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Paul Ehrenfest on the Necessity of Quanta (1911): Discontinuity, Quantization, Corpuscularity, and Adiabatic Invariance

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Contents

Abstract

Our object in this paper is to study the antecedents, contents, implications, and impact of a not well-known or appreciated paper by EHRENFEST in 1911 on the essential nature of the different quantum hypotheses in radiation theory. After a careful analysis of EHRENFEST's notebooks, correspondence, and publications, we conclude that

the essential points of EHRENFEST's paper were not perceived to a large extent, and hence that its implications were not considered thoroughly. Specifically, we show that EHRENFEST contributed significantly to the clarifications of the differences between PLANCK's and EINSTEIN's respective quantum hypotheses, as well as to those of the concepts "discontinuity," "quantization," and "corpuscularity."

We use the following abbreviations for the archives cited

AHQP	Archive for History of Quantum Physics; for the catalogue see KUHN *et al.* (1967).
AL	Archief H. A. Lorentz. We quote from the microfilm version included in the AHQP.
EA	Ehrenfest Archive, in the *Rijksarchief voor de Geschiedenis van de Natuurwetenschappen en van Geneeskunde*, Leiden. For the catalogue see WHEATON (1977), whose abbreviations we adopt, as follows: ESC (Ehrenfest Scientific Correspondence), ENB (Ehrenfest Notebooks), EMS (Ehrenfest Manuscripts), and EPC (Ehrenfest Personal Correspondence). Where possible (the EMS have not been microfilmed) we quote from the microfilm version included in the AHQP.

1. Introduction

Our main theme in this paper is the analysis of the antecedents, contents, and true conclusions of EHRENFEST's article of 1911, "Which features of the hypothesis of light quanta play an essential role in the theory of thermal radiation?"[1] We also discuss the historical context in which EHRENFEST's article was elaborated and explain the reasons for its small influence at the time of its publication, even though, as we will see, it contained subtleties and details that could have contributed significantly to the development of quantum theory.

We are not the first to address these matters; they have been the subject of earlier historical studies. Thus, a note on EHRENFEST's memoir can be found in ROSENFELD (1936), while the longest and deepest analysis to date can be found in KLEIN (1985). In NERI (1986), the statistical approach of EHRENFEST's paper is stressed. Each of these scholars also emphasizes – to different degrees – the appearance of a relationship between adiabatic invariance and quantum theory for the first time in EHRENFEST's paper. We believe, however, that a detailed study of EHRENFEST's paper and of its antecedents, implications, and influence is still needed. We will bring to the foreground several of its aspects that we believe have been overlooked to date.

The idea that quantization of certain physical quantities such as energy and action was necessary was established firmly in the minds of leading physicists after the first Solvay conference in the autumn of 1911. EHRENFEST's paper thus appeared during a period of transition. KUHN, for instance, stresses that in 1911 the number of research

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[1] EHRENFEST (1911).

papers related to the black-body problem became smaller than the number of papers related to other problems in which the quantum hypothesis began to appear (atomic structure, the specific heats of solids, and the like).[2] GARBER considers that during the period 1910–1914 there was a major shift in opinion in the scientific community whereby a minority of defenders of the new ideas overcame their opponents and reduced their influence significantly.[3] Finally, HERMANN places, though on arguable grounds, the end of the genesis of quantum theory in 1913 when BOHR published his trilogy on the atomic structure of matter.[4]

We will show that EHRENFEST's contribution in 1911 deserves much more credit than usually is granted to it for bringing about the acceptance of the new quantum ideas. The Viennese physicist adopted a statistical approach to the black-body radiation problem and obtained what can be considered as a new derivation of WIEN's displacement law. We regard it of paramount importance to go deeply into EHRENFEST's very original use of probability and statistics and into the role he attributed to certain adiabatic invariants. A further question, usually overlooked, is related to the necessity of quantization, which EHRENFEST proved not only for PLANCK's law but also for WIEN's. This will clarify the question of why EINSTEIN formulated his light quantum hypothesis in 1905 starting with WIEN's law rather than PLANCK's. In his 1911 paper, EHRENFEST provided a very clear distinction between EINSTEIN's and PLANCK's quantum hypotheses.

These are but a few examples that support our claim that EHRENFEST's 1911 paper has not yet received the rigorous and detailed attention it deserves. Our paper is intended to fill this gap.

2. EHRENFEST and the theory of radiation before 1911

In 1904 EHRENFEST received his Ph.D. degree from the University of Vienna with a thesis on a generalization of HERTZ's mechanics to fluid media. His first contact with PLANCK's theory had occurred in 1903 when he attended a course given by LORENTZ in Leiden. In 1901 LORENTZ had traced the origin of thermal radiation to the motion of electrons in substances and also had employed certain dimensional arguments that later would be used by EHRENFEST.[5] Prior to 1911, EHRENFEST published two articles and a note on thermal radiation to which we devote the following paragraphs.

2.1. First criticism of irreversibility in PLANCK's theory (1905)

Toward the end of 1905, BOLTZMANN presented to the Vienna *Akademie der Wissenschaften* EHRENFEST's first paper on thermal radiation, "On the physical assumptions of Planck's theory of irreversible radiation processes."[6] PLANCK's law does

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[2] KUHN (1978), 206–232.

[3] GARBER (1976), 121–122.

[4] HERMANN (1971), 2–3.

[5] LORENTZ (1901a and 1901b).

[6] EHRENFEST (1905).

not appear in this systematic study because EHRENFEST's critique does not depend on it: he questions the uniqueness of the black-body spectral distribution and the physical mechanism causing irreversibility. He also questions PLANCK's earlier work when he tried to derive WIEN's law. He reveals the weakness of PLANCK's theory using dimensional arguments, deepening LORENTZ's arguments, and concludes that it is impossible, by assuming only damped oscillators and an aether (including "natural radiation"[7]), to obtain an analogue of BOLTZMANN's *H*-theorem for radiation, as PLANCK had claimed to have done. He also identifies the differences between the function that PLANCK had called the entropy and the thermodynamic function bearing the same name. In PLANCK's theory, in sum, EHRENFEST shows that there are infinitely many natural-radiation states with the same total energy yet with different spectral densities. This would be equivalent, in BOLTZMANN's gas theory, to the Maxwellian velocity distribution not being determined unambiguously.[8]

In the final part of his article, EHRENFEST considers PLANCK's new approach in which he introduces combinatorics and reproduces BOLTZMANN's analysis of 1877.[9] All of the microstates compatible with the macroscopic constraints are equally probable, and BOLTZMANN's *H*-quantity – the negative of the entropy – has an extremal property: it has the minimum value compatible with all macroscopic data. According to EHRENFEST, the application by PLANCK of this method to the black-body problem introduces two new hypotheses:

(i) the energy distributions amongst resonators are equiprobable, and
(ii) the radiant energies of various colors are composed of smallest particles of magnitude $E_\nu = \nu \cdot 6.55 \cdot 10^{-27}$ erg · sec,

where ν is the frequency of the corresponding color. EHRENFEST stresses the similarity of the first hypothesis with BOLTZMANN's, while he simply comments that the second is purely formal, with no analogue in BOLTZMANN's theory, and that it must be reformulated.

EHRENFEST momentarily does not attribute too much significance to the quantization of the energy inside the cavity, while PLANCK had connected quantization to the energy exchanged by the resonators. This may appear paradoxical, given EHRENFEST's stated purpose of clearing up any confusions. KLEIN related his attitude to the possibilities it opened up for a more comfortable application of statistical methods.[10] KUHN instead attributed his "anomalous reading" to the influence of his preceptor LORENTZ, who also applied quantization directly to the radiation in his first papers.[11]

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[7] The concept of "natural radiation" was introduced by PLANCK in an attempt to extend BOLTZMANN's hypothesis of "molecular chaos" to the problem of radiation. See KUHN (1978), 76–82. Einstein also referred to the notion of "natural radiation" in 1905 when he stated that "the radiation may be considered as the most disordered process imaginable," an idea he briefly explained in a footnote. See BECK (1989), 89.

[8] EHRENFEST (1905). In KLEIN (1959a), 96–97.

[9] PLANCK (1901).

[10] KLEIN (1985), 240.

[11] KUHN (1978), 138.

We have written "smallest particles," which is a literal translation that also has been used by others,[12] but this term requires some clarification. EHRENFEST used the word *Energieteilchen*, not *Energieelemente*, which is the word PLANCK had used. This can lead to a misunderstanding, namely, to think that EHRENFEST endowed the Planckian energy elements with some kind of particle character. EHRENFEST presented his work to the Vienna *Akademie* several months after EINSTEIN had published his light-quantum hypothesis,[13] and EHRENFEST probably was aware of EINSTEIN's paper. EINSTEIN does not use the term *Energieteilchen*; rather, he uses the terms *Energiequanta* and *Lichtquanta*, which were not associated with particle properties at the time.[14] Given the rigor that EHRENFEST exhibited in his writings, his term "smallest particles" cannot be interpreted as associating a corpuscular character to radiant energy, for he would have emphasized this point had it been his intention to do so.

2.2. *On the sufficiency of quantization (1906)*

Certain details in EHRENFEST's paper (1906b) partly anticipate the methodology he will use later in his rigorous analysis of 1911 of the relationship between thermal radiation and the quantum hypothesis. EHRENFEST refers to PLANCK's *Vorlesungen*, which had just been published, in which PLANCK presents a systematic exposition of his theory and interprets the constant h as an element of action based on its representation in phase space.[15]

EHRENFEST begins by noting that, according to PLANCK's theory, radiation left to itself does not become black but totally disordered.[16] In addition, using an analogy based on the kinetic theory of gases, he shows that thermal radiation cannot reach an equilibrium state through the processes described in PLANCK's theory. As EHRENFEST had already proved in his 1905 paper, PLANCK's theory implies the existence of infinitely many stable states that do not correspond to the black-body spectral density.

EHRENFEST's main goal is to analyze PLANCK's interpretation of BOLTZMANN's entropy using what EHRENFEST calls "complexion theory." For this purpose he uses RAYLEIGH and JEANS's representation of normal modes in a cavity in which the large number of independently moving particles in a gas is replaced with a large number of modes of oscillation with independent phases and amplitudes. EHRENFEST writes for the entropy,

$$S = const. - k \int_{0}^{\infty} d\nu N(\nu) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} df\, dg\; F(\nu, f, g) \log F(\nu, f, g), \qquad (1)$$

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[12] See, for instance, KLEIN (1985), 234.

[13] EINSTEIN (1905).

[14] For an explanation concerning the meaning of the Latin word "quantum" and its derivatives in that period, see KLEIN (1985), 253–254, footnote 59.

[15] PLANCK (1906).

[16] EHRENFEST (1906b). In KLEIN (1959a), 120–122.

where f is the oscillation amplitude, g its momentum, and $N(\nu)d\nu F(\nu, f, g)df dg$ is the number of modes with frequency between ν and $\nu + d\nu$, amplitude between f and $f + df$ and momentum between g and $g + dg$. The entropy of the radiation in thermal equilibrium inside the cavity, that is, black-body radiation, is obtained as the maximum of (1), subject to two constraints on $F(\nu, f, g)$, one associated with its normalization, the other with the total energy in the cavity. EHRENFEST carried out the calculations just as in the kinetic theory of gases (as also is explained in PLANCK's *Vorlesungen*), whereby the classical RAYLEIGH-JEANS formula is obtained, which agrees with the experimental data only in the low-frequency region. EHRENFEST points out that the RAYLEIGH-JEANS law is consistent with WIEN's displacement law and provides a means of determining PLANCK's constant within its range of validity. EHRENFEST then asks: how was PLANCK's complexion theory able to avoid arriving at the classical RAYLEIGH-JEANS law?

EHRENFEST devotes the rest of his paper to a consideration of a third constraint that leads to PLANCK's law. He stresses that the current lack of knowledge of the fundamental physical processes involved is such that PLANCK's law cannot be justified adequately, and he notes as an example that if the electrons in the cavity cause the radiation, their dimensions and internal structure would limit their permitted normal modes. Thus, he writes down an arbitrary restriction on their normal modes, carries out the calculation of F that maximizes the entropy, and in this way justifies an important result: that any given spectral distribution can be obtained in infinitely many ways, provided that the third constraint is chosen appropriately. That implies that a specific additional constraint was *unnecessary* to obtain PLANCK's law, although it was *sufficient* to avoid obtaining the RAYLEIGH-JEANS law. EHRENFEST shows that the specific constraint that PLANCK actually used was the atomization of energy at each frequency ν, that is, that $\varepsilon_\nu^0 = h\nu = 6.548 \cdot 10^{-27} \cdot \nu$ erg. PLANCK himself recognized that this hypothesis lacked a rigorous foundation.

EHRENFEST ends his article by returning to the question: How can one prevent in PLANCK's theory the runaway energies at the high-frequency modes? He has an intuition about the possible answer, namely, that the quantum energy grows indefinitely with ν, so that for values in the visible spectrum, the quantum energy is of the order of that of a molecule in a gas at $T = 10{,}000$ K.[17] Since the total energy at thermal equilibrium is fixed by the temperature T, it cannot be distributed amongst the very high-frequency modes, because at them a large amount of energy is required to generate a single quantum.

2.3. *Controversy with JEANS (1905–1906)*

Toward the end of his paper (1906b), EHRENFEST inserted a footnote replying to a passage in PLANCK's *Vorlesungen* in which PLANCK had argued that the appearance of the constant h was compelling evidence in favor of his theory. EHRENFEST stressed, on the contrary, that WIEN's displacement law already pointed to the necessity of a

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[17] EHRENFEST actually writes $T = 1{,}000$; as the equipartition theorem shows, this is a typographical error.

new constant that would render the product λT dimensionless.[18] This was precisely the central theme of a polemic that EHRENFEST initiated with JEANS in the *Physikalische Zeitschrift*. EHRENFEST critized a paper of 1905 by JEANS in which he deduced WIEN's displacement law on dimensional grounds, enabling him to write down the radiation constants appearing in that law and in the STEFAN-BOLTZMANN law in terms of known universal constants.[19]

EHRENFEST locates his criticism precisely in his short note: In JEANS's dimensional analysis, one can play with 7 universal constants and 5 quantities, from whence two dimensionless monomials can be formed. This is a trivial consequence of BUCKINGHAM's Π theorem, but that theorem was published only in 1914 and hence unknown at the time.[20] The pair of monomials JEANS chose led him to WIEN's displacement law, but EHRENFEST showed that JEANS's choice of that specific pair was arbitrary, and also that had JEANS chosen a different pair, he would have been led to expressions that violated WIEN's displacement law.[21]

JEANS replied within two months,[22] rejecting EHRENFEST's criticism. Two months later, EHRENFEST tried to counter JEANS's new arguments,[23] but because their debate was centered essentially on dimensional analysis, which does not play a role in our study here, we omit the details of their controversy.

2.4. *EHRENFEST on radiation: Further details*

We can detect in EHRENFEST's notebooks and correspondence certain aspects of his research that are not apparent in his published papers. His first annotations related to black-body radiation date to 1903, beginning probably after he returned from a two-month stay in Holland that spring.[24] His annotations reveal LORENTZ's influence, since they dwell a great deal on the theory of electrons. Only in 1905, when he published his first paper on radiation, does this become one of the main topics in his notebooks. His annotations deal with a number of questions related to the three articles we discussed above, but we now emphasize those that are connected closely to his paper of 1911.

We find that a common tool that EHRENFEST employed was to analyze an adiabatic-compression process. He asked, for example, if black-body radiation at temperature T_o, when compressed adiabatically until it reaches temperature T, is still black-body radiation. He checks his analysis to see if it is consistent with the second law of thermodynamics, and he resorts to kinetic models that enable him to recover KIRCHHOFF's law,

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[18] EHRENFEST (1906b). In KLEIN (1959a), 124, footnote 3.

[19] EHRENFEST (1906a) and JEANS (1905). For the first formulation of WIEN's displacement law, see WIEN (1894), KANGRO (1976), 37–47 and 90–100. A later and interesting analysis and derivation of the same law within the framework of thermodynamics can be found in BUCKINGHAM (1912).

[20] BUCKINGHAM (1914).

[21] EHRENFEST (1906b). In KLEIN (1959a), 120.

[22] JEANS (1906).

[23] EHRENFEST (1906c).

[24] For instance: note 361, June 1903, ENB:1–02; in EA, microf. AHQP/EHR-1. Concerning EHRENFEST's stay in Leiden in 1903, see KLEIN (1985), 45–46.

the STEFAN-BOLTZMANN law, and WIEN's displacement law, also proposing for the last two to study their dependence on the number of dimensions in the system.[25]

In 1906 EHRENFEST begins to look into the uniqueness of the entropy function that PLANCK had used, and here we can detect his strong conviction that WIEN's displacement law and the STEFAN-BOLTZMANN law contain all of the thermodynamic consequences that can be drawn *a priori* from the frequency-distribution law. He writes down the CLAUSIUS-SZILY theorem, which he will use later to sustain his adiabatic hypothesis, although he apparently considers here only an ideal gas and not black-body radiation. He thinks that a through understanding of WIEN's displacement law and the STEFAN-BOLTZMANN law requires an understanding of how an oscillating system responds to a continuous variation in its normal modes.[26]

On 30 May 1906, a month before the date stamped on EHRENFEST (1906b), he compiled the various questions he was addressing on black-body radiation. He probably was referring to these questions when he announced at the beginning of his article that the ensuing considerations belong in a longer work yet to be published.[27] His points range from *a* through to *z*.[28] A few are devoted to some of the above criticisms of PLANCK's theory and to questions related to the H function, which EHRENFEST constructed for radiation just as BOLTZMANN had for gases. In point *n* an issue appears for the first time that would recur often in EHRENFEST's research: he explicitly opposes BOLTZMANN's method of distributing molecules in energy domains [*sic*] to PLANCK's in which energy is distributed among molecules.[29] In point *o* EHRENFEST proposes to derive WIEN's displacement law by maximizing his proposed H function, and in p by studying the infinitely slow (or fast) variation of the cavity's characteristic frequencies. In point q the issue of the influence of the system's dimensionality also appears.

We are interested particularly in EHRENFEST's annotation entitled "Proof of Wien's displacement law."[30] He starts from the relationship between the variation of the energy E_k of a normal mode and its frequency p_k in an adiabatic compression:

$$\begin{aligned} p'_k &= \rho \cdot p_k \\ E'_k &= \rho \cdot E_k \end{aligned} \tag{2}$$

to infer WIEN's displacement law in the form

$$\varphi = p^3 \psi\left(\frac{\gamma^{1/4}}{p}\right), \tag{3}$$

where γ is the total energy and p the frequency. EHRENFEST's justification of equations (2) is found in another notebook, one more difficult to date.[31] We also find, undated, what

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[25] Notes 266, 269, 270 and 275, April 1905, ENB:1–05; in EA, microf. AHQP/EHR-1.

[26] Notes 595, 638, 640 and 778, February and May 1906, ENB:1–07; in EA, microf. AHQP/EHR-1.

[27] EHRENFEST (1906b). In KLEIN (1959a), 120.

[28] Note 786, 30 May 1906, ENB:1–07; in EA, microf. AHQP/EHR-1.

[29] Actually PLANCK distributed energy elements among resonators.

[30] Note 787, 30/31 May 1906, ENB:1–07; in EA, microf. AHQP/EHR-1.

[31] ENB:2–13; in EA, microf. AHQP/EHR-7.

looks like drafts of articles.[32] One has the title "On the radiant cavity spectral density concept and Wien's displacement law." EHRENFEST states his objective at its outset: to find a derivation of WIEN's displacement law that displays the usefulness of the normal modes in the thermodynamical treatment of black-body radiation. He quotes LORENTZ, who also tried to avoid notions that were apparently alien to thermal radiation, such as rays or wave fronts, even though his treatment differs clearly from LORENTZ's.[33]

By resorting to the normal modes in the cavity, EHRENFEST affirmed that RAYLEIGH founded this method of analysis in kinetic theory and the thermodynamics of radiation, but he had not yet read RAYLEIGH's work, which he knew about only through JEANS's papers, and then inferred the adiabatic invariants (2). Thus EHRENFEST assumed that RAYLEIGH's method would lead him to the simplest proof of WIEN's displacement law.

Other drafts, probably from the same period, have such significant titles as "Adiabatic influence of an oscillating system and Wien's displacement law" and "Elementary deduction of Wien's displacement law."[34] EHRENFEST never published these; nevertheless, they provide clear indications of his interests at this time. He then soon began to ask himself in his notebooks, timidly at first, about the asymptotic properties of the function $f(T/\nu)$ in WIEN's displacement law. Thus, in early 1907 we find a primitive formulation of what he will call the "red condition" in his 1911 paper, and also an attempt to find a definition of entropy when it is invariant in an adiabatic compression.[35] *Energieatome*, as EHRENFEST calls light quanta in his notebooks, hardly appear, and when they do only in brief annotations such as, "if one thinks of energy atoms, how can one then deduce Wien's displacement law and Boltzmann's law?!" And he again insists on the differences between the energy distributions that were adopted by PLANCK and BOLTZMANN.[36]

A notebook of particular significance dates to May 1909, after EHRENFEST and his wife had moved to St. Petersburg. EHRENFEST and his new friend, A. F. IOFFÉ, had been studying the problem of the energy atoms,[37] and he wrote on this subject in his notebook and also gave detailed accounts of the colloquia, including the names of the participants, that he and his wife organized there.[38] Thus, at the first colloquium on 15 October 1908 (RC),[39] EHRENFEST talked about energy atoms. In the second on 28 October (RC), he talked about black-body radiation and "IOFFÉ's hypothesis" was

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[32] EMS:1; in EA (EMS are not microfilmed in the AHQP).

[33] LORENTZ(1901b). Actually, near the head of EHRENFEST's draft we see crossed out the text "Boltzmann's and Wien's laws of radiation," precisely the title of LORENTZ's article.

[34] EMS:1; in EA.

[35] Notes 938, 38 and 57, November 1906 and March/April 1907, ENB:1–08; in EA, microf. AHQP/EHR-1.

[36] Notes 388 and 390, May/July 1907, ENB:1–09; in EA, microf. AHQP/EHR-1. Of course, when the author of an English translation is not specified, as in this case, it means it is ours.

[37] IOFFÉ was from the Ukraine. He got his Ph.D. degree in Munich under RÖNTGEN and settled in St. Petersburg in 1906. For details see GRIGORIAN (1978).

[38] ENB:5–01; in EA, microf. AHQP/EHR-14. See KLEIN (1985), 85–86.

[39] The abbreviation (RC) indicates that a date refers to the Russian (Julian) calendar; it is thus necessary to add 13 days to it to have the corresponding Western (Gregorian) date.

discussed. In the third on 6 November (RC), he talked on "PLANCK's energy atoms," and IOFFÉ committed himself to defending them.

We know of at least two letters that IOFFÉ sent to EHRENFEST in the summer of 1910[40] in which he sketched some of the results he would publish the following year in the *Annalen der Physik*. In one of them, IOFFÉ raised a question that EHRENFEST soon would explore deeper: How was it possible for PLANCK to obtain his radiation law on the basis of his elementary quanta?[41] According to IOFFÉ, one should expect to obtain WIEN's law, simply because it follows from the MAXWELL-BOLTZMANN velocity distribution by changing the variables to the radiant energy density u_ν and frequency ν. EHRENFEST's notebooks indicate that he did not address this issue directly at this time. However, they do contain a few annotations on the analogy between gases and radiation, attempts to analyze thermodynamically a cyclic adiabatic process in the black-body cavity, and various proposals for an entropy function.[42]

Toward the end of December 1910, EHRENFEST reproduced a formula that had appeared in an article by EINSTEIN and HOPF (1910) that month in the *Annalen*.[43] He tried to generalize their representations of different radiation laws, especially PLANCK's and WIEN's. EHRENFEST thus followed the leading journals closely. He also cited EINSTEIN and DEBYE in the context of "energy atoms in the aether,"[44] commented on JEANS's 1910 paper,[45] and referred to contributions of LARMOR and WILSON.[46] To keep his knowledge up to date, he eventually created a journal that contained excerpts from foreign journals, brief reviews, a bibliography, and the like.[47]

2.5. *On EINSTEIN's light-quantum hypothesis (1905–1911)*

EINSTEIN based his light-quantum hypothesis of 1905 on an analogy between the probabilities for a state of an ideal gas and of thermal radiation. He adopted BOLTZMANN's principle and for the ideal gas introduced a "statistical probability" that enabled him to calculate its change in entropy when its volume changed from V to V_0 as

$$S - S_0 = k \log \left(\frac{V}{V_0}\right)^n , \tag{4}$$

where n is the number of gas molecules. He treated thermal radiation differently: he assumed it obeyed WIEN's law and found that its change in entropy when it underwent a change in volume is given by

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[40] IOFFÉ to EHRENFEST, 13 July (RC) and August 1910. In MOSKOVCHENKO and FRENKEL (1990), 267–270, 271–273.

[41] *Ibid.*, 272.

[42] Notes 662, 664 and 689, September/October 1910, ENB:1–11 and note 836, March 1911, ENB:1–12; in EA, microf. AHQP/EHR-2.

[43] Note 764, December 1910, ENB:1–12; in EA, microf. AHQP/EHR-2. See BECK (1993), 229; this paper, EINSTEIN-HOPF (1910), was received by the *Annalen* on 29 August 1910.

[44] Note 839, March 1911, ENB:1–12; in EA, microf. AHQP/EHR-2.

[45] Note 970, May 1911, ENB:1–13; in EA, microf. AHQP/EHR-2. The paper is JEANS (1910).

[46] WILSON (1910), LARMOR (1910).

[47] KLEIN (1985), 89.

$$S - S_{\text{o}} = k \log \left(\frac{V}{V_{\text{o}}} \right)^{E/h\nu} . \tag{5}$$

Comparing these two expressions, EINSTEIN came to his celebrated conclusion:

> Monochromatic radiation of low density (within the range of validity of Wien's radiation formula) behaves thermodynamically as if it consisted of mutually independent energy quanta of magnitude $h\nu$.[48]

One year later, EINSTEIN (1906) stressed the sufficiency of quantization to obtain PLANCK's radiation law and hence to avoid the RAYLEIGH-JEANS law. His article begins:

> In a study published last year... I was lead to the view that light of frequency ν can only be absorbed or emitted in quanta of energy $h\nu$ .... This relationship was developed for a range that corresponds to the range of validity of Wien's radiation formula.
>
> At that time it seemed to me that in a certain respect Planck's theory of radiation constituted a counterpart to my work. New considerations, which are being reported in §1 of this paper, showed me, however, that the theoretical foundation on which Mr. Planck's radiation theory is based differs from the one that would emerge from Maxwell's theory and the theory of electrons, precisely because Planck's theory makes implicit use of the aforementioned hypothesis of light quanta.[49]

Physicists who were beginning to accept PLANCK's energy quanta, however, for the most part rejected EINSTEIN's light-quantum hypothesis. PLANCK himself considered in 1910 that its only supporters were EINSTEIN, LARMOR, STARK, and J. J. THOMSON.[50] There was hardly any reference to light quanta at the Solvay conference of 1911, while PLANCK's energy quanta were discussed widely. The main objection to EINSTEIN's light quanta was that they apparently were incompatible with MAXWELL's electromagnetic waves.

In 1910 WILSON published a paper in the *Philosophical Magazine* in which he used PLANCK's law to derive the number of degrees of freedom of each energy element, finding

$$\bar{\varepsilon} = 2.7\, kT, \tag{6}$$

which seemed to imply, assuming equipartition of energy, that each energy element has 5.4 degrees of freedom.[51] Reasoning from the thermodynamics of gases and radiation, WILSON then suggested that "the elements of disturbance [as LARMOR had called them] ought to have energy corresponding to six degrees of freedom instead of only 5.4, but the energy is not distributed among the elements in the same way as among the gas molecules."[52] To recover six degrees of freedom, WILSON calculated the mean energy

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[48] EINSTEIN (1905). In BECK (1989), 97. For simplicity we employ today's notation.

[49] EINSTEIN (1906). In BECK (1989), 192.

[50] PLANCK (1910), 761.

[51] WILSON (1910), 123.

[52] *Ibid.*, 124.

$\bar{\varepsilon}$ assuming that "the chance that an element is in V_1 when the volume is V_2 is V_1/V_2."[53] Note that this is the "statistical probability" that EINSTEIN had used in 1905 for gases, but WILSON now applied it to radiation.

We emphasize two aspects of WILSON's analysis. First, it is striking that he does not mention that the value $3kT$ for the mean energy per element is obtained by exactly the same procedure that led him to (6), except that then WIEN's law is required instead of PLANCK's, as EINSTEIN had emphasized in 1905 and as WILSON knew, since he cited EINSTEIN at the beginning of his paper. Second, WILSON recognizes EINSTEIN as the promoter of the quantum interpretation of the energy of radiation, as opposed to PLANCK's quantum interpretation of the energy of resonators. In other words, WILSON emphasized the difference between these two quantum interpretations even though PLANCK's law can be obtained from both of them.

In 1910 JEANS also published a paper in the *Philosophical Magazine* that is often considered as containing the first traces of his conversion to the emerging quantum theory.[54] JEANS opens by praising LARMOR's attempts to formulate PLANCK's theory "in terms of continuous motion, or mathematically in terms of differential equations," but he then asks:

> Can any system of physical laws expressible in terms of continuous motion (or of mathematical laws expressible in terms of differential equations) be constructed such that a system of matter and aether tends to a final state in which Planck's law is obeyed? It will be found that the answer obtained is in the negative.[55]

JEANS, however, still refused to accept the quantum hypothesis. He suggested that PLANCK's law does not describe a real equilibrium state and proposed "an alternative method of arriving at Planck's law."[56] Its central feature was his assumption that a high frequency mode has a low probability of having a unit of energy $\varepsilon = h\nu$. We will see that EHRENFEST made a similar assumption in 1911, although he introduced a general "weight function" rather than resort to the canonical distribution, as JEANS had done. We find it at least curious how widely statistical methods were used during this period in trying to locate the essence of the quantum hypothesis, especially when it is borne in mind that such methods, including the equipartition principle, had been designed for gases, and the validity of their extension to radiation could not be taken for granted.[57]

In the same volume of the *Annalen der Physik* that EHRENFEST's paper of 1911 was published, IOFFÉ published a paper in which he tried to deepen or modify EINSTEIN's hypothesis to account better for the experimental results.[58] EHRENFEST's

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[53] *Ibid.*

[54] JEANS (1910).

[55] *Ibid.*, 944.

[56] *Ibid.*, 953.

[57] GIBBS had made his opinion clear on the non-viability of statistical mechanics to explain thermal radiation: GIBBS (1902), 167. Regarding the complex relationship between the equipartition theorem and the evolution of the quantum theory of radiation see BERGIA and NAVARRO (1997).

[58] IOFFÉ (1911). This paper was received by the *Annalen* on 24 July 1911 and published in November. EHRENFEST (1911) was received 8 July 1911, and published in the October issue.

notebooks clearly reveal his close collaboration with IOFFÉ on his radiation research, especially during the first half of 1911. Although IOFFÉ's investigations did not have a strong impact on the development of quantum theory, his presentation of them in St. Petersburg did attract attention. As EPSTEIN in Munich wrote to EHRENFEST: "I have heard that IOFFÉ may have invented a new theory of radiation. Can you tell me anything about that?" [59]

IOFFÉ was one of the few who recognized the difference between PLANCK's and EINSTEIN's quantum hypotheses and, at least after 1908, strongly supported the latter.[60] EHRENFEST visited SOMMERFELD, PLANCK, RÖNTGEN, and WIEN in early 1912 and learned that IOFFÉ's work, to which he had contributed, was underappreciated.[61] Nevertheless, while IOFFÉ differed with EHRENFEST, his paper contained a number of suggestions and comments to which EHRENFEST would respond implicitly in his paper of 1911. IOFFÉ indicated his preference for EINSTEIN's theory over PLANCK's at the beginning of his article of 1911:

> The theory of radiation, as developed mainly by W. Wien and M. Planck, is a theory of "black radiation." Although this is a fundamental problem, it affects only a fraction of all of the radiative phenomena. The rapidly increasing experimental research in recent years on "purely luminous effects" (photoelectricity, photochemistry, fluorescence, photoionization) renders such a theory really infertile.
>
> A. Einstein has succeeded in explaining many empirical regularities in the cited phenomena by applying and extending the hypothesis of energy quanta. A quantitative development of the theory, however, is still missing.[62]

IOFFÉ proposed to attribute new properties to radiation to explain the experimental results and to obtain a unique derivation of the spectral-distribution law. To this end, he introduced the following state quantity for radiation:

$$P = \frac{U}{\bar{\nu}}, \tag{7}$$

where U is the total energy and $\bar{\nu}$ some average frequency. In view of the advantages he thought EINSTEIN's hypothesis offered, he proposed to quantize P by assuming that $P = Nh$. His quanta would be indestructible and have energy $\varepsilon = h\nu$ for monochromatic radiation and $\varepsilon = h\bar{\nu}$ for multicolored radiation; he likened them to electrons (quanta of electricity) and to atoms (quanta of mass).

Regarding the friendship between EHRENFEST and IOFFÉ, see KLEIN (1985), 84–86. For their correspondence, in Russian, see MOSKOVCHENKO and FRENKEL (1990).

[59] EPSTEIN to EHRENFEST, 1 December 1910; in EA, microf. AHQP/EHR-19, Section 10. EPSTEIN was born in Warsaw and lived in Moscow from 1901 to 1910, first as a student, later as a teacher, and then moved to Munich to do his Ph.D. degree under SOMMERFELD.

[60] See footnote 40.

[61] EHRENFEST to his wife TATIANA, 20/21, 31 January and 1 February 1912. In EA, microf. AHQP/EHR-29, Section 5. In particular, PLANCK told EHRENFEST that he was unhappy with an inappropriate quotation by IOFFÉ of a privately communicated comment he had made to him. See IOFFÉ (1911), 536, footnote 1.

[62] IOFFÉ (1911), 534.

IOFFÉ devoted the last section of his paper to establishing an analogy between black-body radiation and gas molecules, stressing the limitations of such an analogy, however, because the number of radiation quanta is not conserved. He proposed to find the most probable spectral-energy distribution similarly to the way in which the velocity distribution of molecules is found, but he cautioned that the result will not be unique: The form of the spectral-distribution law depends on additional conditions, as EHRENFEST had proved in 1905.[63] IOFFÉ claimed that to determine the spectral-energy distribution, the behavior of P must be established previously by introducing a specific physical hypothesis, and that some degree of correlation among the quanta must be assumed to recover PLANCK's law. He maintained that available experimental data were insufficient to decide on a precise quantum hypothesis, and thus radiative phenomena other than cavity radiation would have to be studied.[64]

3. EHRENFEST's paper of 1911

EHRENFEST and IOFFÉ addressed the same problem: To make the meaning of the quantum hypothesis precise, and to justify its necessity on the basis of the experimental data. While IOFFÉ insisted that a new formulation of the quantum theory should be developed based on the behavior of black-body radiation as well as other phenomena, EHRENFEST tried to establish which aspects of the quantum theory were necessary to accept based on the experimental data on black-body radiation. Initially, EHRENFEST evidently wanted to begin his paper of 1911 by analyzing EINSTEIN's 1905 derivation, because his manuscripts contain a draft of its first section, entitled "The deduction, presented by EINSTEIN (1905), of the hypothesis of light quanta from WIEN's spectral equation."[65] He decided, however, to omit this section and to consider the meaning of EINSTEIN's light-quantum hypothesis directly.

3.1. EHRENFEST's paper

In presenting the main points EHRENFEST made in his paper, we will not follow its original order but one better suited to our purposes.

A. Prerequisites to which the radiation law must comply. EHRENFEST states as his objective to establish, by analyzing the properties of thermal radiation, those features of EINSTEIN's light-quantum hypothesis that can be considered as definitively settled and can be expressed as constraints on the "weight function" (*Gewichtsfunction*)

$$\gamma(\nu, E)dE \tag{8}$$

representing the probability that an individual normal mode of frequency ν has an energy between E and $E + dE$. This boils down to finding the form of the weight function

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[63] *Ibid.*, 548–550. IOFFÉ doesn't cite EHRENFEST.

[64] *Ibid.*, 550.

[65] EMS:5; in EA.

in light of the theoretical and experimental properties of black-body radiation. Those properties are:

(I) The entropy of the radiation in a cavity with totally reflecting walls remains constant in a reversible adiabatic compression, whether or not the radiation is black-body radiation. This property had been used by PLANCK and even earlier by BOLTZMANN when he derived the STEFAN-BOLTZMANN law. It also entered in a key way in the existing proofs of WIEN's displacement law, for example the one that PLANCK presented in his *Vorlesungen*.[66]

(II) WIEN's displacement law is valid; EHRENFEST writes it as

$$\rho\,(\nu, T)\,d\nu = \alpha\,\nu^3 f\left(\beta\frac{\nu}{T}\right) d\nu. \tag{9}$$

This law does not impose any restriction *a priori* on the form of the function f. Restrictions emerge from the following conditions:

(III) The RAYLEIGH-JEANS law applies to "very long wavelengths." In terms of the function f, this forces f to satisfy what EHRENFEST calls the "red condition" (*Rotforderung*):

$$\mathrm{Lim}_{\sigma\to 0}\,\{\sigma \cdot f(\sigma)\} = 1, \tag{10}$$

where $\sigma = \beta\frac{\nu}{T}$. EHRENFEST states explicitly that the law WIEN had proposed, wherein f takes the form of an exponential $e^{-\sigma}$, does not satisfy this condition; in that case the limit is zero.

(IV) EHRENFEST wants to avoid what he calls the "RAYLEIGH-JEANS catastrophe in the ultraviolet" region of the black-body spectrum. To this end, the spectral-distribution function $\rho(\nu, T)$ must decrease more rapidly than $1/\nu$ for large values of ν, which requires the "violet condition" (*Violettforderung*):

$$\mathrm{Lim}_{\sigma\to\infty}\left\{\sigma^4 \cdot f(\sigma)\right\} = 0. \tag{11}$$

(V) Given that WIEN's law accounts satisfactorily for the experimental results at large σ, EHRENFEST suggests a "strong" alternative to condition (11) based upon an extrapolation from experimental data:

$$\mathrm{Lim}_{\sigma\to\infty}\left\{\sigma^n \cdot f(\sigma)\right\} = 0, \text{ for arbitrarily large } n. \tag{12}$$

This he calls the "strengthened violet condition" (*verstärkte Violettforderung*).

(VI) Since the black-body radiation formulas proposed by WIEN and PLANCK have the same behavior at large values of σ, EHRENFEST imposes what he calls the "WIEN-PLANCK violet condition" (*Wien-Plancksche Violettforderung*), namely, that there exists a finite and non-zero value of L such that the limit

$$\mathrm{Lim}_{\sigma\to\infty}\left\{\frac{f(\sigma)}{e^{-L\sigma}}\right\} = M \tag{13}$$

holds, where M is a finite non-zero constant. This condition clearly is satisfied by the f functions associated with both WIEN's and PLANCK's formulas.

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[66] PLANCK (1988), 314–332.

EHRENFEST puts conditions III and IV into the category of indispensable requisites that must be satisfied by any radiation law. The RAYLEIGH-JEANS law, however, which was deduced from the principle of equipartition of energy and leads to the ultraviolet catastrophe, is in good agreement with experiment at long wavelengths. EHRENFEST thus bases the validity of condition III on direct experimental evidence, while the validity of condition IV is justified by the finiteness of the total energy in the cavity. Conditions V and VI, which only apply to the limit $\sigma \to \infty$, go beyond the available experimental evidence. Condition VI is more specific than V; hence, EHRENFEST says, "it would be wrong... to reject all those $f(\sigma)$ which do not satisfy equality (13)."[67]

B. Formalism of normal modes of vibration. EHRENFEST gives two starting points to describe equilibrium, either by the normal-modes method that was introduced by RAYLEIGH and JEANS, or in terms of Planckian oscillators. He refers to PLANCK's *Vorlesungen*[68] for the calculation of the number of independent normal modes $N(\nu)$ in a perfectly reflecting cubic cavity of side length l with frequencies between ν and $\nu + d\nu$, which yields

$$N(\nu)\,d\nu = \frac{8\pi\, l^3 \nu^2}{c^3}\, d\nu. \tag{14}$$

EHRENFEST also mentions an adiabatic invariant (although he does not use that terminology) for the cavity: If its walls are contracted infinitely slowly, then the energy of each normal mode increases (at the expense of the work done against the radiation pressure) linearly with frequency, hence inversely with the length l of the cube's side, so that

$$\frac{E'_{\nu'}}{\nu'} = \frac{E_\nu}{\nu} \qquad \nu' l' = \nu l. \tag{15}$$

EHRENFEST then refers to RAYLEIGH (1902) for a derivation of the STEFAN-BOLTZMANN law and states that Eq. (15) permits the "simplest possible derivation of *WIEN's displacement law*."[69] We will return to this point later.

C. Properties of the weight function. Section 3 of EHRENFEST's paper is crucial to an understanding of the essence of his paper. It is entitled "the theoretical probabilistic formalism," and in it EHRENFEST applies a method that was developed by BOLTZMANN in studying a mixture of different gases. EHRENFEST likens the number of normal modes of different frequencies to the number of atoms of different gases in the mixture, but adds an important innovation: He considers a statistical weight that does not have to be proportional to the phase space "(q, p)–volume."[70] From Eq. (8), he calculates the probability that of the $N(\nu)d\nu$ modes of frequency ν , there will be a_1 in the interval dE_1, a_2 in dE_2, etc., which he writes as

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[67] EHRENFEST (1911). In KLEIN (1959a), 187.

[68] PLANCK (1988), 420–425.

[69] EHRENFEST (1911). In KLEIN (1959a), 188, footnote (emphasis in the original).

[70] *Ibid.*, 189.

$$\left[\gamma(\nu, E_1)\cdot dE_1\right]^{a_1}\cdot\left[\gamma(\nu, E_2)\cdot dE_2\right]^{a_2}\cdots\frac{[N(\nu)\cdot d\nu]!}{a_1!a_2!...}. \tag{16}$$

He then maximizes the total probability *W*, which he deduces from products of expressions like (16), using STIRLING's approximation and imposing the constraints of the total number of modes and the total energy of the system. He finally obtains

$$a(\nu, E) = N(\nu)\,\frac{\gamma(\nu, E)\,e^{-\mu E}}{\int\limits_0^\infty dE\cdot\gamma(\nu, E)\,e^{-\mu E}}, \tag{17}$$

where $a(\nu, E)$ is the initial distribution of the modes and the multiplier μ depends on the total energy *E* for a given weight function $\gamma(\nu, E)$.

EHRENFEST then moves over to the language of statistics: If (17) is to match property (I), that is, if the entropy does not change in an adiabatic reversible transformation, then the quantity $\log W$ must remain constant in such a process, independent of the initial distribution $a(\nu, E)$. This obviously assumes the validity of BOLTZMANN's principle,

$$S = k\log W,^{71} \tag{18}$$

which, together with the adiabatic invariant in (15), permits EHRENFEST to obtain a key result: The weight function must be of the form

$$\gamma(\nu, E) = Q(\nu)\cdot G\left(\frac{E}{\nu}\right), \tag{19}$$

where $Q(\nu)$ is an irrelevant multiplicative factor.

To calculate the energy density $\rho(\nu, T)$ corresponding to a given frequency ν, it now suffices to take Eqs. (17) and (19) into account to obtain the most probable distribution,

$$\begin{aligned}\rho(\nu, T)\,d\nu &= \frac{N(\nu)}{l^3}\cdot\frac{\int\limits_0^\infty dE\cdot E\cdot e^{-\mu E}\gamma(\nu, E)}{\int\limits_0^\infty dE\cdot e^{-\mu E}\gamma(\nu, E)}d\nu\\ &= \frac{8\pi\nu^3}{c^3}\cdot\frac{\int\limits_0^\infty dq\cdot q\,e^{-\mu\nu q}G(q)}{\int\limits_0^\infty dq\cdot e^{-\mu\nu q}G(q)}d\nu = \frac{8\pi}{c^3}\nu^3 f(\nu\mu)\,d\nu,\end{aligned} \tag{20}$$

where $q \equiv E/\nu$.[72] For (20) to now satisfy property (II), it is necessary and sufficient that $\mu = \beta/T$. We emphasize that EHRENFEST has introduced a significant innovation: He has shown that a probabilistic formulation leads to WIEN's displacement law by applying the methods of statistical mechanics to the normal modes of vibration in a radiating cavity.

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[71] In 1914, EHRENFEST would make a more general analysis of the conditions the weight function must satisfy so that BOLTZMANN's principle still will be applicable. See EHRENFEST (1914).

[72] EHRENFEST (1911). In KLEIN (1959a), 194.

D. Generalization of the weight function. EHRENFEST introduces a general weight function that, in addition to the usual continuous spectrum (*Streckenbelegung*), may contain a possible discrete spectrum (*Punktbelegung*). To this end, he assigns finite singular weights $G_0, G_1, G_2, \dots$ to the points $q_0, q_1, q_2, \dots$ and easily shows that the relationship between the weight function $f\ (\sigma)$ and the radiation law is

$$C \cdot f(\sigma) = -\frac{d}{d\sigma}\{\log\ Q\ (\sigma)\}, \tag{21}$$

where C, σ, and Q are defined by

$$C = \frac{\alpha c^3}{8\pi};\ \sigma = \frac{\beta \nu}{T}$$

$$Q\ (\sigma) = \sum_{r=0}^{\infty} e^{-\sigma q_r}\ G_r + \int_0^{\infty} dq \cdot e^{-\sigma q} G\ (q), \tag{22}$$

and α and β are the constants that appear in WIEN's displacement law (9).[73] This is the most general form of the weight function having the properties that the entropy remains constant in an adiabatic compression and the adiabatic invariant (15) holds. It obviously leaves the question of the continuity or discontinuity of the weight function open.

E. Limitations on the form of the weight function

(a) Violet condition. This is not satisfied for a purely continuous domain of $G(q)$. The weight function must include a discrete domain with a non-zero singular weight G_0 at $q = 0$. In addition, if the violet condition is to be satisfied, then $G(q)$ must approach zero faster than q^2 as $q \to 0$. And if the strengthened violet condition is to be satisfied, then $G(q)$ must approach zero faster than q^n for arbitrary n.

(b) Red condition. The implications of this condition appear at large values of q (*i.e.*, at large energy): $G(q)$ cannot decrease arbitrarily for increasing values of q. EHRENFEST shows that if this condition is met, then the expression

$$\sum_1^{\infty} q_r \cdot G_r + \int_0^{\infty} dq \cdot q \cdot G(q) \tag{23}$$

cannot have a finite value. Thus, EHRENFEST's speculation of 1906 on why the total energy does not blow up at high frequencies now acquires mathematical rigor. Indeed, at increasing frequencies (*i.e.*, at decreasing q), the probability that energy will be distributed in the corresponding normal modes ("high tones") decreases. To avoid the ultraviolet catastrophe requires also the imposition of an unexpected singularity at $E = 0$.[74]

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[73] Note that the Q's in (19) and (22) are not the same.

[74] The same conclusion is reached in POINCARÉ (1912), though independently and by a different method: the finiteness of the total energy in a radiant cavity requires that a singularity be present at $E = 0$ (for a monochromatic resonator in this case). This paper of POINCARÉ is discussed in McCORMMACH (1967) and in PRENTIS (1995).

EHRENFEST illustrates all of this with an example. He proposes the weight function

$$G_o = A \neq 0 \quad \text{for} \quad q = 0 \quad \text{(discrete spectrum)} \tag{24}$$

$$G(q) = \begin{cases} 0 & \text{for} \quad 0 \leq q \leq R \\ & \\ B & \text{for} \quad q > R \end{cases} \qquad \text{(continuous spectrum).}$$

A simple calculation permits us to write equation (21) in the form

$$C \cdot f(\sigma) = \frac{1 + \sigma^{-1}}{1 + \sigma\, e^{\sigma}}, \tag{25}$$

where we have set $A = RB$ and chosen suitable units so that $R = 1$. This function verifies the strengthened violet condition (hence also the violet condition),[75] as well as the red condition. For both small and large values of σ, Eq. (25) can be recast in the form

$$C \cdot f(\sigma) = \frac{e^{-\sigma}}{\sigma}. \tag{26}$$

Here EHRENFEST cites the behavior of the empirical formula that RAYLEIGH proposed in 1900 as a candidate for the radiation law:

$$\rho(\nu, T) = \alpha \nu^2 T e^{-\beta \frac{\nu}{T}}. \tag{27}$$

This corresponds to Eq. (26)[76] but does not verify the WIEN-PLANCK violet condition. We thus have here the first genuinely statistical analysis of one of the radiation laws. EHRENFEST has shown how a formula, Eq. (25), can be obtained that coincides with RAYLEIGH's formula (27) in both the low and high frequency limits. But Eq. (25) was derived by assigning the same non-zero statistical weight to all energy values, except in the range between $R = 0$ and $R = 1$. In addition, the zero energy value has a non-zero singular weight. This example may have a value beyond being just illustrative: It could be interpreted as showing the existence of a resonator-excitation threshold. Thus, if one sets $A = R = 0$, that is, if there exists only a continuous range above $q = 0$ and equiprobability is satisfied, then Eq. (21) can be written as

$$C \cdot f(\sigma) = \frac{1}{\sigma}, \tag{28}$$

which leads to the RAYLEIGH-JEANS radiation formula.

F. Application to WIEN's and PLANCK's formulas. Using some of the results above, EHRENFEST concluded that if the WIEN-PLANCK condition (13) is satisfied, then in addition to the point $q_0 = 0$ another point say $q_1 = L$, with a non-zero singular weight must necessarily exist, and between these two points there must not exist another value of q with a singular weight different from zero. He warns the reader that:

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[75] The violet condition would be violated if $A = 0$ or if $R = 0$.

[76] EHRENFEST (1911). In KLEIN (1959a), 199, footnote 2.

> *While the necessity of a singular weight for $q_0 = 0$ follows directly from the obvious equality* [(11)], *we only obtain the necessity of a singular weight for a second point* $q_1 \neq 0$ if we subject $f(\sigma)$ to the equality [(13)], which essentially goes beyond any experimental control. Inappropriate use will be made of the ensuing statement then if, guided only by the good coincidence between [WIEN's radiation law] and experimental data at high ν/T, all of the $G(q)$ that do not fulfil condition C [the existence of another $q_1 \neq 0$ with a non-zero singular weight] are dismissed.[77]

EHRENFEST thus once again shows his consideration of both high and low-frequency experimental data (which seems logical, given that the lower limit of ν is bounded while the upper limit is not). He also anticipates the weights that correspond to WIEN's and PLANCK's formulas:

$$G(q) = 0; \quad q_r = r; \quad G_r = 1/r!, \quad \text{for WIEN's formula :}$$

$$C \cdot f(\sigma) = e^{-\sigma}$$

$$G(q) = 0; \quad q_r = r; \quad G_r = A, \quad \text{for PLANCK's formula:}$$

$$C \cdot f(\sigma) = \frac{1}{e^{\sigma} - 1}. \tag{29}$$

G. Summary and conclusions. The last section of EHRENFEST's paper, which is also the longest one, is the richest one from our point of view. We now interpret and comment on his results. EHRENFEST not only shows the origins of discontinuity, he also shows why the corresponding interval must be proportional to the frequency ν, namely, because $\gamma(\nu, E)$ has the form $G(E/\nu)$.[78] He stresses that a loss of precision occurs in passing from a description in terms of normal modes of vibration (RAYLEIGH-JEANS) to the terminology of resonators (PLANCK), and he then states his conclusion in new language:

> *A sufficiently rapid rate of decrease in the radiation curve for infinitely high ν can be accomplished only if the resonators present some sort of "excitation threshold"* [Reizschwelle], *whose value is anyway proportional to the resonator frequency.* [79]

EHRENFEST specifies the "peculiar features presented by the hypothesis of light quanta in the fashion in which EINSTEIN makes use of it" as follows:

A) A resonator of frequency ν can show only discrete values of the energy: $0, h\nu, 2h\nu, \ldots$

B) These values are made effective by the joint storage of elementary magnitudes of energy, independent of one another and of value $h\nu$.

C) These light quanta do not behave like atoms only in emission and absorption phenomena, they also possess an existence of their own in empty space.[80]

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[77] *Ibid.*, 201 (emphasis in the original).

[78] *Ibid.*, 204. We find interesting ROSENFELD's comment on this issue. See COHEN and STACHEL (1979), 230; particularly on his difference with POINCARÉ.

[79] EHRENFEST (1911). In KLEIN (1959a), 204 (emphasis in the original).

[80] *Ibid.*, 204–205.

EHRENFEST cites here EINSTEIN's papers of 1905, 1906, and 1909. EINSTEIN's first paper is not as clear as EHRENFEST's above statements on light quanta, even if EINSTEIN insisted on statement (C) in his 1909 paper in which he analyzed the energy and momentum fluctuations in black-body radiation. EHRENFEST regards (A) as confirmed by the singularity at zero energy, the extremely small probability of neighboring energy values, and their proportionality to ν . He stresses the essential point that his conclusions are based on the behavior that $\rho(\nu, T)$ must have at limiting values of ν/T. Hence, we see that his arguments so far cannot be considered definitive in justifying the necessity of something as revolutionary as light quanta.

EHRENFEST's treatment allows us to prove rigorously the necessity of energy quantization by inverting the procedure he used to obtain formulas (29). To this end, it is expedient to combine Eqs. (21) and (22) to obtain

$$\sum_{r=0}^{\infty} G_r\, e^{-q_r\sigma} + \int_0^{\infty} dq \cdot G(q)\, e^{-q\sigma} = e^{-\int C\cdot f(\sigma)d\sigma}. \tag{30}$$

The weights now are given by the solution to this functional equation, in which the radiation law determines the datum appearing on its right-hand side. Thus, knowledge of $f(\sigma)$, that is, of the radiation law, and not just its asymptotic behavior, leads to the necessary weights, both discrete and continuous, that are required to recover that law. Today the functional equation (30) can be solved without particular difficulty by finding the "spectral decomposition" of the right-hand side after substitution of the corresponding expression for $f(\sigma)$, given by equation (29), for either WIEN's or PLANCK's law.[81] In EHRENFEST's day these difficulties obviously were greater.

EHRENFEST cites a paper by RIEMANN in which he solved equation (30) without the summation term by means of integration in the complex plane. It thus seemed that weights now could be inferred from PLANCK's and WIEN's formulas, rather than the reverse, as always had been the case to date. EHRENFEST, however, indicates only that he owes the solution of Eq. (30) to an unspecified "intimate colleague."[82] In any case, he finds that $G(q) = 0$, and that non-zero singular weights occur for $q_r = 0, 1, 2, \ldots$.

Near the end EHRENFEST makes a comment – to which little attention has been paid – on a subtlety concerning the difference between EINSTEIN's light quanta and PLANCK's energy elements. EHRENFEST returns to the three properties of EINSTEIN's light quanta noted above and suggests that assumption (A) has been proven to be valid. He then emphasizes that EINSTEIN's assumption (C), that light quanta exist in a vacuum, which is alien to PLANCK's theory, is widely known. EHRENFEST also believes that, strictly speaking, EINSTEIN and PLANCK also differ in assumption (B). This is a confusion that is partly caused by the two different derivations PLANCK gave of his distribution law when he calculated the most probable distribution:

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[81] See, for instance, COHEN and STACHEL (1979), 229.

[82] This appears to be Prof. HERGLOTZ, as we can read in some of the article's drafts. For some reason EHRENFEST ultimately decided not to publish the name of his colleague. See EMS:5; in EA.

a) of the *resonators in* different *energy* domains
b) of the *energy in* different *resonators* (§150 and §148 of Planck's book, respectively), which is in turn based on:
α) Each individual resonator of frequency ν can only have energies 0, $h\nu$, $2h\nu, \ldots,$ all of them with the same probability.
β) The energy of the radiation of frequency ν is distributed in elementary finite quanta of value $h\nu$ among resonators of frequency ν. Each elementary quantum has equal probability of going into all resonators, and each elementary quantum must be considered independent and non-interacting with the others. [83]

EHRENFEST considers, on the one hand, that no equivalent derivations can be considered, since method (a) is not based, nor can be founded on (β). But, on the other hand, the two methods in PLANCK's case do not imply different counting strategies. Keeping the somewhat cryptic style of EHRENFEST's final section in mind, we read:

> It can be proved that: *assumption β) does not lead to Planck's radiation formula, but rather to a practically quasi infinite number of radiation formulas, wherein selection of a privileged one requires some additional condition.*[84]

EHRENFEST's statement reminds us of IOFFÉ's view that it is necessary to endow energy quanta with some additional property to determine the radiation law unambiguously.[85] Summing up, EHRENFEST claims that EINSTEIN's and PLANCK's hypotheses differ in both assumptions (B) and (C), and not only in (C) as was generally held at the time. This is a highly non-trivial conclusion that does not have a clear connection to the calculations preceding it. As we will see, EHRENFEST returns frequently to this issue in his notebooks, and it is conceivable that when writing his 1911 paper he still may not have had as clear and rigorous proof of it as he desired. This is precisely the theme of the footnote with which EHRENFEST closes his article, where he announces his intention of returning to his analysis of the distinction between EINSTEIN's and PLANCK's quantum hypotheses, a subject that he recalled giving a talk on to the St. Petersburg Physical Society in April 1911.[86]

3.2. On the elaboration of EHRENFEST's paper

Let now return to our analysis of EHRENFEST's notebooks, picking up where we had left it in Sect. 2.4. In March 1911, his annotations on radiation again dominated. We can grasp them in light of the results that appeared in his paper of 1911. EHRENFEST refers to a letter to IOFFÉ, which is no longer extant, in which he posed what he calls "IOFFÉ's problem,"[87] namely, to find the law describing the distribution of N h-elements [*sic*] with total energy $D = AT^4$ in the most probable form in ν -space [ν -*Scala*]. He writes (where an "*h*" must be understood as a quantum):

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[83] EHRENFEST (1911). In KLEIN (1959a), 207 (emphasis in the original).
[84] *Ibid.*
[85] IOFFÉ (1911), 550.
[86] This happened on 19 April 1911 (RC). See the article's manuscripts, EMS:5; in EA.
[87] Note 838, March 1911, ENB:1–12; in EA, microf. AHQP/EHR-2.

$\gamma(\nu)\Delta$ a priori probability that an individual h have frequency between ν and $\nu + d\nu$
$h\omega(\nu)$ energy quantum each h has
$a(\nu)\Delta$ number of h-elements between ν and $\nu + d\nu$

- - - - o - - - -

$$W = (\gamma_1\Delta)^{a_1\Delta} \cdots (\gamma_n\Delta)^{a_n\Delta} \cdot \frac{N!}{(a_1\Delta)! \cdots (a_n\Delta)!}$$

And on the following page, after a few calculations, he writes *log W* and then:

Boundary conditions

$$(1) \qquad \int_0^\infty d\nu \cdot a(\nu) = N \quad (¡¡\text{au}!!)$$

$$(2) \qquad \int_0^\infty d\nu \cdot a(\nu) \cdot \omega(\nu) = D = AT^4$$

We note that he here leaves the energy of the quantum unspecified.

In the same annotation, he gives WIEN's displacement law in the form

$$h\omega(\nu) \cdot a(\nu) = \alpha\nu^3 \cdot f\left(\frac{\beta\nu}{T}\right), \tag{31}$$

and he assumes, as a simplifying hypothesis, that $\omega(\nu) = \nu$.[88] Shortly thereafter, in an annotation of 21 March, the question of combinatorics appears. We read:

> On Planck's entropy
> P spheres in N urns
> N^P types of distribution
> Planck says: $\dfrac{(N+P-1)!}{(N-1)!(P-1)!}$
> this must be wrong.
>
> - - - - o - - - -
>
> It is to be expected that N^P must somehow lead (like in Einstein's philosophy) to Wien's distribution.– But how.[89]

EHRENFEST had long been aware that PLANCK, even though he resorted to BOLTZMANN's combinatorics, had done so in a way that had important consequences: As he had written in a letter to IOFFÉ, PLANCK's use of energy quanta leads unavoidably to WIEN's law. Now, in March 1911, EHRENFEST proposed to clarify whether PLANCK's distribution of energy quanta among resonators leads to PLANCK's law.[90] Under the title "Distribution of normal modes on energy," EHRENFEST calculated the frequency distribution for radiation in a cubic cavity of unit side by quantizing the energy of the normal modes. He concluded that PLANCK's law is obtained from a distribution "à la BOLTZMANN" (normal modes in phase space) rather than from distributing energy quanta amongst normal modes.

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[88] Notes 840 and 841, March 1911, ENB:1–12; in EA, microf. AHQP/EHR-2.
[89] Note 843, 21 March 1911 (RC), ENB:1–12; in EA, microf. AHQP/EHR-2.
[90] Notes 844 and 846, March 1911, ENB:1–12; in EA, microf. AHQP/EHR-2.

On 20 March (RC), EHRENFEST spoke in a colloquium about EINSTEIN's light quanta of 1905 and IOFFÉ's problem.[91] Around this time, he structured his research on two fronts: Analyzing the distribution of h-elements in ν-space (IOFFÉ's problem), and attempting to apply BOLTZMANN's formalism to normal modes, as eventually appeared in his 1911 paper. The weight function makes its first appearance around this time, together with the necessity of discretization.[92] He writes:

> (1) $\int_0^\infty dx \cdot \gamma\,(\nu, x)\, e^{-\mu x} = \dfrac{1}{1 - e^{-\nu h \mu}}$
> find a <u>non</u> discrete sol[ution] $\gamma(\nu, x)$!
> (2) To calculate the Planckian entropy of Boltzmann.
> (3) To oppose energy on resonators-resonators on energy.[93]

His only hesitation to accept the uniqueness of PLANCK's discrete solution seems to concern the dependence of μ in the exponential in point (1) on parameters other than the temperature.

On March 25 (RC), EHRENFEST relates adiabatic invariants to the weight function and WIEN's displacement law, and he also stresses the existence of a ν-dependent multiplicative factor, which, however, is devoid of physical meaning:

> the form of $\gamma(\nu, x)$ could instead be restricted, because of the displacement law, to the following:
>
> $$dx \cdot \gamma(\nu, x) = d\left(\frac{x}{\nu}\right) \cdot \varphi\left(\frac{x}{\nu}\right)$$
>
> or
>
> $$\underline{\underline{\gamma(\nu, x) = \frac{1}{\nu} \cdot \varphi\left(\frac{x}{\nu}\right)}}$$
>
> Proof?!!
>
> May be like this: the entropy of any radiation, also monochromatic, must remain constant in adiabatic compressions. Hence, for each normal mode x and $\underline{\nu}$ will vary in such a way that x/ν const.?[94]

Or, more explicitly:

> It must follow from an adiabatic compression that (!!!)
>
> $$\gamma\,(\nu, E) = f\left(\frac{E}{\nu}\right) \cdot g\,(\nu)\,.^{95} \tag{32}$$

EHRENFEST worries now about finding a mechanical argument to infer this result, which is more in accordance with the methods of statistical mechanics. We read further:

> Problem: it follows from Wien's displacement law (more precisely: <u>from the invariance of probability in adiabatic compressions</u>) that phase-space points of the normal modes of

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[91] ENB:4–06; in EA, microf. AHQP/EHR-11.

[92] Notes 852 and 854, March 1911 (RC), ENB:1–12; in EA, microf. AHQP/EHR-2.

[93] Note 855, 25 March 1911 (RC), ENB:1–12; in EA, microf. AHQP/EHR-2 (x denotes energy).

[94] Note 857, 25 March 1911 (RC), ENB:1–12; in EA, microf. AHQP/EHR-2.

[95] Notes 858, March 1911; ENB:1–12; in EA, microf. AHQP/EHR-2. EHRENFEST writes $\ni$ instead of E.

> oscillation are not distributed on the surface $dpdq$ – or dE – but rather on the surface $\frac{dp\cdot dq}{\nu}$,
> which is precisely $\frac{dE}{\nu}$
> Weight function $f\left(\frac{E}{\nu}\right)$.[96]

We detect here a sketch of EHRENFEST's 1911 paper. After posing the problem "à la Boltzmann," EHRENFEST resorts to WIEN's displacement law, which he needs to identify the coefficient μ as the inverse temperature. This, and the uniqueness of the solution of Eq. (30), are two of the issues EHRENFEST was concerned with at this time. At the end of note 858, he indicates that he will consult HERGLOTZ on these matters. A letter from HERGLOTZ of 9 April 1911 may well be his response to EHRENFEST.[97] It has a marked mathematical character, and we will not discuss it in detail here; we only comment that it contains the solution to the integral Eq. (30) for WIEN's law (also a discrete solution), and also confirms the uniqueness of the solution for PLANCK's law, as EHRENFEST already had determined. It appears, however, that HERGLOTZ too was unable to find a rigorous proof that μ is the inverse of T. In 1914, EHRENFEST presented a rigorous justification of this relationship, one that is valid for certain systems but not in general.

On 31 March (RC), EHRENFEST notes the reception of a letter from HERGLOTZ, which might well be the one mentioned above.[98] On that same day, he sends IOFFÉ a brief note explaining that, just as he was close to solving the "problem of the weight function of the spectral density," he received a letter from HERGLOTZ claiming that he solved the problem completely. EHRENFEST explains schematically that the weight function associated with WIEN's law also is purely discrete.[99]

On 28 March (RC), EHRENFEST opened a new notebook that he will devote mostly to the black-body problem, and more specifically to the preparation of his 1911 paper, which he submitted to the *Annalen der Physik* on 22 June (RC). He studies the asymptotic properties of the weight function for various radiation laws.[100] He first seeks the feature that "will free us from the Rayleigh-Jeans catastrophe."[101] In a colloquium on 8 April (RC), he spoke about the behavior of the weight function for small values of E/ν.[102]

On 22 May, EHRENFEST wrote in his diary: "Ioffé's problem solved. Rayleigh-Rayleigh formula [*sic*]."[103] He indeed found a general solution for the radiation law satisfying the conditions of IOFFÉ's problem, as follows:

$$\rho\left(\nu, T\right)=e^{N}\alpha\nu^{3}\left(\frac{h\nu}{kT}\right)^{L}e^{-c_{1}\frac{h\nu}{kT}}.\text{[104]} \tag{33}$$

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[96] Note 859, March 1911; ENB:1–12; in EA, microf. AHQP/EHR-2 (emphasis in the original).

[97] HERGLOTZ to EHRENFEST, 9 April, 1911. In EA, microf. AHQP/EHR-21, Section 6.

[98] Entry 31 March 1911 (RC), ENB:4–06; in EA, microf. AHQP/EHR-11.

[99] EHRENFEST to IOFFÉ, 31 March (RC) 1911. In MOSKOVCHENKO and FRENKEL (1990), 75.

[100] Note 866, 28 March 1911 (RC), 867 and 876, March/April 1911, ENB:1–13; in EA, microf. AHQP/EHR-2.

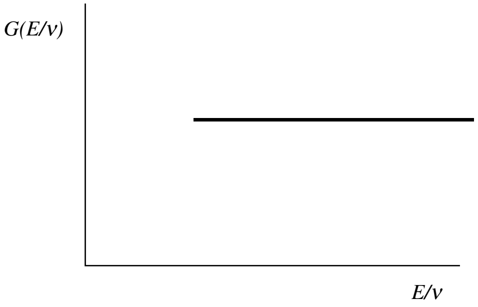
[101] Note 872, March/April 1911, ENB:1–13; in EA, microf. AHQP/EHR-2.

[102] ENB:4–06; in EA, microf. AHQP/EHR-11.

[103] Entry 22 May 1911 (RC), ENB:4–06; in EA, microf. AHQP/EHR-11.

[104] Note 980, 22 May 1911 (RC), ENB:1-13; in EA, microf. AHQP/EHR-2.

When $c_1 = 1$ and $L = -1$, RAYLEIGH's formula is reproduced, while different values of these constants yield different formulas. We assume that this is the proof that EHRENFEST refers to in his article.[105] He must have considered it significant given the annotation preceding it, where he worries about a radiation law corresponding to a weight function as shown on the following plot:



which can be interpreted as displaying the existence of an excitation threshold in the resonators. He made his preference for a solution of this kind clear in an undated letter to IOFFÉ[106] in which he says that he is confident he will be able to avoid energy atoms and employ something more similar to an excitation threshold. This interpretation would be possible with a formula like Eq. (26). EHRENFEST occasionally refers to equation (26) in his notebooks, and to Eq. (25), which he says is "mine." Even before he solved IOFFÉ's problem, he had written:

> Next tasks:
>
> (1) Compare $\frac{e^{-\sigma}}{\sigma}\left(\frac{\sigma+1}{\sigma+e^{-\sigma}}\right)$ with experiments.
> (2) Prove that the weight function must have the form $\frac{1}{\nu}\varphi\left(\frac{\varepsilon}{\nu}\right)$.
> (3) Prove that WIEN's distribution follows from the hypothesis of the energy atoms, if these are distributed amongst resonators.
> (4) Find the weight function for $\varphi(\sigma) = \frac{e^{-\sigma}}{\sigma}$.[107]

In these we easily can recognize RAYLEIGH's and EHRENFEST's formulas.

The weight function associated with the former does not appear in EHRENFEST's paper of 1911. It seems that months later HERGLOTZ indicated its form to him, which is neither simple nor easy to interpret, and EHRENFEST became aware of it only after he submitted his manuscript for publication.[108] It seems that even though he never published anything on a weight function corresponding to an excitation threshold – which

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[105] See the text corresponding to our footnote 84.

[106] EHRENFEST to IOFFÉ. In MOSKOVCHENKO and FRENKEL (1990), 53–54. In view of EHRENFEST's notebooks and of the course of his research, this letter must have been written toward the end of May 1911. We do not understand why the editors of this correspondence date the letter to 1909.

[107] Note 937, April 1911, ENB:1–13; in EA, microf. AHQP/EHR-2.

[108] HERGLOTZ to EHRENFEST, 28 August 1911. In EA, microf. AHQP/EHR-21, Section 6.

possibly would have led to an "EHRENFEST's law"– he remained hopeful after his article was published that it might be valid. This probably is why EHRENFEST insisted so much in his paper that the high-frequency experimental data were less reliable than the low-frequency data and therefore that functions not satisfying the "Wien-Planck condition," Eq. (13), should not be discarded, since his formula deviates more clearly away from PLANCK's in the low-frequency region, as can be seen in Fig. 1.

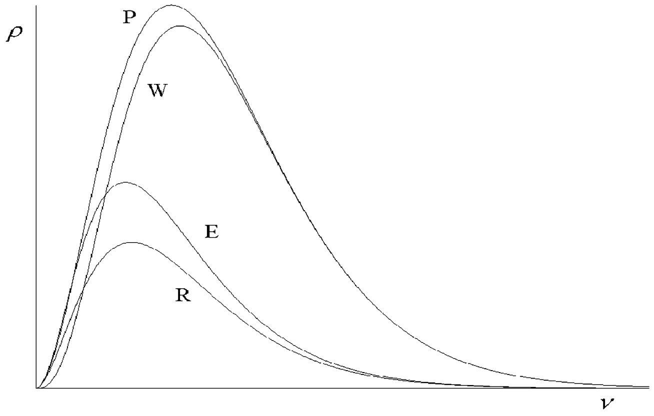

Fig. 1. Various energy densities ρ as a function of frequency ν, for $T = 7{,}500$ K. Following the order of maxima we have: EHRENFEST (E), RAYLEIGH (R), PLANCK (P), and WIEN (W)

After EHRENFEST's paper was published, we again find references to his formula in his notes, although only to dismiss it. He discussed with ISAKOV how to calculate the maxima in the various radiation laws and compare them with the experimental results.[109] On 9 November (RC), EHRENFEST exclaimed "Debacle," and the following day noted "Calculating the entire morning for tragic finale."[110] He apparently checked the theoretical values of the maxima against HOLBORN's observations and found that both his formula and RAYLEIGH's predicted values too far removed from the experimental data. We have not found any further references to his formula in his notes after that "tragic" day in the autumn of 1911. We stress that this represented EHRENFEST's attempt to avoid discretization of energy by resorting to fairly common concepts at the time, in this case of an excitation threshold. But even before his "debacle," his work must have been unsatisfactory, since toward the end of June we read of his attempt "to find a good radiation formula [from the] excitation threshold."[111]

EHRENFEST required 19 days to write up his paper of 1911 for publication, during which time he talked continuously with his wife TATIANA and IOFFÉ.[112] Soon

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[109] Entries 2,3,4,6 November 1911 (RC), ENB:4–08; in EA, microf. AHQP/EHR-11. And notes 297, 299, 300 and 307, 3/9 November 1911 (RC), ENB:1–15; in EA, microf. AHQP/EHR-2.

[110] Entries 9 and 10 November 1911 (RC), ENB:4–08; in EA, microf. AHQP/EHR-11.

[111] Note 57, June 1911, ENB:1–13; in EA, microf. AHQP/EHR-2.

[112] Entry 3 June 1911 (RC), ENB:4–06; in EA, microf. AHQP/EHR-11.

thereafter, IOFFÉ also submitted his paper of 1911 for publication.[113] A number of EHRENFEST's annotations during this time address questions that appear in IOFFÉ's paper, but not in EHRENFEST's own paper, such as an attempt to find an analogy between the behavior of gas molecules and radiation.[114] His notebook ends toward 1 July (RC), cutting off any annotations that might have shed light on the genesis of his 1911 paper. Naturally, however, EHRENFEST did not stop working completely on these questions. For example, he continued to search for a few years for a weight function that would lead to a solution to the integral Eq. (30). In 1920 his former student KRUTKOW sent him a nostalgic letter from St. Petersburg, saying that a friend had solved Eq. (30) in a very elegant way by applying STIELTJES's theory of integration.[115]

3.3. The germ of the adiabatic hypothesis

"Adiabatic motions" were introduced into mechanics toward the end of the nineteenth century by HELMHOLTZ and HERTZ.[116] "Adiabatic invariants" are mechanical quantities, generally associated with periodic motions, that remain constant when certain parameters in the expression for the potential energy undergo extremely slow changes. This is a mechanical definition, but the thermodynamical terminology is retained to stress that the work done on the system to change these parameters results exclusively in changes in its energy.

In RAYLEIGH's paper of 1902, which EHRENFEST cites in 1911, adiabatic invariants appear, although not under that name, for a series of oscillating mechanical systems, including one that RAYLEIGH used in deriving the STEFAN-BOLTZMANN law. This is the earliest relationship that we have found between adiabatic invariants of a mechanical system and radiation, and it implies that electromagnetic radiation can be modelled mechanically. That hypothesis eventually lost weight as radiation phenomena acquired specific distinctive properties of their own.

In reading RAYLEIGH's paper of 1902, one experiences a certain amount of bewilderment, because the adiabatic invariant in Eq. (15) does not appear, at least not explicitly. RAYLEIGH, probably the world's leading authority on wave theory at the time, devotes his short paper to an attempt to generalize the concept of radiation pressure to all kinds of vibrations:

> The importance of the consequences deduced by Boltzmann and W. Wien from the doctrine of the pressure of radiation has naturally drawn increased attention to this subject. That aethereal vibrations must exercise a pressure upon a perfectly conducting, and therefore perfectly reflecting, boundary was Maxwell's deduction from his general equations of the electromagnetic field; and the existence of the pressure of light has lately been confirmed experimentally by Lebedew. It seemed to me that it would be of interest to

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[113] IOFFÉ (1911). Entry 5 July 1911 (RC), ENB:4–07; in EA, microf. AHQP/EHR-11.

[114] Note 979, May 1911 and 50, 52, 53, 54, June 1911, ENB:1–13; in EA, microf. AHQP/EHR-2.

[115] KRUTKOW to EHRENFEST, 6 October 1920 (RC); in EA, microf. AHQP/EHR-22, section 10.

[116] JAMMER (1966), 97. We may recall incidentally that EHRENFEST's Ph.D. thesis was about an extension of HERTZ's mechanics. See KLEIN (1959a), 1–76.

> inquire whether other kinds of vibration exercise a pressure, and if possible to frame a general theory of the action.[117]

RAYLEIGH then develops a framework to address arbitrary kinds of vibrations, including electromagnetic vibrations. EHRENFEST refers to RAYLEIGH's paper in his notebooks in 1910, precisely when he resumed his research on black-body radiation.[118] Then, in 1913, he resorted to a theorem of CLAUSIUS and BOLTZMANN that allowed him to generalize RAYLEIGH's invariant for vibrations to more general periodic motions.[119] In that generalization, the role of the adiabatic invariant E/ν in vibrations is played by $\bar{T}/\nu$, where $\bar{T}$ is the temporal average of the kinetic energy over one period of motion.[120] Even though EHRENFEST claims in some of his manuscripts that he did not consult RAYLEIGH's paper,[121] there can be no doubt that the invariant shown in it played an important role in EHRENFEST's developing ideas on the relationship between adiabatic invariants and quantum theory. As EHRENFEST wrote in 1923:

> even more important was the fact that *Lord Rayleigh* had already made in 1902 a mechanical theorem he subsequently applied to prove *Boltzmann's* radiation law [the Stefan-Boltzmann law]. This makes possible to group together all the mechanical-electrodynamic ingredients of the deduction of Wien's displacement law in an extremely precise way, more accurate than in the traditional descriptions where for example light rays and the Doppler principle are used. . . . This theorem by *Rayleigh* decisively boosted the effort to clarify that the situation of the *displacement law* fits in a truly exact way *within Planck's radiation theory*. Let me, after this, be a bit more precise; for at this point – even if, initially, only in a unique and rather paradigmatic case – the role of the adiabatic invariants in the general quantum theory, and also in particular in quantum statistics, began to be disclosed.[122]

We insist that without RAYLEIGH's invariant, EHRENFEST in 1911 hardly could have justified that the weight function depends on a single variable, a result, as we have seen, that leads directly to WIEN's displacement law.

In stating that EHRENFEST in 1911 inferred WIEN's displacement law from RAYLEIGH's invariant, we are being somewhat inaccurate, since he still had to justify a few minor details. In 1914 he published a paper in which he cleaned up some of those details.[123] In particular, he proved the validity of BOLTZMANN's principle for weight functions other than BOLTZMANN's (a uniform distribution). Thus, what in 1911 was for EHRENFEST a generalization of BOLTZMANN's methods to the analysis of radiation, now is extended to systems of molecules. He now proves that BOLTZMANN's principle retains its validity (once BOLTZMANN's hypothesis that $G = 1$ is dropped) so long as the weight function satisfies a certain condition that he calls the "δG-condition."

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[117] RAYLEIGH (1902), 338.

[118] ENB:1–11; in EA, microf. AHQP/EHR-2.

[119] EHRENFEST (1913).

[120] *Ibid.* In KLEIN (1959a), 342. In the same page, EHRENFEST states that the extension to non-periodical systems is not at once possible.

[121] ENB:2–13; in EA, microf. AHQP/EHR-7.

[122] EHRENFEST (1923). In KLEIN(1959a), 464 (emphasis in the original).

[123] EHRENFEST (1914).

In sum, we think it is fully justified to regard EHRENFEST's paper of 1911 as the first in a short series of papers that will lead him to a precise formulation of his adiabatic hypothesis five years later, and to use it to extend the quantization concept to quantities other than energy, and to systems other than radiation. Nonetheless, from our study of his notebooks, we only can infer that towards 1911 he resorted to adiabatic invariants as a tool for developing his intuition of the central role played by WIEN's displacement law; they motivated his research only after about 1913.

4. EHRENFEST's paper of 1911 and the development of quantum theory up to 1914

We will not go beyond 1914 in this section because BOHR's atom model of 1913, the subsequent enunciation of the quantization rules and their applications in atomic physics, and the outbreak of the Great War in 1914, resulted in diminished research activity on thermal radiation. This does not mean, however, that EHRENFEST himself stopped developing his ideas on quantum theory prior to 1914: He applied his adiabatic hypothesis, whose germ, as we have seen, appeared in his paper of 1911, to the determination of the permitted states of a wide variety of mechanical systems.[124]

4.1. First reactions

The first Solvay conference, which took place in Brussels from 29 October to 3 November 1911 on the subject, "The theory of radiation and quanta," gathered together the leading physicists of the period.[125] No one, however, gave a lecture on Einstein's light-quantum hypothesis, so that a significant part of the considerations that EHRENFEST advanced in his paper of 1911, which was published in October, were not discussed there.

Planck presented four different ways of recovering the radiation law from the quantum hypothesis in his lecture at the Solvay conference, referring to papers by EINSTEIN, LARMOR, LORENTZ, DEBYE, and others. He does not cite EHRENFEST. PLANCK does cite EHRENFEST's paper of 1911, however, in the second revised edition of his *Vorlesungen* published in 1913, but then only in a footnote to its last paragraph, and then only in the context of the inability of PLANCK's treatment to explain how equilibrium among resonators is reached. PLANCK makes no reference to the necessity of discontinuity, which was the main theme of EHRENFEST's paper.[126] The English edition of 1914 goes no further. The translator included an appendix "with Professor *Planck's* permission" giving "a list of the most important papers on the subjects treated in this book and others closely related to them."[127] Among those cited are EHRENFEST (1911), IOFFÉ (1911), JEANS (1910), DEBYE (1910), NATANSON (1911), and POINCARÉ

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[124] EHRENFEST (1916).

[125] LANGEVIN and DE BROGLIE (1912).

[126] PLANCK (1988), 229.

[127] *Ibid.*, 3.

(1912). Nothing is said about EHRENFEST's paper, while POINCARÉ's is credited for proving the necessity of discontinuity.[128]

Thus, the immediate impact of EHRENFEST's paper of 1911 was almost nil, and a few years later PLANCK and his followers regarded it as little more than one of many publications on the subject.

EHRENFEST visited PLANCK in Berlin in January 1912 as he was travelling in German-speaking countries in search of a stable position.[129] EHRENFEST's tour, which included around twelve European cities, at least served as a reminder of EHRENFEST's existence, even though he was living in Russia, and provided him with many opportunities to explain his work in his incomparable way. In Berlin, he verified that PLANCK had browsed his paper, though only partly understood it. He explained to PLANCK certain of its details, particularly the general validity of the equation

$$\log W = \int \frac{\delta Q}{T}, \tag{34}$$

which PLANCK admitted using many times even though its applicability had not been proven.[130] PLANCK also displayed interest in the relationship of energy levels to light quanta and in the conditions necessary to avoid the ultraviolet catastrophe, and he reproached EHRENFEST for not publishing these matters. That PLANCK did not have a thorough knowledge of EHRENFEST's 1911 paper, however, was apparent to EHRENFEST. He told his wife TATIANA in a letter that PLANCK "had never considered these matters from this point of view."[131]

A few days later, EHRENFEST travelled to Leipzig, where HERGLOTZ lived, and he spoke there on his work on radiation.[132] While he was in Leipzig, POINCARÉ's note appeared in the *Comptes Rendus* in which he published his proof of the necessity of introducing discontinuity into quantum theory.[133] EHRENFEST sensed immediately after reading POINCARÉ's note that he would never get credit for this result, even though it was one of the main results in his own paper of 1911.[134] After his prophecy was fulfilled, EHRENFEST never ceased asserting his priority, nor bemoaning his misfortune: "Well, POINCARÉ did it wonderfully, but he did so many wonderful things, and this is one of the few things I have done nicely. . . . So please, please say that I did it."[135]

EHRENFEST read the proceedings of the Solvay conference prior to their publication when he visited SOMMERFELD in Munich in January 1912 during his job-seeking tour. He sent his wife TATIANA a postcard in which he wondered what might

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[128] *Ibid.*, 237–238.

[129] KLEIN (1985), 171–180.

[130] EHRENFEST to TATIANA, 20/21 January and 22 January 1912; in EA, microf. AHQP/EHR-29, section 5.

[131] EHRENFEST to TATIANA, 22 January, 1912; in EA, microf. AHQP/EHR-29, section 5.

[132] Entries 9,13 January and 5, 6 March 1912 (RC), ENB:4–09; in EA, microf. AHQP/EHR-11.

[133] POINCARÉ (1911). POINCARÉ's approach was very different from EHRENFEST's.

[134] EHRENFEST to TATIANA, 26/27 January 1912; in EA, microf. AHQP/EHR-29, section 5.

[135] Quoted by L. BRILLOUIN in interview of L. BRILLOUIN by T. S. KUHN, P. P. EWALD, and G. UHLENBECK, 29 March 1962. There is a transcription in AHQP, microf. AHQP/OHI-1.

have happened had he published his paper two or three months earlier than he did. [136] EHRENFEST also talked with LAUE, EPSTEIN, WAGNER, and others in Munich about his "work on radiation."[137] LAUE told him two months later that he was reading his article on statistical mechanics for the *Encyklopädie* as well as his article on light quanta, about which he asked a few casual questions.[138] EHRENFEST also visited WIEN in Würzburg (near Munich), and talked with him about IOFFÉ's work and BOLTZMANN's principle.[139]

SOMMERFELD knew about EHRENFEST's paper before it was published in October 1911. The preceding month, EHRENFEST wrote to SOMMERFELD, proposing to do a second doctorate under SOMMERFELD's supervision.[140] SOMMERFELD agreed and suggested that EHRENFEST should extend the work in his paper.[141] EHRENFEST replied euphorically,[142] stating that he was elaborating his work on "radiation quanta" in two respects: (A) By deepening the foundations of his analysis by investigating if the ratio $\delta Q/T$ is an exact differential, and under which conditions the equality

$$\frac{\delta Q}{T} = \delta \log W \tag{35}$$

holds, since, EHRENFEST said, it is easy to verify that it is not valid for arbitrary systems. (B) By expanding his considerations on the important differences between PLANCK's and EINSTEIN's quantum hypotheses. He noted that EINSTEIN's hypothesis (energy atoms distributed over resonators) does not lead to PLANCK's law, but to WIEN's or RAYLEIGH's laws or, more generally, to a law of the form

$$\alpha \nu^3 \cdot \left(\frac{T}{\nu}\right)^m e^{-\frac{h\nu}{kT}}, \tag{36}$$

which we recognize as EHRENFEST's solution to IOFFÉ's problem, which he had found in March, that is, Eq. (33), where L is now m and where certain constants do not appear.

EHRENFEST told SOMMERFELD that within two weeks he would send him something readable on the subject. To our knowledge, he never did. Among his manuscripts are two partial attempts that might have complied with his promise. The title of one is "On the probabilistic-theoretical foundations of radiation theory," that of the other "On Planck's theory of the 'most probable' distribution of light quanta over resonators."[143] These eventually will materialize in EHRENFEST (1914) and EHRENFEST

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[136] EHRENFEST to TATIANA, 29 January 1912; in EA, microf. AHQP/EHR-29, section 5. See also KLEIN(1985), 173–174.

[137] Entries 16, 17, 21, 23, 24 January 1912 (RC), ENB:4–09; in EA, microf. AHQP/EHR-11.

[138] LAUE to EHRENFEST, 24 March 1912; in EA, microf. AHQP/EHR-23, section 2. English version of the article for *Encyklopädie* in EHRENFEST, P. and T. (1990).

[139] Entries 18 and 19 January 1912 (RC), ENB:4–09; in EA, microf. AHQP/EHR-11.

[140] KLEIN (1985), 166–171. See also letter from EHRENFEST to SOMMERFELD, 17 September 1911 (RC). In SOMMERFELD (2000), 402–404.

[141] Entry 2 September 1911 (RC), ENB:4–08; in EA, microf. AHQP/EHR-11. We are thus led to assume that SOMMERFELD knew of this article even before it was published.

[142] EHRENFEST to SOMMERFELD, 3 October 1911 (RC). In SOMMERFELD (2000), 406–408.

[143] EMS:1 and EMS:5; in EA.

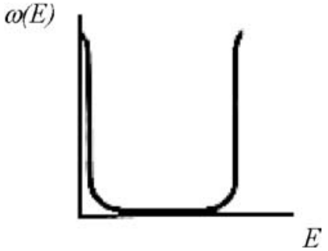
and KAMERLINGH-ONNES (1914), the latter containing an appendix that has a structure essentially identical to that of the second manuscript.

EHRENFEST also visited EINSTEIN in Prague during his job-seeking tour and gave a lecture that EINSTEIN praised soon thereafter when he recommended EHRENFEST as DEBYE's successor in Zürich (who EHRENFEST also visited): "He gave such a good lecture on the radiation problem before our mathematical society that my colleagues want very much to have him here."[144] EINSTEIN also recommended EHRENFEST as his own successor in Prague, referring to EHRENFEST's paper of 1911 as "a through and ingenious study of the question: what statistical properties must we attribute to radiation in order to satisfy the radiation formula, insofar as the latter is confirmed by experience."[145]

EINSTEIN also was aware of EHRENFEST's 1911 paper before the Solvay conference. As he wrote to BESSO on 21 October 1911:

> The question as to what can be concluded about $\omega(E)$ from the radiation formula has recently been discussed by Ehrenfest in Annalen. The following character of the ω-curve seems to be necessary so that Wien's limiting law can be obtained from a law of the character
>
> $$W = const\colon e^{-E/kT} \cdot \omega(E).$$[146]

EINSTEIN then adds a drawing that stresses that $\omega(E)$ is different from zero only at certain points, as follows:



Of the physicists who attended the Solvay conference, not only SOMMERFELD and EINSTEIN knew about EHRENFEST's paper of 1911 before going to Brussels. LORENTZ, PLANCK, and WIEN also likely knew about it, since the *Annalen* was published widely and rapidly at this time. In any case, in January 1912 EHRENFEST explained the subtleties of his work to many leading physicists of the time during his job-seeking tour. DEBYE too knew about EHRENFEST's article before the Solvay conference.[147] EHRENFEST also evidently sent reprints of it to others, including

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[144] EINSTEIN to KLEINER, 3 April 1912. In BECK (1995), 285.

[145] Report to the Philosophical Faculty of the German University on a Successor to the Chair of Theoretical Physics. Prague, before 23 May 1912. In BECK (1995), 301. EHRENFEST's talk on radiation in Prague is recorded in his diary on 27 February 1912. Entry 27 February 1912, ENB:4–11; in EA, microf. AHQP/EHR-12.

[146] EINSTEIN to BESSO, 21 October 1911. In BECK (1995), 215.

[147] DEBYE to EHRENFEST, 13 October 1911; in EA, microf. AHQP/EHR-19, Section 3.

POINCARÉ, LANGEVIN, RAYLEIGH, and JEANS.[148] LORENTZ was impressed with EHRENFEST's ability to disentangle a complex theoretical problem,[149] and POINCARÉ had no reservation in admitting to EHRENFEST in a letter that he had been anticipated in his proof of discontinuity.[150] Unfortunately, he died shortly thereafter, before he was able to make his recognition public.[151]

Incidentally, another of the few physicists who went into EHRENFEST's work deeply also was French. In his thesis of 1912, BAUER reproduced some of EHRENFEST's results and used them to refute a new radiation law proposed by BOISSOUDY.[152] Many years later, in 1963, BAUER said in an interview that what convinced him "of the necessity of quanta was the work of EHRENFEST."[153]

The case of JEANS is curious. EWALD wrote a report of the *British Association* meeting of 1913 for the *Physikalische Zeitschrift*, noting that JEANS had stated that POINCARÉ had concluded that the failure of equipartition of energy ensuing from PLANCK's radiation law did not depend on the exact validity of that law. Now, near POINCARÉ's name a footnote is inserted that reads "and by Ehrenfest (speaker's observation)."[154] We understand that JEANS ordered EWALD to include this footnote in his summary for the *Physikalische Zeitschrift*, but this should not be taken to mean that JEANS cited EHRENFEST's paper of 1911 at the meeting itself. In fact, JEANS did not even cite EHRENFEST's paper in his *Report on radiation and the quantum-theory* that he published in 1914, although he did cite POINCARÉ's paper.[155]

4.2. EINSTEIN's quanta and PLANCK's quanta

We finally assess the work of physicists that contributed to the clarification of the differences between EINSTEIN's and PLANCK's quantum hypotheses and that bears on the contents of EHRENFEST's paper of 1911.

4.2.1. The controversy between WOLFKE and KRUTKOW (1913–1914)

In 1913 WOLFKE published two papers giving a new derivation of PLANCK's law that was based on earlier ideas of EINSTEIN and STARK who, according to WOLFKE, stressed that the energy of light displays a discontinuous character, not only in emission

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[148] Entry 23 January 1911 (RC), ENB:4–09; in EA, microf. AHQP/EHR-11.

[149] KLEIN (1985), 184.

[150] POINCARÉ to EHRENFEST, ca. January 1912; in EA, microf. AHQP/EHR-24, Section 8.

[151] KLEIN (1985), 174, 251–253. Also see McCORMMACH (1967), 51.

[152] BAUER (1913), BOISSOUDY (1913). See also BAUER to EHRENFEST, 25 March 1913; in EA, microf. AHQP/EHR-17, section 2.

[153] Interview of E. BAUER by T. S. KUHN, 8 January 1963. There is a transcription in AHQP, microf. AHQP/OHI-1.

[154] EWALD (1913). See the footnote on page 1298.

[155] JEANS (1914).

and absorption processes, as PLANCK's theory seemed to suggest, but also in empty space.[156] WOLFKE added the hypothesis that "light atoms cannot be either created or destroyed by themselves."[157] Thus, a perfectly reflecting surface reflects the same number of light atoms as incident on it, even if their energy and frequency is changed.

WOLFKE pictures a monochromatic beam of light of energy U_1 consisting of N light atoms each of energy ε_1 and frequency ν_1,which is incident on a mirror and then reflected to yield a new monochromatic beam with corresponding characteristics U_2, N, ε_2 and ν_2. Using the relation $\frac{U_1}{U_2} = \frac{\nu_1}{\nu_2}$, as proved by ABRAHAM, he concludes that $\frac{\varepsilon_1}{\nu_1} = \frac{\varepsilon_2}{\nu_2}$, or equivalently, that

$$\frac{\varepsilon}{\nu} = \alpha, \tag{37}$$

where α is a universal constant.

WOLFKE calls Eq. (37) the "fundamental equality of light atoms" that relates their two basic characteristics, their energy and frequency, to each other.[158] He claims that this justifies the relationship that had been obtained by EINSTEIN based on a statistical treatment of WIEN's law; he makes no reference to EHRENFEST's derivation. Finally, he obtains the spectral-distribution law by following PLANCK's line of reasoning of 1901, using his expression for the number of different ways that N_ν atoms can be distributed into ω_ν receptacles:

$$W_\nu = \frac{(\omega_\nu + N_\nu - 1)!}{(\omega_\nu - 1)!N_\nu!}. \tag{38}$$

In his second paper, WOLFKE starts from the relativistic expression

$$m = \frac{\varepsilon}{c^2}, \tag{39}$$

which allows him to assign mass to the light atoms.[159] From the available experimental data, he estimates the value of the constant α as $6.42 \cdot 10^{-27}$ erg·sec.This implies that the atoms of light are extremely light as compared to ordinary atoms, and even to electrons, whose mass is on the order of a million times larger.[160]

KRUTKOW, who was then studying with EHRENFEST in Leiden, replies sharply to WOLFKE,[161] referring to EHRENFEST's paper of 1911. He emphasizes that WOLFKE has derived PLANCK's law by assuming an atomic constitution of radiation while PLANCK himself did not make such an assumption. Instead, EINSTEIN in 1905 assigned to light quanta the atomistic properties that EHRENFEST attributed to them in 1911. These quanta, KRUTKOW continues, following EHRENFEST, differ from PLANCK's by the properties EHRENFEST denoted by (B) and (C), and he proves that by assuming properties (A) and (B) WIEN's law is recovered.[162] He proves this by

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[156] WOLFKE (1913a) and WOLFKE (1913b).

[157] WOLFKE (1913a), 1123.

[158] *Ibid.*, 1125.

[159] WOLFKE (1913b).

[160] *Ibid.*, 1218. Calculations make reference to an atom of light with a wavelength of 0.5 μ.

[161] KRUTKOW (1914a).

[162] See the text corresponding to our footnote 80.

drawing on the analogy of balls and urns that appears, as we indicated earlier, in EHRENFEST's notebooks. Just as P independent balls can be distributed into N urns in N^P different ways, the same holds for quanta distributed among resonators (always translatable into the language of modes of vibration). Thus instead of Eq. (38), as WOLFKE maintained, KRUTKOW states that the starting point should be

$$\frac{N_\nu^{\omega_\nu}}{\omega_\nu!}, \tag{40}$$

which agrees with EINSTEIN's assumption for light quanta and leads to WIEN's law just as Eq. (38) leads to PLANCK's. KRUTKOW also takes the opportunity to emphasize the cogency of EHRENFEST's analysis on this question.[163]

WOLFKE replies immediately,[164] attempting to explain why he and KRUTKOW arrive at different results even though their starting points are seemingly the same. He specifies that the independence he assumes is that the probability of an atom of light of a given frequency being in a given volume at a certain time is independent of how many atoms of light of that frequency already exist there. EINSTEIN, WOLFKE insists, assumes instead spatial independence, namely, that the probability of an atom of light to be at a given location is independent of whether another atom of light of the same frequency is also there. Accordingly, EINSTEIN's theory leads to WIEN's law.

KRUTKOW replies, astonished by WOLFKE's spurious argument.[165] WOLFKE does no better in a further reply: He limits himself to stating that assumptions (A) and (B), on which KRUTKOW essentially has based his criticism, have nothing to do with his derivation of PLANCK's law:

> This formula [our (38)] does not mean "the number of equiprobable distributions of N_ν independent elements over the ω_ν resonators (or normal modes of vibration)" but rather the number of equiprobable distributions of N_ν atoms into ω_ν possible realizations in one and the same frequency interval $d\nu$.[166]

It seems that this was a dialogue of the deaf, and both protagonists must have viewed it as such, since there is no evidence that it went any further. We have discussed this minor polemic because it was one of the very few instances in which EHRENFEST's paper of 1911 was cited positively, albeit by his disciple KRUTKOW, who stressed that EHRENFEST's weight-function approach clarified the problem, permitting one to identify the conditions necessary to obtain WIEN's and PLANCK's formulas.

4.2.2. EHRENFEST and KAMERLINGH-ONNES (1914)

KRUTKOW had shown, as IOFFÉ had before him, although on different grounds, that a derivation based on the statistical independence of quanta does not lead to

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[163] KRUTKOW (1914a), 135–136.

[164] WOLFKE (1914a); this was received 17 February. KRUTKOW (1914a) had been received 6 January.

[165] KRUTKOW (1914b).

[166] WOLFKE (1914b), 463.

PLANCK's but to WIEN's law. To obtain PLANCK's law, an additional condition is required, namely, a certain correlation among quanta that limits or removes their independence. Neither KRUTKOW nor anyone else, however, was able to specify such a condition physically. That was precisely the problem that EHRENFEST and KAMERLINGH-ONNES addressed in 1914 in a paper so short that its footnotes and appendix occupy more space than the body of its text. The appendix sets *Energiestufen* in opposition to *Lichtquanta*, and thus probably was written by EHRENFEST.[167]

EHRENFEST and KAMERLINGH-ONNES develop an ingenious procedure to deduce formula (38) for the distribution of quanta among resonators used by PLANCK and others.[168] Their procedure is widely known, but not always attributed to them. We will not go into detail here but only stress that they state in a footnote that in the earlier proof, which was based on the "transition from n to $n+1$," that is, on mathematical induction, a method was used that "taken as a whole does not give an insight into the origin of the final expression."[169] In their appendix, entitled "The contrast between Planck's hypothesis of the energy-grades and Einstein's hypothesis of energy-quanta," they address this issue directly. They conclude:

> More than once the analogous, equally formal device used by Planck, viz. distribution of P energy-elements over N resonators, has by a misunderstanding been given a physical interpretation, which is absolutely in conflict with Planck's radiation formula and would lead to Wien's radiation formula.
>
> As a matter of fact Planck's energy-elements were in that case almost entirely identified with Einstein's light-quanta and accordingly it was said... that the latter assumes the existence of mutually independent energy-quanta also in empty space, the former only in the interior of matter, in the resonators. The confusion which underlies this view has been more than once pointed out [EHRENFEST (1911) and KRUTKOW (1914a and 1914b) are cited]. Einstein really considers P similar quanta, existing *independently of each other*.[170]

In other words, EHRENFEST's proof in 1911 of the necessity of discontinuity in the energy distribution of each mode of vibration did not imply a corpuscular nature of radiation. We have seen how EHRENFEST after 1905 addressed the black-body problem through the normal modes of vibration and in 1911 presented a corpuscular description of EINSTEIN's hypothesis, with the specific purpose in mind of differentiating it clearly from PLANCK's hypothesis which, according to EHRENFEST, does not presume the existence of any kind of particles. We stress that EHRENFEST does not take sides on the hypothesis of light quanta; he simply questions the interpretation of PLANCK's hypothesis and never makes any statements about the possible existence of any particular kind of quanta. Thus, his 1914 paper with KAMERLINGH-ONNES helps us to understand EHRENFEST's meaning about the necessity of quanta in his paper of 1911. For EHRENFEST, quantization means discontinuity, not corpuscularity.

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[167] EHRENFEST to LORENTZ, 24 October 1914; in AL, microf. AHQP/LTZ-5.

[168] This procedure is shown, for instance, in KLEIN (1959b), 47, and in DARRIGOL (1991), 253.

[169] EHRENFEST and KAMERLINGH-ONNES (1914). In KLEIN (1959a), 354, footnote 1.

[170] *Ibid.*, 355 (emphasis in the original).

4.2.3. On the law of photochemical equivalence: EINSTEIN, ISHIWARA, and EHRENFEST

Around 1912 a debate about the law of photochemical equivalence triggered some discussion about EINSTEIN's light-quantum hypothesis very much along the lines proposed by EHRENFEST in 1911. Although EINSTEIN then was concentrating on his research on relativity, he nevertheless devoted some effort to understanding the quantum nature of radiation.[171] We refer here to his work on the law of photochemical equivalence, that the decomposition of one gram equivalent of any chemical substance by light of frequency ν requires radiation of energy $E = Nh\nu$, where N is Avogadro's number. This law follows in a straightforward way from the quantum hypothesis, but EINSTEIN showed that "the quantum hypothesis is not required, rather it can be deduced from a few simple hypotheses on photochemical processes following a purely thermodynamical way."[172] We will not reproduce EINSTEIN's derivation here but emphasize an aspect of it that bears on our concern, namely, the appearance in the ensuing debate about it of PLANCK's and WIEN's radiation laws, or equivalently, of a comparison of the nature of PLANCK's energy elements and EINSTEIN's light quanta.

Let three chemically different gases of molecular weights m_1, m_2, and m_3 be enclosed in volume V. Let n_1, n_2, and n_3 be the corresponding number of gram moles of the three gases. Assume now that a molecule of the first gas absorbs energy ε of monochromatic radiation of frequency ν and is decomposed into molecules of the second and third gases. These in turn can recombine later with the emission of energy ε. We make the following hypotheses:

(i) The decomposition of a molecule of the first gas does not depend on the concentration of the other two gases.

(ii) The probability per unit time that a molecule of the first gas decomposes is proportional to the radiation energy density ρ, so that the number Z decomposing per unit time is given by

$$Z = A \cdot \rho \cdot n_1. \tag{41}$$

(iii) The recombination of the second and third gases is described by the law of mass action. The number Z' of molecules of the first gas produced per unit time by recombination of the second and third gases is then given by

$$Z' = A' \cdot V \cdot \frac{n_2}{V} \cdot \frac{n_3}{V}. \tag{42}$$

By equating the rates of decomposition and recombination to achieve a state of equilibrium, EINSTEIN obtains

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[171] EINSTEIN (1912a). See on this matter *Editorial note: Einstein on the law of photochemical equivalence*. In KLEIN *et al.* (1995), 109–113.

[172] EINSTEIN (1912b). In KLEIN *et al.* (1995), 172. This excerpt is found in EINSTEIN's response to STARK's claims of fatherhood of the derivation of that law, which he pretended to have obtained already in 1908.

$$\rho = \frac{A'}{A}\alpha \cdot e^{-\frac{N\varepsilon}{RT}}. \tag{43}$$

He proves that the constants A, A', and α do not depend on the temperature T and concludes that the above hypotheses lead to good agreement with WIEN's law provided that

$$\frac{A'}{A}\alpha = \frac{8\pi h\nu^3}{c^3} \quad \text{and} \quad \varepsilon = h\nu. \tag{44}$$

To EINSTEIN this is a non-trivial conclusion, since the hypotheses that led to it did not include one on the corpuscular nature of the radiation. Thus he proved the law of photochemical equivalence and established the value of the energy ε within the range of validity of WIEN's radiation law.

EINSTEIN's considerations constitute a clear precedent for his derivation of PLANCK's law in 1916 in terms of three elementary processes: spontaneous emission, induced emission, and induced absorption.[173] Here he considers only two processes: spontaneous emission and absorption.[174] His treatment provoked certain reactions because PLANCK's law did not appear in it. Thus, ISHIWARA objected in 1912 and proposed a new interpretation of PLANCK's law.[175] He explained how a connection can be established between PLANCK's law and the law of photochemical equivalence. He wrote PLANCK's law as a series expansion and compared it with WIEN's law and discovered that different multiples of the energy $h\upsilon$ could participate in photochemical processes, and not simply quanta of energy $\varepsilon = h\nu$. He concluded, with no further calculation, that by using EINSTEIN's method PLANCK's law could be recovered only by assuming that the energy consists of "molecules of radiation" of energy $ih\nu$.[176]

Even though EHRENFEST never published anything on the law of photochemical equivalence, he certainly was well aware of this debate, as can be seen in his correspondence with EINSTEIN of this period. EHRENFEST did not miss any opportunity to explore PLANCK's law, even though he too was busy with research on relativity at this time. IOFFÉ also became involved in these discussions.[177] Around the end of March 1912, EHRENFEST sent EINSTEIN two unsuccessful attempts he and his wife had made to obtain PLANCK's law based on EINSTEIN's method.[178] The first was purely "formal" and hence "unattractive." The second was "informal" in the sense that they had

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[173] EINSTEIN (1916).

[174] For a possible relationship between EINSTEIN's investigations on the law of photochemical equivalence and his subsequent contributions to quantum theory, see BERGIA and NAVARRO (1988).

[175] ISHIWARA (1912). The paper was received in October. ISHIWARA had been in Europe since March. For details on this visit, which stretched until spring 1914, see SIGEKO (2000).

[176] ISHIWARA (1912), 1144–1145.

[177] See, for example, entry 9 April 1912 (RC), ENB:4–13; in EA, microf. AHQP/EHR-12.

[178] Letter (draft) from EHRENFEST to EINSTEIN, before 3 April 1912. English translation in BECK (1995), 280–285.

tried to find a model like EINSTEIN's that would lead to PLANCK's law rather than WIEN's. Despite their difficulties, EHRENFEST wrote:

> It would nevertheless be interesting to establish by what *reasonable* modifications of your initial posits one could free oneself from *Wien's* radiation law.– We shall retain a part of your assumptions unchanged *not* because we view them as physically evident, but because nothing more whatsoever can be calculated without them.[179]

They then proposed to modify expressions (41) and (42), replacing them with others in which the radiation density depended also on the temperature T. This is reminiscent of EHRENFEST's 1911 paper and notebooks, but they recognized finally that they were not obtaining reasonable results. In his response, EINSTEIN categorically rejected their proposals on the ground that they do not lead to a true equilibrium state.[180] EINSTEIN used an identical argument in rejecting two similar attempts by SCHIDLOF.[181]

5. Conclusions

In his paper of 1911, EHRENFEST demonstrated the necessity of discontinuity from the asymptotic properties of any candidate for the radiation law, rather than from some specific one. As we have shown, his contemporaries did not appreciate his achievement. He conceived an innovative approach in analyzing the meaning, implications, and differences between PLANCK's and EINSTEIN's quantum hypotheses. He clarified why EINSTEIN was able to justify his heuristic light-quantum hypothesis of 1905 starting from WIEN's law rather than from PLANCK's, showing that discrete statistical weights correspond to either law. His disciple KRUTKOW completed the analysis, showing by the use of combinatorics that the assumption of corpuscular quanta does not allow one to go beyond WIEN's law. To recover PLANCK's law, "something more" is required, as EHRENFEST and EHRENFEST and KAMERLINGH-ONNES showed with remarkable clarity and simplicity.

The complexity in making precise comparisons among different approaches makes it compulsory to be precise regarding the meaning of a phrase like "different proofs of the necessity of the quantum hypothesis." EHRENFEST proved specifically that the statistical weight function necessarily must have a singular non-zero value at the zero energy point, a property that can be made more precise by taking into consideration other asymptotic properties of the radiation law. He thus left open the possibility that other radiation laws that do not require the same energy quantization proposed by PLANCK may be equally valid. EHRENFEST made clear distinctions between the discontinuity of the weight function and energy quantization. We therefore consider it more appropriate to speak of the "necessity of discontinuity" instead of the "necessity of quantization." The same applies to "corpuscularity." It thus appears utterly imprecise, to say the least, to affirm that EHRENFEST and POINCARÉ obtained the same result independently,

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[179] BECK (1995), 282 (emphasis in the original).

[180] EINSTEIN to EHRENFEST, 25 April 1912. English translation in BECK (1995), 287–288.

[181] EINSTEIN to SCHIDLOF, 17 June and 5 July 1913. English translation in BECK (1995), 339 and 341.

when their assumptions and approaches were so very different. A rigorous analysis of these differences still remains to be carried out.

Adiabatic invariants play an important role in EHRENFEST's paper of 1911, even if they are not granted specific relevance in it. In light of his notebooks and other publications, EHRENFEST conceived the concept of adiabatic invariants while analyzing the essence of WIEN's displacement law, a classical law that remained valid in quantum theory. We have stressed that adiabatic invariants do not lead to the discrete character of the weight function; they only impose condition (19) on it. Thus, our analysis of EHRENFEST's 1911 paper helps us to localize both the germ of his adiabatic hypothesis and the way in which he arrived at it.

The small impact of EHRENFEST's 1911 paper possibly can be traced partly to its difficulty in reading, since he chose a statistical route in addressing the radiation problem, generalizing the methods of his master BOLTZMANN. EHRENFEST was in a privileged position to pursue this task, yet almost none of his colleagues at the time was able to appreciate his results. It probably is no accident that most of the few positive responses came from connoisseurs of statistical methods such as EINSTEIN, JEANS, and SOMMERFELD. It seems, however, that even EINSTEIN did not understand EHRENFEST's arguments completely, as can be seen in the correspondence the two men had on EHRENFEST's analysis of the conditions necessary for BOLTZMANN's principle to be valid for weight functions different from unity, that is, in the absence of traditional equiprobability.[182]

The small impact of EHRENFEST's 1911 paper also has been attributed to his low scientific reputation at the time.[183] This clashes, however, with the high recognition LORENTZ granted him when he proposed EHRENFEST as his successor for the chair of theoretical physics in Leiden only a few months after EHRENFEST's paper was published. LORENTZ clearly was impressed with EHRENFEST's work and abilities at the time and did not regard him as an unknown scientist or an outsider to the physics community. Nevertheless, geography may have played a role. EHRENFEST was working in St. Petersburg, far from the Western European centers of research in quantum theory in Germany, France, Switzerland, Holland, and Great Britain. His geographical isolation thus may have contributed to the neglect of his 1911 paper even though it was published in the widely read *Annalen der Physik*. The work of IOFFÉ, NATANSON, and ISHIWARA suffered a similar fate. We are not in a position, however, to go into this question further at this time.

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[182] EINSTEIN to EHRENFEST, 18 and 25 May 1914; letters (drafts) from EHRENFEST to EINSTEIN, 20 and 21 May 1914. English translation in HENTSCHEL (1998), 14–15, 21–22, 15–16 and 17–21.

[183] See for instance, McCORMMACH (1967), 51.

References

BAUER, E. (1913): “Sur la loi du rayonnement noir et la théorie des quanta. Remarques sur un travail de M. J. de Boissoudy.” *Comptes Rendus* **153**, 641–649.

BECK, A. (1989): *The Collected Papers of Albert Einstein*. Vol. 2.*The Swiss years: writings, 1900–1909*. English translation. Princeton University Press, Princeton.

BECK, A. (1993): *The Collected Papers of Albert Einstein*. Vol. 3.*The Swiss years: writings, 1909–1911*. English translation. Princeton University Press, Princeton.

BECK, A. (1995): *The Collected Papers of Albert Einstein*. Vol. 5. *The Swiss years: correspondence*, *1902–1914*. English translation. Princeton University Press, Princeton.

BERGIA, S., LUGLI, N., and ZAMBONI, N. (1979): “Zero-point energy, Planck’s law and the pre-history of stochastic electrodynamics. Part I: Einstein and HOPF’s paper of 1910.” *Annales de la Fondation Louis de Broglie* **4**, 295–317.

BERGIA, S. and NAVARRO, L. (1988): “Recurrences and continuity in Einstein’s research on radiation between 1905 and 1916.” *Archive for History of Exact Sciences* **38**, 79–99.

BERGIA, S. and NAVARRO, L. (1997): “Early quantum concepts and the theorem of equipartition of energy in Einstein’s work (1905–1925).” *Physis* **34**, 183–223.

BOISSOUDY, J. DE (1913): “Sur une nouvelle forme de la loi du rayonnement noir et de l’hypothèse des quanta.” *Comptes Rendus* **153**, 385–396.

BUCKINGHAM, E. (1912): “On the deduction of Wien’s displacement law.” *Philosophical Magazine* **23**, 920–931.

BUCKINGHAM, E. (1914): “On physically similar systems; illustrations of the use of dimensional equations.” *Physical Review* **4**, 345–376.

COHEN, R. S. and STACHEL, J. J. (eds.) (1979): *Selected Papers of Léon Rosenfeld.* (Boston Studies in the Philosophy of Science, Vol. XXI.) D. Reidel, Dordrecht.

DARRIGOL, O. (1991): “Statistics and combinatorics in early quantum theory, II: Early symptoma of indistinguishability and holism.” *Historical Studies in the Physical Sciences* **21**, 237–298.

DEBYE, P. (1910): “Der Wahrscheinlichkeitsbegriff in der Theorie der Strahlung.” *Annalen der Physik* **33**, 1427–1434.

EHRENFEST, P. (1905): “Über die physikalische Vorausetzungen der Planck’schen Theorie der irreversiblen Strahlungsvorgänge.” *Sitzungberichte*, *Akademie der Wissenschaften*, *Wien*, Abteilung **II**, 1301–1314. Reprinted in KLEIN (1959a), 88–101.

EHRENFEST, P. (1906a): “Bemerkung zu einer neuen Ableitung des Wienschen Verschiebungsgesetzes.” *Physikalische Zeitschrift* **7**, 527–528. Reprinted in KLEIN (1959a), 119–120.

EHRENFEST, P. (1906b): “Zur Planckschen Strahlungstheorie.” *Physikalische Zeitschrift* **7**, 528–532. Reprinted in KLEIN (1959a), 120–124.

EHRENFEST, P. (1906c): “Bemerkung zu einer neuen Ableitung des Wienschen Verschiebungsgesetzes. Antwort auf Herr Jeans’ Entgegnung.” *Physikalische Zeitschrift* **7**, 850–852. Reprinted in KLEIN (1959a), 125–127.

EHRENFEST, P. (1911): “Welche Züge der Lichtquantenhypothese spielen in der Theorie der Wärmestrahlung eine wesentliche Rolle?” *Annalen der Physik* **36**, 91–118. Reprinted in KLEIN (1959a), 185–212.

EHRENFEST, P. (1913): “A mechanical theorem of BOLTZMANN and its relation to the theory of energy quanta.” *Proceedings Amsterdam Academy* **16**, 591–597. Reprinted in KLEIN (1959a), 340–346.

EHRENFEST, P. (1914): “Zum Boltzmannschen Entropie-Wahrscheinlichkeits-Theorem.” *Physikalische Zeitschrift* **15**, 657–663. Reprinted in KLEIN (1959a), 347–352.

EHRENFEST, P. (1916): “On adiabatic changes of a system in connection with the quantum theory.” *Proceedings Amsterdam Academy* **19**, 576–597. Reprinted in KLEIN (1959a), 378–399.

EHRENFEST, P. (1923): "Adiabatische Transformationen in der Quantentheorie und ihre Behandlung durch Niels Bohr." *Die Naturwissenschaften* **11**, 543–550. Reprinted in KLEIN (1959a), 463–470.

EHRENFEST, P. and T. (1990): *The conceptual foundations of the statistical approach in mechanics* (English translation by J. Moravcsik). Dover Publications, New York. (Originally published in 1959 by Cornell University Press, Ithaca.) The original German version appeared in 1912: *Encyklopädie der Mathematischen Wissenschaften*. B. G. Teubner, Leipzig, IV 2, II, Heft 6. Reprinted in KLEIN (1959a), 213–302.

EHRENFEST, P. and KAMERLINGH-ONNES, H. (1914): "Simplified deduction of the formula from the theory of combinations which Planck uses as the basis of his radiation theory." *Proceedings Amsterdam Academy* **17**, 870–873. Reprinted in KLEIN (1959a), 353–356.

EINSTEIN, A. (1905): "Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtpunkt." *Annalen der Physik* **17**, 132–148. Reprinted in STACHEL (1989), 149–169. English translation in BECK (1989), 86–103.

EINSTEIN, A. (1906): "Zur Theorie der Lichterzeugung und Lichtabsorption." *Annalen der Physik* **20**, 199–206. Reprinted in STACHEL (1989), 349–358. English translation in BECK (1989), 192–199.

EINSTEIN, A. (1909): "Über die Entwickelung unserer Anschauungen über das Wesen und die Konstitution der Strahlung." *Physikalische Zeitschrift* **10**, 817–825. Reprinted in STACHEL (1989), 563–583. English translation in Beck (1989), 379–394.

EINSTEIN, A. (1912a): "Thermodynamische Begründung des photochemischen Äquivalentgesetzes." *Annalen der Physik* **37**, 832–838 and **38**, 881–884. Reprinted in KLEIN *et al.* (1995), 114–121 and 165–170.

EINSTEIN, A. (1912b): "Anwort auf eine Bemerkung von J. Stark:„ Über Anwendung des Planckschen Elementargesetzes… "." *Annalen der Physik* **38**, 888. Reprinted in KLEIN *et al.* (1995), 171–173.

EINSTEIN, A. (1916): "Zur Quantentheorie der Strahlung." *Physikalische Gesellschaft Zürich. Mitteilungen* **16**, 47–62. A reedition of this paper was published in 1917 in *Physikalische Zeitschrift* **18**, 121–128; this is the paper usually quoted. Reprinted in KOX *et al.* (1996), 381–398. English translation in ENGEL (1997), 220–233.

EINSTEIN, A. and HOPF, L. (1910): "Statistische Untersuchung der Bewegung eines Resonators in einem Strahlungsfeld." *Annalen der Physik* **33**, 1105–1115. Reprinted in KLEIN *et al.* (1993), 270–280. English translation in BECK (1993), 220–230. English translation and commentary in BERGIA *et al.* (1979).

ENGEL, A. (1997): *The Collected Papers of Albert Einstein*. Vol. 6.*The Berlin years: writings, 1914–1917*. English translation. Princeton University Press, Princeton.

EWALD, P (1913): "Bericht über die Tagung der British Association in Birmingham (10 bis 17. September)." *Physikalische Zeitschrift* **14**, 1297–1307.

GARBER, E. (1976): "Some reactions to Planck's law, 1900–1914." *Studies in History and Philosophy of Science* **7**, 89–126.

GIBBS, J. W. (1902): *Elementary principles in statistical mechanics*. Yale University Press, Yale. Reprinted in 1981: Woodbridge (Connecticut), Ox Bow Press.

GILLISPIE, C. C. (ed.) (1978): *Dictionary of Scientific Biography*. Charles Scribner's Sons, New York. (8 Vols.)

GRIGORIAN, A. T. (1978): "Ioffé, Abram Fedorovich." In GILLISPIE (1978), Supplement I, 251–252.

HENTSCHEL, A. M. (1998): *The Collected Papers of Albert Einstein*. Vol. 8. *The Berlin years: correspondence*, *1914–1918*. English translation. Princeton University Press, Princeton.

HERMANN, A. (1971): *The genesis of quantum theory (1899–1913).* MIT Press, Cambridge. (English translation by Claude W. Nash.) Original German version, 1969: *Frühgeschichte der Quantentheorie (1899–1913).* Physik Verlag, Mosbach/Baden.

IOFFÉ, A. (1911): "Zur Theorie der Strahlungserscheinungen." *Annalen der Physik* **36**, 534–552.

ISHIWARA, J. (1912): "Das photochemische Gesetz und die molekulare Theorie der Strahlung." *Physikalische Zeitschrift* **13**, 1142–1151.

JAMMER, M. (1966): *The conceptual development of quantum mechanics*. Mc-Graw Hill, New York.

JEANS, J. H. (1905): "On the laws of radiation." *Proceedings of the Royal Society of London* **76**, 545–552.

JEANS, J. H. (1906): "Bemerkung zu einer neuen Ableitung des WIENschen Verschiebungsgesetzes. Erwiderung auf Herrn P. Ehrenfests Abhandlung." *Physikalische Zeitschrift* **7**, 667.

JEANS, J. H. (1910): "On non-Newtonian mechanical systems, and Planck's theory of radiation." *Philosophical Magazine* **20**, 943–954.

JEANS, J. H. (1914): *Report on radiation and the quantum-theory*. The Electrician, London.

KANGRO, H. (1976): *Early history of Planck's radiation law*. Taylor and Francis. London. Original German version, 1970: *Vorgeschichte des Planckschen Strahlungsgesetzes*. Franz Steiner Verlag GmbH, Wiesbaden.

KLEIN, M. J. (ed.) (1959a): *Paul Ehrenfest: collected scientific papers*. North-Holland, Amsterdam; Interscience, New York.

KLEIN, M. J. (ed.) (1959b): "Ehrenfest's contributions to the development of quantum statistics. I and II." *Proc. Koninklijke Akademie van Wettenschapen te Amsterdam* **B62**, 41–50, 51–62.

KLEIN, M. J. (1985): *Paul Ehrenfest*. Vol. 1. *The making of a theoretical physicist*. Elsevier Science Publishers, Amsterdam. First edition 1970.

KLEIN, M. J., KOX, A. J., RENN, J., and SCHULMANN, R. (eds.) (1993): *The Collected Papers of Albert Einstein*. Vol. 3. *The Swiss years: writings, 1909-1911*. Princeton University Press, Princeton.

KLEIN, M. J., KOX, A. J., RENN, J., and SCHULMANN, R. (eds.) (1995): *The Collected Papers of Albert Einstein*. Vol. 4. *The Swiss years: writings, 1912–1914*. Princeton University Press, Princeton.

KOX, A. J., KLEIN, M. J., and SCHULMANN, R. (eds.) (1996): *The Collected Papers of Albert Einstein*. Vol. 6. *The Berlin years: writings, 1914–1917*. Princeton University Press, Princeton.

KRUTKOW, G. (1914a): "Aus der Annahme unabhängiger Licht-quanten folgt die Wiensche Strahlungsformel." *Physikalische Zeitschrift* **15**, 133–136.

KRUTKOW, G. (1914b): "Bemerkung zu Herrn Wolfkes Note: Welche Strahlungsformel folgt aus der Annahme der Lichtatome?" *Physikalische Zeitschrift* **15**, 363–364.

KUHN, T. S. (1978): *Black–body theory and the quantum discontinuity, 1894–1912*. Oxford University Press, New York.

KUHN, T. S., HEILBRON, J. L., FORMAN, P., and ALLEN, L. (1967): *Sources for history of quantum physics. An inventary and report*. The American Philosophical Society, Philadelphia.

LANGEVIN, P. and DE BROGLIE, M. (eds.) (1912): *La théorie du rayonnement et les quanta*. Gauthier-Villars, Paris.

LARMOR, J. (1910): "On the statistical theory of radiation." *Philosophical Magazine* **20**, 350–353.

LORENTZ, H. A. (1901a): "The theory of radiation and the second law of thermodynamics." *Proceedings Amsterdam Academy* **3**, 436–450.

LORENTZ, H. A. (1901b): "Boltzmann's and Wien's laws of radiation." *Proceedings Amsterdam Academy* **3**, 607–620.

LORENTZ, H. A (1910): "Alte und neue Fragen der Physik." *Physikalische Zeitschrift* **11**, 1234–1257.

McCORMMACH, R. (1967): "Henri Poincaré and the quantum theory." *Isis* **58**, 37–55.

MOSKOVCHENKO, N. Ia. and FRENKEL, V. Ia. (eds.) (1990): *Ehrenfest-Ioffe. Nauchnaya perepiska 1907–1933 gg*. Nauka, Leningrad.

NATANSON, L. (1911): “Über die statistische Theorie der Strahlung.” *Physikalische Zeitschrift* **12**, 659–666.

NERI, D. (1986): “Una nota su come Ehrenfest giunse alla formulazione del principio adiabatico.” *Rivista di Storia della Scienza* **3**, 375–383.

PLANCK, M. (1901): “Ueber das Gesetz der Energieverteilung in Normalspectrum.” *Annalen der Physik* **4**, 553–563. Reprinted in PLANCK (1958), Vol. 1, 717–727.

PLANCK, M. (1906): *Vorlesungen über die Theorie der Wärmestrahlung*. J. A. Barth, Leipzig. Reprinted in PLANCK (1988), 241–470.

PLANCK, M. (1910): “Zur Theorie der Wärmestrahlung.” *Annalen der Physik* **31**, 758–768. Reprinted in PLANCK (1958), Vol. 2, 237–247.

PLANCK, M. (1958): *Physikalische Abhandlungen und Vorträge*. 3 Vols. F. Vieweg und Sohn, Braunschweig.

PLANCK, M. (1988): *The theory of heat radiation*. Tomash, Los Angeles. This book contains the original German edition of *Vorlesungen über die Theorie der Wärmestrahlung*, 1906; it also contains the English translation, 1914, of the second German edition, 1913.

POINCARÉ, H. (1911): “Sur la théorie des quanta.” *Comptes Rendus* **153**, 1103–1108.

POINCARÉ, H. (1912): “Sur la théorie des quanta.” *Journal de Physique Théorique et Appliquée* **2**, 5–34.

PRENTIS, J. J. (1995): “Poincaré’s proof of the quantum discontinuity of nature.” *American Journal of Physics* **63**, 339–350.

RAYLEIGH, LORD (1902). “On the pressure of vibrations.” *Philosophical Magazine* **3**, 338–346.

ROSENFELD, L. (1936): “La première phase de l’évolution de la théorie des quanta.” *Osiris* **2**, 149–196. English translation in COHEN and STACHEL (1979), 193–234.

SIGEKO, N. (2000): “Ishiwara Jun’s Quantum Theory.” *Historia Scientarum* **71**, 112–119.

SOMMERFELD (2000): *Wissentschaftlicher Briefwechsel.* Band 1. *1892–1918.* Deutsches Museum, München.

STACHEL, J. (ed.) (1989): *The Collected Papers of Albert Einstein.* Vol. 2. *The Swiss years: writings, 1900–1909*. Princeton University Press, Princeton.

WHEATON, B. (1977): *Catalogue of the Paul Ehrenfest Archive at the Museum Boerhaave. Leiden.* Communication 151 of the National Museum for the History of Science and Medicine “Museum Boerhaave”, Leiden.

WIEN, W. (1894): “Temperatur und Entropie der Strahlung.” *Annalen der Physik und Chemie* **288**, 132–165.

WILSON, H. A. (1910): “On the statistical theory of heat radiation.” *Philosophical Magazine* **20**, 121–125.

WOLFKE, M. (1913a): “Zur Quantentheorie. Vorläufige Mitteilung.” *Deutsche Physikalische Gessellschaft, Verhandlungen* **15**, 1123–1129.

WOLFKE, M. (1913b): “Zur Quantentheorie. Zweite vorläufige Mitteilung.” *Deutsche Physikalische Gessellschaft, Verhandlungen* **15**, 1215–1218.

WOLFKE, M. (1914a): “Welche Strahlungsformel folgt aus der Annahme der Lichtatome?” *Physikalische Zeitschrift* **15**, 308–310.

WOLFKE, M. (1914b): “Antwort auf die Bemerkung Herrn Krutkows zu meiner Note: Welche Strahlungsformel folgt aus der Annahme der Lichtatome?” *Physikalische Zeitschrift* **15**, 463–464.

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