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Paul Ehrenfest: The Genesis of the Adiabatic Hypothesis, 1911–1914

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Abstract

We analyze the evolution of EHRENFEST's thought since he proved the necessity of quanta in 1911 until the formulation of his adiabatic hypothesis in 1914. We argue that his research contributed significantly to the solution of critical problems in quantum

physics and led to a rigorous definition of the range of validity of BOLTZMANN's principle.

We use the following abbreviations for the archives we cite:

AHQP	Archive for History of Quantum Physics; for a 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 a 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). Wherever possible we quote from the microfilm version included in the AHQP (the EMS have not been microfilmed).
NB	Niels Bohr Archive. We quote from the microfilm version included in the AHQP.

1. Introduction

In a recent paper,[1] we analyzed the main features and immediate impact of EHRENFEST's article of 1911 on the nature of the various quantum hypotheses in radiation theory.[2] We argued that EHRENFEST deduced the "necessity of discontinuity" rather than the "necessity of quantization," and that he clarified the deep differences that existed between PLANCK's and EINSTEIN's quantum hypotheses. His disciple KRUTKOW completed his analysis, showing by means of combinatorics that the assumption of corpuscular quanta does not allow one to go beyond WIEN's law. Further, to recover PLANCK's law, a correlation among quanta that removes their independence is required. We also showed the important role that adiabatic invariants played in EHRENFEST's paper, even though they did not lead him either to certain quantization rules or to the discrete character of the weight function, but instead imposed a factorization condition on the weight function that was essential for him to obtain his main results. Our analysis allowed us to localize the germ of his future adiabatic hypothesis in this paper. Its origin and appearance will be the main topics of our present paper.

We first will analyze the reasons that led EHRENFEST to address questions that were not directly related to the black-body radiation problem. Specifically, we will consider EHRENFEST's paper of 1913 on the specific heat of hydrogen,[3] in which he made an original use of adiabatic transformations that constitutes a big step toward his adiabatic hypothesis. We also will investigate the reasons why EHRENFEST wrote this

[1] NAVARRO and PÉREZ (2004).
[2] EHRENFEST (1911).
[3] EHRENFEST (1913a).

paper which at first sight only seems to be a simple alternative to an earlier paper by EINSTEIN and STERN.[4] Then, in another article of 1913 on a mechanical theorem of BOLTZMANN,[5] EHRENFEST already employed a primitive adiabatic hypothesis but did not formulate it clearly. He used it instead to deduce a set of quantization rules that differed from the usual ones and specifically obtained the quantization rule for the motion of a rigid rotator. In this way adiabatic invariants began to play a role in the development of quantum theory. He also posed for the first time a question that would become the target of continuing debate: What is the relationship between classical mechanics and the new quantum mechanics?

We also will show in light of EHRENFEST's correspondence and notebooks that the dates and contents of his publications of 1913 do not provide a fair basis for an account of the evolution of his ideas on the role of adiabatic invariants in quantum theory. In particular, we will examine the circumstances that led him to postpone the publication of his considerations on the adiabatic hypothesis for almost one year.

In 1914 EHRENFEST posed another question of extreme importance to those who ascribed great value to the methods of statistical mechanics: In which measure was BOLTZMANN's traditional approach compatible with the emerging quantum developments?[6] In other words, since the number of microstates compatible with a certain macrostate plays such a prominent role in BOLTZMANN's statistical mechanics, and since this number is incomparably smaller in quantum treatments than in classical ones, to what extent was it possible to continue to refer to BOLTZMANN's statistical methods, once quantum restrictions were accepted? EHRENFEST answered this question with his usual rigor by means of the weight function he had introduced in 1911: He proved that the necessary and sufficient condition to guarantee compatibility between BOLTZMANN's methods and quantum theory was the so-called "δG-condition," whose meaning we will analyze in detail. This condition, as EHRENFEST stressed, was satisfied trivially by the quantization rules that had been formulated to date, so that compatibility between BOLTZMANN's statistical methods and the emerging quantum theory was guaranteed, at least for a time.

As was often the case, these important contributions of EHRENFEST during 1913 and 1914 were not very well known even by leading physicists at the time. Then, during 1915 and 1916 different generalizations of PLANCK's quantization rule (for sinusoidal vibrations) and of BOHR's (for uniform circular motions) appeared. EHRENFEST's ideas on the connection between adiabatic invariants and quantum theory now offered a theoretical framework for these different quantization rules. On the one hand, all of them could be understood on the basis of a unique principle, EHRENFEST's adiabatic hypothesis. On the other hand, that hypothesis now offered a definite procedure for obtaining new quantization rules from the older ones.

We will examine the special circumstances that led EHRENFEST, perhaps motivated by the appearance of the last of SOMMERFELD's papers on quantum theory,[7] to write

[4] EINSTEIN and STERN (1913).
[5] EHRENFEST (1913b).
[6] EHRENFEST (1914).
[7] KLEIN (1985), 284–287.

an article introducing his adiabatic hypothesis in a transparent and rigorous form and illustrating how to use it in the new theoretical panorama presented by quantum theory. We will stop with the appearance of EHRENFEST's paper of 1916,[8] whose contents, impact, and applications during the old quantum theory we will discuss in a future paper.

2. From black-body radiation to rotational specific heats (1913)

In early 1912 EUCKEN published the results of his experiments in Berlin on the specific heat of hydrogen.[9] His measurements showed that the rotational contribution to the specific heat reached an almost constant value at about 60°K. But at lower temperatures the specific heat seemed to behave like that of a monoatomic gas, in accordance with the equipartition theorem.

At the beginning of 1913 EINSTEIN and STERN provided a theoretical explanation of earlier experimental results of EUCKEN,[10] in which they resorted to the concept of zero-point energy, an assumption in PLANCK's second quantum theory of 1911.[11] EHRENFEST suggested an alternative explanation of EUCKEN's results in 1913 without going beyond the framework of his paper of 1911, that is, by combining statistical-mechanical techniques and quantum theory without making use of the concept of zero-point energy.[12] His notebooks show, however, that he developed the main ideas in this paper during 1912, and its essential points are mixed in with other ideas that he published in a second paper in 1913.[13] In his notebooks we can glimpse a first formulation of his adiabatic hypothesis and how to use it to find quantization rules for general periodic motions.

2.1. EINSTEIN and STERN's proposal in support of a zero-point energy

In his second quantum theory, PLANCK assumed that black-body resonators absorb radiation continuously, as in classical electromagnetism, but emit radiation in discrete energy quanta and that the emission is subject to statistical laws. His second theory also led to his original radiation law of 1900, but instead of the mean energy $\overline{E}$ of a monochromatic resonator of frequency ν at absolute temperature T being given by

$$\overline{E} = \frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1}, \tag{1}$$

it now was given by

$$\overline{E} = \frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} + \frac{h\nu}{2}. \tag{2}$$

8 EHRENFEST (1916a).
9 EUCKEN (1912).
10 EINSTEIN and STERN (1913).
11 PLANCK (1911a and 1911b).
12 EHRENFEST (1913a).
13 EHRENFEST (1913b).

In PLANCK's view, the additional $h\nu/2$ term could not be measured experimentally, because expression (2) led to the same radiation law as expression (1). Further, it did not contribute to the specific heat, because its derivative with respect to temperature is zero.[14]

Nevertheless, in view of EUCKEN's measurements of the specific heat of hydrogen at low temperatures, EINSTEIN and STERN saw the possibility to use them to differentiate between these two expressions and consequently to test the zero-point energy hypothesis. They saw that if they could identify an oscillating system in which its frequency depended on its temperature, then the additional term would indeed contribute to the specific heat. The system they analyzed was that of rotating diatomic gas molecules. Thus the rotational kinetic energy E_r of a diatomic molecule is given by

$$E_r = \frac{1}{2} L (2\pi\nu)^2, \tag{3}$$

where L is its moment of inertia and ν its rotational frequency.[15] After a slight justification, which included their assumption that "approximately, all dipoles of our gas rotate with the same speed at a given temperature"[16] (that is, the frequency ν is the same for all of the molecules), they equated the rotational kinetic energy E_r to twice the mean kinetic energy of a Planckian resonator (that is, to the mean energy of the resonator) of the same frequency, which, depending on whether they adopted expression (1) or (2) for the mean energy, led to either

$$T = \frac{h}{k} \frac{\nu}{\ln\left(\frac{h}{p\nu} + 1\right)}, \tag{4}$$

or

$$T = \frac{h}{k} \frac{\nu}{\ln\left(\frac{h}{p\nu - \frac{h}{2}} + 1\right)}, \tag{5}$$

where $p = 2\pi^2 L$. The rotational specific heat c_r is therefore

$$c_r = \frac{\mathrm{d}E_r}{\mathrm{d}T} = \frac{\mathrm{d}E_r}{\mathrm{d}\nu} \cdot \frac{\mathrm{d}\nu}{\mathrm{d}T}, \tag{6}$$

where they calculated $\mathrm{d}E_r/\mathrm{d}\nu$ from Eq. (3) and $\mathrm{d}\nu/\mathrm{d}T$ from either Eq. (4) or (5).

EINSTEIN and STERN plotted the results of their calculations as shown in Fig. 1, where EUCKEN's experimental data is represented by the small crosses. They obtained Curve I from Eq. (5), that is, by assuming a zero-point energy, and found reasonable agreement with EUCKEN's experimental data, in contrast to Curve II, which they obtained from Eq. (4), that is, by assuming no zero-point energy. They obtained Curve III by assuming a zero-point energy but also that ν is independent of T, and Curve IV by assuming a zero-point energy equal to $h\nu$; both also exhibit the correct asymptotic behavior at low temperatures, but at higher temperatures Curve I fits EUCKEN's experimental data better.

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[14] PLANCK (1911a), 146. In PLANCK (1958), Vol. 2, 257.

[15] EINSTEIN and STERN (1913) denoted the moment of inertia by J, but we adopt EHRENFEST's notation L.

[16] EINSTEIN and STERN (1913), 553. In BECK (1996), 138.

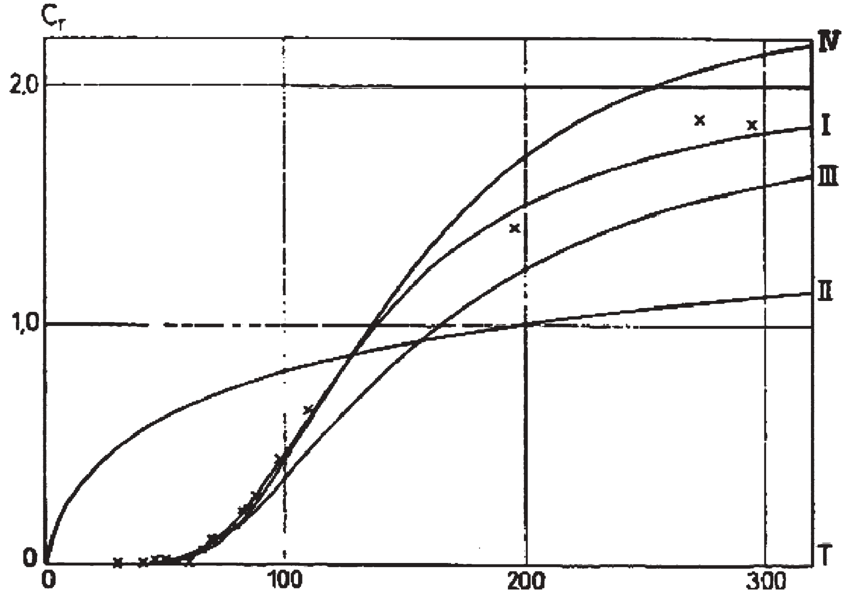

Fig. 1. EINSTEIN and STERN's plots assuming a zero-point energy (I, III, IV), and not assuming one (II). EUCKEN's experimental data are represented by the small crosses

EINSTEIN and STERN, however, went further. In the second part of their paper, they used a formalism that EINSTEIN and HOPF introduced in 1910 to study the heat balance between a system of resonators and electromagnetic radiation.[17] They divided the effect of the radiation on the resonators into a continuous part associated with the radiation pressure and a stochastic part related to the change in momentum of the system induced by radiation fluctuations, in a way similar to EINSTEIN's earlier analyses of momentum fluctuations.[18] But now a great novelty appeared: While EINSTEIN and HOPF (1910) arrived at the RAYLEIGH-JEANS law without quantizing the energy of the resonators, EINSTEIN and STERN (1913) now obtained PLANCK's law, also without quantizing the energy of the resonators, but by assuming the existence of a zero-point energy of $h\nu/2$. They concluded:

> 1. Eucken's results on the specific heat of hydrogen make probable the existence of a zero–point energy equal to $h\nu/2$.
> 2. The assumption of the zero-point energy opens a way for deriving Planck's radiation formula without recourse to any kind of discontinuities. Nevertheless, it seems doubtful that the other difficulties can also be overcome without the assumption of quanta.[19]

Despite this cautious conclusion, it would have frustrated EHRENFEST, who believed that he had established the necessity of quanta rigorously in 1911. Still, he could

[17] EINSTEIN and HOPF (1910).
[18] See, for instance, BERGIA and NAVARRO (1988), 84–85.
[19] EINSTEIN and STERN (1913), 560. In BECK (1996), 145.

immediately see a way out based upon EINSTEIN and STERN's excessive simplification of the problem by assigning an average frequency to all of the molecules of the gas instead of a distribution of frequencies.

2.2. EHRENFEST's counter-proposal: Quantize the rotational motion of diatomic molecules

EHRENFEST's paper (1913a) can be understood as a standard application of statistical mechanics. Starting from a distribution of the frequencies of rotation of diatomic hydrogen molecules, EHRENFEST obtained reasonable agreement with EUCKEN's experimental data – at least as good as EINSTEIN and STERN's – without recourse to a zero-point energy. He begun by stating two assumptions:

A. In rotating about a fixed axis, the only allowed angular frequencies are those for which the rotational kinetic energy is an integral multiple of $h\nu/2$:

$$\varepsilon_n = \frac{L}{2}(2\pi\nu)^2 = n\frac{h\nu}{2} \quad (n = 0, 1, 2, \dots). \tag{7}$$

B. If q is the angle of rotation and the corresponding momentum is

$$p = L\dot{q} = L(2\pi\nu), \tag{8}$$

then condition (7) implies that in the phase plane (q, p) of the molecule the only allowed regions are:

the point $q = p = 0$,

$$\text{and the pairs of segments } p = \pm\frac{h}{2\pi}, \pm 2\frac{h}{2\pi}, \pm 3\frac{h}{2\pi}, \dots . \tag{9}$$

This means that all of these elements – the point and every pair of segments – had to be treated for statistical purposes as "equally probable."[20]

EHRENFEST attached footnotes to each of these two assumptions to clarify their meaning. Regarding assumption A, he stated that he followed LORENTZ's approach at the Solvay conference of 1911, according to which the energy of rotation could only be an integral multiple of $h\nu$, but he was going to assume instead integral multiples of $h\nu/2$ that could be obtained from a more general approach, which he did not specify. Expression (7), however, showed that the choice between $h\nu/2$ and $h\nu$ was as secondary as the numerical value of L, which had to be determined by the experimental data.

Regarding assumption B, EHRENFEST imagined an adiabatic modification of the system such that the possible vibrations of the Planckian resonators were transformed into rotations of the molecule that could be obtained from those vibrations by slowly increasing their kinetic energies. Referring to these changes in the phase plane (q, p) of the molecule, this meant that the initial ellipses around $q = p = 0$ were transformed into the regions of phase space given by Eq. (9). Assumption B then states that in an

[20] EHRENFEST (1913a), 453. In KLEIN (1959), 335.

adiabatic change – stimulated, for example, by a slowly varying electric field acting upon the molecular dipoles – the possible initial motions (vibrations) transform into molecular rotations maintaining their equiprobability. We will return to this point later.

Calculating, in the usual way, the most probable distribution corresponding to a system of N molecules in thermal equilibrium at temperature T, EHRENFEST found that the total rotational energy E_R is given by

$$E_R = N \frac{\sum_0^\infty \varepsilon_n \exp\left(-\frac{\varepsilon_n}{kT}\right)}{\sum_0^\infty \exp\left(-\frac{\varepsilon_n}{kT}\right)}, \tag{10}$$

where the rotational kinetic energy ε_n of the molecule, as deduced from Eq. (7), is given by

$$\varepsilon_n = n^2 \frac{h^2}{8\pi^2 L} \quad (n = 0, 1, 2, \ldots). \tag{11}$$

Substituting (11) into (10) and differentiating the result with respect to T, EHRENFEST found that the total contribution of the rotational motion of diatomic molecules to the specific heat is given by:

$$C_R = 2Nk\sigma^2 \frac{\mathrm{d}^2 \log Q(\sigma)}{\mathrm{d}\sigma^2}, \tag{12}$$

where he defined

$$\sigma = \frac{h^2}{8\pi^2 LkT},$$
$$Q(\sigma) = 1 + \exp(-\sigma) + \exp(-4\sigma) + \exp(-9\sigma) + \cdots + \exp(-n^2\sigma) + \cdots, \tag{13}$$

and introduced the factor 2 to take into account the two degrees of freedom that he assigned, without comment, to the rotational motion of the hydrogen molecule.

To simplify the numerical evaluation of Eq. (12) in the limits of high and low temperatures (small and large values of σ), EHRENFEST presented some possible approximations for the function Q. He also included graphical representations of EUCKEN's experimental data, EINSTEIN and STERN's (1913) curve obtained with a zero-point energy, and his own curve given by Eq. (12), in which he had previously adjusted L in accordance with EUCKEN's experimental data. He stressed that at low temperatures his equation fit EUCKEN's data well (see Fig. 2), while at higher temperatures it approaches the equipartition value Nk, reaches a maximum at T$\approx$ 250°K and then decreases to a minimum at T$\approx$ 550°K (not shown), all of which was in clear contrast, he affirmed, with the well-known monotonically increasing behavior of Planckian resonators. Finally, he pointed out that the larger values BJERRUM measured in 1911–1912 in the range from 1700°K to 2700°K had to be interpreted "naturally" as stemming from the appearance of additional degrees of freedom.[21]

[21] *Ibid.*, 456–457 and 338–339.

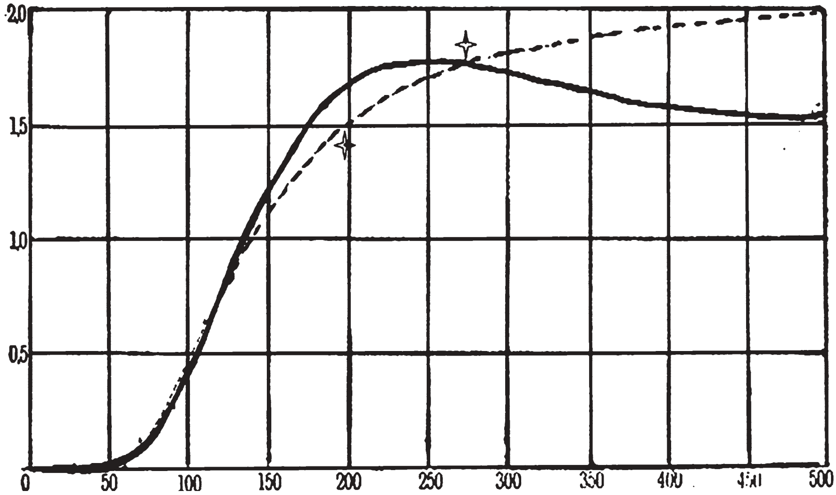

Fig. 2. EHRENFEST's plots of the total specific heat c_R of a system of diatomic hydrogen molecules *versus* the absolute temperature T. The continuous line corresponds to his expression (12), and the dotted one to EINSTEIN and STERN's Curve I of 1913. We have highlighted the only two points of EUCKEN's experimental data corresponding to the central zone ($T \approx 195$°K and $T \approx 270$°K). At low temperatures both curves fit EUCKEN's data very well

2.3. EHRENFEST versus *EINSTEIN and STERN*

We now turn to a critical comparison of the methods and hypotheses found in EHRENFEST (1913a) and EINSTEIN and STERN (1913). Some of their differences appear explicitly in these articles, while others do not.

In their treatments of the contribution of the molecular rotational motion to the specific heat of hydrogen, both EINSTEIN and STERN (1913) and EHRENFEST (1913a) introduced novelties pertaining to the rotational frequency. EINSTEIN and STERN introduced a dependence of the frequency on the absolute temperature, but they assumed a unique value for all of the molecules that could be determined from Eq. (5) by assuming a zero-point energy. They also assumed that "at equilibrium the kinetic energy of a dipole must be twice as great as that of a one-dimensional resonator of the same frequency,"[22] which was a key assumption that appeared without any comment. By contrast, for EHRENFEST, at any given temperature the molecules can rotate with any of the infinite number of frequencies that can be deduced from Eq. (7), that is,

$$\nu = \frac{nh}{4\pi^2 L} \quad (n = 0, 1, 2, \ldots), \tag{14}$$

where the range of possible frequencies for any given molecule is fixed by the parameter L. The temperature T then does not determine a unique frequency of rotation, but a distribution of the possible frequencies given by Eq. (14) or, equivalently, the possible

[22] EINSTEIN and STERN (1913), 553. In BECK (1996), 138.

energies given by Eq. (11). This distribution, the canonical distribution, is the basis for the statistical approach that allowed EHRENFEST to obtain Eq. (12). In other words, whereas each of the Planckian resonators had a characteristic frequency and its energy could have an infinite number of discrete values, now every diatomic molecule has a characteristic moment of inertia L, and its frequency of rotation and its corresponding energy can have an infinite number of discrete values according to Eqs. (14) and (11), respectively. Thus, EHRENFEST's procedure was closer to the quantization of electronic orbits in BOHR's atomic model, in which the frequencies of rotation of the electron were quantized, than to PLANCK's original treatment, in which the frequency was not subject to any restriction and was the essential characteristic of a monochromatic resonator. At the same time, although both EHRENFEST's and BOHR's papers appeared in 1913, we will later offer reasons to believe that EHRENFEST was unaware of BOHR's ideas before they were published in the *Philosophical Magazine*.[23]

The new quantization rule that EHRENFEST introduced for the uniform rotation of a diatomic molecule about its axis, as expressed by (11) or (14), could be interpreted as a contribution to the generalization of quantum theory, once he had established the necessity of quantization in EHRENFEST (1911). By contrast, EINSTEIN and STERN (1913) represents an attempt to eliminate any vestige of quantization:

> In what follows it shall be shown how, on the basis of the assumption of a zero-point energy, one can derive Planck's radiation formula in an unforced, though not quite rigorous way, and without assuming any discontinuities.[24]

As EHRENFEST wrote some years later to BOHR,[25] when he sent his work in for publication he did not know about a previous work by BJERRUM (1912) on molecular spectra.[26] In this work the author employed expression (7), with quanta $h\nu$. Though BJERRUM did not complete his calculations with the corresponding statistical treatment, he actually presented the first successful application of quantum notions to infrared spectroscopy.[27]

Concerning agreement with EUCKEN's experimental data on the specific heat of hydrogen, since only two of his measurements were at temperatures in the central zone in EHRENFEST's plot (Fig. 2), it cannot be said that his curve fit them better than EINSTEIN and STERN's curve. This is still the case even if one includes the minimum at higher temperatures, which EHRENFEST did not represent in his article, but which DEBYE did the following year (Fig. 3). EHRENFEST's ultimate concern, it seems, was to rebut EINSTEIN and STERN's argument against the necessity of introducing a quantum discontinuity and to support having recourse to a zero-point energy. EHRENFEST's claim was strongly reinforced by his theoretical explanation of EUCKEN's measurements at low temperatures. Indeed, in a first draft of his article, there is a brief comment,

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[23] BOHR (1913).

[24] EINSTEIN and STERN (1913), 556. In BECK (1996), 141–142.

[25] EHRENFEST to BOHR, 8 May 1922. In AHQP, microfilm AHQP/BSC-2.

[26] Of course, this work is not the two papers of BJERRUM quoted in EHRENFEST (1913a) to which we referred in Sect. 2.2.

[27] BJERRUM (1912).

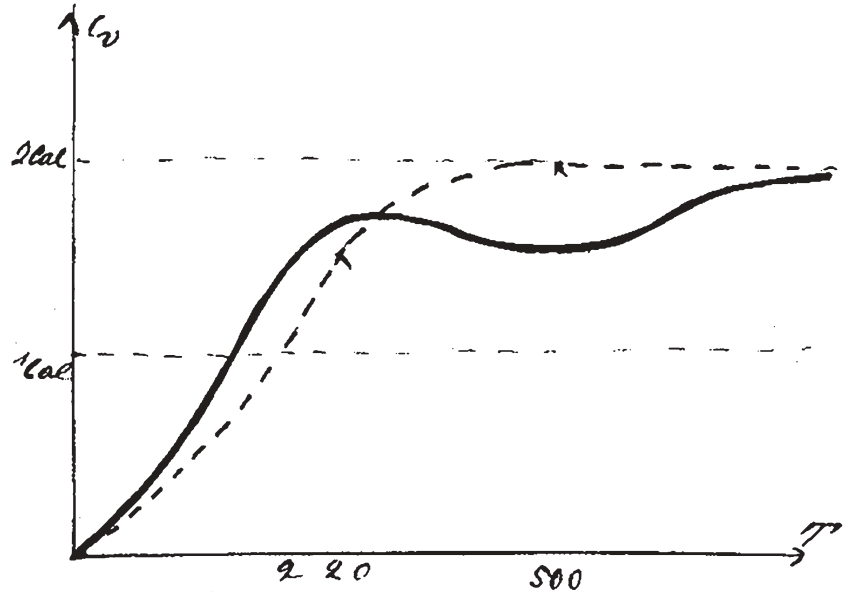

Fig. 3. Plots of the specific heat of hydrogen as a function of temperature. The solid line represents EHRENFEST's curve. We have extracted this curve from DEBYE's notes of the course he gave on "Quantentheorie" at the University of Göttingen in the winter semester 1914–15. DEBYE obtained it by applying his own generalization of PLANCK's quantum hypothesis, recognizing that EHRENFEST had obtained it earlier in 1913[29]

which he eliminated later, in which he pointed out that his curve was no worse than others when compared with the observations at high temperatures.[28]

EHRENFEST's notebooks confirm that EINSTEIN and STERN's contention that the specific heat of diatomic gases at low temperatures, as well as the characteristics of black-body radiation, could be explained without recourse to quantization stimulated his thoughts and offer insight into the evolution of his ideas on the necessity of quantization around 1913. At the same time, to understand EINSTEIN and STERN (1913), it is necessary to understand the formalism in EINSTEIN and HOPF (1910), its predecessor, which was published in the *Annalen* on 20 December 1910. That same winter EHRENFEST made an entry in his notebook entitled "Zu Einstein-Hopf,"[30] in which he generalizaded their treatment and obtained a common expression for both WIEN's and PLANCK's laws, writing the spectral-distribution function $\rho(\nu, T)$ for black-body radiation as

$$\rho(\nu, T) = \nu^3 f\left(\frac{\nu}{T}\right) = \frac{8\pi h\nu^3}{c^3}\frac{1}{\exp\left(\frac{h\nu}{kT}\right) + C}. \tag{15}$$

[28] EMS:7.

[29] "Quantentheorie," 17. In "P. Debye Lectures on Quantum Theory," microfilm AHQP-24.

[30] Note 764, December 1910 - January 1911, ENB:1-13. In EA, microfilm AHQP/EHR-2.

Later notes probably written during the first months of 1911 suggest that EHRENFEST thought about publishing something on EINSTEIN and HOPF (1910),[31] just at the time he began his investigations that culminated in EHRENFEST (1911).

Although fluctuations play a prominent role in EINSTEIN and HOPF (1910), much in line with EINSTEIN's earlier research on momentum fluctuations in black-body radiation,[32] nothing on them appeared in EHRENFEST (1911). However, immediately after he published this paper, fluctuations began to attract his attention, as can be seen in some of his frequent and rigorous statistical treatments.[33] Then, several annotations concern "Einstein's fluctuations," and he calculated energy fluctuations associated with various black-body radiation laws, including his own of 1911, which he continued to refer to as "mine,"[34] based upon the assumption of only one discontinuity owing to the existence of an excitation threshold. He found the following results for the energy fluctuations associated with the various black-body radiation laws:

$$\begin{array}{ll} \text{Wien} & \overline{\varepsilon^2} = h\nu\rho \\ \text{Planck} & \overline{\varepsilon^2} = h\nu\rho + kT\rho\frac{\sigma}{e^{\sigma}-1} \\ \text{Rayleigh} & \overline{\varepsilon^2} = h\nu\rho + kT\rho \\ \text{Rayleigh - Jeans} & \overline{\varepsilon^2} = kT\rho \\ \text{Ehrenfest} & \overline{\varepsilon^2} = h\nu\rho\frac{\sigma+1}{\sigma+e^{-\sigma}} + kT\rho\frac{1}{1+\sigma} \end{array} \qquad (16)$$

In 1912, now installed as LORENTZ's successor in Leiden, EHRENFEST again considered EINSTEIN and HOPF (1910).[35] It seems that LORENTZ, as director of FOKKER's doctoral dissertation, proposed that he should use ideas contained in EINSTEIN and HOPF (1910) to calculate the mean energy of an electron in a radiation field.[36] According to FOKKER, EHRENFEST declined to supervise his investigations, but a letter that he wrote to EHRENFEST suggests that the two discussed the role that fluctuations played in FOKKER's calculation.[37]

Around the end of 1912, EHRENFEST began to make annotations on ideas and projects that would lead him to write EHRENFEST (1913a). Thus, in November he made a note entitled "energy content of a rotating dipole in a Planck's radiation field."[38] Then, in December, EINSTEIN announced in a letter to EHRENFEST that he was studying the problem of the rotational specific heat of hydrogen,[39] and in January 1913 EHRENFEST noted his intention to study EINSTEIN's fluctuations, which he had constantly postponed.[40] Next, in March 1913, a few days after the publication of EINSTEIN and

[31] ENB:1-13. In EA, microfilm AHQP/EHR-2.

[32] See, for example, BERGIA and NAVARRO (1988), 80–85.

[33] See, for example, notes 75, 78, 79, 80, 81, 82, 83, 85, 86, July 1911, ENB:1-14. In EA, microfilm AHQP/EHR-2.

[34] NAVARRO and PÉREZ (2004), 118–124.

[35] Note 891, 9 November 1912, ENB:1-17. In EA, microfilm AHQP/EHR-3.

[36] Interview of A. FOKKER by J. L. HEILBRON, 1 April 1963. Microfilm transcription AHQP/OHI-2.

[37] FOKKER to EHRENFEST, 24 December 1912. In EA, microfilm AHQP/EHR-20, Sect. 4.

[38] Note 892, 19 November 1912, ENB:1-17. In EA, microfilm AHQP/EHR-3.

[39] EINSTEIN to EHRENFEST, 20/24 December 1912. In KLEIN, *et al.* (1993), 508–509.

[40] Note 934, 9 January 1913, ENB:1-17. In EA, microfilm AHQP/EHR-3.

STERN (1913), EHRENFEST decided to analyze PLANCK's hypothesis of zero-point energy, either by means of EINSTEIN's fluctuations, or by introducing an infinite set of frequencies.[41] Finally, at the end of April 1913, EHRENFEST attended the Wolfskehl lectures in Göttingen, which were delivered by PLANCK, DEBYE, SMOLUCHOWSKI, SOMMERFELD, LORENTZ, and others, on the kinetic theory of matter and electricity.[42] It thus seems plausible that while he was in Göttingen EHRENFEST wrote the note (which included a sketch of our Fig. 4 below) entitled "specific heat of rotating molecules according to the quantum theory,"[43] a topic that turned out to be central to EHRENFEST (1913a). Indeed, many of the lecturers mentioned the hypothesis of zero-point energy: DEBYE cited EINSTEIN and STERN (1913);[44] KAMERLINGH-ONNES and KEESOM referred to the hypothesis when they suggested a nonzero energy for the fundamental state of a monatomic gas;[45] and PLANCK and SOMMERFELD also commented on the hypothesis.[46] EHRENFEST lost little time in writing his paper after returning to Leiden,[47] which suggests that the Wolfskehl lectures were a strong stimulus for him to take a position against the hypothesis of zero-point energy and to find another basis on which to calculate the specific heat of hydrogen.[48]

Soon after he sent his paper in for publication EHRENFEST wrote in his notebook: "Calculation of the specific heat of the ideal gases according to the theory $h\nu/2$,"[49] which was precisely the topic treated by KAMERLINGH-ONNES in Göttingen. This note probably constitutes the beginning of a further project in which EHRENFEST analyzed – and eventually rejected – arguments in favor of a new hypothesis of zero-point energy for translational degrees of freedom according to the guidelines set out in EINSTEIN and STERN (1913). By then EHRENFEST had reproduced several of his earlier calculations in his notebooks, but now redone by introducing zero-point energy.[50] He did not pursue his results, however, because he soon dropped the hypothesis of zero-point energy. EHRENFEST's decision probably was decisively influenced by his discussions with EINSTEIN when he and his wife visited EINSTEIN in Zurich in June and July 1913. By then EINSTEIN no longer considered his and STERN's treatment of fluctuations to be valid. As EHRENFEST explained to LORENTZ in a letter he wrote while still in Zurich:

[41] See, for instance, notes: 981, 26 March 1913; 984, 16 April 1913; 985, 17 April 1913. ENB:1-17. In EA, microfilm AHQP/EHR-3.

[42] PLANCK, *et al.* (1914).

[43] Note 989, end of April or beginning of May 1913, ENB: 1-17. In EA, microfilm AHQP/EHR-3.

[44] PLANCK, *et al.* (1914), 19.

[45] *Ibid.*, 193–194.

[46] *Ibid.*, 14 and 138–139.

[47] EHRENFEST (1913a) was received by the *Annalen* on 24 May.

[48] Notes 995–1000, May 1913, ENB:1-17. In EA, microfilm AHQP/EHR-3.

[49] Note 1001, 4 June 1913, 892, ENB:1-17. In EA, microfilm AHQP/EHR-3.

[50] Notes 1003, 1004, 1006 and 1007, June 1913, ENB:1-17. In EA, microfilm AHQP/EHR-3.

> In the field of the quantum question, Einstein has discovered a serious shortcoming in the treatment of fluctuations in his last work published with Stern. He has asked me to inform you verbally about it.[51]

EINSTEIN publicly renounced the hypothesis of zero-point energy that October, at the second Solvay conference in Brussels, where he declared:

> I must also point out in this respect that the arguments which I put forward with Mr. Stern in favor of the existence of an energy at absolute zero, I do not consider anymore as valid. By developing further the considerations that we have made regarding the deduction of Planck's radiation law, I have found indeed that this procedure, based on the zero-point energy hypothesis, leads to contradictions.[52]

EINSTEIN also conveyed his change of heart a few days later in a letter to HOPF in which he stated that soon after the publication of EINSTEIN and STERN (1913) he realized the futility of maintaining the zero-point energy hypothesis.[53] He conveyed the same message to EHRENFEST in a letter at the beginning of November in which he also referred to adiabatic transformations, which he was beginning to use as a promising tool in his calculations.[54]

These, however, were not EINSTEIN's last words on the subject. In July 1914 he wrote to EHRENFEST again, proposing that EHRENFEST should redo his calculations of the previous summer on the specific heat of hydrogen, but now assuming quantization of the rotational energy and the existence of a zero-point energy.[55] If the result "also did not conform to experience, it would get the adiabatic theorem in trouble and surely also quantum theory in general. If you do, write me how the matter stands."[56] The implication probably was that EINSTEIN and EHRENFEST had agreed that none of the earlier calculations were in satisfactory agreement with measurements. Although we have found no documentary evidence for it, we assume that EHRENFEST told EINSTEIN that the inclusion of zero-point energy did not change his earlier results.

In sum, taking into account EHRENFEST's notebooks, his concern with the hypothesis of zero-point energy seems to have been only momentary. He could well have felt that the admission of this hypothesis would have been tantamount to the denial of the essential result he had obtained in 1911: The necessity of introducing some discontinuity to explain the experimental behavior of black-body radiation. Our view here is reinforced by a letter that EHRENFEST wrote to JOFFÉ soon after he wrote EHRENFEST (1913a), in which he stressed the incorrectness of EINSTEIN and STERN's treatment, the inade-

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[51] EHRENFEST to LORENTZ, 2 July 1913. In AL, microfilm AHQP/LTZ-4; our translation.

[52] GOLDSCHMIDT, *et al.* (1921), 108; our translation. The conference took place in Brussels from 27–31 October 1913 on the subject, "The structure of matter."

[53] EINSTEIN to HOPF, 2 November 1913. In KLEIN, *et al.* (1993), 562–563.

[54] EINSTEIN to EHRENFEST, before 7 November 1913. In KLEIN, *et al.* (1993), 564.

[55] In EINSTEIN's opinion, there existed new approaches that suggested reconsidering these hypotheses. He was possibly referring to SACKUR (1914), although he did not specify it.

[56] EINSTEIN to EHRENFEST, 8 July 1914. In HENTSCHEL (1998), 31.

quate justification of the zero-point energy hypothesis, and the correctness of his recent work:

> This is interesting, because it is possible to operate *without* the introduction of the "absolute zero energy"! And the fact is that Einstein obtained his [and STERN's] curve by means of a not completely correct calculation, in which he turned out to have been bound to have recourse to this "absolute zero energy," to obtain again through a not very correct way the form of the curve of this sort [EHRENFEST here draws its horizontal asymptote]. Here, however, we achieve an absolutely correct calculation without employing the "absolute zero energy."[57]

In short, EHRENFEST believed that in his work of 1913 he had shown the incorrectness of EINSTEIN and STERN's calculation of the specific heat of hydrogen. Further, he had stressed the absence of a rigorous justification of the hypothesis of zero-point energy, whose only role in EINSTEIN and STERN's treatment seemed to have consisted in rectifying the errors they had committed in their calculations. By contrast, EHRENFEST's calculation was based on a correct application of statistical mechanics and on the introduction of a new quantization rule for the rotational motion of a diatomic molecule around a fixed axis, in a way that LORENTZ and others had suggested earlier. He therefore believed that his results were not less worthy than EINSTEIN and STERN's as an explanation of EUCKEN's experimental data.

2.4. *Toward an adiabatic hypothesis*

The first connection between adiabatic transformations and quantum theory appears in EHRENFEST (1913a), in his reasoning to obtain the quantization of angular velocity of the molecules by means of Eq. (7). To justify the equiprobability that he assigned to the allowed regions in phase space given by Eq. (9), he described the relationship between PLANCK's resonators and rotating molecules as follows:

> For a moment, one assumes that an orienting field acts on the molecule (dipole). For very small values of the kinetic energy [relative to the energy of the applied field] the molecule would then oscillate sinusoidally. The corresponding phase curves in the q-p plane space would be ellipses around the point $q = p = 0$, as for PLANCK's resonators; but with this one treats the ellipses "equally possible" among themselves and with the point $q = p = 0$. For higher kinetic energies the molecule inverts and rotates in one or another sense: the ellipse has resolved itself into a pair of undulating curved pieces between $q = \mp\pi$. For still higher kinetic energies these curved pieces degenerate into the pairs of segments [(9)]. By infinitely slow diminution of the orienting field, one can transform all of the oscillating molecules "adiabatically" into uniformly rotating ones: the ellipses around $q = p = 0$ into the pairs of segments [(9)].[58]

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[57] EHRENFEST to JOFFÉ, 22 May 1913. In MOSKOVCHENKO and FRENKEL (1990), 121; our translation.

[58] EHRENFEST (1913a), 453–454, footnote 2. In KLEIN (1959), 335–336; our translation.

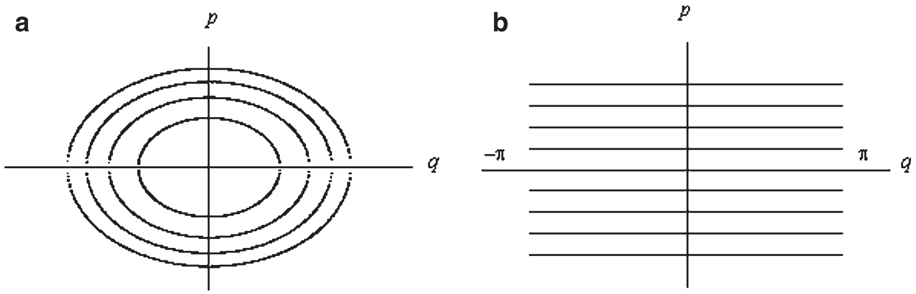

Fig. 4. (a) The ellipses about the point (0,0) in phase space constitute the equiprobable allowed regions in phase space for PLANCK's resonators. (b) Following EHRENFEST (1913a), the pairs of segments and the point (0,0) – obtained from (a) by an adiabatic transformation – play the identical role for uniform rotations of a diatomic molecule around its axis

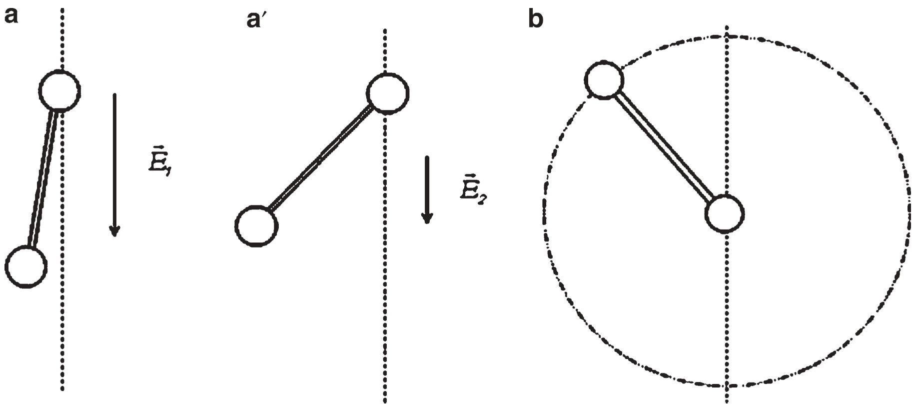

Fig. 5. In (a) a dipole oscillates harmonically in the presence of a strong orienting field (the dipole's kinetic energy is small relative to the field's potential energy); the dipole behaves like a Planckian resonator. In (a′) the dipole oscillates anharmonically in the presence of a weak orienting field. In (b) the dipole rotates in the absence of an orienting field; it now behaves like a rotating molecule

In Fig. 4 (which EHRENFEST did not include in his paper) we show a graphical representation of the two different regions in phase space that EHRENFEST notes in the last sentence of the above quotation. In Fig. 5 we represent three different motions for a dipole corresponding to the two regions (a) and (b) depicted in Fig. 4. Note that EHRENFEST implicitly assumes that two regions of phase space that can be related by means of an adiabatic transformation preserve their respective probabilities, that is, possible motions in one region will transform into possible motions in the other region with the same probability (equiprobability in the case of Planckian resonators and thus also in the case of rotating molecules), and forbidden motions will transform into forbidden motions.

Although adiabatic transformations did not appear explicitly in EHRENFEST's papers before EHRENFEST (1913a) (recall that his manuscript was received by the

Annalen on 24 May), his notebooks clearly show that at least as early as November 1912 adiabatic transformations and their possible role in the generalization of quantum theory were among his favorite topics of investigation. He was especially interested in searching for adiabatic invariants, that is, mechanical quantities in different mechanical systems that remain constant under an adiabatic transformation; he also frequently highlighted their possible relativistic invariance.[59] At the same time, it seems that EHRENFEST began to suspect that a theorem of SZILY might provide a new route to extend the quantum theory to more general systems than those that he had treated by a new and suitable use of adiabatic invariants.[60]

EHRENFEST gave two different, but closely related applications of adiabatic transformations in his paper: the determination of the possible rotational motions of a dipole (mechanics) and that of the corresponding allowed regions in phase space (statistical mechanics). In line with his investigations in 1911, he first detected the adiabatic invariance of E/ν (mechanics), and he then found that the weight function was a function of this invariant (statistical mechanics). This was the moment in which he generalized the adiabatic invariant E/ν before Christmas of 1912, his first one in Leiden. His notebooks at this time contain a large number of entries on the possible relationships among adiabatic invariants, relativistic invariants, and quantum theory, as well as comments that anticipate a large part of EHRENFEST (1913a) and even of EHRENFEST (1913b). For example, on 20 December he wrote:

> Let θ be the period of a motion with <u>one</u> degree of freedom – E its amount of energy. Maybe there is not a very numerous class of systems in which for an adiabatic influence
>
> $$\delta(E\theta) = 0$$
>
> Anyhow, check it for the following cases:
>
> 1) $\ddot{\varphi} = -\frac{\varepsilon}{M}\varphi$
> 2) Force of a free molecule between two walls
> 3) Rotating point
> 4) Ball that moves in a gravitational field.[61]

And also:

> a) Relationship with Szily's theorem?
> b) Dependence with the virial theorem
> c) Mono and polycycles
> d) Invariance of $\int_{t_1}^{t_2} H dt$ in the theory of relativity.[62]

Although EHRENFEST's study of the pendulum and other mechanical systems seemed to indicate that he had not yet completely grasped the true meaning of adiabatic invariance, he found, with the help of his wife TATIANA, the relationship:

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[59] Notes 876, 879, 880, 5 November 1912, ENB: 1-17. In EA, microfilm AHQP/EHR-3.
[60] Notes 882, 883, 5 November 1912, ENB: 1-17. In EA, microfilm AHQP/EHR-3.
[61] Note 900, 20 and 21 December 1912, ENB: 1-17. In EA, microfilm AHQP/EHR-3.
[62] Note 901, 20 and 21 December 1912, ENB: 1-17. In EA, microfilm AHQP/EHR-3.

$$\delta'(\theta \cdot 2\bar{K}) = 0, \tag{17}$$

where δ' denotes a reversible adiabatic variation and $\overline{K}$ represents the mean kinetic energy.[63] Furthermore, EHRENFEST detailed explicitly the essential questions to be solved:

a) The question of invariance under the relativity principle! (Sommerfeld, Planck, Laue)
b) Extension to nonperiodical motions
c) In those problems where $\overline{K}$ is a fixed ratio of E, is $\delta'(\theta E) = 0$ also valid
d) Extension to the general Hamilton principle.[64]

It seems that on 23 December EHRENFEST deduced one of the first consequences of his ideas about the connections between adiabatic transformations and quantum theory, a feature that also would have to play an essential role some months later in his paper on the specific heat of diatomic gases. He wrote:

> If quanta – $(T, \overline{K})$ and not quanta – (T, E) are universal, then to go on from resonators to free molecules and to rotating dipoles it has to be taken into account that quanta – $(T, \overline{K})$ are $= \frac{h}{2}$ and $\neq h$![65]

It seems that to EHRENFEST, PLANCK's quanta were like double universal quanta, because in treating radiation problems the total energy was quantized, not the kinetic energy, which was part of the adiabatic invariant that he had just determined. This did not invalidate PLANCK's quantization or the results of EHRENFEST (1911), because in both cases the total energy appeared, but the true essence of quantization remained hidden.

On 23 December EHRENFEST also wrote a letter to LORENTZ, who was responsible for his appointment in Leiden, offering an example of his new work, "a small thing ('on the quantum hypothesis') that I found yesterday, and which I have been investigating fruitlessly for a long time."[66] Let us examine this "small thing" in more detail, because we see it as a crucial step on his route to his adiabatic hypothesis.

EHRENFEST raised the following question about the adiabatic invariant E/ν, which is characteristic of black-body radiation:

> If now we convey it from sinusoidal vibrations to any other periodic motion: which quantity is the one that remains constant (in the place of E/ν) in an "adiabatic-reversible" influence?[67]

The answer to this question, EHRENFEST continued, not only would permit the extension of the quantum hypothesis, it also would provide a better understanding of the second

[63] Note 909, 21 December 1912, ENB: 1-17. In EA, microfilm AHQP/EHR-3.
[64] Note 910, 21 December 1912, ENB: 1-17. In EA, microfilm AHQP/EHR-3.
[65] Note 913, 23 December 1912, ENB: 1-17. In EA, microfilm AHQP/EHR-3.
[66] EHRENFEST to LORENTZ, 23 December 1912. In AL, microfilm AHQP/LTZ-4.
[67] *Ibid.*; his emphasis.

law of thermodynamics. He then asked a second question: "How must the light-quantum hypothesis be extended from sinusoidal oscillations to other (periodic) motions?" Incidentally, it seems surprising that EHRENFEST wrote here light-quantum when referring to PLANCK's hypothesis, especially since one of the topics that he treated best in his paper of 1911 was delineating the clear difference between PLANCK's and EINSTEIN's hypotheses.[68]

In his letter to LORENTZ, EHRENFEST answered his first question by considering a mechanical system with n degrees of freedom whose time-independent Lagrangian is represented by an arbitrary function of the coordinates $q_1, q_2, \ldots, q_n$, an homogeneous quadratic function of the velocities $\dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n$, and an arbitrary function of some external parameters $r_1, r_2, \ldots, r_k$. He also assumed that for any set of values of these parameters the possible motions of the system are strictly periodic, with the periods of the motions depending upon the different values of these parameters and upon the different motions that are compatible with a given set of these values. He gave as an illustration a pendulum oscillating with a finite amplitude: Its period depends upon its length (r_1), the force of gravity (r_2), and its amplitude, which, however, is not an external parameter but an initial condition that determines the kind of motion it undergoes. In any reversible adiabatic influence (*Beeinflussung*) on such a system, in which the external parameters change infinitely slowly, transforming all of its work into energy and vice versa, EHRENFEST declared that

$$\delta'(T \cdot \bar{K}) = 0 \quad \text{or} \quad \delta'\left(\frac{\bar{K}}{\nu}\right) = 0, \tag{18}$$

where δ' denotes the reversible adiabatic variation, T is the period of motion, ν its frequency, and $\bar{K}$ its mean kinetic energy over one period. He told LORENTZ that the first equation can be deduced from HAMILTON's principle or from BOLTZMANN-CLAUSIUS-SZILY's variational theorem, as he would show in detail if requested. In those cases in which the mean kinetic energy $\bar{K}$ is proportional to the total energy E, as for example in sinusoidal oscillations where $E = 2\bar{K}$, then

$$\delta'(T \cdot E) = 0 \quad \text{or} \quad \delta'\left(\frac{E}{\nu}\right) = 0. \tag{19}$$

EHRENFEST concluded that any adequate generalization of the quantum hypothesis should involve the quantum $\bar{K}/\nu$ instead of E/ν; in other words, the value of the true quantum should be $h/2$, and not PLANCK's h. He emphasized that he was worried about two aspects of this surprising result: First, in considering the possible extension of expression (18) to nonperiodic systems, he sensed that periodicity was not essential to obtain it. Second, he asked himself about the possible relativistic invariance of the above adiabatic invariant, stating that this was not clear to him at present.

LORENTZ paid little attention to EHRENFEST's questions in his brief reply,[69] and they do not reappear in EHRENFEST's notebooks for more than two years. In any case, at the beginning of 1913, EHRENFEST began to consider applying the quantization of

[68] PÉREZ (2002).

[69] LORENTZ to EHRENFEST, 27 December 1912. In EA, microfilm AHQP/ESC-27, Sect. 4.

the energy of rotating molecules to diatomic gases in terms of $h/2$, writing for example in his notebooks: "To translate Debye's method of specific heats to gases," and "Statistical equilibrium of rotating dipoles."[70] That and much more was reflected in a long letter he wrote to his friend JOFFÉ,[71] at the end of February, in which he essentially repeated his arguments to LORENTZ and considered the possibility of using $h/2$ in tackling the problem of the specific heats of diatomic gases:

> Don't you also get a little fun out of the fact that h is displaced by the cheaper $h/2$? If the quantum hypothesis is somehow carried over to ideal gases (e.g. to the specific heat of diatomic gases) the $h/2$ can play a role since the potential energy is zero there.[72]

2.5. *Some reactions*

As we noted in Sect. 2.3, EINSTEIN retracted the main arguments in EINSTEIN and STERN (1913) at the second Solvay conference in October 1913 during the discussion following VON LAUE's talk on the interference of X rays where a main topic was the hypothesis of zero-point energy and its possible application to solids.[73] No one, however, mentioned EHRENFEST (1913a), which had appeared a few months earlier. There also is no reference to his paper in EUCKEN (1914) or SACKUR (1914), both of which, even though they are devoted to the specific heat of monoatomic gases, discuss the validity of the hypothesis of zero-point energy.[74] EUCKEN's omission here is particularly surprising, since in his paper he argued for the definitive abandonment of this hypothesis. Thus he clearly did not consider EHRENFEST (1913a) germane to his argument.

EHRENFEST (1913a) was appreciated, however, by those who were trying to account theoretically for the experimental data on the specific heat of hydrogen. Thus, HOLM published a paper in September of 1913, prior to the second Solvay conference, in which he tried to eliminate the anomalous minimum in EHRENFEST's curve (Fig. 3) by assuming, as in EINSTEIN and STERN (1913), the existence of a zero-point energy. HOLM treated the specific heat of hydrogen in a rigorous statistical-mechanical way (which EINSTEIN and STERN had not done),[75] and managed to eliminate EHRENFEST's minimum, but his curve did not fit EUCKEN's data better than any of the earlier ones (Fig. 6).

In January 1914 FOKKER referred to EHRENFEST (1913a) in connection with his attempt to calculate the energy distribution of electric dipoles in a radiation field, but

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[70] Notes 916 and 951, 3 January and 3 February 1913, ENB:1-17. In EA, microfilm AHQP/EHR-3.

[71] EHRENFEST to JOFFÉ, 20 February 1913. In MOSKOVCHENKO and FRENKEL (1990), 113–118. Translated into English in KLEIN (1985), 261–263.

[72] MOSKOVCHENKO and FRENKEL (1990), 117. In KLEIN (1985), 263.

[73] GOLDSCHMIDT, *et al.* (1921), 105–108.

[74] EUCKEN (1914), SACKUR (1914).

[75] HOLM (1913).

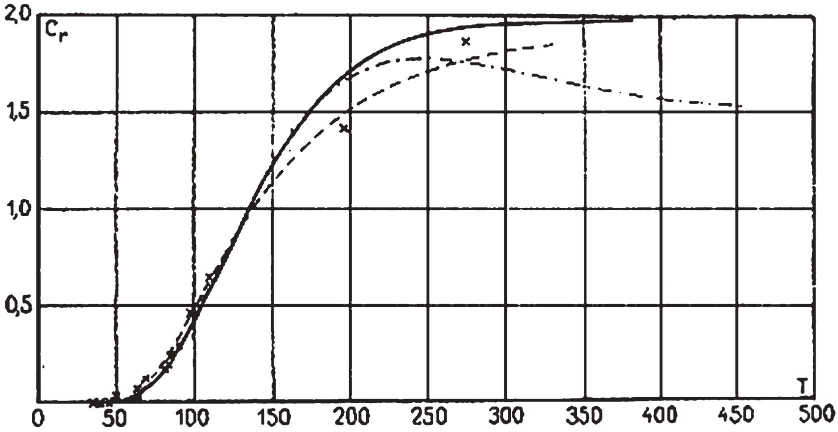

Fig. 6. HOLM's plot of the specific heat of hydrogen as a function of temperature is represented by the solid line. The two other curves represent EHRENFEST's and EINSTEIN and STERN's calculations. Note that HOLM's curve departs from EUCKEN's experimental points more than the other two at intermediate temperatures

his attempt was no better than those of his predecessors.[76] Then, at the end of 1914, PLANCK wrote to EHRENFEST, asking him for additional clarification of his use of quanta of magnitude $h\nu/2$ instead of $h\nu$,[77] and also asked FOKKER for his proof of the Brownian-motion formula he used at the beginning of FOKKER (1914).[78] PLANCK was following the research on the quantum treatment of diatomic gases closely, pursuing a path that would lead him in 1917 (prior to FOKKER) to the FOKKER-PLANCK equation.[79] In 1915 he had written:

> Just as the investigation of Holm uses the thermodynamic method, I would like to outline here briefly the electrodynamic method, and then to continue Fokker's exposition on my part, as Holm did with that of Ehrenfest.[80]

PLANCK wrote a paper in 1915 devoted to improving "HOLM's method," applying his second quantum theory to a system of diatomic molecules as a whole and not separately to every degree of freedom,[81] obtaining a new curve (Fig. 7) for the specific heat. He of course, mentioned EHRENFEST (1913a) in this context.

There is no evidence that EHRENFEST (1913a) influenced BOHR or that BOHR (1913) influenced EHRENFEST, even though EHRENFEST's quantization of the rotational energy of diatomic molecules and BOHR's quantization of the angular momentum of electrons in circular orbits are equivalent in a certain sense. EHRENFEST submitted

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[76] FOKKER (1914).
[77] PLANCK to EHRENFEST, 28 December 1914. In EA, microfilm AHQP/EHR-24, Sect. 7.
[78] See footnote 36.
[79] PLANCK (1917).
[80] PLANCK (1915a), 314. In PLANCK (1958), Vol. 2, 337; our translation.
[81] PLANCK (1915b).

his paper for publication in May 1913, two months before the first part of BOHR's trilogy had appeared in print (although it was dated 5 April), with the second and third parts appearing in September and November and also containing no reference to EHRENFEST (1913a).[82]

EHRENFEST on his part did not respond warmly to BOHR's new atomic theory. He did not refer to it in his next paper of November 1913, which we will discuss in detail in our next section, because he distrusted it as he made clear in a letter to LORENTZ on 28 August 1913: "Bohr's paper on the quantum theory of the Balmer formula has plunged me into despair. If he reaches his goal by this route I will have to renounce my chores in physics."[83] Similarly, he wrote his friend JOFFÉ three days later: "Bohr's paper leads me to despair: if Balmer's formula can be obtained *in this way*, I must throw all physics into the garbage heap (and also myself . . .)."[84]

By 1916, however, EHRENFEST clearly understood the great significance of BOHR's contributions to quantum theory, placing them on the same plane as PLANCK's, DEBYE's, and SOMMERFELD's.[85] By then SOMMERFELD also had informed EHRENFEST that his adiabatic hypothesis had attracted BOHR's attention.[86] Thus, in 1916 BOHR wrote a paper that was to appear that April in the *Philosophical Magazine* but actually was published only in 1921,[87] in which he displayed a deep knowledge of both of EHRENFEST's 1913 papers, using a result that EHRENFEST had derived in them to carry out a new calculation of the specific heat of diatomic gases. BOHR now quantized rotational motion as a whole, not separately for each degree of freedom, and obtained a theoretical curve that fit the experimental data better than the one that PLANCK had obtained from his second quantum theory, as seen in Fig. 7. As BOHR wrote, explicitly citing EHRENFEST's papers:

> The agreement between the measurements at higher temperatures and curve I. is also better than that obtained in previous papers by P. Ehrenfest and E. Holm on assumptions corresponding to Planck's first and second theory respectively, but in which the two degrees of freedom are considered as independent of each other.[88]

SOMMERFELD, in a long two-part article "On the quantum theory of spectral lines" of 1916,[89] also cited EHRENFEST (1913a) as the one in which he calculated the specific heat of diatomic gases.[90] Two years earlier, BJERRUM had published a brief note in which he compared quanta of energy $h\nu$ to quanta of energy $h\nu/2$, using the numerical value he deduced from the spectrum of the chlorine molecule; as a result of this

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[82] BOHR (1913).

[83] EHRENFEST to LORENTZ, 25 August 1913. In AL, microfilm AHQP/LTZ-4; our translation.

[84] EHRENFEST to JOFFÉ, 28 August 1913. In MOSKOVCHENKO and FRENKEL (1990), 122; our translation.

[85] EHRENFEST (1916a), 578. In KLEIN (1959), 380.

[86] SOMMERFELD to EHRENFEST, 30 may 1916. In SOMMERFELD (2000), 561.

[87] BOHR (1916).

[88] *Ibid.* In HOYER (1981), 458, footnote.

[89] SOMMERFELD (1916).

[90] *Ibid.*, 11. In SOMMERFELD (1968), Vol. 3, 182.

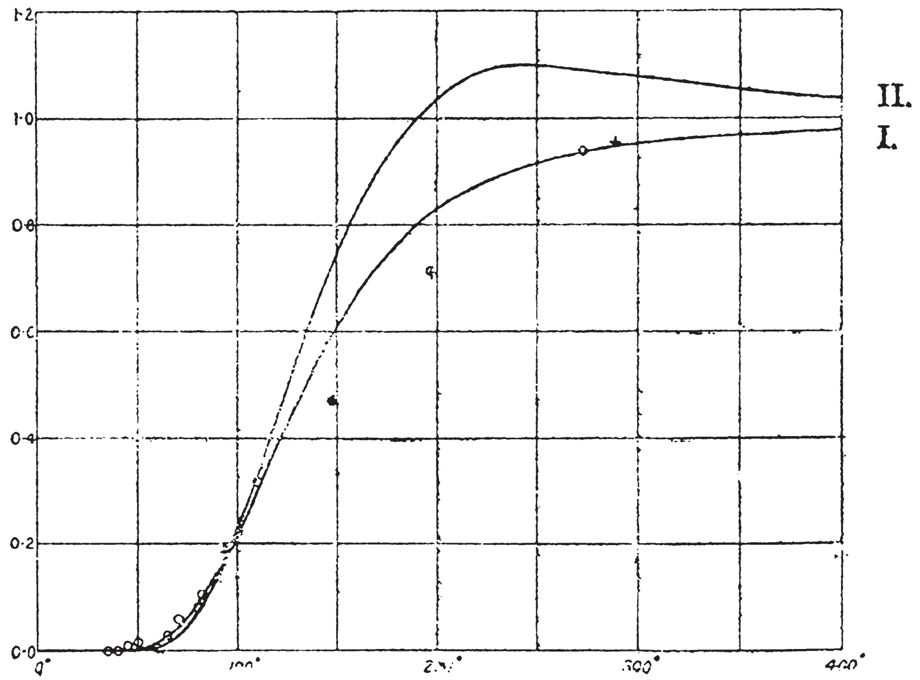

Fig. 7. BOHR's plot (I) of the specific heat of hydrogen as a function of temperature as compared to PLANCK's (II). This figure appeared in BOHR's paper that was to be published in April 1916. BOHR's curve evidently fits the experimental data much better than PLANCK's

comparison he refuted EHRENFEST's arguments in support of quanta of energy $h\nu/2$.[91] As we also have seen, DEBYE too referred to EHRENFEST's work in his lecture notes for a course on quantum theory at the University of Göttingen in the winter semester 1914–1915.[92] EHRENFEST's work thus was well known among researchers and their students.

3. From black-body radiation to periodic mechanical systems (1913)

On November 29, 1913, LORENTZ communicated a paper by EHRENFEST to the Amsterdam Academy on mechanical systems with periodic motions.[93] The quantum properties of radiation now became only a guide for EHRENFEST to the quantum properties of mechanical systems. His paper contained an application of a theorem of BOLTZMANN on a certain property of adiabatic transformations in classical mechanics. EHRENFEST now showed that BOLTZMANN's theorem offered possibilities for

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[91] BJERRUM (1914).
[92] See footnote 29.
[93] EHRENFEST (1913b).

generalizing PLANCK's quantum hypothesis. Thus, if we detected the germ of the adiabatic hypothesis in EHRENFEST's paper of 1911, then we could say that his present paper represented the final phase in its gestation, since it was followed by a series of papers in which adiabatic invariants came to be the forefront in his research.

3.1. Application of a mechanical theorem of BOLTZMANN

In his introduction to EHRENFEST (1913b), he refers to a result "of fundamental importance for the purely *thermodynamic* derivation of WIEN's law." When radiation, whether black-body radiation or not, is compressed reversibly and adiabatically in a perfectly reflecting cavity, each of its principal modes of vibration obeys the relation

$$\delta\left(\frac{E_p}{\nu_p}\right) = 0 \quad (p = 1, 2, \dots, \infty), \tag{20}$$

where E_p and ν_p are the energy and the frequency of the pth mode. This relation is essential for every statistical theory of radiation, since WIEN's displacement law is nothing but a manifestation of the second law of thermodynamics as applied to radiation and "it is also the basis" of PLANCK's quantum hypothesis, which is "in harmony both with relation [(20)] and with the second law of thermodynamics."[94] In view of the several extensions of PLANCK's quantum hypothesis, however, two questions arose:

1. Does there continue to exist an adiabatic relation analogous to Eq. [(20)] in the transition of systems vibrating sinusoidally (in which the motion is governed by linear differential equations with constant coefficients) to general systems?
2. If so – how can it be applied heuristically, when PLANCK's assumption (2) [quantization of energy] is extended to systems vibrating not sinusoidally?[95]

He would show that the answer to the first question was affirmative, but that he could give an answer to the second question only by means of an example.

To answer his first question, EHRENFEST resorted to "a mechanical theorem found by BOLTZMANN and CLAUSIUS independently of each other," as follows: Given a mechanical system such that its potential energy depends upon generalized coordinates and on some slowly varying external parameters, let its kinetic energy T be a homogeneous quadratic function of the generalized velocities. If all of its possible motions are strictly periodic under every adiabatic change, then

$$\delta'\left(\frac{\bar{T}}{\nu}\right) = \delta' \int_0^P dt \cdot T = 0, \tag{21}$$

where δ' denotes an infinitesimal adiabatic change, ν is the frequency of the motion, and $\bar{T}$ is the time average of the kinetic energy over the period P. Thus the quotient of $\bar{T}$ and ν is an adiabatic invariant or, equivalently, the action calculated over the period P is constant under adiabatic changes, which EHRENFEST declared "is nothing but a

[94] *Ibid.*, 591. In KLEIN (1959), 340.
[95] *Ibid.*, 591–592 and 340–341.

special case of the thesis of BOLTZMANN, CLAUSIUS and SZILY, the derivation and formulation of which may be found in BOLTZMANN's 'Vorlesungen über Mechanik', Vol. II, § 48."[96] That section is devoted to the establishment of analogies between certain results for mechanical systems and the kinetic theory of heat.[97]

For a mechanical system under the above conditions on its kinetic and potential energies and undergoing periodic motions, BOLTZMANN proved that

$$\delta' Q = \frac{2}{P}\delta'(P \cdot \bar{T}), \tag{22}$$

where $\delta' Q$ is the difference between the infinitesimal variation of the mechanical energy (kinetic plus potential) and the work done on the system by external means.[98] If the process is adiabatic (that is, if all of the work done on the system changes its mechanical energy), then it turns out that $\delta' Q$ vanishes and expression (22) reduces to (21) as a special case.

Concerning the relationship of expressions (21) and (20), EHRENFEST made three remarks, as follows: (a) If the potential energy of the system is a fixed fraction of its kinetic energy, or if its potential energy is zero, then expression (21) can be rewritten as (20) for these particular cases. (b) It would be desirable to find an extension of expression (21) to nonperiodic motions because BOLTZMANN's extension of his theorem to nonperiodic systems "essentially rests on the untenable hypothesis of ergodes."[99] (c) Expression (21) must be reconsidered if the adiabatic process leads to a singular motion.

EHRENFEST's first two remarks would become especially important; he clarified the third with an example that HERZFELD provided to him in a discussion. Consider a point particle that moves back and forth freely in a tube. If a repulsive force appears in the midpoint of its motion, and if this force grows infinitely slowly, then at some time the particle will oscillate in one of the two halves of the tube with its same kinetic energy but twice its frequency. This is a singular case: The original motion of the particle has divided into two separate motions during the adiabatic process so that relation (21) is no longer valid and requires some modification.

3.2. *Adiabatic invariants appear on the quantum scene*

So far neither BOLTZMANN's theorem (22), nor its particular case (21) bore any relationship to quantum theory; they simply stated some properties of a wide class of mechanical systems undergoing periodic motions. Next, however, EHRENFEST gave an example involving rotating dipoles in which he showed how the adiabatic invariance of $\overline{T}/\nu$ could be used to generalize PLANCK's quantum hypothesis for harmonic oscillations to the quantization of physical quantities in more general motions.

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[96] *Ibid.*, 342 and 593; his emphasis. EHRENFEST cites the corresponding three papers in a footnote.

[97] BOLTZMANN (1897–1904), Vol. 2, 162–212.

[98] *Ibid.*, 182. We have preserved EHRENFEST's notation. BOLTZMANN writes δ instead of δ' and i instead of P.

[99] EHRENFEST (1913b), 593. In KLEIN (1959), 342.

EHRENFEST envisioned a fixed dipole that can rotate freely about a certain axis, say the z-axis, and is subjected to a fixed, strong electrical field parallel to the x-axis that causes the dipole to oscillate harmonically along the x-axis. Since its time average kinetic energy $\bar{T}$ then is half its total energy, PLANCK's quantization condition becomes

$$\left(\frac{\bar{T}}{\nu}\right)_0 = n \cdot \frac{h}{2} \quad (n = 0, 1, 2, \ldots), \tag{23}$$

where the subscript zero applies to its initial harmonic motion. Now, let its angle of rotation be q and its corresponding angular momentum be p. The (q, p) in the phase plane of such a dipole lie only on ellipses determined by the values $0, h\nu_0, 2h\nu_0, \ldots,$ of the total energy of the harmonic oscillations, while the infinite number of points corresponding to rest and equilibrium are associated with zero total energy and are given by $p = 0$ and $q = 0, \pm 2\pi, \pm 4\pi, \ldots$

EHRENFEST then introduces an adiabatic perturbation consisting of an infinitely slow change in both the electric field strength and the dipole moment of inertia, so that the dipole's initial infinitely small amplitudes of oscillation increase and become finite amplitudes. In this way the oscillations can increase their original infinitely small amplitudes until the dipole rotates about the z-axis, its angular velocity becoming constant. The dipole's original harmonic oscillation thus is transformed into a uniform rotation by an adiabatic change, for instance by decreasing the electric-field strength infinitely slowly. EHRENFEST represented this transformation in the (q, p) phase plane of the system in Fig. 8, where PLANCK's ellipses at the center correspond to the dipole's harmonic oscillations, the wavy lines at the top and bottom correspond to its rotations, and the line gH corresponds to the transition through its singular motion. In this transition, one complete oscillation of the dipole corresponds to two complete rotations, so that its corresponding final rotational frequency is $\nu_1 = \dot{q}_1/4\pi$ instead of the usual $\nu_1 = \dot{q}_1/2\pi$.

EHRENFEST now connects the adiabatic invariants to quantum theory by applying BOLTZMANN's theorem (21) to find the dipole's allowed rotational motions, writing, according to Eqs. (21) and (23)

$$\left(\frac{\bar{T}}{\nu}\right)_1 = \frac{4\pi T_1}{\dot{q}_1} = \left(\frac{\bar{T}}{\nu}\right)_0 = 0, \frac{h}{2}, 2\frac{h}{2}, 3\frac{h}{2}, \ldots, n\frac{h}{2}, \tag{24}$$

which, since $T_1 = \frac{p_1 \dot{q}_1}{2}$, also can be written as

$$p_1 = 0, \pm\frac{h}{4\pi}, \pm 2\frac{h}{4\pi}, \ldots, \pm n\frac{h}{4\pi}. \tag{25}$$

EHRENFEST concluded that these are the only allowed values for the angular momentum of the dipole's uniform rotational motion:

> *If other values of p were admitted for a uniformly rotating dipole, it would be possible that by reversal of the described adiabatic process* [i.e., by an infinitely slow increase in the field strength] *sinusoidal vibrations were obtained, with an amount of energy which*

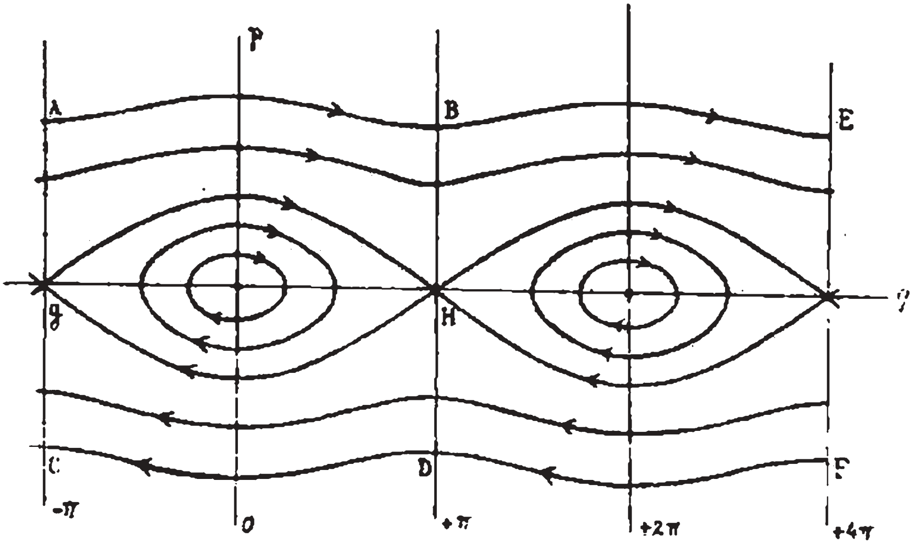

Fig. 8. EHRENFEST's representation of the dipole's motion in the (q, p) phase plane. PLANCK's ellipses, under an adiabatic influence, turn into the wavy lines at the top and bottom. Owing to a printer's error, the first vertical axis on the right corresponds to 3π, not to 4π

> *would come in collision with* PLANCK's *assumptions* (3) *and* (2) [quantization of energy for harmonic oscillations].[100]

In his earlier paper of 1913, EHRENFEST had found the unit of the dipole's angular momentum to be twice as large,[101] but this, he wrote, "has no further influence on the derivations given there than that the numerical value of the moment of inertia L of the hydrogen molecule calculated [here] finally must be divided by four."[102]

EHRENFEST raised and addressed a fundamental issue hovering over not only his own investigations but also over all of quantum theory, namely, the great difficulty in bridging the gap between classical and quantum theory:

> There is no sense – it may be argued – in combining a thesis, which is derived on the premise of the mechanical equations with the antimechanical hypothesis of energy quanta. Answer: WIEN's law holds out the hope to us that results which may be derived from classical mechanics and electrodynamics by the consideration of macroscopic adiabatic processes, will continue to be valid in the future mechanics of energy quanta.[103]

100 *Ibid.* 596, and 345; his emphasis.
101 See expression (9).
102 EHRENFEST (1913b), 596. In KLEIN (1959), 345.
103 *Ibid.*, 592 and 341.

3.3. EINSTEIN's objection and other considerations

EHRENFEST turned to a difficulty that EINSTEIN had called to his attention "in a conversation," which we will refer to as "EINSTEIN's objection." It concerned the statistical treatment of a system of N uniformly rotating dipoles: If their motions were restricted by condition (25), what was their most probable statistical distribution? EHRENFEST suggested two different procedures by which it could be found, as follows:

Procedure A. Start from the ellipses in the phase plane corresponding to N oscillating dipoles and by an adiabatic change transform each ellipse into a pair of segments such as those depicted in Fig. 4. In that way, EHRENFEST wrote, "we are naturally led to treat the just-mentioned pair of lines for the uniformly rotating dipoles as regions of equal probability." That, however, actually was a new assumption that EHRENFEST called "Hypothesis A," namely, the equiprobability of the distributions of the uniformly rotating dipoles (distribution A).[104]

Procedure B. Start, not from the equiprobability of the distribution of the N oscillating dipoles, but from a distribution of them over PLANCK's ellipses in the "most probable" manner. Then, by an adiabatic change, obtain the "most probable" distribution (distribution B) for the rotating dipoles according to condition (25).

We have depicted EHRENFEST's two procedures in Fig. 9. The question he posed amounts to the following: Is the "most probable" distribution obtained from hypothesis A (which we denote as distribution A) the same distribution as distribution B? As EHRENFEST put it: "Is distribution B to be taken as the distribution which corresponds to the state of [thermal] equilibrium, and is therefore the distribution A and the hypothesis A to be rejected?"[105] In the final paragraph of his paper, EHRENFEST argued that procedures A and B did not always lead to the same distribution, in other words, distribution B is not always an equilibrium distribution. Black-body radiation is transformed into black-body radiation in an adiabatic compression, and MAXWELL's velocity distribution for a monatomic ideal gas is conserved "by an infinitely slow shifting of the walls of the vessel." That, however, is not always the case, for instance, "for molecules consisting of more than one atom or for monatomic molecules on which an external field of force acts."[106] As EHRENFEST put it in a footnote, "In an analogous way we can see that a canonical ensemble of gases generally does *not* remain canonical after an 'adiabatic influencing'."[107]

In sum, EHRENFEST's arguments seem to have rested more on intuition than on rigorous reasoning but his paper was a doubly pioneering one. First, it proposed a way to generalize PLANCK's quantum hypothesis for harmonic oscillations to other cases, a goal that EHRENFEST partially attained almost three years later when he formulated his adiabatic hypothesis for mechanical systems with periodic or quasiperiodic motions. Second, he raised a fundamental question: To what extent were the new quantum conceptions, which implied a notable decrease in the number of allowed states, compatible

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[104] *Ibid.*, 596 and 345.
[105] *Ibid.*
[106] *Ibid.*, 597 and 346, respectively.
[107] *Ibid.*; his emphasis.

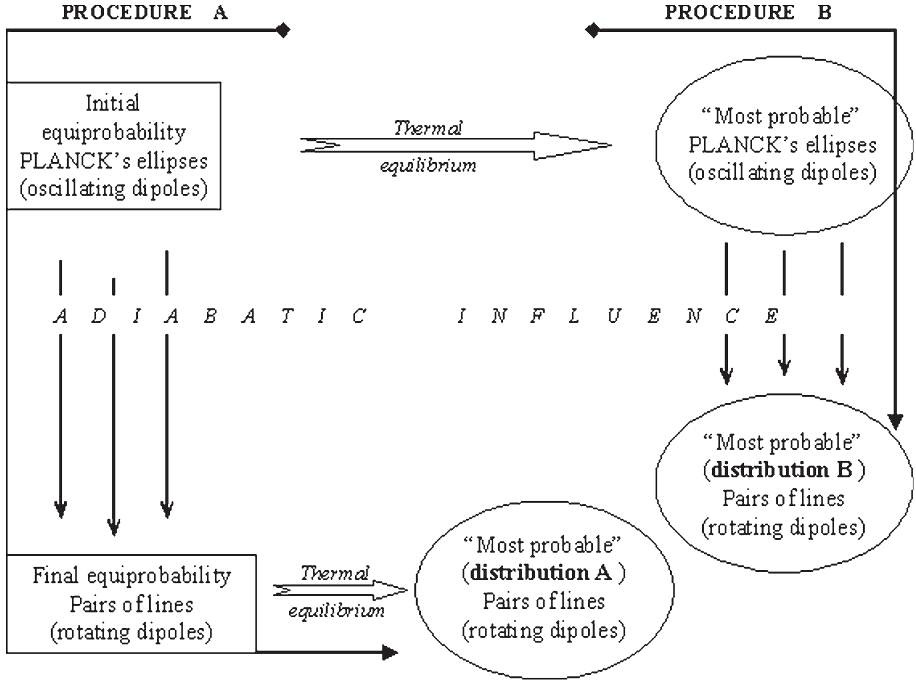

Fig. 9. Our representation of EHRENFEST's two procedures to obtain the "most probable" distribution for a system of uniformly rotating dipoles. By the path indicated as *Thermal equilibrium* we mean the standard procedure used in statistical mechanics to obtain the "most probable" distribution. In current terminology, it represents the step from a microcanonical ensemble (which is adequate to describe isolated systems) to a canonical ensemble (which describes thermal equilibrium)

with BOLTZMANN's classical approach, where the number of allowed states played such a prominent role? EHRENFEST proposed an initial answer to this question a few months later in 1914, in a paper that we will treat in detail next.

4. Inquiries on the validity of BOLTZMANN's statistical mechanics (1914)

The expression

$$S = k \log W, \tag{26}$$

which relates the entropy S to the number of complexions W of a thermodynamic state with a given energy, in other words, the relative probability W of a thermodynamic state, is the keystone in BOLTZMANN's statistical mechanics. "BOLTZMANN principle," as EINSTEIN termed it in 1905,[108] also played an important role in PLANCK's

[108] EINSTEIN (1905), 141. In BECK (1989), 94.

formulation of his quantum hypothesis in 1900, who recognized that it contains two independent assumptions:

> This theorem can be split into two theorems: [1] The entropy of the system in a given state is proportional to the logarithm of the probability of that state, and [2] The probability of any state is proportional to the number of corresponding complexions, or, in other words, any definite complexion is [as] equally probable as any other complexion.[109]

The application of BOLTZMANN's principle was never without difficulties until the creation of quantum statistical mechanics. Assumption [2], especially, was permanently subjected to criticism owing largely to ambiguity in assigning a probability to a thermodynamic state. Regarding assumption [1], EINSTEIN repeatedly tried to undergird it by seeking a rigorous and practical definition for the probability of a thermodynamic state.[110]

EHRENFEST was among those who were convinced that the validity of BOLTZMANN's principle was not fully guaranteed, especially since any quantum hypothesis greatly restricted the number of complexions that are compatible with a given total energy. Thus, in his paper of 1911, he carefully avoided an unconditional application of BOLTZMANN's principle: the just admitted assumption [1] and tried to deduce from it some properties of the weight function he introduced without any assumption of equiprobability.[111]

It is in this context of criticizing the validity of BOLTZMANN's principle that we have to frame EHRENFEST's paper of 1914, "On the Boltzmann Entropy-Probability Theorem." Among its other novelties with respect to his paper of 1911, EHRENFEST abandoned his concern with Planckian resonators and black-body radiation and dealt instead with more general systems. This is a challenging paper owing both to its highly technical character and to its rigorous mathematical framework. These difficulties probably were what caused his contemporaries to pay little attention to it, with the notable exceptions, as we shall see, of EINSTEIN, BOHR, and SMEKAL.

4.1. Criticism of equiprobability

EHRENFEST considered the classes of "weight functions" (the generalization of his *Gewichtsfunktion* of 1911[112]) for which the statistical justification of the second law of thermodynamics would continue to be valid. This justification was provided by BOLTZMANN's relation

$$\frac{\delta E + A_1 \delta a_1 + A_2 \delta a_2 + \dots}{T} = k\delta \log W, \tag{27}$$

where T is the absolute temperature and A_i is the force exerted by the system during the variation of the external parameter a_i. To prove Eq. (27), BOLTZMANN used the

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[109] PLANCK (1900), 243. In TER HAAR (1967), 87.
[110] See, for instance, NAVARRO and PÉREZ (2002).
[111] NAVARRO and PÉREZ (2004), 112–113.
[112] *Ibid.*, 110–118.

hypothesis of equiprobability, namely, that regions of equal volume in the phase space of the system have equal probabilities. In EHRENFEST's terminology, the weight function G was assumed to acquire the same value in all accessible points of the phase space, or

$$G(q, p) = \text{const.} \tag{28}$$

PLANCK also had used BOLTZMANN's principle, Eq. (26), which is equivalent to Eq. (27) and also to

$$F = E - kT \log W, \tag{29}$$

where F is HELMHOLTZ's free energy. PLANCK, however, did not use the hypothesis of equiprobability embodied in (28); instead, he introduced a more general weight function that allowed him to avoid the consequences of the equipartition principle, in particular the "ultraviolet catastrophe." PLANCK, as EHRENFEST noted, thus transformed BOLTZMANN's principle from a result into a postulate, as did EINSTEIN as well.[113]

In the introduction of his paper of 1914, EHRENFEST posed the question:

> For which weight functions $G(q, p; a_1, a_2)$ of the molecular phase space does the expression
>
> $$\delta E + A_1 \delta a_1 + A_2 \delta a_2 + \cdots$$
>
> calculated for the most probable distribution of states possess:
> (a) integrating factors in all cases,
> (b) among these, one such that for the "coupling" between two systems it behaves like T^{-1}?[114]

EHRENFEST asserts that he has found a general condition that weight functions must fulfill to satisfy requirement (a), and that he will present a wide class of weight functions, which include those used by PLANCK and DEBYE, that fulfill both requirements (a) and (b).

4.1.1. The "δG-condition"

EHRENFEST considered a gas of N equal molecules,[115] each having r degrees of freedom, so that its state is determined by a point in its corresponding $2r$-dimensional phase space. Its total energy is a function of its generalized coordinates and conjugate momenta and of the external parameters a_1 and a_2:

$$\varepsilon = \varepsilon\,(q_1, \ldots, q_r; p_1, \ldots, p_r; a_1, a_2)\,, \tag{30}$$

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113 EHRENFEST (1914), 657. In KLEIN (1959), 347; our translation.
114 *Ibid.*, 657–658 and 347–348.
115 We prefer the literal "equal molecules" (for *gleiche Moleküle*) to KLEIN's "independent molecules"; see KLEIN (1958), 280. To use "identical molecules" would be anachronistic.

while its potential energy χ is a function of its generalized coordinates and the external parameters a_1 and a_2:

$$\chi = \chi\left(q_1, \ldots, q_r; a_1, a_2\right). \tag{31}$$

The (generalized) force exerted by a molecule, corresponding to the variation of the external parameter a_i (for instance, the volume), is then given by:

$$-\frac{\partial \chi}{\partial a_i} = -\frac{\partial \varepsilon}{\partial a_i}. \tag{32}$$

EHRENFEST now introduced his fundamental "hypothesis A": For a system with fixed total energy E and arbitrary values of the parameters a_1 and a_2 there exists one and only one stationary distribution function for the states of a molecule: $f(q_1, \ldots, p_r, a_1, a_2, E)$. He then considered an infinitely slowly varying process

$$a_1 \to a_1 + \delta a_1, \quad a_2 \to a_2 + \delta a_2, \quad E \to E + \delta E,$$

and found that the heat transmitted to the gas in such a process is

$$\delta Q = \int d\tau \cdot \varepsilon \delta f, \tag{33}$$

where $d\tau = dq_1 \cdots dq_r \cdot dp_1 \cdots dp_r$ is a volume element in the molecular phase space, assuming implicitly the normalization

$$\int d\tau \cdot f = N. \tag{34}$$

Now, instead of assuming *a priori* equiprobability, that regions with the same volume in phase space have equal probabilities, EHRENFEST introduced a general weight function G such that

$$G\left(q_1, \ldots, q_r, p_1, \ldots, p_r, a_1, a_2\right) d\tau$$

represents the *a priori* probability for the phase of a single molecule to be in the volume element $d\tau$, so that:

$$\int d\tau G = 1. \tag{35}$$

He then found by means of a standard calculation that the most probable distribution for a gas with a fixed number of molecules N and a total energy E is

$$f = N \frac{\exp(-\mu E) \cdot G}{\int d\tau \cdot \exp(-\mu E) \cdot G}, \tag{36}$$ [116]

where the multiplicative factor $\mu = \mu(a_1, a_2, E)$ is determined by the energy constraint

[116] Note that this expression for the most probable distribution only differs from the usual one in classical-statistical mechanics by the factor G, which reflects the now-known possibility of assigning different weights to different points in phase space.

$$N\frac{\int d\tau \cdot \exp(-\mu\varepsilon) \cdot G \cdot \varepsilon}{\int d\tau \cdot \exp(-\mu\varepsilon) \cdot G} = E. \tag{37}$$

EHRENFEST then introduced his "hypothesis B": The stationary distribution, which is unique according to hypothesis A, is precisely the most probable distribution as given by Eq. (36). He stated that a simple calculation (which he did not detail) using (36) to evaluate (33) leads to the equality:

$$\mu\delta Q - \delta \log W = -\frac{N}{Z}\int d\tau \cdot \exp(-\mu E) \cdot \delta G, \tag{38}$$

where

$$Z = \int d\tau \cdot \exp(-\mu E) \cdot G \quad \text{and} \quad \delta G = \frac{\partial G}{\partial a_1}\delta a_1 + \frac{\partial G}{\partial a_2}\delta a_2. \tag{39}$$

Comparing Eq. (38), which is a general result for the most probable distribution of a gas in thermal equilibrium, to Eq. (27), which is equivalent to BOLTZMANN's principle, shows that they are equivalent if the right-hand side of (38) vanishes, which then preserves the validity of BOLTZMANN's principle. EHRENFEST wrote the necessary and sufficient condition (for every value of E, a_1, and a_2) for that in the form:

$$\int_{\varepsilon(q,p,a)=B}^{\varepsilon(q,p,a)=A} d\tau \cdot \delta G = 0, \tag{40}$$

which he called the "δG-condition".[117] It says that the integral of δG between two arbitrary constant energy shells in the phase space of a molecule must vanish to guarantee the validity of BOLTZMANN's principle and thus of BOLTZMANN's statistical interpretation of the second law of thermodynamics. EHRENFEST therefore generalized BOLTZMANN's statistical interpretation in the sense that it no longer required the hypothesis of equiprobability.

4.1.2. Further details

KLEIN has commented that EHRENFEST's "δG-condition" is "a somewhat guarded way of stating that the weight function must be adiabatically invariant if the statistical foundations of the second law are to remain valid."[118] This is not to say, however, that G is an adiabatic invariant, since an adiabatic invariant is any physical quantity whose numerical value is not altered by an adiabatic change, and this is not the case for G, which is neither a physical quantity nor a function that is defined on the phase space of the gas, but only on the phase space of a single molecule. Nonetheless, it would be more or less justified to regard G as adiabatically invariant if $\delta G = 0$, but this is not

[117] EHRENFEST (1914), 659. In KLEIN (1959), 349. This is obviously a sufficient condition; to demonstrate its necessity, EHRENFEST used an auxiliary theorem that he mentioned in a footnote, which we are not concerned with here.
[118] KLEIN (1985), 282.

EHRENFEST's "δG-condition." Further, it seems to us that if that condition could be formulated with complete generality in terms of adiabatic invariants or adiabatic invariance, EHRENFEST, who had introduced these concepts into quantum theory, would have emphasized this, but nowhere in his paper did he refer to adiabatic invariants or to adiabatic invariance.

EHRENFEST devoted the last part of his paper to a particular class of weight functions for which his "δG-condition" is satisfied, and to a rigorous analysis of the analogy between the multiplier μ in (36) and the inverse of the absolute temperature T of the gas. For this special class of weight functions, the validity of BOLTZMANN's principle and that of the statistical interpretation of the second law of thermodynamics is guaranteed, although now one has to work with the most probable distribution as given by Eq. (36).

Let $i(q_1, \ldots, p_r; a_1, a_2)$ denote the $2r$-dimensional volume of the phase space of a molecule enclosed by the energy shell

$$\varepsilon(q_1, \ldots, p_r; a_1, a_2) = \text{constant}, \tag{41}$$

for given values of the parameters a_1 and a_2. EHRENFEST showed (with the help of "an auxiliary geometric theorem" that he had proved earlier) that any weight function of the form

$$G(q_1, \ldots, p_r; a_1, a_2) = \Gamma(i), \tag{42}$$

where Γ is a function of i only, satisfies the "δG-condition" or, more precisely, that the right-hand side of Eq. (38) vanishes, so that

$$\mu \cdot \delta Q = \delta \log W. \tag{43}$$

For this special class of weight functions, therefore, BOLTZMANN's principle is valid, and it is also possible to establish the analogy noted above between μ and T^{-1}. EHRENFEST checked that all of the statistical weights used to date – he referred to BOLTZMANN's, PLANCK's, DEBYE's, and his own – satisfied (42), since for all of them the weight assigned to a point is determined only by the constant-energy hypersurface to which it pertains, and the volume enclosed by this hypersurface is a function only of its energy.

The question arises, however, whether the class of weight functions of the form (42) represents the most general class of weight functions for which BOLTZMANN's principle not only holds, but also which leads to the most probable distribution, Eq. (36), which justifies the analogy between the multiplier μ and the inverse of the absolute temperature T. EHRENFEST answered this question negatively by showing that it is possible to find weight functions for which the right-hand side of (38) vanishes but which are not of the form (42), as occurs frequently for molecules with more than one degree of freedom.[119] EHRENFEST also noted that the integral

[119] EHRENFEST (1914), 661–662. In KLEIN (1959), 351–352.

$$\int_0^\infty di \cdot \Gamma(i)$$

diverges in all of the cases he considered, but at the end of his paper he proposed to interpret his results without resorting to the concept of weight function, thereby avoiding the problem that it did not satisfy the normalization condition required by every probability distribution.

4.2. On the genesis of EHRENFEST (1914) as seen in his notebooks

EHRENFEST's notebooks offer deeper understanding of the origin, evolution, and interpretation of his "δG-condition." We divide our discussion of them into, first, the period immediately following the appearance of EHRENFEST (1911); second, EHRENFEST's response to FOKKER (1914); and third, elaboration of EHRENFEST (1914).

4.2.1. The significance of EHRENFEST (1911)

The first trace we have found in EHRENFEST's notebooks on the question of the general validity of BOLTZMANN's principle appears in August 1911, a few days after he sent EHRENFEST (1911) to the *Annalen*, when he asked himself:

> Which are the more general nonergodically distributed ensembles that lead equally to the analogy with the 2nd law
>
> $$S = \log W.$$ [120]

EHRENFEST's answer was not the one he gave in EHRENFEST (1914); instead, he calculated the probability W without restricting the weight function, calculated also the entropy S, obtained a general condition for the validity of BOLTZMANN's principle, and affirmed that it is valid, specifically, for the MAXWELL-BOLTZMANN distribution, PLANCK's law, his own (*meine*[121]) law, and every distribution satisfying WIEN's displacement's law.[122] He evidently was not fully satisfied with his general condition, although he proved that the weight functions for which $\log W$ remained constant in an adiabatic compression verified it.[123]

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[120] Note 182, 29 August 1911 (RC), ENB:1-14. In EA, microfilm AHQP/EHR-2. 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.

[121] For more on EHRENFEST's law see, for instance, NAVARRO and PÉREZ (2004), 122–123.

[122] Notes 253, 27 September, 254, 1 October and 256, 2 October, 1911 (RC), ENB:1-14. In EA, microfilm AHQP/EHR-2.

[123] Notes 256 and 262, beginning October 1911 (RC), ENB:1-14. In EA, microfilm AHQP/EHR-2.

At the end of the summer of 1911, PAUL and TATIANA EHRENFEST wrote an appendix to their famous article of 1909 on the foundations of statistical mechanics in the *Encyklopädie der Mathematischen Wissenschaften* in which they discussed important papers that had been published in the meantime. Specifically, in section 29, they observed that the statistical-mechanical approach based on ergodically distributed ensembles of systems was not enough to explain thermal equilibrium satisfactorily and commented on the trick that EINSTEIN used several times to save BOLTZMANN's principle.[124] They wrote:

> We need, however, more experimental and theoretical investigations to determine which are the nonergodic ensembles leading to the energy distributions realized in nature, and for which among these the analogies with the second law and especially the relationship between entropy and "probability" are preserved. From this point of view the trick which Einstein uses systematically deserves special attention. He retains the relationship:
>
> Entropy = Logarithm of the "probability"
>
> and then, reversing Boltzmann's procedure, he calculates the relative "probability" of two states from the experimentally determined values of the entropy. In this way he calculates – always appropriately adapting the meaning of "probability" – the average values, in time or otherwise, of the parameters of the state of the system. In those applications where we know from experience that there is a violation of the theorem of the equipartition of kinetic energy, this procedure goes essentially beyond the range of validity of the methods of Boltzmann.[125]

These ideas would become the focus of continuing discussions between EINSTEIN and EHRENFEST, as we will see in Sect. 5.

The EHRENFESTs referred again to the need for analyzing the validity of the statistical interpretation of the second law of thermodynamics in connection with a paper EHRENFEST intended to submit to a Russian journal for publication:

> In providing that $\delta Q: T$ is a perfect differential, both Boltzmann and Gibbs always use ergodically distributed ensembles of systems. It is only in connection with his criticism of the Helmholtz monocycle analogies... that Boltzmann also investigates a few special examples of nonergodically distributed ensembles of systems in order to show that for these the analogies to thermodynamics generally fail. In connection with the problem of thermal radiation P. Ehrenfest (Journ. d. russ. phys. ges., 43 [1911]) constructs a very general class of nonergodically distributed ensembles, for which the relation $\delta Q : T = \delta \log W$ remains valid.[126]

EHRENFEST's paper, however, would never appear in print.[127] Among his unpublished manuscripts, however, is one entitled "On the probabilistic-theoretical foundations of the quantum theory," which may have been a draft of it,[128] and in which EHRENFEST cited

[124] For EINSTEIN's varied use of BOLTZMANN's principle between 1905 and 1911 see, for instance, NAVARRO and PÉREZ (2002).

[125] EHRENFEST (1990), 76–77.

[126] *Ibid.*, 105–106, note 246.

[127] EHRENFEST (1914), 657, footnote 2. In KLEIN (1959), 347.

[128] EMS:1. This manuscript is not dated, although it could have been written in October 1911.

PLANCK's theory of black-body radiation as the first example where BOLTZMANN's statistical methods were applied to a system whose kinetic energy was not distributed uniformly among all of its degrees of freedom. Since neither the equipartition theorem nor ergodicity are valid for an ensemble of Planckian resonators, *a priori* neither BOLTZMANN's principle nor BOLTZMANN's statistical methods could be applied to it.

PLANCK's statistical-mechanical treatment, however, had led to results in close agreement with experiment, so that it made good sense to consider general cases to which BOLTZMANN's statistical methods could be applied, dispensing with equiprobability, the equipartition theorem, or ergodicity; three sufficient and practically equivalent properties that guarantee the validity of those methods. That issue, however, EHRENFEST believed could not be addressed only by theoretical arguments; experiments had to play a role in generalizing BOLTZMANN's principle and his methods. The experiments that he mentioned in this manuscript pertained to thermal balance (electrons in metals, systems at very low temperatures) and to energy transfer (photoelectric effect, photochemical effect, fluorescence), referring in the latter case to EINSTEIN's light-quantum hypothesis.

Further annotations confirm that EHRENFEST was worried about the generalization of BOLTZMANN's statistical methods. In October 1911, for instance, EHRENFEST explored the possibility of obtaining a doctorate under SOMMERFELD, which would allow him to contend for an academic position in Germany, since he was finding it increasingly difficult to obtain one in Russia.[129] He wrote to SOMMERFELD proposing a dissertation topic involving a problem on which he had already been working:

> A:) *Deepening in the foundations:* For
> a.) $\delta Q/T$ be an exact differential
> b.) that it is equal to $\delta \log W$ (probability) has been proved by Boltzmann and Gibbs only for "ergodically" distributed ensembles of systems.– The Planckian ensembles of resonators are *not* ergodic ensembles. The results of Nernst's school on specific heats at low temperatures show that also in this region it is necessary to operate with nonergodic ensembles. My work on light quanta operates with nonergodic ensembles.

EHRENFEST wondered further:

> *For which nonergodically distributed ensembles the analogy with the second principle remains valid*? (it can be easily seen that it does not remain valid for all of them). And for this, $\delta Q/T = \delta \log W$ holds?[130]

EHRENFEST did not reach agreement with SOMMERFELD and hence did not send him any new work. Thus it is possible that the dissertation topic he proposed to SOMMERFELD and the paper he intended to submit to the above Russian journal for publication referred to the same project, the first phase of which was the above draft manuscript.

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[129] Entries 17, 18, 25 and 26 October 1911 (RC), ENB:4-09; in EA, microfilm AHQP/EHR-11

[130] EHRENFEST to SOMMERFELD, 3 October 1911 (RC). In SOMMERFELD (2000), 406–407; his emphasis.

Although never published, EHRENFEST did discuss these ideas with PLANCK in Berlin, WIEN in Würzburg, and others.[131]

EHRENFEST was constantly concerned with the meaning and applications of the invariance of the logarithm of the probability beginning in the winter of 1911, as he indicated in his letters a year later to LORENTZ and to JOFFÉ, as noted above.[132] He seems to have had two closely related topics of research in mind, the extension of BOLTZMANN's principle and his statistical methods to more general systems than ergodically distributed ensembles, and the search for more general quantization rules than PLANCK's for harmonic oscillators. The first topic is closely related to EHRENFEST (1914), and we see that already much earlier he recognized the decisive importance of the adiabatic invariance of the logarithm of the probability, as he made clear in his letter to LORENTZ of 23 December, 1912:

> *The a priori probability must always depend on only those quantities which remain invariant under adiabatic influencing, or else the quantity* log W *will fail to satisfy the condition, imposed by the second law on the entropy, of remaining invariant under adiabatic changes.*[133]

EHRENFEST did not find a satisfactory answer to its puzzle, as he admitted explicitly in EHRENFEST (1913b); indeed, we have no indications in his notebooks that he made substantial progress on it until the beginning of 1914.

4.2.2. FOKKER's ensembles

EHRENFEST's lack of progress should not be interpreted as lack of interest in analyzing the compatibility between traditional statistical methods and the emergent quantum theory. He no doubt thought deeply about this fundamental issue, especially since he was familiar with contributions to quantum theory in which, explicitly or implicitly, the validity of BOLTZMANN's principle was taken for granted. Nevertheless, there are hardly any annotations in his notebooks on this fundamental issue after the Wolfskehl lectures in Göttingen in the spring of 1913.

A notable increase in the number of his annotations related to the content and elaboration of EHRENFEST (1914) could well have been prompted by the publication of an article by FOKKER to which he seems to refer indirectly at the end of its first paragraph:

> In a later note I will show that certain stationary distributions of states, with which one works at present, can not be represented any longer by such "most probable" distributions,

[131] PAUL to TATIANA EHRENFEST, 20/21 January and 22 January 1912. In EA, microfilm AHQP/EHR-29, Sect. 5. See also entry 19 January 1912 (RC), ENB:4-09; in EA, microfilm AHQP/EHR-11.

[132] See footnotes 66 and 71.

[133] EHRENFEST to LORENTZ, 23 December 1912. This paragraph is reproduced in KLEIN (1985), 261; his emphasis.

> and I will discuss its relationship to Boltzmann's principle on the one hand and to the second law [of thermodynamics] on the other.[134]

EHRENFEST never published this "later note," but he seems to refer here to the class of distributions that he called in his notebooks "FOKKER's ensembles." In fact, three days after EHRENFEST (1914) was received for publication, he drafted a fourteen-page letter to EINSTEIN, listing his considerations on the weight function in nine points, the eighth of which was:

> Then I hope also to be able to present to you orally my reflections on why the Fokker systems satisfy the 2nd law *even though it is impossible to describe them as the "most probable" distributions* (!!!).[135]

FOKKER studied mining engineering at the Technical University in Delft and physics at the University of Leiden, where he obtained his doctorate under LORENTZ in 1913. That fall he then traveled to Zurich to continue his studies with EINSTEIN at the Eidgenössische Technische Hochschule. EINSTEIN wrote to EHRENFEST in November 1913, telling him that:

> With Fokker I have already discovered something that is as interesting as it is curious, namely that mechanics, electrodynamics – applied to the rotating dipole – and Jeans's radiation law are not compatible with each other; rather, the quasi-monochromatic Planck oscillator occupies a special position here. The calculation that we employed is absolutely flawless. This conflicts with H. A. Lorentz's general result. I wonder if we might not yet find a handle for the modification of the theory with the help of our methods.[136]

LORENTZ had proved – his "general result" – that the RAYLEIGH-JEANS law was the only black-body radiation law that is compatible with classical physics.[137] He announced that conclusion in a lecture entitled "Le partage de l'énergie entre la matière pondérable et l'éther" that he delivered in Rome in the spring of 1908,[138] and three years later it came up for discussion at the first Solvay conference in Brussels.[139] EINSTEIN thus knew that the MAXWELL-BOLTZMANN distribution was no longer valid for an ensemble of electric dipoles in a radiation field, as he wrote to LORENTZ only a few days after the conference:

> The rotational motion of a dipole in a radiation field can easily be found by means of a trick if one assumes the validity of mechanics for this case. For according to your general study, if mechanics is valid and if one takes Jeans's law as a basis, one must obtain the Maxwell

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[134] EHRENFEST (1914), 658. In KLEIN (1959), 348; our translation.

[135] Letter (draft) EHRENFEST to EINSTEIN, 21 May 1914. In SCHULMANN, *et al.* (1998), 26. English translation in HENTSCHEL (1998), 20; his emphasis.

[136] EINSTEIN to EHRENFEST, second half November 1913. In KLEIN, *et al.* (1993), 568. English translation in BECK (1995), 362.

[137] For the evolution of LORENTZ's ideas on radiation laws and on the validity of the equipartition theorem, see, for instance, BERGIA and NAVARRO (1997), 189–194.

[138] LORENTZ's lecture was published later under the same title in *Revue Générale des Sciences Pures et Appliqués* **20** (1909), 14–26.

[139] LANGEVIN and DE BROGLIE (1912), 417 and 447.

> distribution.... But I do not believe that the result thus obtained is correct, because the laws of mechanics probably do not hold for the rotating dipole. Or in other words: An ensemble of rigid dipoles will probably *not* be distributed according to Maxwell's law in a radiation field.[140]

This is precisely the result that EINSTEIN and FOKKER proved two years later: An ensemble of electric dipoles in a RAYLEIGH-JEANS radiation field does not have a MAXWELL-BOLTZMANN velocity distribution. FOKKER soon corrected that result, however, writing to LORENTZ from Zurich at the end of 1913 that he was investigating "the average energy of an electrical dipole that is in the radiation field and can rotate around a fixed equatorial axis."[141] He continued by saying that he had generalized a method that LORENTZ had suggested to him and that he used in his dissertation "for deriving a differential equation to determine a stationary distribution function." For one degree of freedom (rotation around a fixed axis), he had obtained the following differential equation:

$$Wf(q)\tau - W\bar{R} + \frac{1}{2}\frac{\partial^2}{\partial q^2}\left[W\overline{R^2}\right] = \text{const} = 0, \tag{44}$$

where q is a quantity that determines the state of the system, $W(q)dq$ is the number of dipoles in the interval $(q, q + dq)$, $f(q)$ is the decrease in q per unit time, and R is the (irregular) change in q in the infinitesimal time interval τ. This equation, FOKKER showed, proved, contrary to what he and EINSTEIN had thought previously, that the RAYLEIGH-JEANS law actually was compatible with the MAXWELL-BOLTZMANN distribution:

> With this equation we first investigated whether Maxwell's distribution corresponds to the radiation formula of Rayleigh and Jeans (which is needed for the calculation of R). We did not achieve agreement as long as we assumed $\bar{R}$ to be equal to zero. This seemed so plausible to us. We eventually realized though that it was not so and I have succeeded in calculating the value of $\bar{R}$. Agreement has now been achieved.[142]

FOKKER also obtained the distribution function that corresponds to PLANCK's radiation law and calculated the specific heat of hydrogen as a function of the absolute temperature T, finding that his curve departed noticeably from EUCKEN's experimental data: His theoretical curve had a vertical tangent at $T = 0$, while EUCKEN's measurements showed that it is horizontal. "This is the result which, of course," he declared laconically, "I would have liked to be different."[143]

Still, as we have already noted in Sect. 2.5, FOKKER published a paper in 1914 entitled "The average energy of a rotating electric dipole in a radiation field," which was one of several attempts at the time to explain theoretically EUCKEN's experimental data.[144] FOKKER cited EHRENFEST's curve of 1913 as the one that best fit

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[140] EINSTEIN to LORENTZ, 23 November 1911. In KLEIN, *et al.* (1993), 359. English translation in BECK (1995), 227–228; his emphasis.

[141] FOKKER to LORENTZ, 4 December 1913. In KLEIN, *et al.* (1993), 579.

[142] *Ibid.*

[143] *Ibid.*

[144] FOKKER (1914).

EUCKEN's experimental data. He presented Eq. (44) as a stationarity condition and considered it to be a generalization of EINSTEIN's second paper on Brownian motion of 1906.[145] FOKKER sent EHRENFEST a copy of his paper prior to publication,[146] and that EHRENFEST took it seriously is indicated in a draft of a letter that he wrote to FOKKER on 21 January 1914:

> For the rest, your formula for W has a very strange property: it might be expected that your distribution W could be obtained by means of Boltzmann's method of "complexions," also as a "most probable" distribution for a given total energy, only by choosing the corresponding "weight" $G(\varepsilon)d\varepsilon$ (a priori probabilities). – However, it can be immediately seen that no election of weights
>
> independent of T
>
> can lead to your distribution W. – And the fact is that for that it should have the form
>
> $$W(\omega) = C \cdot G(\omega) \cdot e^{-\frac{L\frac{\omega^2}{2}}{kT}},$$
>
> that is not the case.
> This is very, very curious.–[147]

FOKKER's distribution function, as it appeared in FOKKER (1914),[148] was considerably more complicated than the most probable distribution corresponding to an arbitrary weight function G, Eq. (36), which EHRENFEST published in 1914, which for a system of rotating dipoles leads to:

$$f = N \frac{\exp\left(-\mu \frac{L\omega^2}{2}\right) \cdot G(\omega)}{\int d\omega \cdot \exp\left(-\mu \frac{L\omega^2}{2}\right) \cdot G(\omega)}, \tag{45}$$

where ω is the angular velocity and L the moment of inertia of the dipole. This is the distribution function that EHRENFEST anticipated in the draft of his letter to FOKKER on 21 January 1914. That same day EHRENFEST wrote in his notebook:

> See, in general, when the Brownian movement can lead to something that can not be obtained from the theory of complexions [of Boltzmann].
> Translational electrons, rotating dipoles, resonators in a Planck's radiation field have a distribution of states such that (at least partly) it can not be obtained by means of the theory of complexions.[149]

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[145] EINSTEIN (1906).
[146] FOKKER (1914) is dated 11 December 1913 in Zurich, and was received by the *Annalen* twelve days later.
[147] Letter (draft) EHRENFEST to FOKKER (catalogued under FOCKER), 21 January 1914; in EA, microfilm AHQP/EHR-20, Sect. 3; our translation. This draft is incorrectly catalogued, because EHRENFEST began by writing "Lieber Herr Focker," which seems to have led to classifying it under FOCKER. In his notebooks EHRENFEST makes this same error several times.
[148] FOKKER (1914), 819.
[149] Notes 1074 and 1077, 21 January 1914, ENB:1-17. In EA, microfilm AHQP/EHR-3.

This is only the first of EHRENFEST's long series of annotations that reveal his particular interest in "FOKKER's ensembles," paying special attention to their behavior under an adiabatic influence.[150] He immediately focused his efforts now on searching for a general criterion or condition that would guarantee the applicability of BOLTZMANN's combinatorial method, always keeping in mind the question of the validity of BOLTZMANN's principle;[151] all of which would crystallize a few weeks later in EHRENFEST (1914).

We see that EHRENFEST's research had undergone a dramatic reorientation over the past two years. In 1911, the focus of his ideas was the nature of the various quantum hypotheses that had been proposed to account for black-body radiation; now, by early 1914, he was concentrating on the problem of clarifying the relationship between the emerging quantum concepts and BOLTZMANN's statistical methods. "FOKKER's ensembles," which EHRENFEST constantly mentioned in his notebooks before and after his publication of EHRENFEST (1914),[152] played a significant role in this reorientation of his research.

4.2.3. Elaboration of EHRENFEST (1914)

In a letter to BOHR in the spring of 1918, EHRENFEST recalled the problems with which he had dealt four years earlier:

> It is still extremely interesting that there is a pre-established harmony between the "δG-condition," necessary for the second law to hold (see my 1914 note in the *Physikalische Zeitschrift*), and the adiabatic invariance of the quantum conditions. Oh, if you knew how much I had to fret before I succeeded in convincing anyone that there is a problem here: that we had lost the basis for Boltzmann's old proof of the second law in principle, as soon as we followed Planck in abandoning Boltzmann's old assumption that $G = 1$.[153]

EHRENFEST's letter confirms that he did not clearly recognize the close link between his investigations on nonergodic ensembles and his ideas on adiabatic transformations prior to 1914. He still did not recognize that link in EHRENFEST (1914), where he rigorously analyzed nonergodic ensembles, but adiabatic transformations do not yet appear. Similarly, in a letter to SOMMERFELD in the spring of 1916, EHRENFEST regretted that he did not treat adiabatic transformations in his 1914 paper:

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150 See, for instance, notes 1082, 24 January 1914, ENB:1-17; 1174 and 1209, 6 and 12 April 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.

151 See, for instance, notes 1102, 1103 and 1152, 10 February and 22 March 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.

152 See, for instance, notes 1308, 1309 and 1326, 29 May and 8 June 1914, ENB:1-18; 4358 and 4359, 23 September and 28 November 1914, ENB:1-19; 4409, 25 December 1914, ENB:1-20; 5130, May 1918, ENB:1-24. In EA, microfilm AHQP/EHR-3. (If the numbering of the notes were correlated, instead of 4358, 4359, 4409 and 5130, they should be 1358, 1359, 1409 and 2130, respectively).

153 EHRENFEST to BOHR, 10 May 1918. Quoted in KLEIN (1985), 283.

> Oh! If I could tell you even more verbally, about this whole adiabatic question and its combination with my hardly readable note in Physikal. Zeitschrift [in 1914], however to write or print it completely so it can be read is impossible![154]

That EHRENFEST used the word combination (*Kombination*) here seems significant to us, since we believe that it supports our contention that his concerns with adiabatic transformations and adiabatic invariants, and with the validity of BOLTZMANN's statistical methods, did not arise in his mind at the same time, so that the former did not play an important role in EHRENFEST (1914). We can find confirmation for our contention in EHRENFEST's notebooks of early 1914.

Thus, in early February 1914 EHRENFEST noted that he intended to investigate a question that he had postponed for more than two years, namely, for which class of nonergodic ensembles does the statistical-mechanical conception of the second law of thermodynamics remain valid?[155] From then on, although he frequently also raised various questions about "FOKKER's ensembles," he developed ideas and made calculations that would appear three months later in EHRENFEST (1914).[156]

EHRENFEST's first annotations confirm that his primary goal was to establish the range of validity of BOLTZMANN's principle in view of the new quantum conception,[157] especially by clarifying the relationship between the second law of thermodynamics and the most probable distribution. Adiabatic transformations did not seem to him to be destined to play an essential role in that clarification, although he discussed several considerations on them.[158] Further, he made several annotations in which he mentioned "EINSTEIN's fluctuations method," but he soon convinced himself that that too would not lead him to his goal.[159]

Concurrently, EHRENFEST opened a new route for attacking this problem, a route that he would not abandon until he found his "δG-condition." He found a first formulation of it by the end of the second week of April, and by then he also had demonstrated that for "FOKKER's ensembles" the statistical interpretation of the second law of thermodynamics remained valid.[160] He then immediately verified that PLANCK's distribution for harmonic resonators satisfied his "δG-condition," and he began to look for generalizations of PLANCK's distribution that also would satisfy it, thus guaranteeing the validity of the traditional statistical methods. He also dealt with other related questions, writing for instance:

> 1. For Planck's ellipses in the surface-(q, p), $G(q, p)$ depends <u>explicitly</u> upon α and β, where

[154] EHRENFEST to SOMMERFELD, April/May 1916. In SOMMERFELD (2000), 557.

[155] Note 1098, 10 February 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.

[156] These notes go approximately from number 1098 until number 1286. All of them are included in ENB:1-18. In EA, microfilm AHQP/EHR-3.

[157] Note 1103, 10 February 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.

[158] Notes 1142–1146, 4 March 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.

[159] See, for instance, the final pages of the notebook ENB:1-17. In EA, microfilm AHQP/EHR-3.

[160] Notes 1212 and 1213, 12 and 13 April 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.

$$\varepsilon = \frac{\alpha^2}{2} q^2 + \frac{\beta^2}{2} p^2 \qquad \nu = \frac{\alpha\beta}{2\pi}$$

$$\frac{\alpha}{2\beta} q^2 + \frac{\beta}{2\alpha} p^2 = n \frac{h}{2\pi}$$ are the ellipses of Planck.

Revise how $\mu\delta Q$ is here d.[exact differential][161]

EHRENFEST's "δG-condition," written in the same form as in EHRENFEST (1914), first appeared in his notebooks (although he did not yet give it that name) on 14 April,[162] and from then on he concentrated on its interpretation and on searching for an equivalent but more understandable statement of it. For example, in continuing his investigations on PLANCK's ellipses, he became aware of the adiabatic invariance of the surfaces they enclosed, although he still was unable to relate this property clearly to the validity of BOLTZMANN's principle.[163] In any case, he failed in his search for a more understandable formulation of his "δG-condition."

Only a few days later, on 19 April, EHRENFEST for the first time asked himself explicitly: "How is the distribution of weights related... to the adiabatic theorem?"[164] By "adiabatic theorem" (*Adiabaten Theorem*) EHRENFEST meant the invariance of the volume of a region in phase space under an adiabatic transformation. HERTZ had proved this theorem in 1910 in a long paper on the mechanical foundations of thermodynamics.[165] We emphasize, however, that neither this theorem nor adiabatic transformations appear or play any role in EHRENFEST (1914). His notes instead reveal his focus on finding more general weight functions that are compatible with BOLTZMANN's principle.[166] Even on 11 May, the day he dated his paper, we have found an annotation stating that functions of the type $\Gamma(i)$ (see Sect. 4.1.2 above) verify the "δG-condition."[167]

EHRENFEST's manuscript shows that after he received the galley proofs of his 1914 paper, he added all of the references to the "δG-condition" to it, as well as the last section and a footnote in the second section in which he pointed out that PLANCK's weight function actually depends on certain external parameters. All of these changes, as we will see in the next section, were motivated in part by his discussions with EINSTEIN in April and May 1914, before he had sent his paper in for publication.[168]

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[161] Note 1218, 13 April 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.
[162] Note 1225, 14 April 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.
[163] Note 1237, 16 April 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.
[164] Note 1254, 19 April 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.
[165] HERTZ (1910), 544–549.
[166] Note 1276, 2 May 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3.
[167] Note 1283, 11 May 1914, ENB:1-18. In EA, microfilm AHQP/EHR-3. This manuscript was dated "Leiden, May 1914"; it was sent on 11 May and received by the *Physikalische Zeitschrift* on 18 May.
[168] EMS:7

5. EINSTEIN and EHRENFEST's hypothesis

EINSTEIN's first reference to adiabatic transformations that we have found in his correspondence with EHRENFEST is in a letter of November 1913 in which he wrote:

> I hope that we will manage to accomplish something useful together. I cannot get your idea of adiabatic transformations off my mind. This may be our most valuable resource in our state of general hopelessness, especially since the zero-point energy is now as dead as a mouse. Mr. Keesom has badly aggravated its condition, even though he took great pains to improve it.[169]

EINSTEIN's enthusiasm for adiabatic transformations evidently was stimulated by his conversations with the EHRENFESTs when they visited the EINSTEINs in Zurich the preceding June.[170] In April 1914, however, EHRENFEST and EINSTEIN opened up an intense correspondence on various aspects of the possible compatibility of BOLTZMANN's statistical methods with the new quantum conceptions.

Their correspondence was motivated by "EINSTEIN's objection" (see Sect. 3.3 above): Will an adiabatic change of an equilibrium state necessarily lead to a new equilibrium state? They had discussed a related question personally, when EINSTEIN visited EHRENFEST in Leiden for a week at the end of March 1914,[171] namely, what happens to the motion of a rotating electric charge, which for quantum reasons can only assume rotational velocities of

$$0, \pm\omega_1, \pm\omega_2, \dots , \tag{46}$$

when it undergoes an adiabatic transformation? An adiabatic change in an external magnetic field perpendicular to the plane of its motion shifts all points of its trajectory in the same sense through induction, so that when the magnetic field again becomes constant, the new possible values of ω are distributed asymmetrically around $\omega = 0$, which is a strange result because in statistical mechanics there is no essential difference between situations with and without a constant external magnetic field. In his letter of April 1914 to EHRENFEST, EINSTEIN wrote:

> That is why I doubt that through adiabatic influence in the sense of conventional mechanics possible conditions change again into possible conditions. How do you find your way out of that? Frankly speaking, I have no solution.[172]

EHRENFEST responded immediately:

> In answer to your comment about rotating electrons in a magnetic field.

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[169] EINSTEIN to EHRENFEST, before 7 November 1913. In KLEIN, *et al.* (1993), 563–564. English translation in BECK (1995), 359.

[170] KLEIN (1985), 293–295.

[171] EINSTEIN to EHRENFEST, before 10 April 1914. In SCHULMANN, *et al.* (1998), 12–14. English translation in HENTSCHEL (1998), 9–10.

[172] *Ibid.*, 13 and 10.

I protest against your assertion (or assumption): "*with a constant magnetic field the statist. mechanics of the structure ought surely hardly to differ from those without a magnetic field.*"–
With a concise argument I can force you to admit the contrary. (And then the paradoxes indicated by you disappear!)
Here right away is the crux of the problem:
When an electron rotates in the H field its "*moment*" is *not*

$$mr^2\omega$$

but

$$r^2\left(m\omega + \frac{eH}{2c}\right)$$

[You should not forget that the ether's "electrokinetic" energy contains a term of the form $\frac{er\omega}{c} \cdot \frac{rH}{2}$].[173]

It took more than one month for EINSTEIN to answer.[174] He raised doubts about certain aspects of the motion of rotating charges in a magnetic field, and then criticized EHRENFEST for using, in his statistical treatments, weight functions G that depend upon external parameters, because such a dependency is "completely contrary to BOLTZMANN's conception." EINSTEIN's answer showed clearly that he had not studied EHRENFEST's ideas thoroughly, which prompted EHRENFEST to draft a rapid and incisive reprimand:

Cordial thanks for your letter!— I am triumphant! This time *I* am the brighter one. You protest that in the weighting function $G(q, p, a_1, a_2)$, a_1, a_2 offend Boltzmann's spirit— I do not want to dispute the *latter—but you yourself have been working* with such a $G(q, p, \underline{a})$ *for almost 10 years*!!!!
Namely with Planck's assumption of the quantization of energy [*Energiestufenannahme*]— this *is* a $G(q, p, \underline{a})$.[175]

EHRENFEST proceeded to show that PLANCK's quantum hypothesis leads to a weight function G that depends upon two parameters, "the resonator intensity" α and "the reciprocal factor of inertia" β, the energy of the resonator being given by

$$E(q, p, \alpha, \beta) = \frac{1}{2}\left(\alpha^2 q^2 + \beta^2 p^2\right).$$

EHRENFEST also wrote that HERZFELD used a weight function that depended upon not only external parameters but also upon the absolute temperature, which he called an indecency (*Schweinerei*). EHRENFEST wrote a second draft of his letter to EINSTEIN

[173] Letter (draft) EHRENFEST to EINSTEIN, 10 April 1914 or later. In SCHULMANN, *et al.* (1998), 15. English translation in HENTSCHEL (1998), 11; his emphasis. (We have added the missing square bracket at the end).
[174] EINSTEIN to EHRENFEST, 18 May 1914. In SCHULMANN, *et al.* (1998), 19–20. English translation in HENTSCHEL (1998), 14–15.
[175] Letter (draft) EHRENFEST to EINSTEIN, 20 May 1914. In SCHULMANN, *et al.* (1998), 21. English translation in HENTSCHEL (1998), 15; his emphasis.

the following day. His analysis here was in line with that of his earlier draft but was much more precise and extensive. Nonetheless, he clearly explained his basis idea. Thus, if one admits that in the absence of a magnetic field the angular momentum of the rotating electric charge is

$$mr^2\omega = 0, \pm\frac{h}{2\pi}, \pm 2\frac{h}{2\pi}, \dots,$$

then after the magnetic field H exerts an adiabatic influence on the electron,

$$mr^2\omega + \frac{eH}{2c}r^2 = 0, \pm\frac{h}{2\pi}, \pm 2\frac{h}{2\pi}, \dots .$$ [176]

Perhaps, however, EHRENFEST presented his most insightful point under the heading "On the $G(q, p, \underline{a})$ question." He again criticized EINSTEIN's position, insisting that both PLANCK's quantum hypothesis and DEBYE's generalization of it in his Wolfskehl lecture in April 1913 implied weight functions that depend upon certain parameters. EHRENFEST then addressed an issue that (as we have seen in Sect. 4.1) merited special attention in EHRENFEST (1914): For which class of weight functions is $\mu\delta Q = \delta \log W$, relation (43), satisfied? His answer was that "in all extensions of the quanta approach, we remain within the weight class $G(q, p, a) = \Gamma(i)$."[177] He summarized his ideas for EINSTEIN in a lengthy "*closing remark*":

> a) Planck, Einstein, Debye work with $G(q, p, \underline{a})$, therefore it is worthwhile to examine why these people do come up with $\mu\delta Q = \delta \lg W$ with such anti-Boltzmann spirited G's.
> b) Only *once* did anyone work with $G(q, p, a, \underline{T})$: Herzfeld. This displeases me.
> c) Ideal gas can "of its own accord" happen to shrink to half its volume on one occasion and to 1/3 on another, as if labeled item (a) had compelled it.—Classical Hertzian resonators at frequency ν_0 could "*by coincidence*" all be "stunned" at once. On arrival at the Planck ellipses they will belong in frequency $\nu(\alpha_1, \beta_1)$, in another instance *by chance* to Planck ellipses that belong in frequency $\nu(\alpha_2, \beta_2)$—*as if* they had been *pressed* on to these ellipses through corresponding α, β values with the aid of the quantum hypothesis lever.—*Calculate the quotients of the probabilities of both these coincidences.*
> Yes sir—*this* would be the entropy calculation in Boltzmann's spirit.
> You see *I understand* your comment.
> But did Planck, *you*, and Debye calculate *it like this*?—No!—Rather with $G(q, p, a)$ see e.g., *Einstein, Ann. D. Phys.* 22 (1907) p. 182 bottom.[178]

After EHRENFEST sent his paper in for publication in the *Physikalische Zeitschrift*, he wrote a long letter to EINSTEIN on 21 May 1914 in which he recalled several of the points to be discussed during his next trip to Berlin. He now considered reformulating his treatment without resorting explicitly to the weight function, so that his results would be more accessible to other physicists:

> To come as quickly as possible to the objective, I do so in the following theses:

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176 *Ibid.*, 23 and 17. We have corrected a minor error: $\frac{eH}{c}r^2\omega$ should read $\frac{eH}{2c}r^2$. EHRENFEST himself warned that there was "perhaps a little coefficient error" in this term.

177 *Ibid.*, 25–26 and 20.

178 *Ibid.*, 26 and 20; his emphasis.

> *I define my problem by complete elimination of the concept of $G(q, p, a)$, fully adopting your dictum*. And I then draw up the solution to your problem using this terminology as well.[179]

That his arguments had convinced EINSTEIN of their validity was clear from EINSTEIN's immediate response:

> You are entirely right, you impetuous boy. I had already noticed it before your incensed letter arrived. Quantum theory requires that the G's be made dependent on parameters or that such a dependency be permitted [here Einstein presents an example]....
> Finally, I beg you not to hold against me my rash assertion in my last letters that the G's were independent of a![180]

EHRENFEST was delighted with EINSTEIN's capitulation, as he wrote to JOFFÉ on 3 July 1914:

> I already wrote to you about a quite nice piece that I finished in Easter. Einstein has liked it very much. Not long ago it has gone out to see the light in Z. Phy. [*sic*]. I gladly would reserve it for the anthology for [V.] Kirpichev. Will it be published or not?[181]

Serious differences between EHRENFEST and EINSTEIN still existed, however, on the range of validity of BOLTZMANN's principle and on the concept of the probability of a state. To clarify them, we must examine EINSTEIN's paper, "Contributions to Quantum Theory," which he read at a meeting of the German Physical Society on 24 July 1914,[182] in which he showed that PLANCK's radiation law and NERNST's heat theorem (that the entropy tends to a constant at absolute zero) "can be derived in a purely thermodynamical manner, utilizing basic ideas of quantum theory but not enlisting the help of the BOLTZMANN's principle."[183]

EINSTEIN considered a gas whose molecules were represented by resonators, much as he did in EINSTEIN and HOPF (1910), but now quantized their energies, so that their allowed energies were $nh\nu$. He treated the gas as a mixture of chemical components, each of which consisted of molecules with the same energy, which meant that two molecules were considered to be chemically different if the energies of their resonators were different, so that the concepts of physical and chemical change of a molecule lost their essential distinction. This was the first time that EINSTEIN assumed quantization of energy for molecules, and although it may seem that he was influenced here by the appearance and success of BOHR's atomic model, he made no reference in his paper to BOHR or to BOHR's trilogy of 1913.[184] Instead, in some sense, EINSTEIN's paper

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179 EHRENFEST to EINSTEIN, 21 May 1914. In SCHULMANN, *et al.* (1998), 22–27. English translation in HENTSCHEL (1998), 17–21; on 21; his emphasis.

180 EINSTEIN to EHRENFEST, 25 May 1914. In SCHULMANN, *et al.* (1998), 28. English translation in HENTSCHEL (1998), 21–22.

181 EHRENFEST to JOFFÉ, 3 July 1914. In MOSKOVCHENKO and FRENKEL (1990), 137; our translation.

182 EINSTEIN (1914).

183 *Ibid.*, 820. English translation in ENGEL (1997), 20.

184 BOHR (1913).

constituted a bridge between his paper on photochemical reactions of 1912,[185] and his celebrated paper on the quantum theory of radiation of 1916.[186]

EINSTEIN touched on EHRENFEST's concerns when he noted that "the entropy constants of all components of our mixture [of molecules] are equal, even though the components differ in the resonator energy."[187] He found by means of a standard thermodynamical treatment that the average internal energy of the mixture at thermal equilibrium was given precisely by PLANCK's expression for the average energy of a resonator. More germane to EHRENFEST's ideas on adiabatic transformations was EINSTEIN's consideration of a gas in contact with an infinite heat reservoir whose thermodynamical state is defined by its absolute temperature and a set of additional parameters λ (for example, its volume). EINSTEIN used the MAXWELL-BOLTZMANN distribution to obtain the average energy of a gas having a large number of degrees of freedom, from which he derived its entropy,

$$S = \frac{R}{N} \ln Z, \tag{47}$$

where R is the ideal gas constant, N is Avogadro's number, and Z is the number of elementary states "possible under quantum theory."[188] BOLTZMANN's principle thus was no longer a hypothesis but a theoretical result that, as EINSTEIN stressed in a footnote, he obtained by replacing a canonical ensemble (the MAXWELL-BOLTZMANN distribution) with a microcanonical ensemble (BOLTZMANN's principle).[189]

EINSTEIN's deduction of Eq. (47) rested on his assumption that the changes in the system take place by keeping λ constant. Would this equation still be valid if λ was not kept constant during the transformation? That question, EINSTEIN wrote, cannot be answered without resorting to an additional hypothesis:

> The most natural hypothesis which offers itself is Ehrenfest's adiabatic hypothesis, which can be formulated thus: With reversible adiabatic changes of λ, every quantum-theoretically possible state changes over into another possible state.[190]

EINSTEIN went on to write that EHRENFEST's adiabatic hypothesis implies that the number Z of the elementary states "possible under quantum theory" does not change after an adiabatic transformation, and this also holds for the entropy S. Therefore, as a direct consequence of EHRENFEST's adiabatic hypothesis, BOLTZMANN's principle, as given by Eq. (47), is valid even under infinitely slowly changes of λ.

EINSTEIN's paper of 1914 shows that his discussions with EHRENFEST did not completely clarify EINSTEIN's ideas. Using what he baptized "EHRENFEST's adiabatic hypothesis" in it, EINSTEIN's conclusion seems to have ignored all of EHRENFEST's efforts to establish rigorously the range of validity of BOLTZMANN's principle. EINSTEIN took for granted that the number Z of elementary states retains its meaning

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185 EINSTEIN (1912).
186 EINSTEIN (1916).
187 EINSTEIN (1914), 822. English translation in ENGEL (1997), 21.
188 *Ibid.*, 826 and 24.
189 *Ibid.*, 826 and 25.
190 *Ibid.*

and value during an adiabatic transformation. Thus, it was highly ironic that EINSTEIN used EHRENFEST's adiabatic hypothesis to arrive at this false conclusion as well as his belief in the general validity of BOLTZMANN's principle. As EHRENFEST showed, that was guaranteed if and only if his "δG-condition" was satisfied.

EINSTEIN recognized this serious error only three years later, after he read EHRENFEST's paper of 1916 in which EHRENFEST rigorously clarified the role of adiabatic transformations in quantum theory, and in which he added a short remark discrediting EINSTEIN's application of his adiabatic hypothesis.[191] EINSTEIN tried to justify his lapse in a letter to EHRENFEST in November 1917:

> Your objection to my quantum paper of 1914 [EINSTEIN (1914)] is thoroughly justified; I became aware of the same recently upon studying your paper of 1916 [EHRENFEST (1916b)]. I do believe, though, that the matter can very probably be corrected in this way: The equation $S = \lg Z$ is initially only proven for purely thermal changes. It was wrong, now, to conclude the invariability of Z, according to the adiabatic hypothesis. Instead I avail myself of the circumstance that I can choose the system's external conditions and that, depending on this choice, other processes are "purely thermal." Hence, for ex[ample], a rise in temperature with a constant volume is a purely thermal process or a rise in temperature at constant pressure, depending on the choice of these conditions. Therefore any state of the system is attainable through "purely thermal" changes. That is why the equation $S = \lg Z$ applies generally if it is valid for purely therm. processes.[192]

EHRENFEST apparently did not react to EINSTEIN's proposal, since a year later in answer to a letter in which EHRENFEST alluded improperly to EINSTEIN's 1914 paper, EINSTEIN responded:

> Your observation on the entropy constant is absolutely correct. My paper to which you wanted to allude is probably the one of 1914, not the one of 1916; there the number of possible quantum-like elementary states at absolute zero is indicated as
>
> $$\prod(n!),$$
>
> as it obviously is. Planck will not be talked out of his metaphysical probability concept. When considering his type of inspirations, an irrational residue is left that I cannot assimilate (I then always have to think of Fichte, Hegel, etc.). At the time, you uncovered a false conclusion in my paper of 1914 (wrong application of your adiabatic hypothesis). I informed you once how a correction would be possible. You never let me know whether you approved of this change in the chain of reasoning. Did you ever receive my message then?[193]

We have found no reaction of EHRENFEST to EINSTEIN's proposal.

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[191] EHRENFEST (1916b), 343.

[192] EINSTEIN to EHRENFEST, 12 November 1917. In SCHULMANN, *et al.* (1998), 555. English translation in HENTSCHEL (1998), 407.

[193] EINSTEIN to EHRENFEST, 4 September 1918. In SCHULMANN, *et al.* (1998), 865. English translation in HENTSCHEL (1998), 634.

6. Epilogue: EHRENFEST's adiabatic hypothesis (1916)

We summarize in Fig. 10 the structure and principal points of EHRENFEST's papers of 1913 and 1914,[194] which have constituted the main focus of our analysis. We stress the outstanding role played by EHRENFEST in the extension of the old quantum theory. In the fall of 1913 he published a theorem of BOLTZMANN that EHRENFEST had employed implicitly some months earlier in his justification of the quantization of the angular momentum of rotating molecules to obtain a theoretical explanation of the experimental data on the specific heat of hydrogen without resorting to the zero-point energy hypothesis. In EHRENFEST's view, BOLTZMANN's theorem was an appropriate tool to extend PLANCK's quantum hypothesis on vibrations to general periodic motions, and adiabatic transformations constituted a central concept for the new approach. In 1914 EHRENFEST made a crucial step in improving the statistical foundations of the old quantum theory by extending the validity of BOLTZMANN's relation between entropy and probability, paying special attention to the compatibility between BOLTZMANN's principle and quantum theory.

Although the need to extend the quantum theory was evident, the influence of EHRENFEST's papers of 1913 and 1914 was very limited. As was the case for EHRENFEST (1911), EHRENFEST (1914) may have been too rigorous and technically difficult for most of EHRENFEST's readers to appreciate its significance, particularly because it seemed that these papers seem to have been focused more on analyzing the theoretical foundations of the emerging quantum theory than on obtaining specific results.

In 1915 and 1916 SOMMERFELD generalized BOHR's quantum conditions to include the relativistic variation of the mass of the electron and in this way explained the fine structure of the spectral lines of hydrogenic atoms. EHRENFEST was deeply impressed with SOMMERFELD's achievement and wrote to him in the spring of 1916 congratulating him on it and pointing out its relationship to his adiabatic hypothesis.[195] SOMMERFELD's lukewarm response may have convinced EHRENFEST of the necessity to clarify his ideas, and over the next few weeks he wrote a long paper on his adiabatic hypothesis – now adopting EINSTEIN's name for it – that LORENTZ communicated to the Amsterdam Academy at its meeting on 24 June 1916 and that EHRENFEST published, with slight modifications, in three different journals, the *Proceedings of the Amsterdam Academy*, the *Annalen der Physik*, and the *Philosophical Magazine*.[196] In contrast to his earlier papers, these were much clearer and skillfully employed both classical-mechanical and quantum-mechanical concepts. He regarded his adiabatic hypothesis as a tool for justifying BOHR's and SOMMERFELD's quantization conditions and illustrated its use in three physical systems, an anharmonic oscillator, an electrical dipole in an external electric field, and a point particle moving on a plane under the influence of a Newtonian attractive force.

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194 EHRENFEST (1913a), EHRENFEST (1913b) and EHRENFEST (1914).

195 EINSTEIN to SOMMERFELD, April/May 1916. In SOMMERFELD (2000), 555–557.

196 EHRENFEST (1916a), EHRENFEST (1916b) and EHRENFEST (1917).

EHRENFEST (1913a) (The specific heat of hydrogen)	EHRENFEST (1913b) (A mechanical theorem of BOLTZMANN)	EHRENFEST (1914) (Quantum theory and BOLTZMANN's principle)
• EUCKEN's experimental data on the specific heat of hydrogen. • EINSTEIN and STERN's explanation: – Only a single frequency at a given temperature – No discontinuity – Zero-point energy hypothesis • EHRENFEST's counter-proposal: – Infinite number of frequencies at a given temperature – Quantization rule for the rotational motion of the molecules. (Tools: Adiabatic changes, equiprobability, and statistical treatment) • Implication: The theoretical explanation of experimental data does not necessarily require the zero-point energy hypothesis.	• A mechanical theorem of BOLTZMANN (without demonstration): – Adiabatic change – Adiabatic invariants and quantum rules – Adiabatic invariance of $\bar{T}/\nu$ • Example: Quantization of the angular momentum of a rotating dipole. • EINSTEIN's objection.	• Criticism of equiprobability. • Necessary and sufficient condition for the validity of BOLTZMANN's principle: – The "δG-condition" • For the usual weight functions this condition holds.

Fig. 10. Summary of the contents of EHRENFEST's papers we discussed, emphasizing those points that are related to the genesis and development of EHRENFEST's adiabatic hypothesis

An important novelty in EHRENFEST (1916) was the way in which he presented his "δG-condition," although he did not call it that. Thus, although he referred to his treatment of 1914, he used new language to establish the relationship between adiabatic transformations and BOLTZMANN's principle for molecules with one degree of freedom:

> *For an ensemble of such molecules (resonators)* BOLTZMANN'*s relation between entropy and probability will exist then and only then when the steady motions are characterized by the condition*:
>
> $$\frac{\overline{2T}}{\nu} = \int\int dq\, dp = \text{fixed numerical values } \Omega_1, \Omega_2 \ldots$$
>
> *which condition is invariant with respect to adiabatic changes*.[197]

[197] EHRENFEST (1916a), 588. In KLEIN (1959), 390; his emphasis.

Here ν is the frequency and $\overline{2T}$ is twice the time-average kinetic energy. This was a much simpler statement of the necessary and sufficient condition for the validity of BOLTZMANN's principle than the one that EHRENFEST had given in 1914, but he still was unable to clarify it for molecules with more than one degree of freedom.

EHRENFEST also commented on what we have called "EINSTEIN's objection" and raised the question at issue with maximum generality: Does a "most probable" distribution of states transform into a "most probable" distribution when the system undergoes a reversible adiabatic change? For EHRENFEST the answer was clear: With some exceptions, the answer must be negative. In the version of his paper that he published in the *Annalen* (presumably the one EINSTEIN would read) EHRENFEST expressed his disagreement with EINSTEIN's use of his adiabatic hypothesis in 1914, since the general condition for the validity of BOLTZMANN's principle had to be, in one form or another, equivalent to his "δG-condition," Eq. (40), in its new form above. As far as we know, EHRENFEST never again dealt with this subject.

Another novelty in EHRENFEST (1916) was EHRENFEST's greater emphasis on singular motions. In addition to his example of 1913 on the transition from vibrations to rotations (see Sect. 3.2 above), he gave the example of a reversible adiabatic transformation from vibrations in an anisotropic field of force into vibrations in an isotropic field of force.[198] He related the difficulties here to those that arose when attempting to extend the treatment to nonperiodic motions. He assigned the investigation of them to BURGERS, who as part of his doctoral thesis of 1917 demonstrated that the action variables are adiabatic invariants in each multiply-periodic motion, whether degenerate or not, and generalized his demonstration to nonseparable systems.[199] Thus, after 1917 EHRENFEST's adiabatic invariants were strongly linked to the development of the old quantum theory along with BOHR's correspondence principle.[200]

In his answer to EHRENFEST's letter of the spring of 1916,[201] SOMMERFELD noted that BOHR had praised his adiabatic hypothesis and that EPSTEIN would soon give a seminar on it in Munich.[202] In March 1916, in light of SOMMERFELD's articles, BOHR decided to postpone the publication of his latest work on quantum theory, and in communicating that decision to SOMMERFELD, BOHR wrote:

> I have myself been working a good deal with the quantum theory in this winter and had just finished a paper for publication in which I had attempted to show that it was possible to give the theory a logically consistent form covering all the different kinds of applications. In this I had made largely use of Ehrenfest's idea about adiabatic transformations which seems to me very important and fundamental, and I had discussed a great number of different phenomena, also the dispersion.... The intention of writing all this is only to tell you how exceedingly glad I was to receive your papers before my paper was published. I

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[198] *Ibid.*, 589–591 and 391–393.
[199] BURGERS (1917).
[200] DARRIGOL (1992), 132–137.
[201] See footnote 154.
[202] SOMMERFELD to EHRENFEST, 30 May 1916. In SOMMERFELD (2000), 561. EPSTEIN's seminar appears in the register of the Münchener Physikalisches Mittwochs-Colloquium, dated 2 March 1917, microfilm AHQP-20.

> decided at once to postpone the publication and to consider it all again in view of all, for which your papers have opened my eyes.[203]

Two years later, in his first letter to EHRENFEST, BOHR enclosed a copy of the first part of his paper, "On the Quantum Theory of Line Spectra,"[204] and told EHRENFEST that:

> As you will see the considerations are to a large extent based on your important principle of "adiabatic invariance." As far as I understand, however, I consider the problem from a point of view which differs somewhat from yours, and I have therefore not made use of the same terminology as in your original papers. In my opinion the condition of the continuous transformability of motion in the stationary states may be considered as a direct consequence of the necessary stability of these states and to my eyes the main problem consists therefore in the justification of the application of ordinary "mechanics" in calculating the effect of a continuous transformation of the system. As it appears to me it is hardly possible to base this justification entirely on thermodynamical considerations, but it seems naturally suggested from the agreement with experiments obtained by calculating the motion in the stationary states themselves by means of ordinary mechanics. I have endeavored to show how from this point of view the characteristic exceptions from the principle in question present themselves in a clearer light.[205]

To BOHR, in 1918 EHRENFEST's adiabatic hypothesis thus became the "condition of the continuous transformability of motion" or the "principle of mechanical transformability,"[206] and in 1923 it became the "adiabatic principle"[207] after experiments forced him to renounce applying classical mechanics systematically to the determination of stationary states. Bohr thus was instrumental in making EHRENFEST's adiabatic hypothesis widely known, used, and debated, as was SMEKAL, who in 1918 had written two papers in which he attempted to improve EHRENFEST's derivation of his "δG-condition" and to generalize it to systems of more degrees of freedom,[208] and who in 1925 published a long article on quantum theory and quantum statistics in the *Encyklopädie der Mathematischen Wissenschaften* in which he discussed EHRENFEST's adiabatic hypothesis.[209]

Earlier, very few physicists referred to EHRENFEST's adiabatic hypothesis;[210] later, many well-known physicists, such as SOMMERFELD, VON LAUE, BORN, and DIRAC, used adiabatic invariants in their investigations,[211] and owing to the work of

[203] BOHR to SOMMERFELD, 19 March 1916. In HOYER (1981), 604.
[204] BOHR (1918).
[205] Letter (draft) BOHR to EHRENFEST, 18 May 1918. In NIELSEN (1976), 11–12.
[206] BOHR (1918), 8. In NIELSEN, 74.
[207] BOHR (1923).
[208] SMEKAL (1918a) and SMEKAL (1918b).
[209] SMEKAL (1925).
[210] One of them was PLANCK (1918).
[211] SOMMERFELD (1919), FERMI (1923a), FERMI (1923b), VON LAUE (1925), BORN (1925), DIRAC (1925) and DIRAC (1926).

FERMI, PERSICO, BORN and FOCK, and others, EHRENFEST's adiabatic hypothesis was reformulated as the "adiabatic theorem,"[212] as it is known today.

EHRENFEST himself, however, saw the reception of his adiabatic hypothesis otherwise, and with his characteristic pessimism wrote to BOHR in the spring of 1922:

> Sommerfeld, in the new edition of his book [*Atombau und Spektrallinien*], has introduced the adiabatic hypothesis through a couple of very elegant changes and footnotes, in such a way that my participation in that can rather appear reduced to — a plagiarism. Lorentz and Einstein have founded the subject, I have given it a name and Burgers has put everything in order. I was first very, very depressed. I know that I have never discovered anything, and quite surely never will discover anything, that I can love so fervently as this line of thought which I found out with so large joy.[213]

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[212] FERMI and PERSICO (1926), BORN (1926), BORN and FOCK (1928).

[213] EHRENFEST to BOHR, 8 May 1922. In NB, microfilm AHQP/BSC-2; our translation, his emphasis.

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