### Einstein's part in the development of quantum concepts

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Einstein's papers on quantum theory over the period 1905–1925 are reviewed. These papers played a fundamental role in the development of quantum concepts. This review traces the relationship between these papers, on the one hand, and Wien's and Planck's theoretical work on thermal radiation and Einstein's own work on statistical thermodynamics, on the other. Einstein's 1905 development of the concept of light quanta from Wien's radiation law, the application of this concept to elementary interactions of radiation with matter, Einstein's 1906–1907 analysis of the Planck radiation law, and Einstein's development of the foundations of a quantum theory of specific heat are all discussed. Particular attention is paid to Einstein's 1909 development of the concept of a particle-wave duality for radiation from a study of the energy and momentum fluctuations in a radiation field. Einstein's 1916 papers on the quantum theory of radiation are analyzed, and it is emphasized that Einstein was the first to suggest a probabilistic interpretation of the particle-wave duality, in addition to introducing coefficients to characterize the probabilities for optical transitions and offering his well-known derivation of the Planck radiation law. There is a special discussion of Einstein's expression, in his 1925 paper on the quantum theory of monatomic ideal gases, of high regard for de Broglie's concept of a particle-wave duality for material particles.

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#### 1. INTRODUCTION

Einstein's papers on quantum theory were an important part of his creative work. In research on the quantum theory of radiation and on the interaction of radiation with matter, beginning with the fundamental 1905 paper<sup>1</sup> published in Annalen der Physik, Einstein advanced the crucial concepts of light quanta (photons) and the particle-wave duality for electromagnetic radiation. He derived a quantum explanation for the elementary processes by which radiation interacts with matter and then introduced coefficients to characterize the probabilities for optical quantum transitions (these coefficients are now called the "Einstein coefficients"); he published his well-known derivation of the Planck law; and he was the first to suggest a probabilistic interpretation of particle-wave duality. Einstein also laid the foundation for the quantum theory of the specific heat of matter. Finally, he applied to monatomic ideal gases the statistical method developed by Bose for radiation; the result was the development of quantum

statistics for systems of particles with symmetric eigenfunctions (Bose-Einstein statistics). The net result was a major contribution to the development of quantum concepts. Einstein continued to think about the problems of quantum theory to the end of his days, and he carried on a celebrated discussion with Bohr regarding the completeness of the quantum-mechanical description of events at the submicroscopic level, which in fact began during the establishment of quantum mechanics.

Einstein's papers on quantum theory are all related to each other and to his work on other questions, especially statistical thermodynamics, and these papers constitute an extremely important part of the work by this eminent figure of 20th century physics. In the extensive literature on Einstein, on the other hand, the emphasis has naturally been on his pioneering work in the theory of relativity, of which he is the primary founder. Only in a comparatively few publications has his work in quantum theory been analyzed adequately. In textbooks and monographs, his work on quantum theory is frequently described in a superficial way and occasionally incorrectly. As an example we might cite the fact that Einstein's first work<sup>1</sup> in this field is usually considered to be his paper on the photoelectric effect, although this paper devotes only a single section to this celebrated equation for the photoelectric effect (the Einstein equation), and the subject covered in the paper is incomparably broader (as was emphasized correctly by Born<sup>2</sup> and in a paper by the well-known physics historian M. Klein<sup>3</sup>). Adequate credit has not been given to Einstein's 1909 papers,<sup>4,5</sup> in which the idea of particle-wave duality for radiation was developed through an analysis of the energy and momentum fluctuations of blackbody (equilibrium) radiation. Discussions of Einstein's 1916 paper<sup>6</sup> on the probabilities for optical quantum transitions, with the crucial derivation of the Planck radiation law, have not paid adequate attention to Einstein's analysis of the problem of momentum exchange between atomic systems and radiation and Einstein's emphasis of the role of chance in a comparison of wave and particle representations (the importance of chance was singled out for particular comment by Pauli in a paper<sup>7</sup> on Einstein's contribution to quantum theory). Einstein's work has figured prominently in books tracing the development of quantum theory $^{8-10}$  (see also Ref. 11), but these books do not discuss in detail the relationship between Einstein's work on quantum theory and his other work, and they do not demonstrate the evolution of his views. There has been no comprehensive examination of the contradictions in Einstein's scientific work: In the second period of his career, while he was working on the development of a unified field theory, Einstein argued against those very ideas of the probabilistic interpretation of quantum mechanics of which he had been one of the originators.

There is a need for a further systematic study of Einstein's work on the development of quantum concepts, an analysis of the origins of this work and its relationship with the work by other founders of quantum theory, a study of the place of this work in Einstein's career, and the writing of special monographs on these questions based on Einstein's extensive correspondence and other materials. Our purpose in the present paper is to review Einstein's most important papers on quantum theory from the period 1905–1925, with special emphasis on the origins of these papers, Einstein's development of the basic quantum concepts, and the evolution of his views.

# 2. ORIGINS OF EINSTEIN'S WORK ON QUANTUM THEORY

In order to understand the formation and evolution of Einstein's ideas on quantum theory, first mentioned in his 1905 papers,<sup>1</sup> we must analyze his earlier papers of 1901-1904, and we must also analyze the situation regarding the problem of thermal blackbody radiation as it existed in 1905. It was in the development of this problem that Planck first introduced quantum concepts. We note at the outset that Einstein's papers on the theory of radiation are not a direct continuation of Planck's work but are related in a more complicated way; to a considerable extent, Einstein leaned on the work by Wien, which preceded Plank's work.

A complete analysis of the origins of Einstein's work on quantum theory requires special research, and in this paper we will discuss only certain of the most important questions, which deal with Einstein's work before 1905 and also the work by Wien and Planck on the theory of blackbody radiation.

Einstein's first papers were on the theory of molecular phenomena.<sup>12,13</sup> Already in these early papers we can see the exceptional physical intuition and the effort to work from an analysis of specific material to find general approaches to the questions under study. In his first paper Einstein took up the question of capillarity, using thermodynamic relations, and he made certain assumptions regarding the potential energy of binary interactions between molecules. Working from experimental data, he calculated the values of the constants of this interaction and drew the following conclusion: "In summary, it can be said that our fundamental assumption is justified: Corresponding to each atom is an attractive molecular field, which is independent of the temperature and independent of the method by which this atom is chemically bound to other atoms."12 In his second paper he developed the thermodynamic theory for the potential difference between a metal and a completely dissociated solution of the salt of this metal, working from the concept of conservative molecular forces in liquids and using equations from his first paper for the binary molecular potentials. This thermodynamic analysis thus had a molecular basis. Taking a similar approach, he posed the problem of a general statistical foundation for thermodynamics, and in 1902-1904 he published three papers on this problem.<sup>14-16</sup> In the first of these papers, he began as follows: "No matter how great the achievements of the kinetic theory of heat in the field of the physics of gases, this theory does not yet have a satisfactory mechanical foundation, since the laws of thermal equilibrium and the second law of thermodynamics still cannot be derived on the sole basis of the equations of mechanics and probability theory, although Maxwell and Boltzmann have nearly succeeded in achieving this aim in their theories. It is the purpose of the present paper to bridge this gap. At the same time, we find a generalization of the second law which is of considerable importance for applications of thermodynamics. In addition, a mathematical expression for the entropy is derived from the standpoint of mechanics."14 Without going into detail on these three very interesting papers, of profound physical content (the importance of these papers has been discussed by Born<sup>2</sup> and by Klein<sup>3</sup>), we must emphasize that Einstein introduced a canonical ensemble (not using this term) independently of Gibbs, with whose work he was not acquainted at the time, gave a general basis for the relationship of entropy and probability, and derived the second law of thermodynamics. Later, after he had become acquainted with Gibbs' work, Einstein wrote,17 in re-

sponse to criticism of the papers in Refs. 14 and 15 by P. Hertz, "In my opinion, preference should be given to the approach proposed by Gibbs in his book, for which the starting point is a canonical ensemble. If I had known about Gibbs' book at the time, I would not have published those papers, and I would have restricted my attention to certain particular questions." Einstein's independent development of statistical thermodynamics in a general form was to play a very important role in his further research on quantum theory. in which he made widespread use of statistical methods, which he understood thoroughly. In addition, Einstein was interested in the elementary molecular interactions in liquids and solutions, as is demonstrated by his earliest papers,<sup>12,13</sup> and he naturally arrived at the problem of the elementary interactions between radiation and matter. In several of his projects we see the characteristic combination of the use of statistical methods and a study of the elementary processes. This combination can be seen in his papers on Brownian motion<sup>18</sup> (which appeared beginning in 1905) and, especially, in his work on quantum theory, with which we are concerned in the present review.

Special note should be taken of the last few sections in Einstein's third paper on statistical thermodynamics,<sup>16</sup> which was published in 1904 and which was the direct predecessor of his 1905 papers on quantum theory,<sup>1</sup> Brownian motion,<sup>18</sup> and the special theory of relativity.<sup>19</sup> At the beginning of his paper Einstein discussed the expression for the entropy of a system, S, in terms of the probability logarithm ln W. He wrote that this expression was "completely analogous to the expression found by Boltzmann for ideal gases and introduced by Planck in his theory of radiation"<sup>16</sup> (this was Einstein's first mention of Planck's theory of radiation). In \$3 ("The meaning of the constant  $\varkappa$  in the atomic-kinetic theory"). Einstein showed that the proportionality factor between S and ln W, which he denoted by  $2\kappa$  (i.e., the Boltzmann constant k, which was first used explicitly by Planck<sup>11</sup> in 1900), was equal to the ratio of the universal gas constant R and Avogadro's number N. Einstein cited Boltzmann's work on the theory of gases and stated that "The quantity  $3\kappa$  is equal to the ratio of the average kinetic energy of an atom to the absolute temperature."<sup>16</sup> Section 4 of that paper (the penultimate section, on the "General meaning of the constant x") was extremely important. In it, Einstein analyzed the difference between the instantaneous value of the energy E and its average value  $\overline{E}$  for a system in contact with "a system having an energy infinitely large in comparison with the first system and an absolute temperature T." He introduced the quantity  $\varepsilon = E - \overline{E}$ , which he called the "energy fluctuation," and he derived the following equation for the mean square fluctuation:

 $\overline{\epsilon^2} = 2 \varkappa T^2 \frac{d\overline{E}}{dT}$ .

(1)

Einstein's further development of the concepts of thermal fluctuations in liquids and solutions led him to the theory of Brownian motion.<sup>18</sup> For our purposes in the present review, however, the point of particular interest is Einstein's application of the energy-fluctuation concept to radiation, in the last section (5) of this paper (which was in fact entitled "Application to radiation"). This step was undoubtedly an important step in the development of his ideas about radiation. At the beginning of the section he stated that Eq. (1) "would allow us to determine the exact value of the universal constant  $\kappa$  if it were possible to find the mean square value of the energy fluctuation of some system." Further on he wrote, "This is not possible, however, in our present state of understanding. It can be concluded from experiment that energy fluctuations occur at all only in physical systems of one particular type. Such a system is empty space containing thermal radiation."<sup>16</sup>

Einstein applied Eq. (1) to the case in which the space filled with the radiation had linear dimensions of the order of the wavelength  $\lambda_m$  corresponding to the maximum of the radiation energy at the given temperature T. He stated that in this case "the fluctuation of the radiation energy will be of the same order of magnitude as the radiation energy in this space," i.e., that  $\sqrt{\overline{\epsilon}^2}$  $\approx \overline{E}$ . Writing  $\overline{E} = av T^4$ , in accordance with the Stefan-Boltzmann law, where the volume is  $v = \lambda_m^3$ , and the constant is  $a = 7.06 \cdot 10^{-15}$ , Einstein found, using Eq. (1),  $\sqrt[3]{v} = 0.42/T$ . This result agrees with experiment, which yields  $\lambda_m = 0.293/T$  (it agrees with the Wien displacement law).<sup>1)</sup> Einstein concluded his paper as follows: "Consequently, both the nature of the temperature dependence and the order of magnitude of  $\lambda_m$  are determined correctly with the aid of the general molecular theory of heat. I believe that this agreement, based on our very general initial assumptions, cannot be dismissed as fortuitous."<sup>16</sup>

For Einstein, therefore, blackbody radiation was a system to which he could apply the general methods of statistical thermodynamics which he had worked out.

We turn now to questions related to the laws of blackbody radiation and to the appearance of quantum ideas (see also the monographs in Refs. 8-10 and 20 and the paper in Ref. 11).

The basic goal of the experimental and theoretical research on blackbody thermal radiation was to establish the form of the universal function describing the spectrum of the radiation energy, which we write for the spectral radiation energy density  $\rho_{\nu} = \rho_{\nu}(T)$  per unit volume per unit frequency interval (we are using the

Einstein wrote, "The quantity  $\overline{\epsilon}^2$  is a measure of the thermal stability of the system; specifically, the larger  $\overline{\epsilon}^2$ , the less stable the system. The absolute constant  $\varkappa$  thus determines the thermal stability of

<sup>&</sup>lt;sup>1)</sup>As can be easily shown, when we use the expressions for the constants in the Stefan-Boltzmann law and the Wien displacement law, with  $v = \lambda_m^3$ , we find  $\overline{E} = avT^4$  to be of the order of kT, i.e., of the order of the energy of a single photon corresponding to the wavelength  $\lambda_m$  (we are ignoring numerical factors of the order of a few units).

definition of  $\rho$  which Einstein used in his papers). The function  $\rho_{\nu}(T)$  is related to the integral radiation energy density  $\rho = \rho(T)$ , which obeys the Stefan-Boltzmann law

$$\rho = aT^4 \tag{2}$$

(a is a constant), by

$$\rho = \int_{0}^{\infty} \rho_{v} dv.$$
 (3)

The law in (2) was first established empirically in 1879 by Stefan and then derived theoretically in 1884 by Boltzmann.<sup>21</sup> Boltzmann worked starting from thermodynamics and from an equation from classical electrodynamics ( $p = \rho/3$ ) which relates the pressure of isotropic radiation, p, to its density  $\rho$ . We note that this general equation remains valid for black body radiation in quantum theory also.

An important step in the establishment of the nature of the function  $\rho_{\nu}(T)$ , which preceded the work by Planck, was the work by Wien,<sup>22, 23</sup> who (like Boltzmann) worked starting from thermodynamics and classical electrodynamics. Considering blackbody radiation in a volume with reflecting walls, and taking into account the change in the wavelength of this radiation in accordance with the Doppler principle upon reflection from the moving wall, Wien derived a law according to which the universal function  $\rho_{\nu}(T)$  should have the general form

$$\rho_{\mathbf{v}}(T) = \mathbf{v}^3 F\left(\frac{\mathbf{v}}{T}\right),\tag{4}$$

where F is an arbitrary function of the ratio  $\nu/T$ .

Wien's original papers<sup>22, 23</sup> dealt with the function  $\rho_{\lambda}(T)$  [for which Wien used the notation  $\varphi(\lambda)$ ], which was calculated per unit interval of the wavelength  $\lambda$  (this approach corresponds to writing  $\rho$  as  $\rho = \int_0^{\infty} \rho_{\lambda} d\lambda$ ), and which has the form

$$\rho_{\lambda}(T) = \frac{1}{\lambda^{5}} f(\lambda T), \qquad (5)$$

where  $f(\lambda T)$  is some arbitrary function of the product  $\lambda T$ . When we use the replacement  $\nu = c/\lambda$ , where c is the speed of light, we find Eq. (4). As Wien wrote in Ref. 22, "In the normal emission spectrum of a blackbody, each wavelength shifts in such a way upon a change in temperature that the product of the temperature and the wavelength remains constant." In particular, for the wavelength  $\lambda_m$ , which corresponds to the maximum radiation energy, we have  $\lambda_m T = \text{const.}$  This is the usual formulation of the Wien displacement law. The expression "Wien displacement law" is also used for Wien's more general equations in (4) and (5).

It is extremely important to note that in Ref. 23 Wien was studying independent monochromatic components of the radiation, and he described these components by means of not only energy densities but also entropy densities and the corresponding temperatures, which are generally different for the different monochromatic components. Wien defined the integral entropy density as the sum of the entropy densities of the monochromatic components; this integral density reaches a maximum in the case of blackbody radiation, for which the temperatures of all components are the same. Wien's results on the entropy of radiation were subsequently used by Einstein in Ref. 1 [see the text preceding Eq. (15) below].

Like the Stefan-Boltzmann law [Eq. (2)], the Wien law in (4) is a general law: It also holds for blackbody radiation in the quantum theory (the Doppler effect can of course also be explained by this theory). It is easy to verify that the law in (2) is a consequence of the law in (4) and relation (3).

The question of the specific form of the function  $F(\nu/T)$ , and thus of the unknown function  $\rho_{\nu}(T)$  [ and also the question of the value of the constant a in the law in (2), which depends on the nature of the function  $F(\nu/T)$ ], cannot be resolved on the basis of general thermodynamic and electrodynamic considerations. This is an extremely difficult problem, which cannot be solved at all by the methods of classical physics. As we are well aware, this problem was solved in 1900 by Planck, who found the radiation law

$$\rho_{\mathbf{v}} = \rho_{\mathbf{v}}(T) = \alpha \mathbf{v}^3 \frac{1}{e^{\beta \mathbf{v}/T} - 1}$$
(6)

[the "Planck equation" (see Ref. 24 and also Refs. 11 and 25); we are writing this law in the notation used by Einstein in Ref. 1].

The constants  $\alpha$  and  $\beta$  are expressed in terms of fundamental constants: the Planck constant h (which first appeared in Planck's 1899 papers<sup>10,11</sup>), the Boltzmann constant k, and the speed of light c,

$$\alpha = \frac{8\pi\hbar}{c^3} \tag{7}$$

and

$$\beta = \frac{h}{k}, \qquad (8)$$

Planck's radiation law in (6) agrees with the general form of the Wien law in (4).

As limiting cases of Planck's law we have the laws obtained for  $\beta \nu/T = h\nu/kT \gg 1$  and  $(\beta \nu/T = h\nu/kT \ll 1)$ .

In the former case, in which the energy quantum  $h\nu$  is much larger than the thermal energy kT, we have  $\exp(\beta\nu/T) \gg 1$  and

$$\rho_{\nu} = \rho_{\nu} \left( T \right) = \alpha \nu^{3} e^{-\beta \nu/T}, \tag{9}$$

This *purely quantum* radiation law had been derived back in 1896 by Wien,<sup>26</sup> on the basis of considerations related to the similarity of the Maxwell distribution of gas molecules with respect to velocity v and the spectral variation of the radiation density at large values of v/T (as was subsequently emphasized by Einstein at the beginning of the paper in Ref. 6). For a Maxwell distribution there is typically an exponential variation with the molecular velocity and the temperature, of the form  $\exp(-\gamma v^2/T)$  (where  $\gamma = M/2k$ , M is the mass of the molecule, and k is the Boltzmann constant). Wien suggested (developing ideas which had been advanced earlier, in 1887, by W. A. Michelson,<sup>27</sup> whom Wien cited) that molecules moving at a velocity v emit and

absorb light at a wavelength  $\lambda$  which is inversely proportional to  $v^2$  (i.e., the light has a frequency v proportional to  $v^2$ ). This assumption would explain the variation of the exponent with  $1/\lambda T$  (i.e., with  $\nu/T$ ), satisfying the Wien displacement law, and it would immediately yield the form of the function  $F(\nu/T)$  in (4) and radiation law (9). It is easy to see that by equating the exponent  $(-\beta \nu/T = -h\nu/kT)$  in (9) to the exponent  $(-\gamma v^2/T = -Mv^2/2kT)$  in the Maxwell distribution we would find  $Mv^2/2 = h\nu$ . In other words, this identification corresponds (from the modern standpoint) to the appearance of a photon with an energy  $h\nu$  due to the kinetic energy of the fast molecules  $(Mv^2/2 = h\nu \gg kT)$ or to the inverse process. Wien's paper<sup>27</sup> thus contained a quantum hypothesis in a hidden form (see p. 24 in the monograph by Hund<sup>8</sup>). Wien's radiation law in (9) with the empirical constants  $\alpha$  and  $\beta$  is supported well by experimental data for large values of  $\nu/T$ .

Actually, of course, the kinetic energy is not directly converted into radiation energy, as Wien suggested for gas molecules (and as Michelson had done earlier for the atoms of a solid<sup>27</sup>). Some of the relative kinetic energy of two colliding molecules is expended on exciting one of these molecules, with the subsequent emission of a photon. The inverse process can also occur: the absorption of a photon by the molecule, with a subsequent conversion of excitation energy into relative kinetic energy in a collision of the second kind.

In the second case, in which the quantum of energy  $h\nu$  is much smaller than the thermal energy kT, we have  $\exp(\beta\nu/T) \approx 1 + (\beta\nu/T), \rho_{\nu} \approx \alpha\nu^{2}T/\beta$ . Noting that we have  $\alpha/\beta = 8\pi k/c^{3}$  from (7) and (8), i.e., noting that Planck's quantum constant cancels out, we find

$$\rho_{v} = \rho_{v}(T) = \frac{8\pi v^{2}}{c^{3}} kT.$$
 (10)

This purely classical law, subsequently named the "Rayleigh-Jeans law," can of course be derived by calculating  $Z(\nu)$ , the number of oscillations of the electromagnetic field per unit frequency interval per unit volume [ it turns out to be  $Z(\nu) = 8\pi\nu^2/c^3$ ], and by assuming that the average energy associated with each such oscillation (with each oscillatory degree of freedom of the electromagnetic field) is kT (according to the classical law for the distribution of energy among degrees of freedom).<sup>28</sup> The proportionality of the spectral radiation density to the absolute temperature which is observed at high temperatures and low frequencies (at large wavelengths) played an important role in Planck's derivation of the radiation law (6). Planck was attempting to find a law which would yield, along with the Wien radiation law in (9) [with which Planck was familiar, and which held at large values of  $\nu/T$ , results which would correspond to experimental results for small values of  $\nu/T$  (there is no evidence that Planck was familiar with Rayleigh's work<sup>28</sup>; see, for example, Refs. 10 and 25).

In the derivation of the radiation law (6), Planck explicitly introduced a quantum hypothesis for the first time. It is very important to have a clear understanding of the basic assumptions used by Planck in his classical papers<sup>24</sup> (see also Refs. 11 and 25). In the first place, Planck adopted a model for the material with which the radiation (with a spectral density  $\rho_{\nu}$ ) was at equilibrium: a set of elementary electric oscillators which are in harmonic oscillation with different frequencies  $\nu$  and which exchange energy with the radiation field as the result of the resonant emission and absorption of electromagnetic waves of the appropriate frequencies. Planck systematically solved two problems for the set of such oscillators (which he referred to as "resonators"). First, there was the problem of relating  $\rho_{\nu}$  to the average energy of one resonator,  $\overline{E}_{\nu}$ . Second, there was the problem of determining this average energy for a given temperature T, common to matter and to radiation, i.e., for complete thermodynamic equilibrium.

As a result of the solution of the first problem, Planck derived the following equation, by using the methods of classical electrodynamics to analyze the absorption and emission of electromagnetic energy by the individual resonators as *continuous* processes:

$$\rho_{\mathbf{v}} = \frac{8\pi v^2}{c^3} \,\overline{E}_{\mathbf{v}}.\tag{11}$$

To solve the second problem — determining  $\overline{E}_{\nu}$ —Planck sought an expression for the average entropy of one resonator of frequency  $\nu$ , i.e.,  $S_{\nu}$ , so that he could use the thermodynamic relation between the energy and the entropy to find  $\overline{E}_{\nu}$ . He first attempted to derive Wien's radiation law in (9), since it agreed with experimental data (Planck was not satisfied with Wien's own derivation in Ref. 26). He managed to find an expression for  $S_{\nu}$  which led to the equation

$$E_{\mathbf{v}} = b\mathbf{v} e^{-a\mathbf{v}/T},\tag{12}$$

where a and b are constants). When this equation was substituted into (11), the result was Wien's radiation law in (9) (Ref. 24).

Planck's expression for  $S_{\nu}$  was<sup>24</sup>

$$S_{\mathbf{v}} = -\frac{\overline{E}_{\mathbf{v}}}{a\mathbf{v}} \left( \ln \frac{\overline{E}_{\mathbf{v}}}{b\mathbf{v}} - 1 \right), \tag{13}$$

where, as it was determined later, b = h and a = h/k. The ratio  $\overline{E}_{\nu}/b\nu = \overline{E}_{\nu}/h\nu$  is thus the average number of energy quanta, and the ratio  $\overline{E}_{\nu}/a\nu = k\overline{E}_{\nu}/h\nu$  is the average number of energy quanta multiplied by the Boltzmann constant k, in agreement with that quantization of the energy of the resonators (i.e., of the harmonic oscillators) which Planck introduced in his subsequent papers. We see that Planck was also using a quantum expression (in this case for the entropy) without knowing it.

Later on, Planck derived the law in (6), which also holds at small values of  $\nu/T$  (after he had first derived it by a semiempirical method). For this purpose he determined the average entropy of a resonator,  $S_{\nu}$ , starting from the Boltzmann equation  $S=k \ln W$  relating the total entropy of the set of resonators of a given frequency, S, and the probability W, and using the fundamental hypothesis that the resonators have discrete energies. According to this quantum hypothesis of Planck, a resonator oscillating at a frequency  $\nu$  could take on only those energies which were equal to some integral multiples of amounts of energy  $\varepsilon = h\nu$  (or energy quanta, as they subsequently came to be known). In other words, the possible energies of an individual resonator are

 $E_{v} = n\varepsilon = nhv,$ where *n* is an integer. (14)

The expression which Planck derived for the average resonator entropy<sup>24</sup> by the probabilistic treatment was more general than Eq. (13). This more general equation led to the consequence  $E_{\nu} = h\nu/[\exp(h\nu/kT) - 1]$ , and a substitution into (11) led to Planck's radiation law in (6) with all the constants.

We should emphasize that Planck's quantum hypothesis in (14) dealt with the quantization of the energy of matter and that Planck treated the absorption and emission of radiation as continuous, in accordance with classical electrodynamics. It is also important to note that Planck was not interested in the specific elementary processes by which the radiation interacted with the matter. These resonators were simply a model which he needed to derive the radiation laws. In particular, he wrote, "It is totally irrelevant whether the oscillations of the elementary resonators are based on conduction currents (in the absence of an electrical resistance, of course) or convection currents (the motion of electrically charged particles)."24 In writing the law in (14) for the quantization of the resonator energy. Planck was not yet thinking about the application of this law to particular atomic systems.

An understanding of these aspects of Planck's approach is very important for analyzing the new ideas which Einstein contributed to quantum theory.

# 3. QUANTIZATION OF RADIATION ENERGY (EINSTEIN'S 1905 PAPER)

It is natural to begin a discussion of Einstein's work on quantum theory with a detailed and systematic analysis of his 1905 paper,<sup>1</sup> in which he first advanced the revolutionary idea of *quantization of radiation energy*. This idea was embodied in the hypothesis of light quanta, which was the major point of that paper (rather than an explanation of the laws for the photoelectric effect; see the discussion above). It is this paper which marked the beginning of the quantum theory of radiation.

Einstein waited no further than the brief introduction to that paper to contrast very clearly the wave theory of light, based on continuity of the electromagnetic field ("which operates with continuous spatial functions"), and the corpuscular theory of light, "excellently justified by its description of purely optical phenomena" according to which "the energy of the light is distributed over space in a discrete manner" and which, in Einstein's opinion, gave a better description of the "phenomenon of the appearance and conversion of light" (Ref. 1).<sup>2)</sup> At the end of the introduction, Einstein wrote, "Below I will describe the direction taken by my thoughts and those facts which led me along this direction, hoping that the opinion offered here ["a heuristic point of view," as indicated in the title of the paper (M.E.)] may be of some use to other investigators in their research."

Of the nine sections of that paper, which was extremely original and rich in content, the first six dealt with the approach to corpuscular ideas regarding radiation and the foundation of these ideas. The last three sections dealt with applications of these ideas regarding light quanta ("photons" in the modern terminology; Einstein used the terms "quantum of energy" and "quantum of light") to the processes by which light appears and is converted.

In \$1 ("On a difficulty in the theory of 'blackbody radiation' ") Einstein analyzed from the classical standpoint the equilibrium between radiation and a material containing "resonator electrons". According to the kinetic theory of gases, the average energy of the vibrational motion of a resonator electron per degree of freedom should be (R/N)T (Einstein did not introduce the Boltzmann constant k; he wrote R/N instead). Using the "dynamical-equilibrium condition" in (11), which had been derived by Planck, Einstein obtained Eq. (10), i.e., the Rayleigh-Jeans law, assuming  $\overline{E}_{\mu} = (R/N)T$ [he cited Planck's paper "On irreversible radiation processes,"24 in which Planck derived the Wien radiation law, working from Eq. (13) for the entropy]. Einstein immediately showed that the condition  $\int_0^{\infty} \rho_{\nu} d\nu = \infty$ holds in this case, and he emphasized that Eq. (10) "not only contradicts experiment but in fact asserts that in our picture [i.e., in the classical picture (M.E.)] we cannot even contemplate any unambiguous distribution of energy between the ether and matter." We thus see that Einstein not only derived the Rayleigh-Jeans law independently but also clearly identified the "ultraviolet catastrophe.'

It is pertinent to note here that neither Planck, in the derivation of Eq. (11), nor Einstein later, in the derivation with the aid of this equation of Eq. (10), treated the expression  $8\pi\nu^2/c^3 = Z(\nu)$ , which appears in Eq. (11), as the number of eigen-oscillations of the electromagnetic field. They treated this expression as simply a proportionality factor relating the spectral density of the radiation,  $\rho_{\nu}$ , to the average energy of the resonator which emits and absorbs this radiation,  $\vec{E}_{\nu}$ . According to classical ideas, the average energy per oscillatory degree of freedom at equilibrium between the radiation and matter should be the same, equal to kT for both the resonators used in the model for the matter and for the eigen-oscillations of the radiation field. For this reason, both approaches-that of Einstein on the one hand and that of Rayleigh, Lorentz, and Jeans,<sup>28</sup> on the other-lead to the result in (10), which is contradicted by experiment at large values of  $\nu/T$ .

In \$2 of that paper there was a further analysis of the limiting classical case of small values of  $\nu/T$  ("On Planck's definition of elementary quanta"). At the beginning of this short section, Einstein wrote: "We will now show that the definition of elementary quanta given

<sup>&</sup>lt;sup>2)</sup>See also Ref. 11, where the entire quotation is given and where the translation from the German original is refined.

by Planck is to some extent independent of the theory which he has derived for blackbody radiation." Then Einstein gave the Planck equation, describing it as "consistent with all experiments which have been carried out to date," in the form in (6), with the numerical values of the constants  $\alpha$  and  $\beta$ . Here Einstein cited Planck's paper "On the energy distribution law in a normal spectrum."<sup>24</sup>

It should be noted (as will be seen below) that the subject here is not the energy quantum  $h\nu$  (in that paper, Planck spoke of an "element of energy"  $\varepsilon = h\nu$ , not yet calling it a "quantum of energy") but the discrete structure of matter and the determination of Avogardro's number N, which Planck has discussed in his paper "On the elementary quantum of matter and electricity."<sup>24</sup>

For small values of  $\nu/T$ , Einstein derived the limiting form of Eq. (6),  $\rho_{\nu} = (\alpha/\beta)\nu^2 T$ , and compared it with Eq. (10), which he had found in the preceding section (with k = R/N). This comparison led him to the value  $N = 6.17 \cdot 10^{23}$  or "precisely the same value as found by Planck" (in the paper just cited).

Einstein finished his analysis of the classical case with the following conclusion: "The higher the energy density and the longer the radiation wavelength, the firmer the foundations for our theory. At short wavelengths and low energy densities, however, these foundations disintegrate completely." Einstein later took up precisely this limiting case of large values of  $\nu/T$ , which is the purely quantum case, in which the Wien radiation law in (9) holds. Einstein wrote, "Below, 'blackbody radiation' will be discussed in connection with experiment, and not on the basis of any ideas regarding the appearance and propagation of radiation."<sup>1</sup> Here Einstein did not build on Planck's work, and he cited it no further. Einstein's approach was fundamentally different from Planck's. While Planck expressed [through (11)] the radiation density  $\rho_{\nu}$  in terms of the average resonator energy  $\overline{E}_{\nu}$ , which is a characteristic of the properties of the material, and which is found as a function of the average entropy of the resonator  $S_{\nu}$ , and used the Boltzmann relation for matter to determine this average entropy, Einstein used the radiation density to find the radiation entropy as a function of the volume and, also using the Boltzmann relation, but applied to the radiation itself, identified the physical meaning of the expression found for the entropy. He reached the fundamental conclusion that radiation exhibits corpuscular properties at large values of  $\nu/T$ . This analysis was carried out in \$\$3-6 of Einstein's paper, and it is extremely instructive to follow his arguments in greater detail.

At the beginning of \$3 ("On the entropy of radiation") Einstein wrote, "The discussion which follows is contained in the famous paper by W. Wien and is reproduced here simply for completeness of exposition." Here he was talking about Ref. 23 (see the discussion above, p. 558), and it should be noted that Einstein discussed the question in a slightly different form than in Wien's paper. For radiation occupying a volume v, Einstein considered the spectral entropy density  $\varphi_{\nu}$  as a function of the spectral energy density  $\rho_{\nu}$  and the frequency<sup>3</sup>  $\nu$ . He defined the total radiation entropy S as a function additive in the frequencies, following Wien, by means of the equation  $S=v\int_{0}^{\infty}\varphi_{\nu}d\nu$ , and he found the maximum of the entropy density  $\int_{0}^{\infty}\varphi_{\nu}d\nu$  at a constant energy density  $\int_{0}^{\infty}\rho_{\nu}d\nu$ , corresponding to blackbody radiation. For this radiation, Einstein derived the following relation, using the relation dS=dE/T between an entropy increment dS and the heat supplied, dQ=dE, for a reversible isochoric process:

$$\frac{\partial \varphi_{\mathbf{v}}}{\partial \rho_{\mathbf{v}}} = \frac{1}{T} \,. \tag{15}$$

This equation holds for all values of the frequency. Regarding Eq. (15) Einstein wrote, "This equation is the law for blackbody radiation. Consequently, the function  $\varphi_{\nu}$  can be used to determine the law of blackbody radiation; conversely, by integrating this law and using  $\varphi_{\nu}$ =0 at  $\rho_{\nu}$  = 0, we can find the function  $\varphi_{\nu}$ ."4) This problem of finding the entropy of blackbody radiation  $\varphi_{\mu}$ from the known energy of this radiation,  $\rho_{\nu}$ , was the subject of \$4 ("Limiting law for the entropy of monochromatic radiation for a low radiation density"). Einstein worked from Wien's radiation law in (9), noting that although this law "does not hold exactly" it is "supported very well by experiment for large values of the ratio  $\nu/T$ ." Einstein thus treated Wien's law as an experimental law, and only much later, in 1916, did he mention<sup>6</sup> Wien's derivation of Eq. (9) (see p. 558 and, for more details, p. 571).

Einstein first determined the quantity  $1/T = -(1/\beta\tau) \ln(\rho_{\nu}/\alpha\nu^{3})$ ; in accordance with the law in (9). Substituting it into (15) and integrating, he found an equation for  $\varphi_{\nu}$ ; when this quantity is multiplied by the volume v and by  $d\nu$ , the result is  $S = v\varphi_{\nu}d\nu$ , the entropy of the radiation in the frequency interval from  $\nu$  to  $\nu + d\nu$ , with an energy  $E = v\rho_{\nu}d\nu$ . Einstein found the following equation for the variation of the entropy with the volume;

$$S - S_0 = \frac{E}{h_{\rm W}} \ln \frac{v}{r_{\rm e}}, \qquad (16)$$

where  $S_0$  is the entropy of the radiation filling the volume  $v_0$ . This expression, which shows "that the entropy of monochromatic radiation of sufficiently low density depends on the volume in the same manner as the entropy of an ideal gas or a dilute solution," was subsequently interpreted by Einstein "on the basis of a principle introduced in physics by Boltzmann, according

<sup>&</sup>lt;sup>3)</sup>In this and the following sections, Einstein wrote  $\varphi_{\nu}$  and  $\rho_{\nu}$  as simply  $\varphi$  and  $\rho$ . For clarity, we will retain the subscript  $\nu$  for spectral quantities, to distinguish them from integral quantities.

<sup>&</sup>lt;sup>4)</sup>Equation (15) was derived by Planck in his 1900 paper "Entropy and the temperature of radiant energy" (Ref. 4, §§5 and 6). Planck used this equation to find  $\rho_{\nu}$ , knowing  $\varphi_{\nu}$  (in Planck's notation,  $\rho_{\nu} = \mathscr{A}$  and  $\varphi_{\nu} = \mathscr{L}$ ).

to which the entropy of a system is a certain function of the probability of the state of this system."

The next section, \$5 ("Study of the dependence of the entropy of gases and dilute solutions on the volume in the molecular theory"), begins with an important general comment: "In a calculation of the entropy by the methods of molecular theory the word 'probability' is frequently used in a sense which is not the definition given it in probability theory. A particularly frequent assumption is the 'case of equal probability' where from the theoretical point of view the problem is sufficiently definite so that one does not need to introduce a hypothesis and argue by deduction." Einstein later examined the question of which states are assumed equiprobable in an analysis of the Planck radiation equation in Refs. 29, 30, and (especially) in Ref. 4. This analysis turned out to be extremely important for bringing out the quantum behavior (see pp. 564 and 566 below).

Einstein later gave a general formulation of the Boltzmann principle. He derived the basic equation

$$S - S_0 = \frac{R}{N} \ln W, \tag{17}$$

where W is the relative probability for the state with entropy S, from a general analysis of two noninteracting systems with entropies  $S_1(W_1)$  and  $S_2(W_2)$ , where  $W_1$  and  $W_2$  are the probabilities for the instantaneous states of these systems. He also assumed that the entropies were additive  $(S = S_1 + S_2)$  and that the probabilities were multiplicative  $(W = W_1 W_2)$ . For the particular case of *n* independent particles, e.g., an ideal gas or dilute solution filling a volume  $v_0$ , the probability that all *n* particles will be in a volume *v* which is some part of the total volume  $v_0$  is

$$W = \left(\frac{v}{v_0}\right)^n ; \tag{18}$$

and, according to Eq. (17),

$$S = S_0 - R \frac{n}{N} \ln \frac{v}{v}.$$
 (19)

Einstein emphasized that "... no assumptions of any kind regarding the motion of the molecules were necessary... to derive this relation."

Equation (16) was compared with Eqs. (17)-(19) in §6 ("Interpretation of the expression for the volume dependence of the entropy of monochromatic radiation obtained on the basis of the Boltzmann principle"), and the fundamental consequences of this comparison were studied. It is this section which contains the hypothesis of quanta of light and which is the central section of Einstein's fundamental paper.<sup>1</sup> When Eq. (16) is written in the form

$$S - S_0 = \frac{R}{N} \ln \left[ \left( \frac{r}{v_0} \right)^{\frac{N}{R} \frac{E}{\beta v}} \right] , \qquad (19')$$

and a comparison with the general equation, (17), is made, it is found that

$$W = \left(\frac{v}{v_0}\right)^{\frac{N}{R}} \frac{\varepsilon}{\beta v}, \qquad (20)$$

in complete analogy with Eq. (18). Correspondingly, Einstein drew the conclusion, "Monochromatic radiation of a low density (within the range of applicability of the Wien radiation law) in the sense of the theory of heat behaves as if it consisted of independent quanta of energy of size  $R\beta\nu/N$ " (i.e., since R/N=k,  $\beta=h/k$ , and  $R\beta/N=h$ , then it would consist of quanta of size  $h\nu$ ; thus the quantity  $NE/R\beta\nu = E/h\nu$  is the number of quanta of light).

Einstein also calculated the average energy of the "quanta of energy of 'blackbody radiation," which is 3(R/N)T (i.e., 3kT) according to Wien's law, (9), and he compared this energy with the average kinetic energy of the motion of the center of gravity of a molecule, (3/2)RT/N [i.e., (3/2)kT].

At the end of \$6 Einstein wrote, "If, however, monochromatic radiation (of sufficiently low density) behaves in the sense of the volume dependence of the entropy as if it were a discrete medium consisting of quanta of energy of size  $R\beta \nu/N$ , then the question suggests itself of whether the laws governing the appearance and conversion of light are of such a nature that they correspond to light consisting of similar quanta of energy." The last three sections of the paper of Ref. 1 dealt with the laws governing the appearance and conversion of light which follow from the hypothesis of quanta of light. Here Einstein dropped the statistical approach to the laws for blackbody radiation and turned instead to the elementary processes by which radiation interacts with matter, working from the concept of discreteness of radiant energy and, correspondingly, the discreteness of the absorption and emission processes themselves.

In \$7 ("The Stokes rule"), Einstein gave a very simple explanation for a relation which had been established by Stokes back in 1852 for photoluminescence. This is the Stokes law or rule, according to which the wavelength of the emitted light,  $\lambda_2$ , is larger than that of the absorbed light,  $\lambda_1$ , or equal to it; i.e., the frequency  $\nu_2 = c/\lambda_2$  is lower than the frequency  $\nu_1 = c/\lambda_1$  or equal to it. If the emitted quantum of light arises solely from the absorbed quantum of light, then energy conservation would require  $h\nu_2 \leq h\nu_1$  (or  $R\beta\nu_2/N \leq R_{\beta}\nu_1/N$ , in Einstein's notation), i.e.,  $\nu_2 \leq \nu_1$ . "This is the well-known Stokes rule," wrote Einstein. He emphasized that "in the case of weak illumination the amount of excited light should-under otherwise equal conditions-be proportional to the intensity of the exciting light," and he pointed out that deviations from the Stokes rule were possible in two cases. The first case is that in which the density of quanta of light is so high that "one quantum of excited light can acquire its energy from many exciting quanta." The second case is that in which there is a deviation from Wien's law, e.g., when "the light is emitted by an object at such a high temperature that Wien's law does not hold for the given wavelength." The first of these cases corresponds to a nonlinear variation of the intensity of the excited light with the intensity of the exciting light; processes of this type-many-photon processes-are of course under widespread study at present. In the second case, the condition  $h\nu \gg kT$  does

not hold; the size of the emitted quantum may be increased at the expense of the thermal energy of the luminescing object (anti-Stokes photoluminscence). We have here an example of Einstein's profound analysis of the essence of the pertinent elementary processes.

In §8 ("On the excitation of cathode rays during the illumination of solids"), Einstein analyzed the photoelectric effect under the assumption "that the exciting light consists of quanta with an energy  $(R/N)\beta\nu$ " (i.e.,  $h\nu$ ). He assumed that "one quantum of light transfers all its energy to one electron" and that "each electron emitted from the object should perform a certain amount of work P (which is a characteristic of the given object)." In other words, Einstein was introducing the concept of the work function. Equating the maximum kinetic energy of the emitted electron,  $R\beta\nu/N - P$ , to the quantity  $\Pi\varepsilon$ , where  $\Pi$  is the magnitude of the retarding potential, and  $\varepsilon$  is the electron charge, Einstein derived his famous equation for the photoelectric effect in the form  $\Pi\varepsilon = R\beta\nu/N - P$  or, in modern notation,

$$eV = hv - P. \tag{21}$$

He wrote, "If this equation is correct, then II would be described as a straight line when plotted as a function of the frequency of the exciting light in Cartesian coordinates, and the slope of this line would be independent of the nature of the particular material." We know that this linear law, from which the ratio h/e can be determined, was subsequently tested very carefully by Millikan (in 1916), by Lukirskii and Prilezhaev (in 1928), and by others.

Einstein noted that regarding the range of applicability of the laws for the photoelectric effect "... it would be possible to make the same comments as regarding the assumed deviations from the Stokes rule." He also stated that in cathode luminescence—the inverse of the photoelectric effect—a large number of quanta of light could be generated from the kinetic energy of a single electron at high accelerating voltages.

In the last section of his paper (§9, "On the ionization of gasses by ultraviolet light"), Einstein used the example of the ionization of individual gas molecules by quanta of ultraviolet light to analyze the question of the number of such processes. If each absorbed quantum causes the ionization of one molecule, then the number of ionized molecules is simply equal to the number of absorbed quanta. This was the original form of the photochemical-equivalent law, which Einstein subsequently formulated for photo-chemical processes.<sup>31</sup>

#### 4. EINSTEIN'S ANALYSIS OF PLANCK'S EQUATION; QUANTIZATION OF THE ENERGY OF MATTER (EINSTEIN'S 1906–1907 PAPERS)

As we saw from the analysis of Einstein's first paper on the quantum theory of radiation, the central concept was the quantization of the energy of radiation, which was based on a statistical analysis of thermal radiation in the limiting case of large  $\nu/T$ . Einstein put a foundation under this concept by working from Wien's law, (9) which holds at large values of  $\nu/T$  and which is of a purely quantum nature. He successfully applied this concept to an analysis of the elementary processes by which radiation interacts with matter, interpreting these processes as discrete processes. At this point, however, the relationship between his approach and Planck's approach—*the quantization of the energy of matter* had not yet been recognized. Einstein developed this relationship in his papers<sup>29, 30</sup> of 1906 and 1907, whose important result was the creation of the basis for a quantum theory of specific heat.

At the beginning of the first of these papers, which was a short but extremely important one,<sup>29</sup> consisting of only two sections, Einstein wrote as follows about his earlier paper (Ref. 1) in which he had "reached the conclusion that light of frequency  $\nu$  can be absorbed and emitted only in quanta of energy  $(R/N)\beta \nu''$ : "Then it seemed to me that Planck's radiation theory [here, as in Ref. 1, Einstein was citing Planck's paper "On the law of the energy distribution in a normal spectrum,"<sup>24</sup> (M.E.)] stands in a certain sense in opposition to my own work. However, the new considerations in \$1 of this paper demonstrate that the theoretical basis of Planck's theory differs from that which would follow from Maxwell's theory and the theory of electrons. Planck's theory actually makes implicit use of the hypothesis of quanta of light mentioned above.

Einstein entitled \$1 of Ref. 29 "Planck's radiation theory and light quanta." He began this section by writing out the Rayleigh-Jeans law, (10), which "contradicted experiment," and raised the question as to why Planck was led to Eq. (6) instead of the Rayleigh-Jeans law. Then Einstein turned to Eq. (11),  $\vec{E}_{\nu} = (c^3/8\pi\nu^2)\rho_{\nu}$ , which had been derived by Planck. He showed that, while the average resonator energy  $\vec{E}_{\nu}$  was determined with the help of an expression for the entropy S which had been found in Ref. 15 on the basis of statistical thermodynamics, Planck's equation (6) was derived only when the assumption was made that the resonator energy was discrete. Einstein concluded: "We can thus assume that Planck's theory is based on the following assertion.

The energy of an elementary resonator can take on only those values which are equal to the quantity  $(R/N)\beta\nu$  multiplied by some integer. The energy of the resonator changes discontinuously during absorption and emission—specifically, by a value which is equal to  $(R/N)\beta\nu$  multiplied by an integer."

Einstein was thus emphasizing that the quantization of the energy of the resonator implied that the absorption and emission processes were discrete (this discrete nature of these processes had been found by Einstein himself in Ref. 1, from the assumption that the radiation energy was discrete; cf. Ref. 11).

Einstein went on to draw a second important conclusion: "If the energy of a resonator can change only discontinuously, then we cannot use the ordinary theory of electricity to find the average energy of a resonator in a radiation field, because the theory does not contain any *special* [Einstein's italics (M.E.)] values of the energy. This assumption is thus embodied in Planck's theory.

Although Maxwell's theory cannot be applied to elementary resonators, the *average* energy of an elementary resonator in the radiation field is equal to the energy calculated from Maxwell's theory of electricity."

Einstein pointed out that  $\overline{E}_{\nu}$  was much smaller than  $\varepsilon = h\nu$  in the range in which Wien's radiation law, (9), held; in other words, only a very few resonators had a nonzero energy.

Einstein summed up the situation in the following manner:

"The discussion above does not, in my opinion, refute Planck's theory of radiation; on the contrary, it apparently shows that Planck introduced in his theory of radiation a new hypothetical element—the hypothesis of light quanta."

We see that Einstein was emphasizing that an important feature of Planck's theory was the relationship between the discrete nature of absorption and emission, on the one hand, and the assumption of special discrete—values of the resonator energy, on the other, i.e., the quantization of the energy of matter. This concept of the discreteness of the energy of matter was subsequently developed in a paper by Einstein<sup>30</sup> which was published in early 1907.

In §2 of Ref. 29 ("Expected quantitative relationship between the threshold for the photoelectric effect and the electromotive series of Volta"), Einstein first derived an equation for the contact potential difference  $V_{12}$  at the boundary between two metals. According to this equation, which was based on the theory of the photoelectric effect which Einstein had set forth in Ref. 1 (see p. 563, Eq. (21) above), the quantity  $eV_{12}$  is equal to the difference between the work functions of the corresponding metals [Einstein introduced the potentials  $V_1$  and  $V_2$ , which correspond to the frequency boundaries of the photoelectric effect,  $\nu_1$  and  $\nu_2$ , in accordance with (in modern notation)  $V_1 = h\nu_1/e$  and  $V_2 = h\nu_2/e$ , where in the case V = 0 we have  $h\nu_1 = P_1$  and  $h\nu_2 = P_2$ , in accordance with Eq. (21)].

Einstein began Ref. 30 by citing his earlier papers<sup>1, 29</sup> in which he had arrived at "a new point of view regarding the absorption and emission of light," and he described the contents of that paper<sup>30</sup> as follows: "In this paper it will be shown that the theory of radiation—especially Planck's theory—leads to a change in the molecularkinetics theory which makes it possible to eliminate certain difficulties with which this theory has previously been afflicted" [he was talking about the specific heat (M.E.)].

First, Einstein used results from his 1903 paper on statistical thermodynamics<sup>15</sup> to give a very simple and fundamentally important "derivation of an equation for the average energy of a Planck resonator which clearly shows the relationship with molecular mechanics." In the case of thermodynamic equilibrium, he used a general equation for the probability dW that the energy E of a subsystem constituting a small fraction of the entire system and described by the independent variables

$$P_{\nu}$$
 ( $\nu = 1, 2, \ldots, m$ ) would lie between E and  $E + dE$ :

$$W = Ce^{-(N/kT)E}\omega (E) dE, \qquad (22)$$

where

d

$$\omega(E) dE = \int_{dE} dp_1 \dots dp_m$$
<sup>(23)</sup>

and where the "integral extends to all combinations  $p_{\nu}$  corresponding to energies between E and E + dE." Einstein was thus considering a general form of the Boltzmann distribution; on the choice of the function  $\omega(E)$ , i.e., on which states were assumed to be equiprobable (see p. 561 above), would depend the particular nature of the distribution function and the average values of physical quantities. For a particle which is executing linear harmonic oscillations, the energy is  $E = ax^2 + b\xi^2$ , where x is the instantaneous distance from this particle to the equilibrium position, and  $\xi$  is the instantaneous velocity (a and b are constants). Equation (23) gives us  $\int_{dE} dx d\xi$  = const dE and thus  $\omega(E)$  = const, and the average energy according to (22) is

$$\overline{E} = \frac{\int E e^{-(N/RT)E} dE}{\int e^{-(N/RT)E} dE} = \frac{RT}{N}.$$
(24)

For an "ion which is vibrating along a straight line," and when Eq. (11) is used (Einstein cited Planck's paper "On irreversible radiation processes," as in Ref. 1; see Ref. 24), this equation leads to Eq. (10), to which Einstein first referred as the "Rayleigh equation." He emphasized that this equation was valid "of course, only in the limiting case of large  $T/\nu$ ."

"In order to arrive at the Planck theory for the radiation of an absolute blackbody," Einstein (citing Planck's lectures on the theory of thermal radiation,<sup>32</sup> which appeared in 1906) retained Eq. (11), making the assumption "that Maxwell's theory of electricity correctly reproduces the relationship between the radiation density and  $\vec{E}$ ," but he discarded Eq. (24), assuming "that the use of molecular-kinetics theory leads to a contradiction with experiment." He worked from Eq. (22) "of the general molecular theory of heat" and, instead of  $\omega$ = const, assumed  $\omega = 0$  for all values of E except those values between 0 and  $0 + \alpha$ , between  $\varepsilon$  and  $\varepsilon + \alpha$ , between  $2\varepsilon$  and  $2\varepsilon + \alpha$ , etc., where  $\alpha$  is infinitesimally small in comparison with c. For these intervals he equated the integrals  $\int \omega dE$  to a constant A, noting that he was "thereby assuming that the energy of this elementary formation takes on only those values which are only infinitesimally different from 0,  $\varepsilon$ ,  $2\varepsilon$ , etc." The average value of the energy turns out to be

$$\overline{E} = \frac{\int Ee^{-(N/RT)E} \omega(E) dE}{\int e^{-(N/RT)E} \omega(E) dE}$$

$$= \frac{0 + Aee^{-(N/RT)E} + A2ee^{-(N/RT)2e} + \dots}{A + Ae^{-(N/RT)e} + Ae^{-(N/RT)2e} + \dots} = \frac{e}{e^{(N/RT)e} - 1},$$
(25)

or, with  $\varepsilon = (R/N)\beta \nu = h\nu$  ("according to the hypothesis of quanta"),

$$\overline{E} = \overline{E}_{\mathbf{v}} = \frac{(R/N)}{e^{\beta N/T} - 1} = \frac{hv}{e^{hv/kT} - 1} , \qquad (26)$$

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so that Planck's equation, (6), is found when (11) is used. Einstein stated that Eq. (26) "gives the temperature dependence of the average energy of a Planck resonator." While Planck's derivation of this equation had been rather complicated, Einstein obtained it immediately by applying the Boltzmann distribution in (22) to quantized states. It is important to note that the simplicity of the derivation was the result of the general and physically justified approach taken by Einstein.

Einstein reached a very important general conclusion: "Up to this point it has been assumed that the motion of molecules obeys precisely the same laws as are obeyed by the motion of the objects in our everyday lives (with only the postulate of total reversibility added), but now it becomes necessary to assume that for those ions which are vibrating at a certain frequency and which are participating in energy exchange between matter and radiation the set of states which these ions can take on is smaller than for the objects of our everyday lives." Here is manifested Einstein's deep understanding of the need to abandon classical mechanics in order to describe the motion of these submicroscopic particles.

Einstein went on to ask, "If those elementary formations whose existence is assumed in the theory of energy exchange between radiation and matter cannot be understood in terms of the present-day molecularkinetics theory of heat, does it not follow that we should also change the theory for other periodically oscillating formations which are dealt with by the molecular theory of heat?" Einstein answered this question in the affirmative, and-assuming that the energy of the vibrational motion of atoms in a solid about their equilibrium. positions was quantized—he derived a theory for the specific heat of solids. For the simplest model, of independent vibrations of the various atoms, Einstein assigned three vibrational degrees of freedom to each atom, finding three times the value in (26) for the average vibrational energy per atom; for a gram-atom he found the energy

$$3R \frac{\beta v}{\epsilon^{\beta v/T} - 1}.$$
 (27)

When this expression is differentiated with respect to the temperature T and summed "over all species of vibrating formations which exist in the given solid," it gives the specific heat as a function of the temperature. At low temperatures, this specific heat vanishes. We will not go into detail here concerning Einstein's development of the quantum theory of specific heat, which began in this paper and which was pursued by other scientists, in particular Debye and, independently, Born and Kármán (see, for example, Klein's paper<sup>33</sup> and also Ref. 10). We would simply like to point out that Einstein was the first to suggest that ions were vibrating in a solid and to calculate the vibration frequencies from the specific heat; these frequencies should be found in the infrared spectra. In particular, for diamond he predicted an infrared absorption peak at  $\lambda = 11 \mu$ . In Ref. 34, however, he rejected his assumption in Ref. 30 "that the heat carriers in solids (insulators) probably consist of only positively charged atomic ions." Einstein stated that "it is extremely likely that there may be uncharged heat carriers which do not participate in optical phenomena." He reached the conclusion, "Then according to the theory it would be expected that either diamond would have an absorption peak at  $\lambda = 11 \mu$  or in diamond there would be no optically observable infrared eigenfrequency at all." We see that Einstein was trying to construct as specific a model as possible for the elementary processes which occur in solids. We also note that Einstein always rejected his own assertions if he found them to be incorrect (see, for example, the two papers in Ref. 35; in the second of these papers, he rejected some assumptions he had made in the first).

#### 5. PARTICLE-WAVE DUALITY FOR RADIATION AND FURTHER DEVELOPMENT OF QUANTUM CONCEPTS (EINSTEIN'S PAPERS IN 1909-1915)

A further development of Einstein's ideas regarding the properties of radiation was reported in two remarkable papers which he published in 1909 in *Physikalische Zeitschrift*. These papers contained the first discussion of the particle-wave duality for radiation a very important step in the development of quantum ideas in general (see Hund's monograph<sup>8</sup> and the paper by Klein in Ref. 3; see also Ref. 11).

We will examine the basic arguments and the extremely important results of those papers. But we will be able to trace only partially the relationships between these papers and Einstein's papers on statistical thermodynamics and the theory of fluctuations (the relationship with both Refs. 14-16 and 18 on the one hand, and the short but important 1907 paper in Ref. 36, on the other, where Einstein took up the question of the probabilities for deviations from thermodynamic equilibrium); this topic requires a separate analysis.

At the beginning of his paper of Ref. 4 on the radiation problem, Einstein noted that Lorentz, Jeans, and Ritz had recently "been publishing in this journal [he was talking about the papers published in *Physikalische Zeitschrift* in 1908 (M.E.)] their opinions on this extremely important problem, making it simpler to give a critical interpretation of the present state of this problem." Einstein set forth his arguments point by point (there were ten of them altogether), "feeling it would be useful to have a discussion among the scientists seriously involved in this problem, even if the discussion does not lead to a final settlement of the matter."

In point 1 Einstein discussed the question of retarded potentials in electrodynamics, whose equations he treated, in contrast with Ritz,<sup>37</sup> as "simply auxiliary mathematical equations." Einstein believed that it is not possible to "assert the irreversibility of *elementary* electromagnetic phenomena." We note that it was also in 1909 that Einstein and Ritz jointly published a note<sup>38</sup> in which they stated their difference in views. At the end of this note it was stated that "... Ritz treats this limitation in the form of retarded potentials as one of the sources of the second law of thermodynamics, while Einstein considers that the irreversibility rests exclusively on probabilistic foundations." Einstein's comments reflect his interest in the relationship between the statistical laws and the laws for elementary processes.

In point 2 Einstein wrote that "the opinion of Jeans [the statistical treatment of the natural oscillations of an electromagnetic field; see p. 559 (M.E.)] can be contrasted with the assertion that it is apparently not correct to apply the general results of statistical mechanics to a cavity filled with radiation." Citing his own paper,<sup>1</sup> Einstein stated that the law in (10) ("the law derived by Jeans") can also be derived from Eq. (11), which relates  $\rho_{\nu}$  and  $\overline{E}_{\nu}$ , for an "oscillating ion" and from the equation  $\overline{E}_{\nu} = RT/N$ , which "necessarily follows from the molecular theory of heat" (see p.560).

Then, in point 3, Einstein emphasized that "there can be no doubt that our present understanding necessarily leads to the law defended by Jeans" [i.e., the law in (10)] and that "with equal confidence we can assert" that this law contradicts experiment. In point 4 Einstein asked, "What is the relationship between Planck's theory of radiation and the theory mentioned in point 2, which is constructed from the present accepted theoretical positions?" (i.e., the classical theory). Einstein wrote that "... In my opinion, the answer to this question is complicated by the fact that Planck's theory is logically somewhat incomplete." Pursuing the thoughts expressed previously in Refs. 1, 29, and 30. Einstein analyzed the question of determining the probability of a state, W, by working from the Boltzmann equation S  $= (R/N) \ln W + \text{const.}$  As Einstein emphasized, "Neither Boltzmann nor Planck gave a definition of W," simply "making the purely formal assumption that W was equal to the number of 'configurations' of the given state.' Einstein showed that if Planck had chosen configurations "such that they were equiprobable in his theoretical picture based on the statistical distribution" he would have arrived at the Rayleigh-Jeans law, (10). Einstein concluded this very important point with the following words: "No matter how overjoyed every physicist might be that Planck fortunately dropped this requirement, still it should not be forgotton that Planck's radiation equation is incompatible with the theoretical foundations on which Planck built." We see that Einstein was involved in an extremely profound analysis of the Boltzmann and Planck relations from a general standpoint.

In point 5, which was short but very important, Einstein cited his papers in Refs. 29 and 36 and showed "how the starting points of Planck's theory could be changed so that the Planck radiation formula would actually be a consequence of the theoretical starting points." First, it was necessary to retain Eq. (11), "derived by Planck from Maxwell's theory" (in an important comment Einstein stated that there could hardly be any doubt that the "electromagnetic theory of radiation gives, at least, the correct time averages"). Second, it was necessary to "alter the statistical theory of heat by introducing the following hypothesis: An electrically charged system which is capable of converting radiation energy into the energy of matter and back by executing vibrations at a frequncy  $\nu$  cannot be in vibrational states of just any arbitrary energy but only those for which the energy is a multiple of  $h\nu$ . Here h is the constant introduced by Planck in his radiation equation" (cf. Refs. 29 and 30; see pp. 563 and 564 above). Beginning with this paper, Einstein used the Planck constant and wrote the energy of the quantum as  $h\nu$ .

Points 6 and 7 in Refs. 4 were the most important. Einstein began point 6 by writing "...Since this modification of the foundations of Planck's theory necessarily leads to extremely profound changes in our physical theories, it is extremely important to seek independent interpretations, as simple as possible, of the Planck equation or of the radiation law in general, under the assumption that it is known. Below we will approach this question in two ways, of exceptional simplicity." These approaches—an analysis of energy fluctuations and one of momentum fluctuations for the radiation were set forth in points 6 and 7, respectively.

Einstein stated that the Boltzmann relation S = (R/N) ln W "has previously been used primarily to calculate the entropy after the quantity W has initially been determined on the basis of some more or less complete theory. However, this relation can also be used for the inverse problem: that of determining the statistical probability for an individual state  $A_{\mu}$  of some closed system from the values of S, found experimentally." This is the approach which Einstein used in Ref. 1 (see pp. 32 and 38), as he himself pointed out. Einstein emphasized that at that time he was "working from Wien's law, which holds only in the limit of large  $\nu/T^{*}$  (actually, "large" was erroneously replaced by "small" in Einstein's original paper and also in the Russian translation in Ref. 4). Now Einstein was working from the Planck radiation law, and in this way he was able to derive fundamental new results.

Einstein examined the energy fluctuations of blackbody radiation for frequencies between  $\nu$  and  $\nu + d\nu$ , in a small volume v, which was communicating with a large volume  $V(V \gg v)$ ; these volumes were assumed to be bounded by diffusely reflecting walls). The values of the energy  $\eta$  differ from the average value of this energy,  $\overline{\eta}$  (which is equal to  $\eta_0 = v\rho_\nu d\nu$ ; see p. 561), and the energy fluctuation is  $\varepsilon = \eta - \eta_0$  (see p. 557). Applying the statistical law which relates the probability of deviations from the average to the entropy (cf. Refs. 16 and 36), and expanding the entropy  $\sigma$  in a power series in  $\varepsilon$ , Einstein derived the equation

$$\overline{\epsilon}^2 = \frac{1}{\frac{N}{R} \left\{ \frac{d^2 \sigma}{d\epsilon^2} \right\}_0},$$
(28)

which contains the equilibrium value of the second derivative of the radiation entropy (in the volume v) with respect to the radiation energy ( $d\varepsilon = d\eta$ ). We note that Eq. (28) can be written in the form (1) (where  $2\kappa$ =k=R/N,  $\overline{E}=\eta_0$ ; see Born's paper<sup>2</sup>). From the known energy density for the blackbody radiation,  $\rho_v$ , it is possible to find  $\overline{\varepsilon}^2$ ; after this calculation, Einstein derived the fundamental equation for the energy fluctuations of blackbody radiation:

$$\overline{\varepsilon^2} = h v \cdot \eta_0 + \frac{c^3}{8 \pi v^2 \, dv} \frac{\eta_0^2}{v}, \qquad (29)$$

which can also be written in the form

$$\overline{\epsilon^2} = \left(h\nu \cdot \rho_{\nu} + \frac{c^2}{8\pi\nu^2} \rho_{\nu}^2\right) \nu \, d\nu. \tag{30}$$

Here  $\eta_0 = v \rho_{\nu} d\nu$  has been taken into account.

With the aid of "simple arguments based on dimensional analysis," Einstein showed that the second term on the right side of Eq. (29) describes the fluctuations according to the wave theory which are caused by the interference of "an infinite number of rays which constitute the radiation in volume v." The first term, on the other hand, "gives those fluctuations of the radiation energy which would occur if the radiation consisted of independently moving point quanta with an energy  $h\nu$ ." This term describes the fluctuations according to the corpuscular theory. Einstein recalled that "the first term makes a larger contribution to the average relative energy fluctuation  $\sqrt{\overline{\epsilon}^2/\eta_0^2}$ , the smaller the energy  $\eta_0$ , and that the relative fluctuation caused by the first term is independent of the magnitude of the volume vfilled by the radiation."

We note that when the absolute values are replaced by relative values, Eq. (29) takes a particularly simple form, and its physical meaning becomes clearest. Dividing both sides of Eq. (29) by  $\eta_0^2 = (v\rho_\nu d\nu)^2$ , we find

$$\frac{\overline{v^2}}{\eta_0^2} = \frac{(\overline{\eta - \eta_0})^2}{\eta_0^2} = \frac{\mu_v}{\eta_0} + \frac{c^3}{8\pi v^2 \, dv \, v} \,. \tag{31}$$

The ratio  $\eta_0/h\nu$  is the average number of photons in the volume v,  $\eta_0/h\nu = \vec{n}$ , and  $8\pi\nu^2/c^3 = Z(\nu)$ , where  $Z(\nu)$  is the number of oscillations of the electromagnetic field per unit volume per unit frequency interval. Thus  $q = 8\pi\nu^2 d\nu/c^3$  is the number of such oscillations in the volume v and in the frequency interval from  $\nu$  to  $\nu + d\nu$ : the number of vibrational degrees of freedom.

We find

$$\frac{\overline{(\eta-\eta_0)^2}}{\eta_0^2} = \frac{\overline{(\eta-\overline{\eta})^2}}{\overline{\iota^2}} = \frac{1}{\overline{\eta}} + \frac{1}{q}.$$
(32)

At high radiation frequencies, at which 1/q is negligible, we have  $(n - \overline{n})^2 = \overline{\Delta n}^2 = \overline{n}$  for purely corpuscular fluctuations. This is the well-known equation for the fluctuations in the number of molecules in an ideal gas or a dilute solution.

In point 7 Einstein dealt with the momentum fluctuations of blackbody radiation. He calculated them for a mirror of area f which was moving freely along the normal to f under the influence of fluctuations in the radiation pressure caused by these momentum fluctuations. Einstein derived the following equation for the momentum  $\Delta$  transferred over the time  $\tau$  as a result of random fluctuations of the radiation pressure to the mirror, which is an ideal reflector at frequencies between  $\nu$  and  $\nu + d\nu$  and transparent for all other frequencies:

$$\frac{1}{c}\frac{\overline{\Delta^2}}{\tau} = \frac{1}{c} \left(hv \cdot \rho_v + \frac{c^3}{8\pi v^2} \ \rho_v^2\right) f \, dv. \tag{33}$$

This equation is completely analogous to Eq. (29), if the latter is written in the form of (30). As Einstein em-

phasized, "Again in this case the equation states that, according to Planck's formula, these two causes of fluctuations appear mutually independent (the terms making up the square of the fluctuations are additive)."

In point 8, Einstein drew the following general conclusion: "From the discussion of both these last points [ energy fluctuations and momentum fluctuations of the radiation, in points 6 and 7 (M.E.)] it indisputably follows, in my opinion, that the radiation must have a structure different from that which we have been assuming." Later he wrote, "The deviation of the observed values from the theoretical values [according to the classical theory (M.E.)] is more pronounced, the larger  $\nu$  and the smaller  $\rho,"$  and he put special emphasis on the point that, "According to the arguments above, it is not sufficient to assume that the radiation can be emitted and absorbed only in the form of quanta of this size and that the problem thus reduces to the property of the emitting and absorbing material [as was believed by Planck and most physicists in this period, and subsequently, until the mid-1920s (M.E.)]. The discussions in points 6 and 7 show that the fluctuations of the spatial distribution of the radiation, just like the fluctuations of the radiation pressure, occur as if the radiation consisted of quanta of this size."

In these results Einstein was thus seeing confirmation of his concept of quanta of light. In point 9 he wrote that "... Experimental study of the consequences of the theory of quanta of light is, in my opinion, one of the most important problems to be solved in present-day experimental physics," and he divided the "consequences which have been obtained to date" into three groups: (a) "determination of the energy of the elementary processes which are involved in the absorption and, correspondingly, the emission of radiation at a certain frequency" (the Stokes law, the photo-electric effect, and cathode luminescence); (b) the equality of the number of elementary events in the absorption of quanta of light to the quantity  $E/h\nu$ , where E is the total absorbed energy, and  $\nu$  is the frequency of the absorbed light; (c) "the modification of the kinetic theory of specific heat" (here Einstein cited his paper in Ref. 30; see p. 565) and "the definite relationships between the optical and thermal properties of objects."

Point 10, the last, was very interesting. Einstein began it as follows: "It is apparently difficult to construct a theory which would completely explain light quanta in the same way that our present-day molecular mechanics, combined with the Maxwell-Lorentz theory, explains the Jeans radiation law. The fact that we are involved with only a *modification* of our present-day theories, rather than a complete *rejection* of them, follows from simply the fact that the Jeans law apparently does hold in the limit (of small values of  $\nu/T$ )" [Einstein's italics (M.E.)]. As is well known, the idea of a relationship between the classical and quantum theories and of a limiting transition from the quantum theory to the classical theory was subsequently developed in Bohr's correspondence principle (see, for example, Ref. 11). Then Einstein stated that "... An indication of how this modification can be made comes

from the dimensional analysis reported by Jeans several years ago, which I believe is extremely important." Here he was talking about Jeans' 1905 paper<sup>39</sup> (which in 1906 Ehrenfest<sup>40</sup> characterized as a "strikingly simple derivation of Wien's displacement law"). Einstein "briefly reproduced" the analysis by Jeans ("altered in a few places") and arrived at the relation  $h = e^2/c$  between Planck's constant and the elementary electric charge. The fact that  $e^2/c$  was equal to  $7 \cdot 10^{-30}$ , while h was equal to  $6 \cdot 10^{-27}$ , and "three whole orders of magnitude are lacking," Einstein attributed to "unknown dimensionless factors" [as we now know, this dimensionless factor is the fine-structure constant  $e^2/\hbar c = 2\pi e^2/hc$  $\approx 1/137$  (M.E.)]. "The most important point in this derivation," wrote Einstein, "is that it reduces the quantum constant of light h to the elementary quantum of electricity e." Einstein offered the opinion that "that modification of the theory which yields the elementary quantum e as a consequence will also incorporate the quantum structure of radiation," and he expressed the hope that a unified theory could be constructed: "However, the large number of possibilities is apparently not so large that we would be frightened away from this problem." Einstein's optimism turned out not to have been warranted, and, as we know, we do not have a unified theory yet. This effort to find the most general approaches was characteristic of Einstein's work, and it was particularly obvious here.<sup>5</sup>

In a short note at the end of Ref. 4, Einstein emphasized in connection with point 4 that "the contrasting arguments in my paper should be understood not as an objection to Planck's theory in the proper sense of this term, but only as an attempt to identify and use the principle of a relationship between entropy and probaability in a clearer manner than has been done previously."

There was a further discussion of the particle-wave duality for radiation on the basis of the results found in Ref. 4 [Eqs. (29) and (33)] in Ref. 5, which was a generalizing report which Einstein made in September 1909 at Salzburg, to the 81th Meeting of German Natural Scientists and Physicians.

The report was delivered to a join section of the physics and mathematics sections. This was Einstein's first appearance before a large number of scientists, among whom were most of the leading physicists of the time from German-speaking countries. In the audience were Planck, Sommerfeld, von Laue, Born, and many other distinguished physicists, both those who had already established their reputation and those who were to do so in the future (Ref. 10, p. 570). Einstein's report, with an exceedingly profound analysis of the problems of contemporary physics, caused a great deal of interest and generated some debate.<sup>41</sup>

Einstein began Ref. 5 by arguing that "the ether hy-

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pothesis must be considered obsolete today," and he stated that "there are many facts dealing with radiation which show that light has several fundamental properties which can be understood much better on the basis of Newton's emission theory than on the basis of the wave theory. I therefore believe that the next step in the development of theoretical physics will give us a theory of light which will in some sense be a blending of the wave theory of light and the emission theory. The purpose of the discussion below is to justify this opinion and to show that we cannot avoid a radical change in our opinions regarding the essence and structure of light."

Einstein recounted the search for laws describing the effect of this hypothetical medium called the ether on optical and electromagnetic phenomena. He described the Lorentz theory and outlined the basic arguments of the theory of relativity. He reached the conclusion that "the theory of relativity changes our views regarding the nature of light in the sense that light emerges as something with an independent existence, like matter." He went on to enumerate those "fundamental properties of optical phenomena" which the wave theory of light could not explain, and he saw the source of difficulty in the absence of reversibility in this theory. He compared the reversibility of each elementary event in the molecular-kinetic theory with the absence of this reversibility "in the wave theory for elementary radiation processes." He wrote that "an oscillating ion, according to the existing theory, creates an outgoing spherical wave. The inverse process does not exist as an elementary process [Einstein's italics (M.E.)], and he suggested that the conclusion that the elementary process by which light is emitted is not reversiblethe conclusion reached in the wave theory-does not correspond to reality. Analyzing the laws for the generation of secondary electrons by x rays, Einstein drew the fundamental conclusion that "the elementary radiation process is apparently directional." Then, following Planck, he discussed the theory for blackbody thermal radiation as furnishing "important initial ideas" regarding the structure of radiation, and he concluded that to adopt Planck's theory was to reject the very foundations of the classical theory of radiation. Einstein felt that this had to be done, as he "had attempted to show previously." Later on, Einstein discussed only one of the two approaches which he had proposed in Ref. 4 (in points 6 and 7; see pp. 566 and 568). The one he selected was that which seemed the most convincing "because of its clarity"; specifically, it was the second approach, which leads to Eq. (33) for the fluctuations in the radiation momentum. He emphasized that for these fluctuations "it is as if there exist two distinct, mutually independent causes," and by analyzing Eq. (33) he concluded that there are nonuniformities in the distribution of the radiation momentum "which, at a low radiation energy density, are far greater" than the spatial nonuniformities which follow from the wave theory. In conclusion, Einstein wrote that, to the best of his knowledge, "it was not yet possible to construct a mathematical theory for radiation which would describe both the wave structure and the structure which

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<sup>&</sup>lt;sup>5</sup>See also Ref. 10 (p. 72) regarding Einstein's attempts in 1909-1910 to resolve the radiation problem and to construct a general theory.

follows from the first term of our equation (the quantum structure)." Expressing the opinion that the assumption "that the appearance of the electromagnetic fields of light should be associated with singularities" is "presently the most natural" assumption, Einstein also wrote, "Until this picture leads to an exact theory, it should not be assigned any particular importance." He "simply wished to use this picture to show that it could not be concluded that the two structures (the wave and quantum structures) which radiation should have simultaneously according to Planck's equation were incompatible."

Einstein's 1909 development<sup>4,5</sup> of the concept of a particle-wave duality for radiation, with the simultaneous existence of two structures—wave and particle—for the radiation, on the basis of an analysis of energy and momentum fluctuations, was an extremely important step in the development of quantum concepts. As was noted correctly by Hund (Ref. 8, p. 51), "with his papers on the statistical fluctuations of radiation Einstein introduced the particle-wave duality for light." It is very important to note that the study of the quantum fluctuations of the momentum of radiation processes; this concept subsequently proved extremely important for understanding the nature of the relationship between the wave and particle properties of radiation (p. 572).

From 1910 to 1915, Einstein published several papers in which he pursued the development of quantum concepts, but in this period he was concerned primarily with the construction of a general theory of relativity. In October 1912, for example, he wrote the following letter to Sommerfeld,<sup>42</sup> who, like many others, was expecting decisive contributions to quantum theory from Einstein: "Your friendly note put me in a difficult position. But I assure you that I have nothing new to say regarding this question of quanta which would be of any interest....I am now occupied exclusively with the problem of gravitation...."

Let us briefly examine some of Einstein's papers from this period (see also the papers by Frankfurt and Frenck; Refs. 43 and 41).

In a paper<sup>44</sup> written jointly with Hopf, he gave an exact derivation of the equation for the mean square momentum fluctuations of radiation,  $\overline{\Delta^2}$ , on the basis of wave representations (in Ref. 4, Einstein simply estimated the analogous term in  $\overline{\epsilon^2}$ ; see p. 566 above). At the end of the paper it was emphasized, with a reference to Ref. 4, "that actually there are still other momentum fluctuations" (i.e., quantum fluctuations).

Among Einstein's series of papers on the quantum theory of specific heat, his report<sup>45</sup> to the First Solvay Congress if of particular interest. In this report Einstein discussed the relationship between the specific heat and the radiation equation (§1), made several theoretical comments regarding the hypothesis of quanta (§2), discussed the general nature of experiments relevant to the hypothesis of quanta (§3), and the rotation of gas molecules (§4).

After discussing the quantum theory of specific heat in

\$1, Einstein raised, in \$2, "the most important but essentially unresolved question" of "how must mechanics be revised in order to give a correct description of the Planck radiation law and the thermal properties of matter?" Examining the "statistical properties of thermal phenomena," Einstein derived an equation [working from the general equation in (1)] for the fluctuations of the vibrational energy in an "ideal, chemically simple solid with a frequency  $\nu$ , which consists of *n* gram-atoms." This equation is

$$\left(\frac{\tilde{e}}{E}\right)^2 = \frac{h\nu}{E} + \frac{1}{3Nn} = \frac{1}{Z_q} + \frac{1}{Z_f},$$
(34)

where

$$E = 3nN \frac{hv}{e^{hv/hT} - 1}$$
(35)

is the average vibrational energy of the object,  $Z_{\sigma} = E/$  $h\nu$  is the "average number of Planck 'quanta' in the object" and  $Z_f = 3nN$  is the total number of all vibrational degrees of freedom. Einstein emphasized that "the relative energy fluctuations of the system caused by the disordered thermal motion correspond to two completely different causes, which are expressed by the two terms on the right side of this equation." We see that this is the first appearance of the concept of phonons, now a familiar concept, and Eq. (34) itself is written in a form completely analogous to the form of Eq. (32) for the fluctuations in the radiation energy. Einstein studied these fluctuations also. He showed that, on the average, the fluctuations in the energy of the absorbed radiation were equal to the fluctuations in the energy of the emitted radiation.

Einstein summarized the results of \$2 in \$3 in the following manner: "If the object acquires or gives up thermal energy by means of a quasiperiodic mechanism, the statistical properties of this process turn out to be the same as if the energy were propagating in integral quanta of size hv." Later on he wrote, "Apparently, those discontinuities which we find so repugnant in Planck's theory actually exist in nature."

In §4 Einstein discussed Sommerfeld's hypothesis regarding the appearance of radiation during the slowing down of electrons,<sup>46</sup> according to which the product of the slowing down time  $\tau$  and the radiation energy emitted is equal to Planck's constant h. Einstein treated this slowing down process as an elementary event (see also Ref. 10, pp. 126-135).

Einstein's report caused a very lively discussion of the questions of quantum theory (see, for example, Ref. 47).

In Ref. 31, Einstein formulated the photochemicalequivalent law: "For the decomposition of a gramequivalent in a photochemical process, radiation energy  $Nh\nu$  is required. Here N is the number of molecules in the gram-molecule, h is the constant from Planck's radiation equation, and  $\nu$  is the frequency of the incident radiation." He cited his basic paper.<sup>1</sup>

In Ref. 48, the only paper published by Einstein on quantum theory in 1914 (it was in 1914 that he published a series of papers on the general theory of relativity, including Ref. 49, the fundamental paper), he discussed questions involved in the derivation of the Nernst theorem.

Finally, in 1915, the results of some experiments by Einstein and W. J. de Haas were published.<sup>6)</sup>

In addition to Einstein's original papers, we should cite his review<sup>50</sup> published in 1915 as part of the book Physics, edited by Lecher. This review was a condensed but very clear exposition of the molecularkinetics theory of heat. In the last section, "Range of applicability of molecular mechanics," Einstein characterized the state of the theory. He pointed out that at low temperatures the specific heat of chemically simple solids (which is due to the vibrational motion) turns out to be, "in contradiction to the results of molecular mechanics," smaller than the theoretical value and that "near absolute zero it in fact becomes vanishingly small!" Later on he wrote that this result "shows that the applicability of the kinetic molecular theory to oscillating formations is poorer, the faster are these oscillations and the lower is the temperature. Without exception, modern physicists believe that the laws of mechanics do not hold for fast oscillatory motions of small masses." [Precisely these questions were discussed at the First Solvay Congress in 1911, where Einstein gave a report<sup>45</sup> (see p. 569 above), and at the Second Solvay Congress in 1913; see Refs. 41 and 47 (M.E.)]. "However, despite all the effort, it has not yet been possible to alter the foundations of mechanics to satisfy experiment in this region also. The theoretical work which has been done to date deals with the Planck radiation theory. Although this work has yielded useful equations, it has not led to a complete theoretical understanding." This understanding was Einstein's goal.

In 1916, after Einstein had been exceedingly successful in deriving a general theory of relativity, he returned to the fundamental problems of the interaction of radiation with matter, working from the results of his earlier research and from Bohr's theory of the atom.<sup>51</sup> In 1913, as is well known, Bohr formulated his famous postulates regarding the existence of stationary states and optical quantum transitions between them. These transitions obeyed the frequency condition  $\varepsilon_m - \varepsilon_n = h\nu$ (where  $\varepsilon_{m}$  and  $\varepsilon_{n}$  are the energies of the two stationary states between which this transition occurs). In Refs. 6 and 52, Einstein succeeded in finding a new approach to the problems of the interaction of radiation with matter, and he made yet another extremely important contribution to the development of quantum concepts. The probabilistic treatment of the elementary processes by which radiation interacts with matter which was set forth in these papers laid down the basis for modern quantum electronics."

#### 6. PROBABILISTIC TREATMENT OF THE ELEMENTARY PROCESSES BY WHICH RADIATION INTERACTS WITH MATTER (EINSTEIN'S 1916 PAPERS)

In Refs. 6 and 52, Einstein introduced probabilistic characteristics of the elementary processes by which radiation is emitted and absorbed by gas molecules, and he examined the statistical equilibrium between molecules and radiation. This approach led to a very simple and fundamentally important derivation of Planck's equation in (6). These results are quite familiar, so we will discuss them very briefly and instead focus on the general approach taken by Einstein, in particular the relationship between his ideas and those of Wien, the directionality of the elementary radiation processes, and the probabilistic interpretation of the particle-wave duality.

In the introduction to his first and briefer paper,<sup>52</sup> Einstein described the path which Planck had taken when, "16 years ago, he created a quantum theory by establishing his radiation equation." Einstein reproduced Planck's equation, (11), stating that Planck had "calculated the average resonator energy  $\vec{E}$  as a function of the temperature on the basis of fundamental new rules of quantum theory which he had proposed." He also stated that Planck's derivation "distinguished itself by its unparalleled boldness but had found brilliant confirmation." "However, no one is satified," wrote Einstein, "that the analysis on the basis of electrodynamics and mechanics which leads to Eq. (11) contradicts the basic concept of quantum theory..." (Einstein had several times previously mentioned this contradiction in Planck's work, as we have seen; see, for example, pp. 563 and 566). Einstein went on to cite Bohr (for the first time in his papers): "From the time that the theory of spectra proposed by Bohr has achieved its remarkable successes, there can hardly be any doubt that the basic concept of quantum theory must be retained. Thus the unity of the theory should apparently be established in such a manner that an analysis with the help of electrodynamics and mechanics, which led Planck to Eq. (11), is replaced by quantum-theory ideas regarding the interaction between matter and radiation [ italics added (M.E.)]. With this goal in mind I have arrived at the following conclusion, which speaks for itself because of its simplicity and generality." This was Einstein's closing of the brief introduction to the paper. In \$1 ("A Planck resonator in a radiation field"), he examined the behavior of such a monochromatic resonator, taking into account emission and absorption in accordance with the classical laws. Along with spontaneous emission, he introduced stimulated emission ("induced radiation"). In \$2 ("Quantum theory and radiation") Einstein made use of quantum theory. He examined the statistical equilibrium for transitions between states with energies  $\varepsilon_m$  and  $\varepsilon_n$  ( $\varepsilon_m > \varepsilon_n$ ), describing spontaneous emission, absorption, and stimulated emission by means of the coefficients  $A_m^n$ ,  $B_n^m$ , and  $B_m^n$  (which are familiar to us as the Einstein A and B coefficients, which determine the probabilities for the corresponding transitions), and he wrote the balance equation  $A_m^n N_m$  $+B_m^n N_m \rho_{\nu} = B_n^m N_n \rho_{\nu}$ , where  $N_m$  and  $N_n$  are the popula-

<sup>&</sup>lt;sup>6)</sup>See the paper by V. Ya. Frenkel' on p. 580 in this issue.
<sup>7)</sup>See the paper by N. V. Karlov and A. M. Prokhorov on p. 576 in this issue.

tions of the energy levels  $\varepsilon_m$  and  $\varepsilon_n$ . Finding the ratio  $N_n/N_m$  from the Boltzmann distribution [ $W_n = p_n \exp(-\varepsilon/kT)$ , where  $p_n$  is the statistical weight] and using  $\rho_\nu \to \infty$  in the limit  $T \to \infty$  (this result yields the equation  $B_n^m p_n = B_m^m p_m$ ), Einstein found the following expression for the spectral density of the radiation:

$$\rho_{\mathbf{v}} = \frac{\alpha_{mn}}{e^{(\epsilon_m - \bar{\epsilon}_n)/kT} - 1}$$
(36)

(where  $\alpha_{mn} = A_m^n / B_m^n$ ). In other words, he derived "Planck's relation between  $\rho_{\nu}$  and T with constants which are yet to be determined." Particular note should be taken of the fact that Einstein wrote here that "the constants  $A_m^n$  and  $B_m^n$  could be calculated directly if we had versions of electrodynamics and mechanics modified on the basis of the hypothesis of quanta." Here Einstein was demonstrating that he had an excellent understanding of the fact that these constants are microscopic characteristics of molecules. As we know, a problem of this type can be solved only in quantum mechanics. Here Einstein used Wien's displacement law, (4), finding that  $\alpha_{mn}$  should be proportional to  $\nu^3$ , while  $\varepsilon_m - \varepsilon_n$ should be proportional to the first power of  $\nu$ ; the result is  $\varepsilon_m - \varepsilon_n = h\nu$ , "where h is a constant" (i.e., it gives the "second postulate of Bohr's theory of spectra"). Einstein thought it extremely probable, because of the "simplicity of the hypotheses and the generality and naturalness of the arguments," that this analysis would "become the basis for future theoretical ideas." This prediction was borne out.

Also in Ref. 52 is a short section, \$3 ("Comment on the photochemical-equivalent law"), where it is emphasized that the absorption of radiation in accordance with  $\varepsilon_m - \varepsilon_n = h\nu$  can lead to the excitation of an intermediate quantum state which would then decay, so that the "absorption of light and the chemical process are independent processes."

We should emphasize in particular here that stimulated emission was studied along with absorption and spontaneous emission in Ref. 52, and this discussion was essentially new and very important. With regard to spontaneous emission, Einstein noted that "the statistical law adopted for spontaneous emission is none other than the Rutherford law for radioactive decay."

Einstein described his approach in more detail in the second of these papers.<sup>6</sup> The introduction was very interesting, beginning with the words, "The formal similarity of the curve showing the wavelength distribution of thermal radiation, on the one hand, and the Maxwell distribution, on the other, is too striking to go undetected for long." He indicated that Wien "had been guided by this similarity to that determination of the radiation law which was subsequently to be so important," and he wrote out Eq. (9) [which, as we have emphasized (see p. 558), is a purely quantum equation], "which even today is correct as a limiting law for large values of  $\nu/T$ ." Then Einstein wrote that when Planck, "in his pioneering study," derived Eq. (6), "from which the quantum theory developed rapidly as a consequence, Wien's discussion which had let to Eq. (9) was naturally forgotten." Citing his previous paper,<sup>52</sup> Einstein continued, "Recently I found an application of Wien's original treatment, based on the main principles of quantum theory, in the derivation of Planck's radiation law, in which we can see a relationship between the Maxwell curve and the wavelength distribution. This derivation deserves attention not only because of its simplicity but also-especially-because it adds some clarity to the process by which radiation is emitted and absorbed by matter, which is not yet understood." Consequently, the analysis of the probabilities for the elementary process of emission and absorption by matter and his derivation of the Planck equation, by a "strikingly simple and general method," was perceived by Einstein as "an application of Wien's original treatment," for which there is the typical combination of the statistical approach and the incorporation of the characteristics of the elementary processes [ which obey quantum laws, but Wien, of course, did not know this (see p. 559), while Einstein understood this point quite well].

Later on, Einstein emphasized that "if these hypotheses regarding the interaction of radiation and matter are correct they must lead to more than simply a correct statistical distribution of the *internal* energy of molecules. In absorption and emission, there is also a transfer of *momentum* to molecules" [Einstein's italics (M.E.)]. As a result, a velocity distribution for the molecules was established which should be the same as the Maxwell distribution, and the average kinetic energy of a molecule (per degree of freedom) should be kT/2, "regardless of the nature of the molecules and regardless of the nature of the frequencies of the radiation which the molecules are absorbing and emitting." In this paper Einstein showed that this important requirement is in fact satisfied.

When we consider momentum exchange we run into the question, "Does the molecule recoil as it absorbs and emits an energy  $\varepsilon$ ?" It will recoil, according to classical electrodynamics, for directional spontaneous emission, while for spherical waves, "there will be no recoil at all." Einstein concluded his introduction by answering his own question: "It turns out that we will find a noncontradictory theory only if all the elementary processes are assumed to be completely directional [Einstein's italics (M.E.)]. This is the basic result of the arguments below."

In the short first section ("Basic hypotheses of quantum theory. Canonical distribution of states"), Einstein treated the Boltzmann distribution  $W_n = p_n \exp(-\epsilon_n/kT)$  as the "widest generalization of the Maxwell velocity distribution."

In §2 ("Hypothesis regarding energy exchange through radiation"), Einstein introduced the coefficients  $A_m^n$ ,  $B_n^m$ , and  $B_m^n$  as in Ref. 52, and he also took up the question of momentum transfer during radiation processes. During absorption, the molecule acquires a momentum  $(\varepsilon_m - \varepsilon_n)/c$  along the direction of the radiation, while in the case of stimulated emission it acquires a momentum in the opposite direction. The stimulated emission (the process inverse to absorption) thus has a radiation direction. Einstein went on to write, "If there is an energy loss as a result of spontaneous emission in the case of a Planck resonator, this resonator as a whole will not acquire any momentum, since the spontaneous emission takes the form of a spherical wave according to the classical theory," and, "as has already been pointed out,...we can find a noncontradictory quantum theory only if we assume that the spontaneous emission is also directional." This assertion led to the statement that the molecule transfers a momentum equal to  $(\varepsilon_m - \varepsilon_m)/c$ " in each elementary spontaneous-emission event."

Section 3 ("Derivation of Planck's radiation law") contains the same results as in §2 of Ref. 52. With regard to the result  $\varepsilon_m - \varepsilon_n = h\nu$ , Einstein wrote that it "is known to form the second basic rule in the Bohr theory of spectra, a rule which can be described as one of the unshakable foundations of our science, after its refinements by Sommerfeld and Epstein."

The last four sections of Ref. 6 (there were only seven sections in this paper) dealt with momentum transfer and momentum fluctuations, and they are extremely important sections.

In §4 ("Method for calculating the motion of molecules in a radiation field"), Einstein derived an equation for  $\Delta$ , the fluctuations in the momentum of the molecule over the time  $\tau$ :

$$\frac{\overline{\Delta^2}}{\tau} = 2RkT, \qquad (37)$$

where R is the constant which appears in the expression Rv for the force which is exerted on the molecule by the radiation. In §5 ("Calculation of R") and §6 ("calculation of  $\overline{\Delta^2}$ "), Einstein found equations for R and  $\overline{\Delta^2}$  in terms of the radiation density  $\rho_{\nu}$ . "If we then write  $\rho_{\nu}$ as a function of  $\nu$  and T in accordance with the Planck law, (6), and substitute the result into (37)," wrote Einstein, "the latter equation must hold identically," Einstein carried out the rather complicated calculation of R in §5, describing the radiation in a coordinate system which was at rest with respect to the molecule under consideration, and using the transformation laws for the frequency from the theory of relativity. All the elementary radiation processes were assumed to be directional. He took into account the transfer of momentum of the molecule during the elementary processes of absorption and stimulated emission (for spontaneous emission, the average momentum transfer is zero). The resulting expression for R is pro-kT), and a function of  $\rho_{\nu}$ . The calculation of  $\Delta^2$ , which is simpler, yields for  $\overline{\Delta^2}/\tau$  an expression which is also proportional to  $B_n^m$  and  $\exp(-\varepsilon_n/kT)$  and which is a function of  $\rho_{\nu}$ .

At the beginning of the final section, \$7 ("Conclusions"), Einstein used the expressions found for R and  $\overline{\Delta^2}/\tau$  to show that Eq. (37) for blackbody radiation with a spectral energy density  $\rho_{\nu}$  is described by the Planck equation, (6), which actually *holds identically*. In this manner it is proved that the momentum acquired by the molecules from the radiation does not disrupt the statistical equilibrium (under the assumption that the elementary radiation processes are completely directional), in accordance with the assertions made in the Introduction.

Summarizing his work, Einstein noted that he had found a "good confirmation of the hypotheses adopted in \$2 regarding the interaction between matter and radiation through absorption and emission, and through spontaneous and induced emission, respectively."

Einstein considered the main conclusion, however, to be the one "dealing with the momentum which is transferred to the molecule during spontaneous and stimulated emission." He considered that it had been definitely proved that during the emission or absorption of an amount of energy  $h\nu$  the molecule always also acquired a momentum  $h\nu/c$ , along the direction of the beam of rays in the case of absorption or in the opposite direction in the case of stimulated emission. Later on, Einstein put particular emphasis on the point that in the case of spontaneous emission "the process is also directional [Einstein's italics (M.E.)]. Spontaneous emission in the form of spherical waves does not exist. In the elementary spontaneous-emission event the molecule acquires a recoil momentum of an amount  $h\nu/$ c, and the direction of this momentum, according to the present state of the theory, is governed only by 'chance." Further, Einstein stated that "these properties of the elementary process which are required by Eq. (37) almost necessarily required the creation of a genuine quantum theory of radiation. The weakness of the theory is that, on the one hand, it does not lead us to a closer linkage with the wave theory and, on the other, that the time and direction of the elementary process are left to 'change.' Incidentally, I am completely confident of the reliability of the method used."

In this manner Einstein arrived at a probabilistic interpretation of the relationship between the particle and wave properties of radiation—a probabilistic interpretation of the particle—wave duality. Subsequently, Born gave a probabilistic interpretation of quantum mechanics, developing the ideas of Einstein,<sup>53</sup> whom he cited (see also Ref. 11).

### 7. THE PERIOD BEFORE THE ESTABLISHMENT OF QUANTUM MECHANICS (EINSTEIN'S PAPERS IN 1917-1925)

After 1916, in the period preceding the actual establishment of quantum mechanics, which occurred in 1925-1928, Einstein continuing to be interested in quantum theory, published several papers in this field developing certain of its ideas.

We will briefly discuss some of these papers (see also Frenck's paper<sup>41</sup>).

In Ref. 54, Einstein examined quantum conditions of the type  $\int p_i dq_i = n_i h$  for systems with many degrees of freedom from the common standpoint of their invariance under coordinate transformations.

Along with Ehrenfest, with whom Einstein shared a close friendship and scientific interests,<sup>55</sup> he wrote two papers on extremely pertinent questions of quantum theory.

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In the first of these papers<sup>56</sup> he discussed the famous experiment by Stern and Gerlach<sup>57</sup> on the deflection of a beam of atoms having a magnetic moment as they passed through an inhomogeneous magnetic field. He took up the question of spatial quantization and of whether it would be possible to have "states which do not satisfy the quantum orientation rules," i.e., states for which the atoms are "not completely quantized."

In the second of these papers,<sup>58</sup> he took up the statistical law proposed by Pauli<sup>59</sup> for the probability of possible elementary events of scattering of radiation by freely moving electrons. Working from the "statistical elementary laws for absorption and emission of light by a Bohr atom" (he cited Ref. 6), he solved the more general problem of the elementary processes of scattering by moving microscopic particles ("molecules, atoms, or electrons"), and he showed that the Pauli equation can be found from the general equation derived for freely moving electrons.

In Ref. 60 we see Einstein's striving to construct a unified field theory, also incorporating quantum theory. At that time Einstein was beginning intense work on various versions of a unified field theory.<sup>61</sup>

A paper of a general nature<sup>62</sup> was written in connection with the discovery of the Compton effect. In this paper it was stated that "now we have two theories of light, both necessary and—as we are forced to admit today—existing without a logical relationship, despite twenty years of colossal effort by theoretical physicists." At the very end of the paper Einstein wrote, "The positive result of Compton's experiment shows that radiation behaves as if it consisted of discrete corpuscles not only in the energy-transfer sense but also in the momentum-transfer sense." Einstein was thus again emphasizing the importance of considering momentum transfer [cf. Ref. 6 and p. 571].

Einstein's most important contribution to the development of quantum ideas in this period after 1916 consisted of his papers on the quantum theory of an ideal  $gas^{63-65}$ : the well-known papers on quantum statistics, since then named "Bose-Einstein statistics."

In 1924 Bose sent Einstein a paper<sup>66</sup> from India containing a derivation of the Planck equation, (6), based on a calculation of the number of possible distributions of light quanta among cells in phase space. Einstein translated this paper from English into German and added the following comment: "The derivation of the Planck equation proposed by Bose is a major step forward, in my opinion. The method which he has used also gives the quantum theory of an ideal gas, which I shall present elsewhere." This theory was set forth in Refs. 63 and 64.

At the beginning of the paper in Ref. 63 Einstein wrote, "No quantum theory for a monatomic ideal gas free of arbitrary assumptions exists at present. This gap is filled below on the basis of a new method which was proposed by Bose and which he has used for an exceptionally interesting derivation of the Planck radiation equation." Einstein gave a brief and exceptionally clear description of this method: "The phase space of some elementary object (in this case, a monatomic molecule) associated with a given (three-dimensional) volume is divided into 'cells' of volume  $h^3$ . If there are many elementary formations, then their microscopic distribution, treated in thermodynamics, is characterized by how the elementary formations are distributed among the cells. The 'probability' of some macroscopically definite state (in the Planck sense) is equal to the number of different microscopic states which can characterize the given macroscopic state. The entropy of the macroscopic state and also the statistical and thermodynamic properties of the system are then determined from the Boltzmann equation."

We will not analyze the content of Einstein's papers in Refs. 63-65, since this would go beyond the scope of the present review; we will simply examine some very important sections of Ref. 64 (§§8 and 9; Refs. 63 and 64 are parts of the same work, and their sections are numbered in a common series).

In §8 ("Fluctuation properties of an ideal gas") Einstein used his method of analyzing fluctuations which had been used in Refs. 4 and 5 in the theory of blackbody radiation (see p. 566). "This fluctuation law," wrote Einstein about the corresponding law for an ideal gas, "turns out to be completely analogous to the fluctuation law found for quasimonochromatic radiation by Planck." For the fluctuations  $\Delta_{\nu}$  in the number  $n_{\nu}$  of monatomic molecules belonging to energy interval  $\Delta E$  in a gas volume V, which communicates with an infinite volume of the same gas, Einstein wrote the fluctuation law as

$$\overline{\left(\frac{\Delta_{v}}{n_{v}}\right)^{2}} = \frac{1}{n_{v}} + \frac{1}{z_{v}},$$
(38)

where  $z_{\nu}$  is the number of phase-space cells which correspond to an infinitesimally small energy interval of the molecules,  $\Delta E$ . We see that Eq. (38) is analogous to Eq. (32) for blackbody radiation and also analogous to Eq. (34) for the fluctuations of the vibrational energy in a solid]. Einstein emphasized that the second term in the case of radiation corresponds to interference fluctuations and that this term "can also be assigned the same meaning in a gas, by associating some radiation process with the gas and calculating the interference fluctuations for this process." Einstein assumed here that "what is involved here is not solely a simple analogy" [italics added (M.E.)]. He cited the dissertation of Louis de Broglie<sup>67</sup> as a work "which deserves every attention" (in a reference to this dissertation, Einstein said that it "contained a very interesting geometric interpretation of the Bohr-Sommerfeld quantum rules"), and he wrote that de Broglie had shown "how a (scalar) wave field could be associated with a mass particle or a system of particles." Einstein reproduced de Broglie's relation between the wave phase velocity V and the velocity of a mass particle,  $v: V = c^2/v$ . In doing so he stated that "v is at the same time the group velocity of this wave process, as de Broglie has shown." Einstein continued:

"It is now easy to see that a scalar wave field can be associated with a gas in this manner. By a direct calculation I have convinced myself that  $1/z_{p}$  is the mean square fluctuation of this wave field. This result corresponds to the energy interval  $\Delta E$  studied above."

In \$9 ("Comment on the viscosity of gases at low temperatures"; it would have been difficult to guess the contents of that section from its title]). Einstein pointed out that as a beam of molecules passes through an aperture it should experience diffraction ("analogous to the diffraction of a light beam"). Here the wavelength  $\lambda = h/mv$  (Einstein reproduced this equation given by de Broglie) must be comparable to the dimensions of the aperture. Einstein examined the possibility of detecting this type of diffraction from the temperature dependence of the viscosity coefficients of gaseous hydrogen and helium at low temperatures, at which  $\lambda$  is comparable to the molecular diamter  $\sigma$ , so that there should be diffraction effects and an increase in the viscosity coefficient (it was assumed here that a diffraction analogous to Fraunhofer diffraction by a disk would occur and that the molecules for which  $\lambda$  was comparable to  $\sigma$  would be strongly deflected).

We see that Einstein not only understood the exceptionally great importance of de Broglie's ideas (de Broglie had developed for microparticles Einstein's own ideas regarding the particle-wave duality) but also was able to find an application for them in quantum statistics. It should be noted that, while Einstein focused on the first term, the *particle* term, for the fluctuations of blackbody radiation, he turned to the second term, the *wave* term, for the fluctuations of an ideal monatomic gas. Another very important point was Einstein's mention of the possible diffraction of microparticles.

We should especially emphasize the fact that Einstein's support for de Broglie's ideas played a major role in their dissemination (see the comments by de Broglie himself<sup>68</sup> and also the articles by Klein in Ref. 3 and by Polak in Ref. 69).

#### CONCLUSION

As a result of his research on quantum theory over a 20-year period beginning in 1905, Einstein played a role in the development of quantum concepts which was exceedingly important in the establishment of quantum mechanics between 1925 and 1928. It was on Einstein's ideas regarding the particle-wave duality that one of the two approaches to quantum mechanics was based. This is the one developed by Schrödinger in early 1926 in the form of wave mechanics<sup>70</sup> (see Ref. 11 for more details). In March 1926, in a paper on the relationship between matrix mechanics and wave mechanics,<sup>69</sup> Schrödinger wrote that his "theory had been stimulated by the work of L. de Broglie" (Ref. 67, where de Broglie, as we emphasized at the end of the preceding section, developed Einstein's ideas for microparticles) and by "brief but very perceptive comments by Einstein" (Ref. 64: see p. 573). However, Einstein did not take direct part in the establishment of quantum mechanics, and his papers<sup>63-65</sup> on guantum statistics remain his last important specific contribution to the development of quantum ideas. When, in 1927, attention turned to questions of the physical interpretation of quantum mechanics on

the basis of the Heisenberg uncertainty relations<sup>71</sup> and Bohr's complementarity principle,<sup>72</sup> a famous discussion between Einstein and Bohr arose regarding the completeness of the quantum-mechanical description of the phenomena of the microworld. (This discussion, mentioned at the beginning of this paper, was preceded by a difference of opinion between Bohr and Einstein between 1923 and 1925 regarding fundamental questions of quantum theory; see Klein's article in Ref. 33.) In 1949, Bohr described this discussion in detail (see Ref. 72 and Einstein's reply<sup>73</sup>: the discussion is described in detail in Ref. 74). The discussion continued until Einstein's death in 1955. Einstein continued to believe that the quantum-mechanical description was not complete. He attempted to construct a unified physical picture of the world, developing a general field theory, and he devoted the second half of his scientific career to this project. He was not satisfied by the physical picture of the world based on the complementarity principle and the probabilistic interpretation of quantum mechanics (see, for example, Born's paper in Ref. 2). Einstein himself had been one of the founders of this interpretation; as early as 1916 he had arrived at the probabilistic interpretation of the particle-wave duality (Ref. 6; see p. 572). He did not accept this interpretation as final, however, and he did not agree that it was necessary to reject classical ideas even more decisively in order to study the microworld, as Bohr and his followers believed. Einstein's views on the methodological questions of modern physics require a separate examination, which would go beyond the scope of the present review.

Note: The references to Einstein's papers are to the Russian translations: A. Einstein, Sobranie nauchnykh trudov (Collected Scientific Works), Vols. I-IV, Nauka, Moscow, 1965-1967. The references to these books in the list below give the volume number, the page number, and the year of publication of the original paper (in parentheses).

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Translated by Dave Parsons