to be, since his new distribution law, equation 5, determined the form of the entropy of an oscillator as a function of its energy. It too had the kind of logarithmic structure that Boltzmann's equation would suggest. Using Boltzmann's great memoir[26] of 1877 as his guide Planck plunged in, and "after a few weeks of the most strenuous work of my life," as he put it, "the darkness lifted and an unexpected vista began to appear."

"An act of desperation"

In order to calculate the "thermodynamic probability" of a state in which a certain energy was shared among many oscillators of the same frequency, that is to say, the number of ways in which this sharing could be accomplished, it was essential that Planck imagine the energy to be composed of a finite number of identical units, each of magnitude ϵ. This by itself would not have been a novel step: Boltzmann had often done it as a computational device, particularly in the 1877 memoir that Planck used as his guide. But Planck had to refrain from taking the accepted next step, namely going to the limit where ϵ vanishes.[27] He had to refrain, that is, if he were to arrive at the entropy formula required by the distribution law that he knew to be the correct one. He was willing to take this step, to restrict the energy of one of his oscillators to multiples of the energy unit or quantum ϵ, radical though he must have known it to be.

Thirty years later, in a letter to R. W. Wood,[28] Planck described what he had done as "an act of desperation," undertaken against his naturally peaceful and unadventurous disposition. "But," he went on, "I had already been struggling with the problem of the equilibrium of matter and radiation for six years (since 1894) without success; I knew that the problem is of fundamental significance for physics; I knew the formula that reproduces the energy distribution in the normal spectrum; a theoretical interpretation *had* to be found at any cost, no matter how high." He described himself as ready to sacrifice any of his previous convictions except the two laws of thermodynamics. When he found that the hypothesis of energy quanta would save the day he considered it "a purely formal assumption, and I did not give it much



THE 1911 SOLVAY CONGRESS brought together many of those who were interested in quantum theory. Planck is standing second from left.

thought except for this: that I had to obtain a positive result, under any circumstances and at whatever cost."

Planck actually did give his assumption of quanta a good deal of thought along one particular line. His theory, which I must omit here, once again contained two universal constants: the constant k, the proportionality constant that related entropy to the logarithm of the "thermodynamic probability," and the constant h, brought into existence by the requirements of the displacement law which made the energy quantum ϵ proportional to the frequency of the oscillator, so that ϵ could be expressed as $h\nu$. These constants were equivalent to those that Planck had emphasized a year earlier: h was the former a and k was the ratio of the former a and β. But now Planck could discuss their detailed physical importance as well as their absolute significance. The constant k, in particular, had to be equal to the ratio of the gas constant R to Avogadro's number N_0, the number of atoms in a gram atomic weight. And Planck's determination of k and h from the measurements on black-body radiation, with the help of his distribution law in the form

$$\rho(\nu,T) = (8\pi\nu^2/c^3)\,(h\nu)\,\{\exp\,(h\nu/kT) - 1\}^{-1} \qquad (6)$$

gave him an accurate value of Avogadro's number and with it the mass of the individual atom.[29]

This was a major achievement. Planck's value for Avogadro's number was far more accurate than any of the existing indirect estimates based on the kinetic theory of gases, and he used it not only to get the mass of the atom but also, together with the Faraday constant, to determine the charge on the recently discovered electron, the natural unit of electric charge. His value of e was 4.69×10^{-10} e.s.u.—at a time when the early attempts at direct measurement gave results from 1.3 to 6.5 in the same units. Unfortunately, Planck's contemporaries did not properly appreciate these results; the handbooks went on printing crude determinations of Avogadro's number, ignoring Planck's value.[30] The first experimentalist to quote Planck's value of e seems to have been Rutherford, in 1908, probably because he and Geiger had obtained essentially the same value, 4.65×10^{-10} e.s.u. from the charge on the alpha particle and were glad to have a confirmation of a result 50% higher than J. J. Thomson's current best determination.[31]

Planck himself laid heavy emphasis on these concrete results of his theory, both in his papers and in his *Lectures on the Theory of Heat Radiation*[32] published in 1906. I am convinced that, with Planck's particular sensitivity to the importance of the natural constants, it was these results that assured him that quanta were more than an ad hoc hypothesis, useful only for arriving at the radiation law. Of course h, the second constant in his equation, the essentially new constant in the theory, was yet unexplored. He remarked in his *Lectures* at several points that h must have some direct electrodynamic meaning, that this meaning must be found before the theory of radiation could be considered fully satisfactory, but that a lot more research would be needed before this meaning was revealed.

The kind of electrodynamic meaning that Planck had in mind for h was suggested in a letter he wrote to Paul Ehrenfest[33] in July 1905. Ehrenfest was engaged in an analysis of Planck's assumptions and had written to Planck asking several questions about them. In his answer Planck pointed out that the existence of a discrete unit of electric charge imposed certain limitations on the electromagnetic field. He went on to write: "Now it seems to me not completely impossible that there is a bridge from this assumption (of the existence of an elementary quantum of electric charge e) to the existence of an elementary quantum of energy h, especially since h has the same dimensions and also the same order of magnitude as (e^2/c). But I am not in a position to express any definite conjecture about this." Planck never published this remark, so far as I can tell. Almost the same thought, however, was expressed by Einstein in 1909 in the course of a dimensional analysis of the displacement law.[34] He too pointed out the dimensional equivalence of h and (e^2/c). But I am not in noted, correctly, that their magnitudes differed by a factor of about a thousand. "The most important thing in this derivation," Einstein went on, "is that it reduces the constant for light quanta h to the elementary unit of electricity e. Now one must remember that the elementary charge e is a stranger in the Maxwell-Lorentz electrodynamics. . . . It seems to me to follow from the relationship, $h=e^2/c$, that the same modification of the theory which contains the elementary charge as one of its consequences will also contain the quantum structure of radiation."

Retreat from energy quantization

I have been trying to give the background for my earlier statement that Planck was fully committed to the quantum, but not necessarily to a quantum theory in Einstein's sense. Planck's work in the years after 1910, when he resumed publication in this field shows him holding fast to the quantum of action but retreating steadily from his earlier strict quantization of the oscillator. In a paper[35] read to the German Physical Society in February 1911 he explained that he was revising his original theory because of the valid criticism to which it had been subjected, particularly by H. A. Lorentz.[36] The objection was basically that the intensity of the radiation at high frequencies was very low, whereas at these frequencies the energy quantum was very large. As a consequence the time it would take an oscillator to absorb one quantum would have to be unreasonably long, and the oscillator might not even be able to absorb one full quantum if the radiation should be cut off. This criticism naturally presupposed that radiation was properly described by electromagnetic waves, and it is interesting to note that Lorentz had used this argument to show how difficult it was to explain phenomena like the photoelectric effect without having recourse to Einstein's light quanta instead of the wave description. Planck, however, did not take it that way.

He proposed instead to give up his hypothesis that the energy of an oscillator had to be an integral multiple of $h\nu$ and could therefore absorb or emit energy only in discrete units. In his new theory the oscillator would absorb energy continuously, just as it did classically, so that Lorentz's criticism could be set aside. The emission process, however, was still quantized. This procedure would eliminate another difficulty, an internal contradiction in the original theory pointed out by Einstein.[37] In that theory Planck had used the classically derived relationship between the radiation density and the oscillator's energy, but that classical derivation was, of course, incompatible with the assumption of quantum states for the oscillator.

Planck gave several versions of his new theory of quantized emission in 1911 and 1912, finally settling on one in which the oscillator, absorbing energy continuously, could emit only when its energy was a multiple of $h\nu$.[38] If it emitted at all it had to emit all the energy it possessed, however many quanta that might be. Whether or not it emitted as its energy reached $nh\nu$, for any n, was governed by a probability η. This probability was fixed by the assumption that the ratio of the probability of no emission to the probability of emission, $(1-\eta/\eta)$, should be proportional to the intensity of the incident radiation. The proportionality constant, in turn, was determined by the requirement of classical behavior in the limit of high intensity radiation. (This is surely one of the first uses of the correspondence principle. There is reason to believe that this paper of Planck's had considerable influence on Bohr's first papers on atomic structure.[39])

This second quantum theory of Planck's led to the same law for black-body radiation as had the first (this must have been an unexpressed boundary condition on the work). But it made an interesting change in the expression for the average energy of an oscillator,

$$\bar{E} = h\nu\,\{\exp(h\nu/kT)-1\}^{-1} + h\nu/2 \qquad (7)$$

The additional term meant that the energy of an oscillator would not vanish at the absolute zero of temperature but would be just $(h\nu/2)$; hence its usual name of zero-point energy. Planck saw a variety of phenomena that might be interpreted as favoring his concept of quantum emission, and also some that supported the reality of the zero-point energy. He suggested, for example, that this might be the source of the energy of particles emitted by radioactive atoms, and that the sharply defined energy of these particles was an example of quantum emission.

The novel idea of zero-point energy attracted a good deal of attention, first of all from Einstein, as one might have expected. Early in 1913 he and Otto Stern discussed its possible relevance for understanding Eucken's new measurements of the heat capacity of hydrogen gas at low temperatures.[40] A number of physicists then tried to apply the zero-point energy to phenomena as diverse as deviations from Curie's law in paramagnetism[41] and the equation of state of gases.[42] The most significant application was made by Debye in his theory of the effect of thermal vibrations on x-ray scattering from crystals.[43] Debye showed that the presence or absence of the zero-point energy could be brought to experimental test by a study of the intensities of x-ray diffraction spots. This was eventually done, and the existence of zero-point energy was confirmed, but by that time it had lost its connection with Planck's largely forgotten second quantum theory.[44]

For Planck the zero-point energy was an interesting by-product of his work, but the important thing was that he had arrived at the radiation law without having to restrict the energy of the oscillator to quantized energies. Actually he was ready to give up even the quantized emission of radiation, and did so in a paper he wrote in 1914, where the crucial h governed only the interaction between oscillators and free particles, and the absorption and emission of radiation followed the classical laws.[45] Planck was always arguing *to* the radiation law and tried to restrict the use of the quantum to the minimum sufficient for deriving that law.

Nernst's law, entropy and quanta

Planck's book on radiation included one important new step in the search for an understanding of h. He constructed an argument showing that h could be interpreted directly as a quantum of action in the sense that h measured the areas of the regions of equal statistical weight in the phase space of the oscillator.[46] The concept of a cell in phase space had already played an important part in Boltzmann's statistical mechanics, but as Planck emphasized in his parallel discussion of the ideal gas, its magnitude was apparently of no significance there since it appeared only in the additive constant in the entropy.

At this stage he did not yet see that there was anything general about the use of h to fix the size of a cell in phase space.

The lectures on heat radiation on which Planck's book were based were delivered during the winter semester of 1905-1906, and while they were going on, Planck's colleague at Berlin, Nernst, reported a significant advance in thermodynamics.[47] This was Nernst's famous heat theorem which, although he did not formulate it that way, amounted to the statement that the entropy differences between all states of a system disappear at absolute zero. It is clear that a new result in thermodynamics of such general import would have been of interest to Planck, but it is not so clear, in view of Planck's background as I have described it, that he should have been the one to probe its statistical significance as well.

He discussed his views in a lecture entitled "On Recent Thermodynamic Theories: Nernst's Heat Theorem and the Hypothesis of Quanta," delivered before the German Chemical Society in December 1911.[48] Planck described the importance of Nernst's theorem, which was really a new and independent postulate, by pointing out the incompleteness of the classical thermodynamics based on the first and second laws. Classical thermodynamics could not lead to a full specification of the conditions for equilibrium (phase equilibrium or chemical equilibrium) precisely because it provided no way of fixing the undetermined constant in the entropy equation. Just this gap was filled by Nernst's law, and Planck stated it in what he considered its simplest and most far-reaching form: the entropy of a chemically pure substance in a condensed phase vanishes at absolute zero. Nernst's law, in other words, allowed one to fix the absolute value of the entropy and therefore represented a major addition to thermodynamics.

Planck then went on to ask for "the real, the more profound physico-chemical meaning" of the law, that is, its meaning on the atomic scale, "not only because this promises greater intuitive insight, but also because only it can help one to discover regularities and relationships . . . which pure thermodynamics cannot touch." And this atomistic interpretation of a law involving the entropy would have to be found, he said, by using Boltzmann's fundamental relationship between entropy and probability. Planck had come a long way in his thinking in the decade or so since he had reconciled himself to trying Boltzmann's methods!

If one wanted to calculate the entropy of a system with the help of Boltzmann's relationship, the whole procedure was fully determined except for one point: there was no *a priori* criterion for choosing the size of the elementary cells in phase space. This lack of definiteness was the exact counterpart of, and could be considered the reason for, the indeterminateness of the entropy constant (as mentioned earlier). Conversely, then, if Nernst's law fixed the entropy constant, this must imply that its "deeper meaning" must be that the sizes of the cells in phase space are not arbitrary but must have definite values. This statement would have been hard to accept, Planck went on, if not for the totally unexpected support it received from the theory of black-body radiation, that is from his own interpretation of h as precisely the size of the phase cell for oscillators of any frequency. Further analysis of the "meaningful and attractive problem" of determining these quite definite elementary cells for calculating the thermodynamic probability was called for, since Planck now saw this as the essential content of the hypothesis of quanta.

He put it this way some months later in the preface to the second edition of his book on heat radiation.[49] "For the hypothesis of quanta as well as the heat theorem of Nernst may be reduced to the simple proposition that the thermodynamic probability of a physical state in a definite integral number, or what amounts to the same thing, that the entropy of a state has a quite definite, positive, value, which, as a minimum, becomes zero, while in contrast therewith the entropy, may, according to the classical thermodynamics, decrease without limit to minus infinity. For the present, I would consider this proposition as the very quintessence of the hypothesis of quanta." Planck must have been thoroughly gratified to have found this way of relating his two favorite concepts—entropy and the quantum of action. He devoted much thought to the general problem of determining the size and shape of the elementary cells in phase space over the next decade,[50] but I cannot discuss that work here.

"A far more significant part"

In the *Scientific Autobiography* that he wrote near the end of his long life Planck frankly discussed the attitude prevalent among many physi-

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cists about his work after 1901.[51] "My futile attempts to fit the elementary quantum of action somehow into the classical theory continued for a number of years, and they cost me a great deal of effort. Many of my colleagues saw in this something bordering on a tragedy. But I feel differently about it. For the thorough enlightenment I thus received was all the more valuable. I now knew for a fact that the elementary quantum of action played a far more significant part in physics than I had originally been inclined to suspect."

It was in this same spirit that he had prophetically closed his lecture to the German Chemical Society in 1911. "To be sure, most of the work remains to be done; . . . but the beginning is made: the hypothesis of quanta will never vanish from the world. . . . And I do not believe I am going too far if I express the opinion that with this hypothesis the foundation is laid for the construction of a theory which is someday destined to permeate the swift and delicate events of the molecular world with a new light." □

All quotations from Planck's unpublished letters are made with the kind permission of Frau Dr. Nelly Planck, to whom I should like to express my thanks.

For an analysis coming to rather different conclusions see Thomas S. Kuhn, Black-Body Theory and the Quantum Discontinuity, 1894–1912 *(New York, 1978). See also Allan A. Needell,* Irreversibility and the Failure of Classical Dynamics: Max Planck's Work on the Quantum Theory 1900–1915 *(Yale Univ. PhD. Diss., 1980).*

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