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Einstein's quantum theory of the monatomic ideal gas: non-statistical arguments for a new statistics

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Abstract In this article, we analyze the third of three papers, in which Einstein presented his quantum theory of the ideal gas of 1924–1925. Although it failed to attract the attention of Einstein's contemporaries and although also today very few commentators refer to it, we argue for its significance in the context of Einstein's quantum researches. It contains an attempt to extend and exhaust the characterization of the monatomic ideal gas without appealing to combinatorics. Its ambiguities illustrate Einstein's confusion with his initial success in extending Bose's results and in realizing the consequences of what later came to be called Bose–Einstein statistics. We discuss Einstein's motivation for writing a non-combinatorial paper, partly in response to criticism by his friend Ehrenfest, and we paraphrase its content. Its arguments are based on Einstein's belief in the complete analogy between the thermodynamics of light quanta and of material particles and invoke considerations of adiabatic transformations as well as of dimensional analysis. These techniques were well known to Einstein from earlier work on Wien's displacement law, Planck's radiation theory and the specific heat of solids. We also investigate the possible role of Ehrenfest in the gestation of the theory.

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Abbreviations

AEA	Albert Einstein Archives, The Hebrew University of Jerusalem, Israel Unpublished correspondence quoted by permission
AHQP	Archive for History of Quantum Physics For a catalogue, see Kuhn et al. (1967)
EHA	Ehrenfest Archive, Rijksarchief voor de Geschiedenis van de Natuurwetenschappen en van Geneeskunde, Leiden, Netherlands For a catalogue, see Wheaton (1977) We quote from the microfilm version included in the AHQP
HPE	Huisbibliotheek van Paul Ehrenfest, Institut Lorentz, Leiden, Netherlands

1 Introduction

It has been said that Albert Einstein's quantum theory of the monatomic ideal gas, the conceptual innovation of Bose–Einstein statistics in the quantum physics of material particles, was his last "positive contribution" to statistical physics.[1] It was presented in three papers published in 1924 and 1925.[2] In these papers, Einstein made an important step in the quantization of the ideal gas, i.e., of a system of free, massive particles confined in a volume.

The historical connections of Einstein's theory with earlier work by Satyendra Nath Bose, on the one hand, and with Erwin Schrödinger's wave mechanics, on the other hand, have already been widely discussed in the literature.

Most historical commentary focuses on Einstein's first two papers, which indeed contain the most significant conclusions of the theory: a new distribution law for the energy, a new way of counting microstates, an analysis of fluctuations, and the prediction of what came to be known as the Bose–Einstein condensation phenomenon. The third paper, in contrast, has rarely been mentioned, and we have not found any work that would analyze it in some detail. Max Jammer,[3] Friedrich Hund,[4] Abraham Pais,[5] Jagdish Mehra and Hans Rechenberg,[6] and Olivier Darrigol,[7] for example, cite the paper but do not comment on it, i.e., they refer to the list of all three publications, but limit their comments to the results of the first two papers only.[8] Martin Klein, in a

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[1] Born (1949, p. 175). In a similar vein, Pais takes the work on the quantum ideal gas to be the last valid achievement in Einstein's intellectual career, when he suggests that his fame was "based exclusively on what he did before 1925," in the infamous dictum about Einstein's later biography that "his fame would be undiminished, if not enhanced, had he gone fishing instead" (Pais 1994, p. 43).

[2] Einstein (1924, 1925a,b).

[3] Jammer (1966).

[4] Hund (1975).

[5] Pais (1982).

[6] Mehra and Rechenberg (1982, 1984).

[7] Darrigol (1991).

[8] Works that contain discussion of Einstein's first two notes but fail to mention the third paper include (Ezawa 1979).

reference article on Einstein and the wave-particle duality, does not even cite the third paper.[9]

Agostino Desalvo, in a long paper, in which he analyzed different attempts of calculating the chemical constant and their relationship to the birth of quantum statistics, discussed Einstein's third paper, albeit only briefly. In fact, his comments suggest that the paper deserves closer attention:

> This paper usually receives less consideration than the former two. However, if one recalls the key role of thermodynamics in Einstein's thought and the discussion of thermodynamics requirements imposed on the theory of gas degeneracy (…) this paper appears to be a *necessary* complement to the other two.[10]

Einstein followed an approach in this paper that was not based only on statistical considerations and that was closer to thermodynamics. He tried to find general conditions that any theory of the ideal gas would have to satisfy, mainly by establishing and exploiting analogies with radiation, where the displacement law at least provided some hints as to what the radiation law should look like.[11]

Paul Hanle, in a general survey of Schrödinger's research on statistics of ideal gases prior to the formulation of wave mechanics,[12] represents another exception. To be sure, his comments are not any more explicit than Desalvo's. He suggested one should understand Einstein's third paper as a response to Paul Ehrenfest's objections against the reality of the condensation phenomenon. But he also suggested that Ehrenfest was not the only addressee and that Einstein took "Ehrenfest's criticism as symptomatic of skepticism toward the theory among his colleagues."[13]

In summary, Einstein's third paper has received very little attention from historians. Neither did it receive a lot of attention at the time of its publication. We hardly have found references to it by contemporaries, and references to the paper are scarce even by Einstein himself.

From a historical point of view, the fact that Einstein wrote a non-combinatorial paper after expounding his new theory of the quantum ideal gas in two prior articles points to a deeper conceptual problem. There are indications that Einstein himself may not have realized the full implications of the new way of counting, despite his earlier work on black-body radiation. For example, Daniela Monaldi has argued in a note on the prehistory of indistinguishable particles that "neither Bose nor Einstein showed any awareness that they were inaugurating the statistics of indistinguishable particles."[14] Such observations raise a methodological problem. Indeed,

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[9] Klein (1964). He did cite the third paper in an interesting article on Ehrenfest's contributions to the development of quantum statistics (Klein 1959a,b).

[10] Desalvo (1992, p. 526). His emphasis.

[11] In the bibliography compiled by Margaret Shields for the book *Albert Einstein: Philosopher-Scientist* this paper is described as follows: "A general condition is deduced which must be satisfied by every theory of a perfect gas" (Schilpp 1949, p. 716). The phrase is almost a literal quote from Einstein's paper. See footnote 66.

[12] Hanle (1977).

[13] Ibid., pp. 176–177.

[14] Monaldi (2009, p. 8).

careful reading of Bose's paper as well as of Einstein's first two notes do not, it seems to us, allow a modern reader to decide whether Einstein or Bose were fully aware, at the time, of the conceptual implications of their new way of counting. We do have, however, parts of an epistolary exchange between Einstein and the Viennese physicist Otto Halpern.[15] The correspondence was initiated by Halpern in response to Einstein's note, and in it we find a very explicit discussion of the new combinatorics, both by Halpern and by Einstein. While it therefore seems that Einstein became aware of the implications of the new conceptual implications of Bose–Einstein statistics, at least, in the period between the publication of the first and the second paper, we also have explicit criticism by his colleague Paul Ehrenfest, which points to the fact that the new way of statistics was rejected just because of these novel implications.

As we will elaborate in this article, the implications of indistinguishability were discussed at the time under the label of "loss of statistical independence."

For a historical reconstruction of the emergence of one of the core conceptual innovations of quantum theory, it is therefore of interest to take a close look at Einstein's third paper on the quantum ideal gas, precisely because it set out to justify this new theory without making use of the new combinatorics.

Our interest in the non-statistical paper on the quantum ideal gas arose initially from our interest in Paul Ehrenfest's adiabatic hypothesis and, more generally, in his work. In the third paper, Einstein used an adiabatic transformation as a part of a process designed to provide an argument to support his new theory of the quantum ideal gas. Indeed, as we will show, a detailed analysis of the paper suggests other interesting relations to Ehrenfest's research. It is well known and has been observed before[16] that Einstein mentioned his good friend in the second paper, but only in relation to the question of loss of statistical independence of the particles.[17] The discovery of a manuscript of that second paper in the professional library of Ehrenfest in Leiden[18] further kindled our interest in what appears to have been a debate between the two physicists in the—more or less—six months of gestation that preceded this third contribution by Einstein on the quantum ideal gas.

In view of all this, our intention is to analyze the content of the third paper without any further analysis of the pair that preceded it, since they have already been studied in detail.[19] We will try to account for its gestation period, in particular as regards the role that Ehrenfest would have taken in it and also compare it with previous and later reflections by Einstein himself. Finally, we will formulate some conjectures as to why this paper met cold reception despite its historical and systematic interest.

In the title of this essay, we refer to the third paper as containing "non-statistical arguments." More accurately, it should state "non-combinatorial arguments." In a certain sense, as we will see, it does contain some statistical results, insofar as it deals with the distribution function of the kinetic energy among the molecules. However,

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[15] See footnote 51.

[16] Pais (1982, p. 430).

[17] See footnote 37.

[18] Huijnen and Kox (2007).

[19] See, for instance, Navarro (2009) and references therein.

Table 1 Chronology of the presentation and publication of Einstein's quantum theory of the monoatomic ideal gas (QTMIG) and some related facts

4 June 1924	Bose writes to Einstein
ca. 2 July 1924	Bose's paper (translated by Einstein) received by *Zeitschift für Physik*
10 July 1924	Einstein's first paper on QTMIG presented to the Prussian Academy (PA)
20 September 1924	Einstein's first paper on QTMIG published (Einstein 1924)
December 1924	Einstein's second paper on QTMIG signed
	Bose's paper published (Bose 1924)
8 January 1925	Einstein's second paper on QTMIG presented to PA
29 January 1925	Einstein's third paper on QTMIG presented to PA
9 February 1925	Einstein's second paper on QTMIG published (Einstein 1925a)
5 March 1925	Einstein's third paper on QTMIG published (Einstein 1925a)

that function is not analyzed starting from the microscopic constituents of the system, but deduced from its macroscopic properties. What Einstein really omitted completely in this paper is any argument of combinatorics. We have kept the word 'statistical' in the title because it was the consideration of the kind of dependence among molecules which Einstein tried to avoid. It was a non-statistical paper in the sense that the way the microstates had to be counted was not discussed.

In Table 1 we have gathered some of the relevant dates for what follows and to which we will refer throughout the paper.

2 Einstein's quantum theory of the monatomic ideal gas

Some time in June 1924, Einstein received a letter from a Bengali physicist, Satyendra Nath Bose, who asked him politely to translate—if he believed it was worth it—and forward for publication a paper on the hypothesis of light quanta, which he had attached.[20] Einstein complied and translated and sent to *Zeitschrift für Physik* Bose's subsequently famous paper.[21] To the published paper, he added the following commentary:

> In my opinion Bose's derivation of the Planck formula signifies an important advance. The method used also yields the quantum theory of the ideal gas, as I will work out in detail elsewhere.[22]

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[20] See Blanpied (1972) and Wali (2006). The editors of *Philosophical Magazine* had earlier rejected Bose's manuscript.

[21] Bose (1924).

[22] "Bose's Ableitung der Planckschen Formel bedeutet nach meiner Meinung einen wichtigen Fortschritt. Die hier benutzte Methode liefert auch die Quantentheorie des idealen Gases, wie ich an anderer Stelle ausführen will" (Bose 1924, p. 181). An English translation of Bose (1924) can be found in Theimer and Ram (1976, p. 1056).

In Bose's paper we find, for the first time, a derivation of the factor

$$\frac{8\pi \nu^2}{c^3} V \mathrm{d}\nu, \tag{1}$$

starting from the quantization of energy (c is the speed of light in vacuum, V the volume). This expression gives the number of cells corresponding to frequencies between ν and $\nu + \mathrm{d}\nu$ or, in wave-theoretical terms, the number of modes with frequency in that same range. With the average energy of a resonator of frequency ν (or of a normal mode) it constitutes Planck's black-body radiation law for the energy density r:

$$r(\nu, T)\mathrm{d}\nu = \frac{8\pi \nu^2}{c^3} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \mathrm{d}\nu \tag{2}$$

(k is Boltzmann's constant and T the temperature). While several different ways had been found to derive the average energy of a resonator based on Planck's quantum hypothesis, the prefactor had previously been derived only classically, without invoking the concept of quantization. Thus, in his 1916 paper Einstein remarked about the prefactor:

> In order to obtain the numerical value of constant α [defined earlier as $\rho = \alpha\nu^3 1/(\exp(-h\nu/kT) - 1)$] one would have to have an exact theory of electrodynamic and mechanical processes. For the time being we must use Rayleigh's limiting case of high temperatures, for which the classical theory applies in the limit.[23]

In order to obtain this factor, Bose divided the six-dimensional phase space of a light quantum into cells of (hyper)volume h^3. He then calculated the probability of a macroscopic state, taking as a microstate only the number of quanta that were contained in each cell, disregarding any information as to which individual quanta were contained in which cell. With that move, and by just applying the orthodox methods inherited from Ludwig Boltzmann, he was able to derive Planck's radiation law.

We will not give any more details about Bose's bold idea and his paper because it is discussed at length elsewhere.[24] Nowadays, Bose's discovery is mostly presented as a striking example of serendipity, since it seems that its author was not fully aware of the significance of the step he was taking.[25]

Einstein was aware of the significance, as is evident from the swiftness with which he translated and submitted Bose's paper, and from the footnote that he attached to it and that we have quoted above. In fact, before receiving Bose's manuscript he had

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[23] "Um den numerischen Wert der Konstante α zu ermitteln, müßte man eine exakte Theorie der elektrodynamischen und mechanischen Vorgänge haben; man bleibt hier voräufig auf die Behandlung des Rayleigh'schen Grenzfalles hoher Temperaturen angewiesen, für welchen die klassische Theorie in der Grenze gilt" (Einstein 1916b, p. 53). Note that Einstein's notation in this quote is inconsistent with the one that we use throughout. In this article, we use r to denote the distribution function for radiation and ρ for material gases.

[24] See, e.g., Klein (1964) and Bergia (1987).

[25] See, e.g., Delbrück (1980), Pais (1982, pp. 424–428) and Bergia (1987).

recently returned himself to an investigation of the theory of light quanta. On 24 April 1924, Einstein gave a presentation in the plenary session of the Prussian Academy of Sciences "about the present state of radiation problem."[26] Only a few weeks before receiving Bose's manuscript, he wrote to a friend:

> As regards scientific work, I am pondering almost exclusively the quantum problem and I now believe to be really on the right track, if it is certain. The best I had achieved in these matters in recent times was the work of 1917 in the *physikal. Zeitschrift*. My new efforts aim at unification of quanta and Maxwell's field. Among the experimental results of recent years, it is only the experiments by Stern and Gerlach and the experiment by Compton (scattering of Röntgen radiation together with a change of frequency) that are of any significance. The first one proves the independent existence of the quantum states, the second one proves the reality of the momentum of light quanta.[27]

Therefore, Bose's manuscript was timely: After the experimental successes by Arthur Compton and Peter Debye, which seemed to confirm that light quanta have momentum as well as energy;[28] after the spectacular discovery of Otto Stern and Walther Gerlach, for many physicists—Einstein among them—the most striking and convincing demonstration of quantization;[29] and shortly after Einstein's return to his own research on light quanta. Probably for this reason it took him so little time to prepare a presentation in which he applied Bose's method to an ideal gas.[30] He presented it at the Prussian Academy on 10 July, only a month after Bose had signed his letter.[31]

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[26] *Sitzungsberichte Preußische Akademie der Wissenschaften, Physikalisch-mathematische Klasse*, 1924, p. 179. The abstract of the *Sitzungsberichte* indicates the content of Einstein's talk: "Statistical properties of radiation. Discussion of Bothe's theory of multiple quanta and of attempts by the author to solve the quantum problem by means of overdetermined systems of equations" ("Statistische Eigenschaften der Strahlung. Betrachtung über Bothes Theorie der mehrfachen Quanten und über Bemühungen des Verfassers, das Quantenproblem durch überbestimmte Gleichungssystem zu lösen.") The reference to Einstein's own work presumably is to Einstein (1923). The abstract in the *Sitzungsberichte* is preceded with a little star (see also the manuscript for the abstract, AEA 05-187, available at www.alberteinstein.info), which indicates that the report was not intended for publication, at least not by the Academy. This implicit use of a star for titles and abstracts of presentations to the Academy listed in its *Sitzungsberichte* had been common since 1902. In earlier issues of the *Sitzungsberichte*, the meaning of the star had been made explicit at the bottom of the page, but during the year 1902, the explicit footnote attached to the star began to be dropped.

[27] "Wissenschaftlich hänge ich fast ununterbrochen dem Quantenproblem nach und glaube wirklich auf der richtigen Spur zu sein—wenns gewiss ist. Das Beste was mir da in späterer Zeit gelungen ist, war die Arbeit von 1917 in der physikal. Zeitschrift. Meine neuen Bestrebungen gehen auf Vereinigung von Quanten und Maxwell'schen Felde. Von den experimentellen Ergebnissen der letzten Jahre sind eigentlich nur die Experimente von Stern und Gerlach sowie das Exp. von Compton (Zerstreuung der Röntgenstrahlung mit Frequenzänderung) von Bedeutung, deren erstes die Allein-Existenz der Quantenzustände, deren zweites die Realität des Impulses der Lichtquanten beweist". Albert Einstein to Michele Besso, 24 May 1924. In Speziali (1972, p. 202), (French paperback edition, p. 120)

[28] See, e.g., Mehra and Rechenberg (1982, pp. 512–532) for a historical discussion.

[29] See ibid., pp. 422–445 for a historical discussion.

[30] Einstein (1924).

[31] In a comparable situation, Einstein surprised his colleague David Hilbert with a swift calculation of the anomalous advance of Mercury's perihelion after giving up his *Entwurf*-equations and reverting to generally covariant field equations, see Hilbert to Einstein, 19 November 1915 (Schulmann et al. 1998, Doc. 149): "If I could do the calculations as rapidly as you, the electron would have to surrender and the

In this paper we find the density of states of (kinetic) energy E for a molecule of mass m of an ideal gas:

$$2\pi \frac{V}{h^3}(2m)^{\frac{3}{2}} E^{\frac{1}{2}} dE, \tag{3}$$

which is the analog of (1): It gives the number of phase cells of a single molecule corresponding to energies between E and $E + dE$. Following Bose's derivation, Einstein maximized the probability of a certain distribution of molecules in phase space, which he had previously divided into cells of volume h^3. He also took into account only how many molecules were in each cell, not which, and introduced the constraint of the total number of particles, a condition that is not invoked in the case of light quanta. He obtained the average occupation number of a state with energy E, and also the equation of state of the ideal gas:

$$p = \frac{2}{3}\frac{\overline{E}}{V} \tag{4}$$

(p is the pressure and $\overline{E}$ the mean energy of the gas). He commented on this result with the remark: "We obtain the notable result that the relation between kinetic energy and pressure is exactly the same as in the classical theory, where it is derived from the virial theorem."[32] We will see below that in the third installment of his theory Einstein tried to take advantage of this coincidence.

In this seminal paper, Einstein also showed how classical results can be obtained by an expansion of expressions corresponding to the new theory in power series of a parameter λ, defined as

$$\lambda \equiv \frac{h^3}{\pi^{\frac{3}{2}}(2\pi m\kappa T)^{\frac{3}{2}}}\frac{N}{V}, \tag{5}$$

and by keeping only the first term ($\lambda \ll 1$). He wrote some expressions that allowed him to see the differences between both theories to that order of approximation. For instance, for the average energy of the system he found[33]:

$$\frac{\overline{E}}{N} = \frac{3}{2}\kappa T\left[1 - 0.1768 h^3 \frac{N}{V}(2\pi m\kappa T)^{-\frac{3}{2}}\right] \tag{6}$$

Footnote 31 continued
hydrogen atom would have to produce a letter from home excusing it from not radiating." The background for Einstein's achievement was, of course, that he had done before detailed calculations of the perihelion problem in the context of the *Entwurf*-theory, which he could readily assimilate to the case of the new field equations, see Earman and Janssen (1993) for a detailed discussion.

[32] "Es ergibt sich also das merkwürdige Resultat, dass die Beziehung zwischen der kinetischen Energie und dem Druck genau gleich herauskommt wie in der klassischen Theorie, wo sie aus dem Virialsatz abgeleitet wird" (Einstein 1924, p. 264).

[33] We correct the wrong numerical factor 0.0318 that appears in the paper. Einstein himself corrected this mistake in the last paragraph of his next paper, without, however, pointing it out, see Einstein (1925a, p. 13). Desalvo and Navarro have already noted this omission (Desalvo 1992, p. 524; Navarro 2009, pp. 200–201).

Einstein pointed out that contrary to what happens in the ordinary theory, the new expression for the entropy of the gas is perfectly compatible with Nernst's principle, in the sense that the entropy vanishes at zero temperature. In fact, in Einstein's theory, at zero temperature, all molecules are in the same cell, leaving only one microstate possible.

At the end of the paper we find an interesting comment on a question that had been and still was widely discussed by his predecessors in the study of the quantum ideal gas: The Gibbs' paradox.[34] In Einstein's theory the entropy of the gas is extensive and, like the classical entropy, additive with respect to different components. If the mixture of two different gases implies an increase of entropy, the *mixture* of the same gas (at equal density), on the other hand, does not. According to Einstein, this prevents one from imagining a continuous variation of the differences between gases.

In the second installment Einstein proposed a solution to this question.[35] The second paper was signed in December and read at the Academy's meeting of 8 January 1925. Since the presentation of the previous paper, Einstein had plenty of time pondering and discussing the subject with his colleagues. The second paper presents further detailed analysis of the consequences implied by the theory expounded in the first paper. Einstein emphasized this fact by numbering both equations and paragraphs in consecutive order with the first one (the second paper begins with the sixth paragraph and with the 24th equation).[36] The most famous results of Einstein's theory are contained in this paper. In this paper indeed, Einstein took the theory considerably further than Bose had done.

First, Einstein discussed an unusual consequence: the condensation at low temperatures or, in other words, the saturated gas. Einstein considered, for the first time, the case of a gas in which, below a certain critical temperature (that depends on N and V), the number of particles in excited states is limited. In the next section, he discussed the loss of statistical independence of the molecules in a famous passage where Ehrenfest's name appears:

> Mr. Ehrenfest and other colleagues have raised the criticism that in Bose's theory of radiation and in my analogous theory of ideal gases the quanta or molecules are not treated as statistically independent entities without explicit mentioning of this feature in our respective papers. This is entirely correct.

And the passage continues:

> If the quanta are treated as statistically independent regarding their localization, one obtains Wien's law of radiation; if one treats the gas molecules in an

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[34] Einstein only refers to "a paradox" ("ein Paradoxon") and does not identify it as Gibbs' paradox. We have no evidence for assuring that Einstein knew Gibbs' paradox. However, Ehrenfest did, see footnote 150 Moreover, Schrödinger had recently published a paper in the *Zeitschrift für Physik* entitled "Isotopie und Gibbsches Paradoxon" (Schrödinger 1921). It is more than likely that Einstein had heard about it before writing this paragraph.

[35] Einstein (1925a).

[36] "For convenience, I write the following formally as a continuation of the paper cited" ("Der Bequemlichkeit halber schreibe ich das Folgende formal als Fortsetzung der zitierten Abhandlung.") (Einstein 1925a, p. 3).

> analogous way, one arrives at the classical equation of state, even if one proceeds in exactly the same way as Bose and I have done.[37]

Then, Einstein elucidated this issue analytically, but he left in the dark what kind of dependence it is that affects the behavior of molecules in the new statistics. He pointed out something that he had already suggested in his previous paper: In classical theory the entropy expression forces one to choose between two different conditions to be fulfilled, that is, Nernst's principle or the extensivity of entropy. In the new theory, the two conditions are satisfied at the same time. Einstein considered this fact a strong support of the deep analogy between radiation and gas on which his theory was founded:

> For these reasons I believe that one has to prefer the conception (a) (i.e., Bose's statistical approach) even if this preference over others cannot be justified apriori. This result in itself lends support for the belief in the deep essential similarity between radiation and gas in that the same statistical conception that leads to Planck's formula produces the agreement between gas theory and Nernst's theorem when applied to ideal gases.[38]

Also in this paper, we find the first appeal by Einstein to a certain duality in terms of the thesis by Louis de Broglie. After analyzing the energy fluctuations of an ideal gas, he described the ideas of the French physicist aimed at overcoming the opposition between waves and particles. The great impact this reference by Einstein to de Broglie's work had on the research of Schrödinger has been noted on many occasions, as Schrödinger never failed to recognize it.[39] Appealing to the wave field that would accompany each particle, Einstein proposed to solve the paradox with which he had closed the previous paper: The interference will only take place in gases composed of molecules of equal mass.

Finally, Einstein suggested two effects of his theory that were possibly accessible to experimental verification. The first one is a decrease in viscosity. The undulatory behavior of the molecules should lead to diffraction effects that might provoke, in gases of low-mass elements such as helium or molecular hydrogen, a dramatic decrease in the friction coefficient of the gas. But after calculating the size of the required

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[37] "Von EHRENFEST und anderen Kollegen ist an BOSES Theorie der Strahlung und an meiner analogen der idealen Gase gerügt worden, daß in diesen Theorien die Quanten bzw. Moleküle nicht als voneinander statistisch unabhängige Gebilde behandelt werden, ohne daß in unseren Abhandlungen auf diesen Umstand besonders hingewiesen worden sei. Dies ist völlig richtig. Wenn man die Quanten als voneinander statistisch unabhängig in ihrer Lokalisierung behandelt, gelangt man zum WIENschen Strahlungsgesetz; wenn man die Gasmoleküle analog behandelt, gelangt man zur klassischen Zustandsgleichung der idealen Gase, auch wenn man im übrigen genau so vorgeht, wie BOSE und ich es getan haben" (Ibid., p. 5).

[38] "Aus diesen Gründen glaube ich, dass der Berechnungsweise a) (d.h. Boses statistischem Ansatz) der Vorzug gegeben werden muss, wenn sich die Bevorzugung dieser Berechnungsweise anderen gegenüber auch nicht a priori erweisen lässt. Dies Ergebnis bildet seinerseits eine Stütze für die Auffassung von der tiefen Wesensverwandtschaft zwischen Strahlung und Gas, indem dieselbe statistische Betrachtungsweise, welche zur Planckschen Formel führt, in ihrer Anwendung auf ideale Gase die Übereinstimmung der Gastheorie mit dem Nernstschen Theorem herstellt" (Ibid., p. 7).

[39] See Klein (1964) and Schrödinger (1926a). Also, Schrödinger to Einstein, 23 April 1926. English translation in Przibram (1967, p. 26).

apertures, Einstein discards standard diffraction experiments for this effect. Second, he proposed to use the statistics of a saturated gas to account for the problem why the electronic contribution to the specific heat of metals is so low. However, in this case, Einstein admits that the difficulties in applying this idea are so big that it can hardly be considered a proof of his theory.

We regard Einstein's second paper on the quanta a milestone in the history of quantum physics, not only because of the unusual amount of new results it contains but also because in a certain sense it closed the circle that was initiated by Einstein himself 20 years earlier with his heuristic hypothesis of light quanta. He was a pioneer in emphasizing the dual nature of radiation in 1909. In 1925, with a completely analogous procedure, he in turn demonstrated the validity of his proposal for the ideal gas.

In short, Einstein developed the analogy between gas and radiation, knowing that despite the evidence he could adduce to support the theory, it was unsure whether his theory was the true theory. In his own words:

> The interest in this theory derives from the fact that it is based on the hypothesis of an extended formal similarity between radiation and gas. According to this theory, the degenerate gas differs from the gas of mechanical statistics in an analogous way as the radiation according to Planck's law differs from the radiation according to Wien's law. If one takes Bose's derivation of Planck's radiation formula seriously, then one cannot ignore this theory of the ideal gas either; because if it is justified to conceive of the radiation as a gas of quanta, then the analogy between a gas of quanta and a gas of molecules must be a complete one.[40]

We finish this brief summary with this quote in order to emphasize the continuity of Einstein's strategy. In the third paper, Einstein insisted on this analogy in order to obtain new arguments for the validity of the theory, but in this case, as he wrote to Ehrenfest, arguments that were independent from the "incrimininated statistics."[41]

3 Ehrenfest's role in the prehistory of the third paper

We will argue that Einstein's third paper is implicitly a response to Ehrenfest's skepticism toward Einstein's new theory. When did Ehrenfest learn about Einstein's new theory? Einstein first communicated to his friend the discovery in a letter:

> The Indian Bose gave a beautiful derivation of Planck's law including its constant on the basis of the lose light quanta. Derivation elegant, but essence remains obscure. I applied his theory to the ideal gas. Rigorous theory of 'degeneracy.'

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[40] "Das Interesse dieser Theorie liegt darin, daß sie auf die Hypothese einer weitgehenden formalen Verwandschaft zwischen Strahlung und Gas gegründet ist. Nach dieser Theorie weicht das entartete Gas von dem Gas der mechanischen Statistik in analoger Weise ab wie die Strahlung gemäß dem PLANCKschen Gesetze von der Strahlung gemäß dem WIENschen Gesetze. Wenn die BOSEsche Ableitung der PLANCKschen Strahlungsformel ernst genommen wird, so wird man auch an dieser Theorie des idealen Gases nicht vorbeigehen dürfen; denn wenn es gerechtfertig ist, die Strahlung als Quantengas aufzufassen, so muß die Analogie zwischen Quantengas und Molekülgas eine vollständige sein" (Einstein 1925a, p. 3).

[41] Einstein to Ehrenfest, 8 January 1925 (AEA 10-097).

> No zero point energy and above no energy defect. The Lord knows whether it's like this.[42]

Einstein presented the first installment on July 10, and this letter was signed on the 12th. At the end of month, the two friends could have discussed the matter in person, since Ehrenfest stopped over in Berlin for some days in his voyage toward Petersburg. However, during those days Einstein was not in Berlin.[43] Ehrenfest took part in the fourth congress of the Russian Society of Physics (this was his first visit after the Revolution and after he moved to Leiden in 1912).[44] In Petersburg, Ehrenfest did not present his friend's new theory, but probably he talked about it with some interested physicists, as Joffé or Krutkow. On the 18th of September, in his presentation on the "theory of quanta," he referred to the struggle that was taking part "in the heart of every physicist" between corpuscular and undulatory theories.[45] Joffé himself spoke the same day about the "light atoms."

There is also no evidence that Ehrenfest met Einstein on his return trip to Leiden at the end of September or beginning of October[46] (after having spent a few days in Moscow to see in situ the center of the communist state). Nevertheless, according to a letter written in October 9 by Ehrenfest to Joffé,[47] we must suppose that those days Einstein was visiting Leiden (in fact, in the previously mentioned letter of 12 July, Einstein already announced a meeting at the "beginning of October"). This is the excerpt of Ehrenfest's letter to Joffé that we are interested in:

> My dear friend!
>
> Precisely now Einstein is with us. 1. We coincide fully with him that Bose's disgusting work by no means can be understood in the sense that Planck's radiation law agrees with light atoms moving independently (if they move *independently* one of each other, the entropy of radiation would depend on the volume *not* as in Planck, but as in W. Wien, i.e., in the following way: $\kappa \log V^{E/h\nu}$).
>
> No, light atoms placed in the same cell of the phase space must depend one on the other in such a way that Planck's formula is obtained. Now we will clarify this question in a *polemic* manner. I, Krutkow and Bursian will publish in the next

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[42] "Der Inder Bose hat eine schöne Ableitung des Planckschen Gesetzes samt Konstante auf Grund der losen Lichtquanten gegeben. Ableitung elegant, aber Wesen bleibt dunkel. Ich habe seine Theorie auf ideales Gas angewendet. Strenge Theorie der, 'Entartung.' Keine Nullpunktsenergie und oben kein Energiedefekt. Gott weiss, ob es so ist." Einstein to Ehrenfest, 12 July 1924 (AEA 10-089). French translation published in Balibar et al. (1992, p. 166).

[43] Einstein was in Switzerland on 29 July (AEA 143-159), returning to Berlin around 18–20 August (AEA 120-908) after also visiting Lautrach (AEA 120-907).

[44] See Frenkel (1971, p. 88).

[45] Ehrenfest (1924). The text we quote appears in Hall (2008, p. 244). We wish to thank Karl Hall for sending us the text of the résumé of Ehrenfest's talk.

[46] Again, Einstein was out of town, arriving in Vienna on 22 September (AEA 92-097) and travelled to Leiden via Innsbruck (AEA 143-163) and Lucerne (AEA 84-567). Nevertheless, Ehrenfest may have visited Einstein's wife and step-daughters on his stopover in Berlin, see, e.g., (AEA 143-168).

[47] Ehrenfest to Joffé, 9 October 1924, in Moskovchenko and Frenkel (1990, pp. 171–172).

> number of Z. Physik a few considerations against, and simultaneously Einstein will give them answer in the same issue.[48]

Unless we are missing a letter, it is obvious from this document that Ehrenfest and Joffé had already discussed about Bose's "disgusting" work. This appellative can be understood as one of the first symptoms of Ehrenfest's future reluctance (which did not imply ignorance) toward the new mechanics; Ehrenfest did not hesitate to qualify it, some months later, as a "sausage- machine-physics-mill."[49]

We have not been able to confirm whether Iurii A. Krutkow (1890–1952) and Viktor R. Bursian (1886–1945)—as the quoted letter suggests—went to Leiden with Ehrenfest on his return trip. We know that Krutkow enjoyed a scholarship from the Rockefeller foundation which allowed him to work in Western Europe in 1925 and 1926, which he did for some time together with Born in Göttingen.[50] In any case, as far as we know, the "considerations," which Ehrenfest referred to in this letter were never published.

It is very likely that Einstein referred to these debates in Leiden in the comment in his 1925 paper in which he referred to Ehrenfest's objections. This does not mean that the "others" Einstein mentioned were the Russian friends of Ehrenfest. At least, the Austrian physicist Otto Halpern had pointed out to Einstein the lack of statistical independence of the molecules in the new approach. He sent Einstein a detailed explanation of how the statistical independence of the elements under consideration had statistical implications. As he himself says, he based his reflections on Ehrenfest's and Krutkow's previous works. In his response, Einstein—who admits Halpern had "illuminated very clearly a point of essential significance"—[51] distinguishes between two hypotheses:

(1) All distributions of the individual quanta over the "cells" are equally probable (Wien's law).
(2) All different quantum-distribution-pictures over the "cells" are equally probable (Planck's law).

And he continued:

> Hypothesis 2 doesn't square with the hypothesis of the independent distribution of individual quanta—but expresses, in the language of the theory of existing quanta—a mutual dependence of the latter among each other.
>
> Without experience one cannot decide between (1) and (2). The concept of independent atom-like quanta calls for (1), but experience demands (2). Bose's derivation therefore cannot be regarded as a genuine theoretical justification of Planck's law, but only as a reduction of that law to a simple, but arbitrary statistical elementary hypothesis.

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[48] His emphasis.

[49] "Wurstmaschine-Physik-Betrieb," Ehrenfest to Einstein, 26 August 1926 (AEA 10-142). English translation in Mehra and Rechenberg (1984, p. 278).

[50] See Frenkel and Josephson (1990).

[51] "Sie haben (…) einen Punkt von wesentlicher Bedeutung klar beleuchtet". Einstein to Halpern, September 1924 (AEA 12-128). Published in French translation in Balibar et al. (1992, pp. 179–180).

Referring to his own extension of Bose's results to material gases, Einstein wrote:

> This therefore also entails the implicit presupposition of certain statistical dependencies between the states of the molecules, a presupposition which the gas theory as such does not suggest. It would therefore be all the more interesting to know whether real gases behave according to this theory.[52]

Einstein's next visit to Leiden took place only in February of the following year, when he participated in the celebration of the fiftieth anniversary of Lorentz's doctorate.[53] On that occasion he spent only a few days in Leiden[54] and the prevailing agitation probably made it difficult for the friends to discuss the matter calmly.[55]

But a possible earlier meeting could have taken place in Berlin, where Ehrenfest spent some time in the beginning of November. This is suggested by a letter written by Ehrenfest, in which, however, he does not say anything related to the question of the gas. But Einstein did comment on the subject in his next letter, dated on November 29, in which he mentioned the condensation phenomenon:

> I am investigating the degeneracy function more thoroughly with Grommer. With a certain temperature the molecules "condense" without attractive forces, i.e., they pile up at the velocity zero. The theory is beautiful but does it also have some truth? I want to try whether one can also relate this to the dependence of the thermo forces at low temperature.[56]

Everything seems to indicate that these days they hardly discussed. Einstein complained about that in another letter:

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[52] "(1) Alle Verteilungen der individuellen Quanten ueber die 'Zellen' sind gleich wahrscheinlich (Wien'sches Gesetz).
(2) Alle verschiedenen Quanten-Verteilungs-Bilder ueber die Zellen sind gleich wahrscheinlich (Planck'sches Gesetz).
Hypothese 2 passt nicht zur Hypothese der unabhaengigen Verteilung individueller Quanten, sondern drueckt—in der Sprache der Theorie existierender Quanten—eine gegenseitige Abhaengigkeit der letzteren von einander aus.
Unabhaengig von der Erfahrung kann zwischen (1) und (2) nicht entschieden werden. Die Vorstellung unabhaengiger atomartiger Quanten verlangt (1), die Erfahrung jedoch velangt (2). Boses Ableitung kann also nicht als eine eigentliche theoretische Begruendung von Planck's Gesetz angesehen werden, sondern nur als dessen Zurueckfuehrung auf eine zwar einfache, aber willkuerlich statistische ElementarHypothese. (…) Es bedeutet dies also ebenfalls die implicite Voraussetzung gewisser statistischer Abhaengigkeiten zwischen den Zustaenden der Molekuele, fuer welche die Gastheorie als solche keine Anhaltspunkte liefert. Es waere also umso interessanter zu wissen, ob sich die wirklichen Gase gemaess dieser Theorie verhalten" (Ibid.).

[53] Since that year the Royal Netherlands Academy of Arts and Sciences awards the Lorentz Medal.

[54] See Einstein to Ehrenfest, 8 January 1925 (AEA 10-098): "Da ich aber im März nach Argentinien muss und hier in Berlin Vorlesung in diesem Semester halte, muss ich gleich wieder zurück von Leiden".

[55] It was presumably during this short trip that Einstein gave Ehrenfest the manuscript of the second paper that was found in Ehrenfest's personal library, see HPE, Document EB22.

[56] "Ich untersuche mit Grommer die Entartungsfunktion der Gase genauer. Von einer gewissen Temperatur an "kondensieren" die Moleküle ohne Anziehungskräfte, d.h. sie häufen sich bei der Geschwindigkeit null. Die Theorie ist hübsch, aber ob auch was Wahres dran ist? Ich will versuchen ob man den Verlauf der Thermokräfte bei tiefen Temperaturen damit in Zusammenhang bringen kann". Einstein to Ehrenfest, 29 November 1924 (AEA 10-093).

> The thing with the quantum gas turns out to be very interesting. It seems to me more and more that something deep and true is hiding there. I am looking forward to—arguing about this with you.[57]

We guess they talked only after Einstein had presented the second paper of his theory in Berlin. Writing to confirm his participation at Lorentz's jubilee (and of his inability to stay longer than a few days), dated January 8 (precisely the day of his second presentation in the Academy), Einstein communicated to his friend that he had found a new way to justify the theory:

> I will then completely convince you about the gas-degeneracy-equation, I found another sound if only not totally complete approach to it, free of the incriminated statistics. But how to set up a mechanics that leads to something like this? Presently I am plagueing myself roughly following Tetrode's, the invisible, prescription (Zeitschr. f. Physik 1922). There is something genial about this man.[58]

Note the third installment was read by Einstein on 29 January. According to this letter, we conclude that when he read the second one he had already thought about how to justify his theory with non-statistical arguments based on the displacement law. Note that up to this point neither Ehrenfest nor Einstein considered Bose's derivation a "theoretical foundation" of Planck's law.

4 The third, non-statistical paper

On 29 January 1925, Einstein presented the third and last paper of his quantum theory of the monatomic ideal gas to the Prussian Academy for publication in its Proceedings. This time, the sections and equations were not labeled consecutively with those of the preceding paper. Below we will return to this question in more detail, but these external aspects already suggest that the third contribution represents a path disconnected from the previous treatments. Or, at least, it seems Einstein wanted to present it this way. In this section, we will paraphrase Einstein's arguments, closely following his original paper.

4.1 Introduction and approach

Einstein stated in the beginning that his theory was justified on the assumption that a light quantum differs, apart from polarization, from a material gas molecule only in

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[57] "Die Sache mit dem Quantengas macht sich sehr interessant. Es kommt mir immer mehr vor, dass da viel Wahres und Tiefes dahinter steckt. Ich freue mich, bis wir darüber—streiten können." Einstein to Ehrenfest, 2 December 1924 (AEA 10-095).

[58] "Ich werde Dich dann völlig überzeugen von der Gas-Entartungs-Gleichung, ich habe noch einen sicheren, aber allerdings nicht ganz vollständigen Zugang zu ihr gefunden, frei von der inkriminierten Statistik. Aber wie die Mechanik aufstellen, die zu so was führt? Gegenwärtig plage ich mich ungefähr nach dem Rezept Tetrodes (Zeitschr. f. Physik 1922), des Unsichtbaren. Es ist etwas Geniales an diesem Mann". Einstein to Ehrenfest, 8 January 1925 (AEA 10-097). Einstein is referring to Tetrode's proposal of extending classical mechanics, which was published in 1922, see Tetrode (1922).

the vanishing of its rest mass. This assumption was not taken for granted by many of his colleagues, nor had many researchers already accepted the statistical method used by Bose and by him. Einstein admitted that this method was "not at all free of doubt" ("keineswegs zweifelsfrei") and that it was only justified a posteriori by its success in the case of electromagnetic radiation. Consequently, in the third paper, he was looking for new arguments in support of the new theory.

Nevertheless, this approach would follow his general heuristics of exploiting the gas-radiation analogy:

> Here we plan to engage in considerations, in the field of gas theory, that are largely analogous, in method and outcome, to those that lead, in the field of radiation theory, to Wien's displacement law.[59]

The results of these considerations will be restrictions on the form of the distribution function

$$\rho = \rho(L, \kappa T, V, m) \tag{7}$$

(L is the kinetic energy, κ the Boltzmann constant, T the temperature, V the volume and m the mass of the molecules).

Einstein began by defining the subject of his investigation: consider a mole of an ideal gas contained in a volume V at a temperature T whose molecules have mass m. The distribution law will be of the form

$$\mathrm{d}n = \rho(L, \kappa T, V, m)\frac{V \mathrm{d}p_1 \mathrm{d}p_2 \mathrm{d}p_3}{h^3}. \tag{8}$$

Here dn designates—for fixed temperature, volume and mass—the number of molecules, whose Cartesian components of the momenta are in the range ($p_1 \ldots p_1 + \mathrm{d}p_1$, $p_2 \ldots p_2 + \mathrm{d}p_2$, $p_3 \ldots p_3 + \mathrm{d}p_3$). Due to the isotropy of the problem, these components will appear in the argument of the distribution function ρ only in the combination

$$L = \frac{1}{2m}(p_1^2 + p_2^2 + p_3^2), \tag{9}$$

i.e., ρ will depend only on the kinetic energy L. Within this approach, knowledge of ρ means knowledge of the equation of state, because

> …there can be no doubt that the pressure is obtained by mechanical calculation based on the collisions of the molecules with the wall.[60]

On the contrary, Einstein did not assume that collisions between molecules be governed by the laws of mechanics. He asserted that if that would be the case, one would

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[59] "Es handelt sich hier darum, auf dem Gebiete der Gastheorie Betrachtungen anzustellen, welche in Methode und Ergebnis weitgehend analog sind denjenigen, welche auf dem Gebiet der Strahlungstheorie zum WIENschen Verschiebungsgesetzführen" (Einstein 1925b, p. 18).

[60] "…nicht daran zu zweifeln ist, daß für den Druck die mechanische Berechnung aus den Zusammenstößen der Moleküle mit der Wand maßgebend ist" (Ibid., p. 19).

arrive at Maxwell's distribution law and the classical equation of state. In fact, as we will see, he neglected interactions among molecules, as is appropriate for an ideal gas.

4.2 Incompatibility with quantum theory

Before beginning the analysis, Einstein commented again on Nernst's principle. However, he did not consider the delicate question of the factor $N!$ (required for S to be an extensive quantity in classical theory), but this time he focused on the dependence of the entropy on volume which is contained in the additive term

$$\kappa \log V. \tag{10}$$

According to the Planckian formulation of Boltzmann's principle,

$$S = \kappa \log W, \tag{11}$$

and ever since Planck's first works on quantum theory, W had always been taken to be a positive integer denoting the number of ways a certain macroscopic (thermodynamic) state can be built up microscopically. Therefore—Einstein added—, it made no sense if W contained additive constants. In his opinion, if one takes into account Nernst's principle, the Planckian formulation (11) becomes almost a necessity: At absolute zero temperature thermal agitation ceases, and then there is only one possible microscopic configuration. That is, at absolute zero, one has:

$$W = 1 \Longrightarrow S = 0, \tag{12}$$

which precisely implies that Nernst's principle is satisfied. Although he did not state it explicitly, it seems Einstein was refining his previous arguments on this subject. Remember that the extensivity of S in the classical theory required the addition of a constant. In the new theory this is not the case.

What Einstein really wanted to emphasize is that this interpretation implies that the entropy cannot be negative. If we consider the Sackur–Tetrode equation of state of an ideal gas,[61]

$$S = N\kappa \left\{ \log \left(\frac{2\pi m \kappa T}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} + \frac{5}{2} \right\}, \tag{13}$$

we see that, if the volume is small enough, the entropy would be negative. Does this mean that real gases, contrary to what is implied by Nernst's theorem, can have negative entropies? No. It simply means that the classical theory of ideal gases can only be taken as valid under certain conditions. This is in analogy, so Einstein, to the case of Wien's radiation law.

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[61] This expression does not appear in Einstein's paper, see Pathria (2007, p. 24).

4.3 Dimensional analysis

According to its definition, (8), the distribution function ρ is dimensionless. Starting from that, Einstein derived some of its properties assuming that Planck's constant, h, is the only dimensional constant contained in ρ (he did not take into account Boltzmann's constant because he assumed that it would always appear in conjunction with temperature; in other words, he avoided selecting a specific temperature scale). Therefore, one can deduce, "in a well known way," as Einstein remarked,[62] that ρ must be of the form:

$$\rho = \Psi\left(\frac{L}{\kappa T}, \frac{m\left(\frac{V}{N}\right)^{\frac{2}{3}}\kappa T}{h^2}\right). \tag{14}$$

Ψ is a universal, but unknown function, which depends on two dimensionless variables; it must satisfy the relation:

$$\frac{V}{h^3}\int \rho \mathrm{d}\Phi = N, \tag{15}$$

where

$$\mathrm{d}\Phi = \int\limits_{L}^{L+\mathrm{d}L} \mathrm{d}p_1\mathrm{d}p_2\mathrm{d}p_3 = 2\pi(2m)^{\frac{3}{2}}L^{\frac{1}{2}}\mathrm{d}L \tag{16}$$

(this is the same expression as (3) in Einstein's first paper, but without a contribution from position coordinates and without division by h^3). Nothing else can be said about ρ on the basis of dimensional analysis alone. But the number of arguments for ρ can be reduced from two to one variable, without introducing additional "questionable" assumptions. Einstein proposed two of those:

1. The entropy of an ideal gas does not change in an "infinitely slow adiabatic" (sic) compression.[63]
2. The required velocity distribution is valid for an ideal gas also in an external field of conservative forces.

Einstein argued that these two properties should be valid disregarding collisions. But the neglect of intermolecular collisions made their assumption unprovable, even if they would be "very natural." In support of both, he announced they would lead not only to the same result, but also to a result according to which Maxwell's distribution law is valid in the region where quantum effects can be neglected.

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[62] "in bekannter Weise," ibid., p. 20.

[63] "bei unendlich langsamer adiabatischer Kompression" (Ibid., p. 20).

4.4 Adiabatic compression

Einstein considered a gas with isotropic velocity distribution confined in a parallelepipedal container with sides of length l_1, l_2, and l_3. Since collisions of the molecules against the walls are elastic, they do not change the velocity distribution, which is stationary. The distribution has the form:

$$\mathrm{d}n = \frac{V}{h^3}\rho \mathrm{d}\Phi, \tag{17}$$

where ρ is an arbitrary function of the kinetic energy L. Although he did not state it explicitly, Einstein did not take up the result here that he had derived using dimensional analysis—(14)—in the previous section. He simply started out from an isotropic distribution law. For an (infinitesimal) adiabatic compression that satisfies

$$\frac{\Delta l_1}{l_1} = \frac{\Delta l_2}{l_2} = \frac{\Delta l_3}{l_3} = \frac{1}{3}\frac{\Delta V}{V}. \tag{18}$$

(the symbol Δ indicates that the process is adiabatic), the distribution will stay of the form (17), but what will it be? The kinetic energy variation will be[64]:

$$\Delta L = \frac{1}{m}\left(|p_1|\Delta|p_1| + \cdots + \cdots\right) = -\frac{2}{3}L\frac{\Delta V}{V}. \tag{19}$$

Since, according to (12), we have

$$\Delta \mathrm{d}\Phi = 2\pi(2m)^{\frac{3}{2}}\left(L^{\frac{1}{2}}\Delta \mathrm{d}L + \frac{1}{2}L^{-\frac{1}{2}}\Delta L \mathrm{d}L\right), \tag{20}$$

it follows that:

$$\Delta(V\mathrm{d}\Phi) = 0. \tag{21}$$

Since an adiabatic transformation does not change the number of molecules, it can be easily seen that:

$$\Delta\rho = 0. \tag{22}$$

As to the entropy, Einstein surmised that it would be of the form:

$$\frac{\mathrm{d}S}{\kappa} = \frac{V}{h^3}s(\rho, L)\mathrm{d}\Phi, \tag{23}$$

---

[64] Einstein wrote δ instead of Δ for the variation of p_i in this equation. We think this is a typographical mistake. See Einstein (1925b, p. 21).

where s is an unknown function. In adiabatic processes one has:

$$\Delta \mathrm{d}S = 0, \tag{24}$$

and, therefore, according to (21):

$$0 = \Delta s = \frac{\partial s}{\partial \rho}\Delta\rho + \frac{\partial s}{\partial L}\Delta L. \tag{25}$$

Finally, using (22), it follows that s is only a function of ρ alone,

$$s = s(\rho). \tag{26}$$

In a next step, Einstein imposed the condition that in thermodynamic equilibrium the entropy is a maximum with respect to variations of ρ, keeping fixed the number of particles and the total energy. The calculation gives:

$$\frac{\partial s}{\partial \rho} = AL + B, \tag{27}$$

where A and B do not depend on L. Since s only depends on ρ, its derivative will do so, too, and Einstein could write:

$$\rho = \Psi(AL + B). \tag{28}$$

In order to determine A, Einstein now considered the process of an infinitesimal isopycnic warming, i.e. a warming that does not alter the density of molecules (a transformation of constant volume in this case). Let $\mathcal{E}$ be the energy of the gas and let D symbolize this process, then

$$D\mathcal{E} = \frac{V}{h^3}\int L(D\rho)\mathrm{d}\Phi \tag{29}$$

will be equal—according to the thermodynamic relation between entropy and energy—to:

$$TDS = \frac{V\kappa T}{h^3}\int (Ds)\mathrm{d}\Phi. \tag{30}$$

Applying the chain rule and taking into account the invariance of the total number of molecules Einstein obtained:

$$\int L(D\rho)(1 - \kappa T A)\mathrm{d}\Phi = 0, \tag{31}$$

that is:

$$A = \frac{1}{\kappa T}. \tag{32}$$

Returning to expression (28), the functional dependence of the energy density with kinetic energy is:

$$\rho = \Psi\left(\frac{L}{\kappa T} + B\right). \tag{33}$$

4.5 Ideal gas in a field of conservative forces

The other path taken by Einstein with the aim of reducing the number of arguments for the distribution function appeals to its stationarity. Consider a gas in dynamic equilibrium in an external field of conservative forces whose single-particle potential energy Π depends on the position of molecules. In addition to neglecting the collisions between them, Einstein assumed that "the motion of the individual molecules under the influence of the external field follows classical mechanics." The condition, which ρ must satisfy to be stationary, is:

$$\sum_i \left(\frac{\partial(\rho \dot{x}_i)}{\partial x_i} + \frac{\partial(\rho \dot{p}_i)}{\partial p_i}\right) = 0 \tag{34}$$

(x_i are the position variables). If we make use of the equations of motion the stationarity condition reads:

$$\frac{\partial \rho}{\partial x_i}\dot{x}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i = 0. \tag{35}$$

It follows that ρ is constant along phase trajectories. Since, as a consequence of the problem's isotropy, the momenta p_i will only appear in the argument in the combination of the kinetic energy L, ρ must be of the form:

$$\rho = \Psi^{\star}(L + \Pi), \tag{36}$$

with $\Psi^{\star}$, again, a universal, but unknown function.

Hence, the volume dependence on the distribution function will only come about through Π.

4.6 Conclusions

The results of the previous sections, (33) and (36), are:

$$\rho = \Psi\left(h, m, \frac{L}{\kappa T} + B\right) \tag{37}$$

$$\rho = \Psi^{\star}\left(h, m, \kappa T, L + \Pi\right) \tag{38}$$

B and Π are universal functions that depend on $h, m, \kappa T$ and V. Ψ and $\Psi^\star$ are universal and dimensionless functions. Taking into account also (14), Einstein derived:

$$\rho = \Psi\left(\frac{L}{\kappa T} + \chi\left(\frac{m\left(\frac{V}{N}\right)^{\frac{2}{3}}\kappa T}{h^2}\right)\right). \tag{39}$$

Here Ψ and χ are universal functions of dimensionless variables. Both are related by equations (15)—the number of particles—and (16)—the density of states—, and the problem was therefore reduced to finding the function Ψ.

In the last paragraph, Einstein looked at the case in which the constant h disappears from dn, i.e. at the classical limit. He defined:

$$u = \frac{Nh^3}{(m\kappa T)^{\frac{3}{2}}V} \qquad \text{and} \qquad v = \frac{L}{\kappa T}. \tag{40}$$

From (8) and (40) we see that h will disappear if and only if $\frac{1}{u}\psi$ does not depend on u. In this case, let $\overline{\psi}(v)$ be the resulting function. With a suitable choice of the function χ (denoted in this particular case by ϕ) it can be achieved that:

$$\psi(v + \phi(u)) = u\overline{\psi}(v). \tag{41}$$

Differentiating first with respect to u and then with respect to v, it can be seen that $\log \psi$ must be a linear function. It is then easy to see that ψ must be the exponential distribution law, i.e., Maxwell–Boltzmann's law[65]:

$$\overline{\psi}(v) = e^{-v}. \tag{42}$$

In contrast, Einstein's statistical theory had produced the expression:

$$\psi(v) = \frac{1}{e^v - 1}. \tag{43}$$

Summarizing, Einstein pointed out that two aims have been achieved:

> First, we found a general condition (Eq. 39), which has to be satisfied by any theory of the ideal gas. Second, it follows from the above that the equation of state which I derived will not be changed by either adiabatic compression or by the existence of conservative force fields.[66]

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[65] Although in the paper this is not the case, we think that this expression must have a bar on the top, as we write. Equation 43 involves another mistake. We will discuss this question below.

[66] "Erstens ist eine allgemeine Bedingung (Gleichung (18)) gefunden worden, der jede Theorie des idealen Gases genügen muß. Zweitens geht aus dem Obigen hervor, daß die von mir abgeleitete Zustandsgleichung durch adiabatische Kompression sowie durch konservative Kraftfleder nicht gestört wird" (Einstein 1925b, p. 25).

5 A displacement law for gases

The novelty of Bose's approach was its statistical (microscopic) reasoning. At a thermodynamic (macroscopic) level, Bose did not obtain any new results, since it was precisely Planck's radiation law that was being derived. On the contrary, for ideal gases there existed no such distribution law that had to be derived, only a distribution law that was valid in the classical limit. Schematically, the situation was as follows:

	Combinatorics	Thermodynamics-Statistical Distribution (→ *indicates the classical limit*)
Radiation	Bose	Planck's radiation law → Rayleigh–Jeans' (Wien's displacement law is always valid)
Gas	Bose–Einstein	Einstein's distribution law → Maxwell–Boltzmann's distribution law

Einstein's theory thus implied developments at both levels. Indeed, the situation was similar to what had taken place some 25 years ago in the study of electromagnetic radiation. At the end of the nineteenth century, neither the radiation law nor the mechanism that is responsible for producing the thermodynamic equilibrium were known or, more precisely, they were known but had led to both empirically and theoretically wrong results. However, at the macroscopic level there was a guide post: Wien's displacement law. It restricts the arguments of the radiation law:

$$r(\nu, T)\mathrm{d}\nu = \frac{8\pi\nu^2}{c^3} f\left(\frac{\nu}{T}\right)\mathrm{d}\nu. \tag{44}$$

Therefore, once the spectrum is known at a certain temperature, it may be extrapolated to other temperatures. The derivations of Wien's law—there were several[67] —always made use, at some point, of the second law of thermodynamics and, specifically, of the connection between states of equilibrium that were related by an adiabatic compression of the radiating cavity, i.e., by an infinitely slow compression in which the work transforms completely into internal energy. Max Planck—who also gave a demonstration in his *Lectures on Heat Radiation*[68] —justified the form of the quantum $h\nu$ appealing to that law.[69]

It is therefore not surprising that Einstein looked for analogous guide posts for derivations of the new distribution law. Nor it is surprising that he used an adiabatic transformation. He himself had suggested in his famous paper of 1905 on energy

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[67] See, for instance, (Wien 1894) and (Lorentz 1901).

[68] Planck (1988, pp. 314–332).

[69] See Planck (1900). In Planck (1958, vol. 1, p. 703).

quanta that one could use an adiabatic compression to reduce the argument of the spectral entropy density $\varphi(r, \nu)$, which was defined as follows:

$$S = V \int_0^\infty \varphi(r, \nu) \mathrm{d}\nu \tag{45}$$

(S is the entropy of radiation, r the density of radiant energy):

> One can reduce φ to a function of a single variable by formulating the assertion that adiabatic compression of radiation between reflecting walls does not change its entropy. However, we shall not enter into this, but will immediately investigate how the function φ can be obtained from the black-body radiation law.[70]

In 1905 Einstein did not elaborate on the argument because he was interested in other properties of φ. Probably, he did not dwell on this result because it was well known by his colleagues. One can show that:

$$\varphi(\rho, \nu) = \frac{8\pi V}{c^3} \nu^2 \xi \left(\frac{r}{\nu^3}\right), \tag{46}$$

which is another way of enunciating Wien's displacement law. In 1925 Einstein may have recalled his own procedure of 20 years earlier.

In our opinion, it was Paul Ehrenfest who gave the most detailed analysis of the radiation law and its derivations. Although his analysis was published over various articles, here we want to refer specifically to a paper of 1911, which we have discussed in more detail in other places.[71] It will be useful to bring it up again here in order to comment on Einstein's non-statistical paper.

In his paper, Ehrenfest set out by listing the conditions that the radiation law necessarily needs to satisfy. Since these conditions comprise the quantum aspects of the radiation law, analogous conditions should hold for the new distribution law ρ that Einstein was trying to justify. Ehrenfest's first three conditions were:

1. The entropy does not change in an adiabatic compression.
2. The radiation law satisfies the displacement law.
3. The classical limit is obtained in the region where ν/T is small.

Three more conditions were related to the violet region (large ν/T) and required the avoidance of the so-called ultraviolet catastrophe (a divergence in the total energy), and, on the other hand, expressed analytically the behavior of Wien's and Planck's radiation laws.

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[70] "Es kann φ auf eine Funktion von nur einer Variabeln reduziert werden durch Formulierung der Aussage, dass durch adiabatische Kompression einer Strahlung zwischen spiegelnden Wänden, deren Entropie nicht geändert wird. Wir wollen jedoch hierauf nicht eintreten, sondern gleich untersuchen, wie die Funktion φ aus dem Strahlungsgesetz des schwarzen Körpers ermittelt werden kann" (Ibid.).

[71] Ehrenfest (1911). See Navarro and Pérez (2004, 2006).

What did Einstein have at his disposal in 1925 to ensure the validity of his material gas distribution law? Initially, it was only the third condition, i.e., the fact that his law produced the Maxwell–Boltzmann's distribution law in the classical limit. But at *low* temperatures (or *high* densities) he did not have anything comparable to Wien's or Planck's radiation laws. In this region, only Nernst's theorem supported the expression for the entropy obtained by Einstein.

Hence, conditions 1 and 2 were not available. As we have said before, in a certain sense, they are both related, and it should be noted here that Ehrenfest listed them separately because his analysis aimed at drawing conclusions at the microscopic level, where the (mechanical) adiabatic invariants play a crucial role. Einstein in 1925, in contrast, was not interested in mechanical invariants because his research remained at the thermodynamic level. According to this scheme, the problem of electromagnetic radiation served Einstein as a guide to explore the case of the degenerate ideal gas.[72] He justified the additivity of the entropy (23) with respect to those portions of gas with different kinetic energy $\mathrm{d}L$, as follows:

> This hypothesis is analogous to the one used in radiation theory, according to which the entropy of the radiation is composed additively from quasi-monochromatic parts. It is equivalent to the assumption that one may introduce semi-permeable walls for molecules of different ranges of velocity.[73]

This is consistent with his justification of writing the total entropy as an integral over the spectral entropy density (Eq. 45 above) in 1905 (the analog to Eq. 23):

> …radiations of different frequencies are to be viewed as separable from each other without expenditure of work and without supply of heat …[74]

It is curious to see how in Ehrenfest's 1911 paper the direction of the justification was just the opposite than in Einstein's 1925 paper. His approach was inspired by gas theory:

> We determine, for given total energy, the "most probable" distribution of oscillations over all possible ranges of excitations according to the same procedure that Boltzmann had used to determine, for given total energy the "most probable" distribution of molecules for a mixture of gases consisting of many kinds of molecules over all possible ranges of velocity. The eigen frequencies of one

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[72] The degenerate gas had been defined in opposition to a perfect gas. As far as we know, it was Nernst who first introduced this terminology, referring to gases at low temperatures, in which their translational contribution to specific heat tended to disappear, see Desalvo (1992, p. 493).

[73] "Diese Hypothese ist in der Strahlungstheorie jener analog, daß die Entropie einer Strahlung sich aus der der quasi-monochromatischen Bestandteile additiv zusammensetze. Sie ist äquivalent der Annahme, daß man für Moleküle verschiedener Geschwindigkeitsbereiche semi-permeable Wände einführen dürfe" (Einstein 1925b, p. 21).

[74] "…Strahlungen von verschiedenen Frequenzen [sind] als ohne Arbeitsleistung und ohne Wärmezufuhr voneinander trennbar anzusehen …" (Einstein 1905, p. 137).

> and the same frequency range dν here play the same role as the molecules of one and the same substance.[75]

In 10 years the reference system and the unknown system switched their roles. Such was the confusion into which quantum discoveries had brought physics at the beginning of the century.

Note that albeit both analogies are not the same they are equivalent. Einstein justifies expressions (45) and (23) as follows. The fact that one can write the total entropy as a summation of all monochromatic or *mono-kineticoenergetic* entropies means that total entropy is additive with respect to frequency (resp. kinetic energy). Ehrenfest, on the other hand, compares different frequencies with different substances, as the entropy of a mixture is also additive with respect to its components. In both cases entropy of radiation is the summation of monochromatic entropies.

The analogies invoked by Einstein do not end here. Although, as we have said, he used the idea of an adiabatic compression to derive something like a displacement law for ideal gases, the whole approach nevertheless rested on dimensional analysis. This approach was modeled on that in a 1909 paper on radiation, in which Einstein himself had given a derivation of the displacement law.

5.1 Dimensional analysis

Einstein had argued that the distribution function can depend only on two dimensionless quantities (cf. Eq. 14):

$$\frac{L}{\kappa T} \quad \text{and} \quad \frac{m\left(\frac{V}{N}\right)^{\frac{2}{3}}\kappa T}{h^2} \tag{47}$$

He did not present the arguments for his claim in any detail, but it is not very difficult to guess what they were. We must remember that Buckingham's theorem (the consequences of which, as we will argue, were certainly known to Einstein, if not by this name) states that the difference between the number of quantities that are assumed to play a role in the physical system under consideration, on the one hand, and the number of fundamental variables involved, on the other hand, gives the number of independent dimensionless monomials which can be constructed.[76] In our case the fundamental variables are mass (M), time (T) and length (L), and the quantities supposed by Einstein to be arguments of the distribution function ρ are

L: kinetic energy $[L] = ML^2T^{-2}$

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[75] "Es wird bei gegebener Totalenergie die „wahrscheinlichste" Verteilung der Eigenschwingungen über alle möglichen Erregungsbereiche nach demselben Verfahren bestimmt, nach welchem BOLTZMANN die—bei gegebener Totalenergie—„ wahrscheinlichste"Verteilung der Moleküle eines aus vielen Molekülsorten bestehenden Gasgemisches über alle möglichen Geschwindigkeitsbereiche bestimmte. Die Eigenschwingungen eines und desselben Frequenzbereiches dν spielen dabei die Rolle der Moleküle einer und derselben Substanz" (Ehrenfest 1911, pp. 94–95).

[76] Buckingham (1914). For historical accounts of dimensional analysis, see, e.g., Bridgman (1922), Carneiro (2000) and Magagno (1971).

κT: temperature (multiplied by Boltzmann's constant), $[\kappa T] = ML^2T^{-2}$
V: volume, $[V] = L^3$
m: mass of the molecules, $[m] = M$

The choice of quantities that play a role in the problem is the crucial point in any dimensional analysis, since the result critically depends on it. Einstein chose the quantities that appear in the distribution law for the classical ideal gas. That is

$$\mathrm{d}n_{\mathrm{clas}} = \frac{1}{V}\left(\frac{h^2}{2\pi m\kappa T}\right)^{\frac{3}{2}} e^{-\frac{L}{\kappa T}} \frac{V\mathrm{d}p_1\mathrm{d}p_2\mathrm{d}p_3}{h^3} \tag{48}$$

$$\Rightarrow \rho_{\mathrm{clas}} = \frac{1}{V}\left(\frac{h^2}{2\pi m\kappa T}\right)^{\frac{3}{2}} e^{-\frac{L}{\kappa T}} = \rho(L, \kappa T, V, m). \tag{49}$$

Taking into account also Planck's constant $[h] = ML^2T^{-1}$—the distinguishing mark of any quantum phenomenon–[77] in the distribution function of the classical gas, albeit not in dn, it follows from Buckingham's Π theorem that only two independent dimensionless monomials can be constructed. One possible pair is the one that Einstein proposed, see Eq. 47. But this choice is not unique. One could also have:

$$\frac{L}{\kappa T} \quad \text{and} \quad \frac{mV^{\frac{2}{3}}L}{h^2} \tag{50}$$

or:

$$\frac{L}{\kappa T} \quad \text{and} \quad \frac{m^2V^{\frac{4}{3}}\kappa TL}{h^4} \tag{51}$$

(Note that the number of particles N does not play a role in these considerations, since it is dimensionless.) In order to have only one monomial, one needs to impose an additional condition. Most likely, Einstein simply decided to choose the monomial that was compatible with the classical result (49). It has the advantage of being a natural one: since the influence of the kinetic energy L in the density function has to be weighted by the temperature κT, both have to appear together in one of the two monomials.

Once the first monomial has been chosen and after excluding from the second one the kinetic energy (for the reason we have explained), the number of possibilities reduces drastically. We now have a problem with four quantities (three quantities and one constant) and three fundamental variables. Thus, in this way, Einstein's result (47) can be considered univocal. Note that the two monomials (47) can also be derived from the form of the classical density (49). Let's now jump to the end of Einstein's paper.

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[77] Of course, the constant h did not appear in the classical expression for dn. However, once the phase space had been quantized, one could relate h with the volume of a microstate. Only in this way can h appear in the classical distribution function, (49). As in the statistical works prior to early quantum developments, what was significant was the quotient of the phase space volumes, the later appearance of h did not retrospectively contradict classical statistical developments.

After having reduced the number of arguments of the density function to a single parameter,

$$\frac{L}{\kappa T}+\chi\left(\frac{mV^{\frac{2}{3}}\kappa T}{h^{2}}\right), \tag{52}$$

Einstein showed that this result is in agreement also with other constraints. He looked at what happens if one assumes that Planck's constant does not appear in the expression for dn, and he obtained Maxwell–Boltzmann's distribution law. There is a mistake in testing that his theory also satisfies this dependence, but the mistake is inconsequential. Einstein wrote that the density can be written as

$$\frac{1}{e^{\frac{L}{\kappa T}}-1}, \tag{53}$$

which is not true. Nevertheless, his theory satisfies the conclusion of the dimensional argument, since ρ is:

$$\frac{1}{\exp\left[\frac{L}{\kappa T}+\chi\left(\frac{m\left(\frac{V}{N}\right)^{\frac{2}{3}}\kappa T}{h^{2}}\right)\right]-1}. \tag{54}$$

Hence, his conclusion is correct but not the reasoning.

To conclude, note that, in fact, the result achieved by Einstein in Eq. 39 does not lead to a true displacement law. This law was named this way because it implied that the maximum of intensity satisfied the relation

$$\frac{\nu_{\max}}{T}=\text{const.} \tag{55}$$

Therefore, the maximum displaces in proportionality with temperature. Due to the form of the argument in Eq. 52, this simple statement cannot be made in the case of molecules. The simple state of affairs in the case of radiation is a consequence of the non-conservation of—or else the lack of sense of the concept of—the number of particles.

Let us now take a look at earlier considerations which may have inspired Einstein and which had helped him before when he was trying to find his way on slippery ground.

5.2 Einstein's deduction of Wien's displacement's law in 1909

In January 1909, the editors of the Physikalische Zeitschrift received the manuscript of one of the subsequently more celebrated papers by Einstein. In it, and in the talk he gave in Salzburg in September of the same year, Einstein suggested and emphasized for the first time the essential dual nature of radiation—corpuscular and undulatory—, starting from a fluctuation analysis of radiation momentum.[78] This paper must be situated in a context where the physics community had not yet realized the implicit contradictions with classical physics inherent in Planck's radiation law.[79] It was only after 1911—after the first Solvay conference—when the position hitherto taken by a small minority would become the received opinion: That it would be necessary to undertake a deep revision of the existing physical theories in order to account for the quantization that Planck had introduced by his black body radiation theory.

In 1909, Einstein was one of the first physicists who had become clearly aware of the exceptional nature of the situation and suggested that perhaps the break did not have to be as traumatic as it may have seemed at first sight. He argued that one should relate to each other Planck's quanta and electricity quanta. The latter did not arise either in any natural way from Maxwellian electromagnetic theory, and maybe a modification of this theory could account for both instances of quantization. In support of the feasibility of this idea, Einstein invoked some dimensional considerations published by James H. Jeans "a few years ago." Although he did not cite the precise source, it is beyond doubt that Einstein referred to the paper "On the laws of radiation," published by the British physicist in 1905.[80]

In it, Jeans gave a derivation of the displacement law, in which he outlined a dimensional argument that allowed him to write the constants that appear in this law and in Stefan's law depending on known universal constants. In other words, he excluded from his consideration Planck's constant. With this derivation, Jeans was trying to advance a new argument for his claim that the problem of specific heats and the black-body problem were both caused by the fact that thermodynamic equilibrium was not established. For this reason, the equipartition of energy could not be applied in the theoretical analysis of either system. In addition, he also argued for the electronic origin of radiation.

Thus, Jeans proposed that electron trajectories are the source of the spectrum (and of its universality), taking up an old idea by Hendrik A. Lorentz.[81] According to Jeans, the radiant energy per volume at temperature T and wavelength λ depends on the following constants[82]:

V: speed of light,
e: electron charge,
m: electron mass,
R: gas constant (the mean kinetic energy of a single particle is $\frac{3}{2}RT$),
K: inductive capacity of the ether (Coulomb's law, $F = K^{-1}q_1q_2r^{-2}$).

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[78] Einstein (1909b). The presentation in Salzburg was transcribed in Einstein (1909a).

[79] Kuhn (1978).

[80] Jeans (1905). See Stachel (1991, p. 549, note 60), where the editors also point out that, in contrast to Einstein's argument, Jeans did not use the Planck constant h, nor does he consider the ratio e^2/c.

[81] Lorentz (1903).

[82] We omit the dependency on some "specific constants" of the body that do not play any role in what follows.

As a dimensional basis, he took length L, mass M, time t, inductive capacity K, and temperature T[83]:

λ: L,
T: T,
V: Lt^{-1},
e: $L^{3/2}M^{1/2}t^{-1}K^{1/2}$,
m: M,
R: $L^2Mt^{-2}T^{-1}$,
K: K.

Since there are five dimensional units and seven quantities, Jeans was able to construct two independent dimensionless monomials. But which ones he chose, is one of the dark spots of his argument. The key step of his derivation was that one of the two monomials that he constructed, $c_1 = RTm^{-1}V^{-2}$, is of order 10^{-8} (at 100°C); he used this fact to justify his claim that the radiation law depends only on the other monomial, which he chose as:

$$c_2 = \frac{\lambda RTK}{e^2}. \tag{56}$$

A few months later, Ehrenfest published a short note in the *Physikalische Zeitschrift*, in which he criticized Jeans's argument.[84] Indicating that he could not follow the reasoning at various steps, he focussed only on the arbitrariness of the choice of the pair of monomials and showed by means of a slightly different choice of monomials, $c'_1 = c_1$, $c'_2 = c_2c_1^{1/8}$, how Jeans's reasoning may lead also to a different result, i.e., not to the displacement law. The British physicist did not accept the criticism.[85] In his view, Ehrenfest's counterexample did not square with his proposal. Ehrenfest wrote another reply, defending himself against Jeans' counter-attack and repeated his criticism of the dimensional argument.[86]

In 1909, in his article "Radiation Theory" for the *Encyklopädie der Mathematischen Wissenschaften*, Wilhelm Wien referred to Ehrenfest's refutation of Jeans's argument like this:

> Another derivation of the displacement law is given by J.H. Jeans. But there is an uncontrollable approximation in it, which must be introduced as a hypothetical assumption; therefore, Jeans's derivation cannot be regarded as a proof of the displacement law.[87]

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[83] As pointed out already in Ehrenfest (1906a), there is a typographical error in Jeans (1905, p. 548), who has the dimension of R as $LMt^{-2}T^{-1}$.

[84] Ehrenfest (1906a).

[85] Jeans (1906).

[86] Ehrenfest (1906b).

[87] "Eine weitere Ableitung des Verschiebungsgesetzes gibt *J.H. Jeans*. Doch kommt in ihr eine nicht kontrollierbare Vernachlässigung vor, welche als hypothetisch Annahme einzuführen ist; daher kann die *Jeans*sche Entwicklung nicht als Beweis für das Verschiebungsgesetz angesehen werden" (Wien 1909).

Although we cannot give further evidence, it appears that Jeans finally admitted the weakness of his argument. His result may be understood as a piece of circumstantial evidence or as an illustration, not as a genuine derivation. Some years later, in his famous *Report on Radiation and the Quantum-Theory* of 1914, Jeans had changed his attitude toward quantum theory and did not mention this result.[88] What makes this omission even more significant is that Jeans here defended practically the same argument that Einstein gave in 1909—which we will discuss at once—, but without quoting him:

> Any attempt to refer back the atomicity of e to the structure of the ether simply discloses the fact that the fundamental equations of the ether are not yet fully known; it implies that if they were fully known they might be expected to contain the quantity e, and this is perhaps the same thing as saying that they would contain the quantity h. It may be that if the equations of the ether were fully known they would be seen to involve the quantum-theory.[89]

For Jeans the possibility of associating the atomicity of the charge with the quantum of energy was still alive in 1924, when he published the second edition of his *Report*.[90] The quoted text remained unchanged after a decade of further developments of quantum theory.

As we have said, Einstein took up Jeans's demonstration in his 1909 paper on the radiation problem but modified it at some points. The most important difference is that he did not assume that the radiation density would depend on the electron mass. This difference renders Ehrenfest's objections invalid, because now there is, according to the Π theorem, only one possible dimensionless monomial. (This does not mean Einstein was aware of the controversy that his colleagues had maintained; we have not found any evidence in this respect.[91])

In a cavity filled with gas molecules, radiation, and ions—the latter allow the energy exchange between the former—, the quantities that—according to Einstein—should be included as arguments of the spectral density are:

RT/N: energy of a molecule (dimensionally speaking),
c: speed of light,
e: quantum of electricity,
ν: frequency.

Only attending to the dimensions of the density of radiant energy r, which are[92] $ML^{-1}T^{-1}$, it can be seen that r must have the form:

$$r = \frac{e^2}{c^4}\nu^3 \Psi\left(\frac{Ne^2}{Rc}\frac{\nu}{T}\right). \tag{57}$$

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[88] Jeans (1914).

[89] Ibid., p. 81.

[90] Jeans (1924).

[91] See also Einstein to H.A. Lorentz, 30 March 1909 (Klein et al. 1993, Doc. 146), where Einstein also refers to Jeans's argument. Einstein and Ehrenfest met in person only a few years later, in 1912, see Klein (1985, Chap. 12), and also Sauer (2007, pp. 172–175).

[92] Einstein wrote ρ instead of r and ϵ instead of e. Now $[e] = L^{3/2}M^{1/2}T^{-1}$.

This is the only possible combination to establish a dimensionless relation for r with the quantities considered by Einstein. Expression (57) is none other than Wien's displacement law, cp. Eq. 44. Comparing now this result with Planck's radiation law,

$$r = \frac{\alpha \nu^2}{c^3} h\nu \frac{1}{e^{\frac{h\nu}{\kappa T}} - 1} \tag{58}$$

(α is a dimensionless factor, cp. Eq. 1), Einstein arrives at:

$$h = \frac{e^2}{c} \quad \text{and} \quad \kappa = \frac{R}{N}. \tag{59}$$

He then observed that the first relation differs from the known results by three orders of magnitude, which in his opinion can be attributed to dimensionless factors. Similar to the way Jeans did it, he speculated about the possibility of reducing the "light quantum constant h" to the "elementary quantum of electricity e" and thus about the unnecessariness of introducing new universal constants.

In a letter Einstein wrote to Lorentz in 6 May 1909, he regarded it as highly significant that the displacement law could be obtained through dimensional considerations, and insisted again on the existence of a relation between e and h.[93] But after reading Einstein's paper, Lorentz responded that he did not regard a discrepancy of three orders of magnitude an insignificant one nor did he agree that the radiation law, which should give evidence of the properties of the ether, should include the electronic charge.[94] But that was precisely Einstein's bet in that state of ignorance and confusion about quantum phenomena.

Thus, in his 1909 analysis of the radiation problem dimensional analysis provided an argument for strengthening a thesis shored up by Einstein in conjunction with other fundamental arguments, such as fluctuation analysis. But it appears that Lorentz, whom he admired deeply, had convinced Einstein of the weakness of the dimensional argument to the effect that he forgot about it. A little more than 2 years later, just before attending the first Solvay conference, in autumn 1911, Einstein responded to a question by Michele Besso as to whether he had ever come across a situation where one had to choose between the quantum of action and e^2 in order to introduce "natural units." Einstein responded that one knew that the ratio was a factor of 900 but that he had never come across this in dimensional considerations, as far as he remembered.[95] And in Brussels, he spent no time on this question in his presentation, although the

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[93] A. Einstein to H.A. Lorentz, 30 March 1909 (Klein et al. 1993, Doc. 163).

[94] H.A. Lorentz to A. Einstein, 6 May 1909 (Klein et al. 1993, Doc. 153).

[95] Einstein to Michele Besso, 11 September 1911, in Klein et al. (1993, Doc. 283). The reference to what it is that Einstein did not remember is unclear in the original German. It could be the factor 900, but more likely it is a response to Besso's question: "Der Unterschied zwischen e^2 und h ist ja Faktor 900. Ist mir noch nicht bei Dimensionalbetrachtungen begegnet, soviel ich mich erinnere."

relation between e and h appeared more than once during the meeting.[96] In 1916 Arnold Sommerfeld introduced in the quantum debates the constant of fine structure,

$$\alpha = \frac{2\pi e^2}{hc}, \tag{60}$$

which contains, in a sense, the numerical relation among e, h and c.[97]

Just before going to Brussels to attend the Solvay meeting, Einstein appealed again to dimensional analysis in a paper that was not directly related to radiation. In it, he admitted that, in general, discrepancies in numerical values should be of the order of unity. However, he admitted exceptions.

5.3 Einstein on the quantum theory of solids

In 1907, Einstein had been a pioneer in applying quantum theory to the study of solids. Following his seminal work, Walther Nernst and his collaborators in Berlin demonstrated the wisdom of Einstein's speculations, at least in a broad sense. However, in 1911, it was clear that the theoretical curve deviated from the experimentally observed data at very low temperatures. Einstein then wrote two new papers with an attempt to leave aside the monochromatic normal modes that had characterized his first approach to the problem.[98] (Shortly before, Nernst and Lindemann had proposed an alternative formula, which Einstein quoted in his 1911 papers.) These new developments in the field of crystalline solids culminated in 1912 with the appearance of the famous contributions by Peter Debye, on the one hand, and by Max Born and Theodor von Kármán, on the other.

In the second paper of 1911, Einstein tried to argue that solids must present a set of frequencies related to the coupling among different forced motions of the atoms. In the third and fourth paragraphs we find two other instances of dimensional analysis.

Here Einstein used it to derive an expression for the proper frequency of an atom in a solid, which he had given already in his earlier paper. He obtained a satisfactory result, since the dimensionless coefficient, which still had to be determined, is of the order of unity (both in the case of his formula and in the case of the Nernst–Lindemann formula). In addition, he used the opportunity to show that Lindemann's formula for the melting temperature of a solid also is in agreement with dimensional arguments.

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[96] Langevin and Broglie (1912, pp. 75–76, 131).

[97] In the late 1940s, Pauli concluded his contribution to the Schilpp volume *Albert Einstein Philosopher-Scientist* with a comment on Einstein's 1909 paper. He observed that "the present form of quantum mechanics is far from anything final, but, on the contrary, leaves problems open which Einstein considered long ago." In the 1909 paper, Pauli continued, Einstein "stresses the importance of Jeans' remark that the elementary charge e, with the help of the velocity of light c, determines the constant e^2/c of the same dimension as the quantum of action h (thus aiming at the now well-known fine structure constant $2\pi e^2/hc$)." But the development of physics had not produced an understanding of the elementary charge flowing from a quantum theory. The determination of the fine structure constant therefore, was "certainly the most important unsolved problem of modern physics" (Schilpp 1949, p. 158).

[98] Einstein (1911a) and Einstein (1911b). These papers are discussed in Bridgman (1922).

In the last section, Einstein tried to find an expression for the thermal conductivity K. Using the dimensional method described earlier in the same paper, he arrives at the following functional dependence[99]:

$$K = C\frac{\nu}{d}\varphi\left(\frac{md^2\nu^2}{\kappa T}\right) \tag{61}$$

(m is the mass of an atom, d the interatomic distance, ν the oscillation frequency and C a constant). In order to determine the function φ Einstein appealed to recently published measurements by Arnold Eucken, which indicated a dependency of K with the inverse of temperature. Accordingly, the final expression should be:

$$K = C\frac{m\mathrm{d}\nu^3}{\kappa T}. \tag{62}$$

This combination of dimensional analysis with an empirical law (referred only to one of the involved quantities) represents, in our opinion, an interesting example of how fruitful this procedure can be.

In this section we have shown another example—the third—in which Einstein used a suitable analyzing method for exploring new territories. Therefore, he used dimensional analysis in radiation, solids, and gases.

We conclude our analysis of Einstein's use of the method of dimensional analysis with a comment on Tatiana Ehrenfest, who, in fact, published a number of papers on this problem. Indeed, in August 1925 she signed a paper, which contains explicit criticism of Einstein's use of dimensional analysis in 1909 and which was communicated to the *Philosophical Magazine* by her husband. In her paper, Tatiana Ehrenfest juxtaposed the method of dimensional analysis with what she called the "theory of similitudes," the latter being based on a mathematical analysis of transformation properties of differential equations. In her comparison, she criticized the use of dimensional analysis in physics as being often misunderstood in its deductive power. The theory of similitudes, in contrast, she commended for being capable of producing definite and reliable results, provided two rules were followed. According to these rules, one needs to consider all "fundamental equations" and one must not introduce "conditional equations" except those that follow from the transformation properties of the fundamental equations. In her concluding paragraph, she attributed value to the method of dimensional analysis only in the case that the theory of similitude is not applicable:

> However, if the fundamental equations of the two problem are unknown, of the two methods there remains only dimensional analysis. It must never be forgotten that in such cases one advances only gropingly, and without experimental or theoretical proof from another quarter one can never be completely certain of the results. Dimensional analysis combined with proof of this kind may be viewed as a systematic method for determining whether in the given problem new and unknown fundamental equations take part which are non-homogeneous relative

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[99] Einstein wrote τ instead of κT.

> to the quantitites considered; i.e., which involve dimensional coefficients or new variables.[100]

Interestingly, she added a footnote here at the end of her paper, in which she referred to Einstein's 1909 paper as providing "a pretty example of such an application of dimensional analysis." However, the reference is not to the example that we have discussed above, but to another instance in this paper, in which Einstein used a "simple dimensional consideration."[101] In this example, he argued that according to a dimensional argument the mean squared energy fluctuation $\overline{\epsilon^2}$ comes out non-classically. It appears likely that she added the reference to Einstein's paper as an afterthought. Despite the praise implicit in the final footnote, she referenced the paper once more in a footnote that she added to a statement where she pointed out that by "erroneously […] overlooking one or another of the fundamental equations" or else by "forgetting" interdependencies of the variables, "there may be projected an illusory definiteness of solution." The footnote here says: "This is the case in the example analyzed by Einstein. Footnote of the final paragraph."[102]

We may extend Tatiana Ehrenfest's praise and criticism of Einstein's use of dimensional analysis in 1909 to the example we have discussed above. In an explicit example that she discussed in her paper, she criticized Lord Rayleigh to have used an unwarranted additional conditional equation, i.e., relating temperature to the average molecular kinetic energy, in violation of the second rule for proper use of the theory of similitudes: "The equation by which temperature is defined as the average kinetic energy of the molecules is not one of the fundamental equations of the problem; it relates quantities (molecular velocity and molecular mass) which do not occur in any of the fundamental equations."[103]

It is quite possible that Tatiana Ehrenfest added the reference to Einstein's 1909 paper at the suggestion of her husband. In any case, we note that the Ehrenfests had a sophisticated understanding of the intricacies of the dimensional analysis and had well-informed and critical opinions on the status of the results based on dimensional considerations, including those put forward by Einstein. However, it is significant for our purposes that nothing is said in Tatiana Ehrenfest's paper about Einstein's dimensional analysis of 1925.

5.4 The adiabatic transformation and the field of conservative forces

Let's go back to the paper of 1925. In it, Einstein pointed out that the dimensional analysis with his initial assumptions has produced only his research—expression (14)—, but that it is possible to go further without making "doubtful hypotheses."[104] He proposed two independent assumptions, which both lead to the same result. He analyzed

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[100] Ehrenfest (1926).

[101] "einfache Dimensionalbetrachtung" (Einstein 1909a, p. 189).

[102] Ibid., p. 266.

[103] Ibid., pp. 268–269.

[104] "ohne Setzung irgendwie zweifelhafter Hypothesen" (Einstein 1925b, p. 20).

how the distribution function ρ is modified by an adiabatic compression and by an external field of conservative forces. Referring to both assumptions, he wrote:

> …but they are very natural, and their correctness is made more probable moreover by the fact that they lead to the same result and that they lead to Maxwell's distribution in the limiting case of vanishing quantum influence.[105]

In order to calculate the change of (kinetic) energy during the adiabatic compression, Einstein resorts to the variation of the molecules' momenta in their collisions against the (mobile) walls. Desalvo found it "remarkable" that starting from such assumption "Einstein obtained the correct dependence of kinetic energy on volume."[106] He apparently referred to the use of the relation between the change in kinetic energy and the change in the volume, i.e., to expression (19). To obtain it, Einstein made an intermediate step, in which he wrote

$$\Delta|p_1| = -|p_1|\frac{\Delta l_1}{l_1}. \tag{63}$$

He claimed that this expression is obtained "easily" by applying the laws of elastic collisions. The calculation proceeds indeed straightforwardly from the consideration of energy and momentum consideration for the case of a material particle bouncing off an infinitely heavy moving piston.[107] It is in this way how, invoking the laws of elastic collisions, a correct expression for the dependence of the kinetic energy on volume can be obtained.[108] However, in the previous installments of his quantum gas theory, Einstein had already deduced that the relation between pressure and energy density for the quantum gas was the same as that in the classical gas (see Eq. 4). Starting from this result, one can immediately calculate the variation of kinetic energy with volume, without using (63). Only in this sense was the use of elastic collisions by Einstein justified in the non-statistical paper.

Picking up the comparison we proposed earlier with Ehrenfest's paper, it must be noted that Ehrenfest—in 1911 but also in the subsequent years in which he developed his idea—always referred to adiabatic transformations as pertaining to mechanical systems. Starting from mechanical variations he established connections between (and sometimes discovered) allowed quantum motions. Then, once he had a hold on the possible motions of the system, he calculated the most probable distribution of states among them and, postulating that this was the state of equilibrium, introduced the notion of temperature. The ideal gas has no mechanical invariants, since those can only be defined properly for periodic motion.[109] The adiabatic transformation

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[105] "…dieselben sind aber sehr natürlich, und ihre Richtigkeit wird außerdem noch dadurch wahrscheinlich gemacht, daß sie beide zu demselben Ergebnis führen, und daß sie in dem Grenzfalle verschwindenden *Quanteneinflusses* zur MAXWELLSCHEN Verteilung führen" (Einstein 1925b, p. 20), our emphasis.

[106] Desalvo (1992, p. 525).

[107] Very similar considerations were applied by Hilbert in his use of Ehrenfest's adiabatic hypothesis for the derivation of the black-body energy density, see Sauer and Majer (2009, pp. 484–500).

[108] For an elementary discussion of adiabatic compression at both the thermodynamic and the molecular level, see Miranda (2002).

[109] See Pérez (2009).

considered by Einstein in 1925 is directly applied to a macroscopic system, i.e., to a thermodynamic system, in an analogous way as he proposed to do it—but did not elaborate on—in 1905 with black-body radiation.[110]

It would be wrong to say that Einstein made use of Ehrenfest's adiabatic hypothesis in this paper, since that would imply—at the very least—that one had identified connected allowed quantum motions. His procedure is closer to the demonstrations of Wien's displacement law in the late nineteenth century.

More significant is what Einstein assumed in the second path to reduce the number of arguments of the density function. Ignoring again collisions between molecules, he assumed that their motions be governed by Hamilton's equations, i.e., that they follow the laws of classical mechanics. In this case, the stationarity of the density function implies, as was known, its dependence on the Hamiltonian, i.e., on the sum of kinetic and potential energy. This result is generally known as Liouville's theorem. Thus, the analysis of the system in an external field allowed Einstein to say something about the dependence of the density on the volume.

Note that due to the failure of the Bohr–Sommerfeld theory to account for many-electron systems, or to the surprising result provided by the experiment of Stern and Gerlach (in the analysis of which Einstein and Ehrenfest themselves had contributed[111]), in early 1925 the validity of Hamiltonian mechanics was seriously questioned. For this reason, it is surprising that Einstein assumed for free particles the validity of classical mechanics. Schematically, these are Einstein's assumptions in this respect:

Interactions between molecules and container walls	Classical elastic collisions
Interactions between molecules	Not taken into account
Free motion of the molecules	According to classical mechanics

These assumptions constitute the definition of an ideal gas. They are, in other words, the necessary assumptions needed to obtain—in statistical mechanics—the relation between total kinetic energy and pressure provided by the virial theorem. Therefore, in utter contradiction to his original intention—and, probably, in awareness of this contradiction—Einstein, it seems, left only one possibility open to right the wrong: statistics. Only in the particular way of counting states, in the transition from mechanics to thermodynamics, could differences between classical and quantum ideal gases be placed.

However, there was another possibility: to build a new mechanics. The first assumption listed in the table was valid in Einstein's theory. The second assumption represents the definition of an ideal gas. Finally, the third and last assumption did not play a decisive role; without it, and using only dimensional analysis, very similar conclusions could be obtained. But Einstein did not make explicit in the paper any conclusion of this kind.

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[110] See Einstein (1905) and the discussion above.

[111] Einstein and Ehrenfest (1922).

6 An ignored attempt

Let us now discuss the immediate contemporary reactions to Einstein's non-statistical paper. First discussions around the question as to how to apply quantization to ideal gases go back to papers by Otto Sackur in 1911, and Hugo Tetrode in 1912.[112] The subject gained attention again in the 1920s, in the course of the developments of theory and also due to the appearance of a widely discussed paper by Ehrenfest and Trkal.[113] The justification of the factorial $N!$ in the partition function was a most widely debated issue. We are not going to analyze this episode here, but refer interested readers to works we have already cited.[114]

Among the physicists who immediately reacted to the appearance of the series of papers by Bose and Einstein, Desalvo mentions Adolf Smekal and Pascual Jordan.[115] Their respective papers were received by *Zeitschrift für Physik* in early July 1925.[116] We find in both papers a favorable disposition toward the new statistics.

On Smekal, a physicist well versed with statistical problems (and also an expert in the meaning and applications of adiabatic transformations), Einstein's third article did not seem to have left any impression. In his paper, he even affirmed that the compatibility of any statistical treatment with the second law of thermodynamics needs the adiabatic invariance of statistical weights.[117] But neither with this point nor with others did Smekal make any explicit reference to Einstein's recent use of adiabatic processes. In an extensive article written for the *Encyklopädie der Mathematischen Wissenschaften*, completed shortly before, he expressed his opinion that the success of the Bose–Einstein approach would be decided by future experiments, i.e., that only future research might corroborate or reject it.[118] This would seem to be a suitable place to mention Einstein's non-statistical arguments in support of the theory, but there is not a single word about them (Smekal gives the reference to Einstein's third paper, but he does not give details nor even refers to any of its content).

The same is true for Jordan, whose interest was focussed on the application of Einstein's new results to the study of the equilibrium between matter and radiation (he also made use of the probability transitions introduced by Einstein (1916a,b). Jordan also cited the third paper but did not engage with its argument.

From Jordan we have available his direct testimony, obtained by Kuhn for the *Archive for History of Quantum Physics*.[119] The German physicist recalled that, during the first half of 1925, there were not many Göttingen physicists particularly interested in Einstein's new gas theory, similar to the way it had happened 20 years before with the hypothesis of light quanta. Nevertheless, during Ehrenfest's annual

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[112] Sackur (1911) and Tetrode (1912a,b).

[113] Ehrenfest and Trkal (1920).

[114] For instance Darrigol (1991) and Desalvo (1992).

[115] Desalvo (1992, pp. 529–531).

[116] Jordan (1925) and Smekal (1925).

[117] Smekal (1926).

[118] Smekal (1926, p. 1214).

[119] Interview with P. Jordan by T.S. Kuhn, 18 June 1963. Microfilm transcription in AHQP/OHI-3.

visit to Göttingen he provoked a debate about the new statistics. It is likely that in a presentation,[120] besides explaining his own analysis of the fluctuations (which a little later would turn into a publication, and which Jordan would translate into the quantum—matrix—formalism[121]), Ehrenfest elaborated on various aspects of Einstein's theory, such as the loss of independence of molecules or the abrupt increase of concentration in the fundamental state below a certain temperature. We do not know whether he mentioned any of the arguments of Einstein's third non-statistical paper.

Planck and Schrödinger were more involved in the debates around the ideal gas and its quantum theory. Both authors published papers soon after the appearance of those by Einstein. Planck presented a communication to the Prussian Academy on 2 February 1925, less than a month after Einstein had presented his third paper.[122] Far from being a reaction to Einstein's theory, Planck recapitulated his previous works, in response to the experimental results by Stern and Gerlach. According to his opinion, the experiments with silver ions had proved that under certain conditions only certain paths in phase space were admissible. With this statement, he was renouncing the kind of quantization that he had defended in his second theory, where only the emission process was quantized, but not the absorption nor the mechanical motion itself.

At the end of his paper, Planck commented on Einstein's theory, pointing out its prediction of a loss of statistical independence of molecules. He neither criticized nor supported the new approach, and limited himself to the remark that the experiments will put it into its right place. But he also pointed out that it would imply a "fundamental modification" of the current ideas on the nature of molecules.

Some months later, and after he had presented on July 23 to the Academy a paper by Schrödinger on the statistical entropy definition for the ideal gas,[123] Planck went back to the question of the entropy of an ideal gas and to Einstein's new theory.[124] Here, as in his last paper on the subject published in *Zeitschrift für Physik*, Planck only referred to the definition of entropy, that is, to the problem of counting and assigning probabilities.[125] But in these papers, with which Planck closed a long series of works dedicated to the study of the ideal gas under the new light of the quantum theory, there is not a single reference to the theoretical tests proposed by Einstein in his third paper.

Something similar happened in the case of Schrödinger.[126] Recall that it had been Einstein's theory, and the ensuing epistolary exchange between both physicists, which had turned Schrödinger's attention to de Broglie's work. The most significant paper of Schrödinger, for our present concern, is "on Einstein's gas theory."[127] In it, he arrived at the same results achieved by his colleague, but he applied Boltzmann's statistics to waves à la de Broglie, i.e., he treated particles as excitations. In the interesting paper

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[120] See footnote 142.

[121] See Born et al. (1926), Ehrenfest (1925), and Duncan and Janssen (2008)

[122] Planck (1925b).

[123] Schrödinger (1925).

[124] Planck (1925a).

[125] Planck (1926).

[126] About Schrödinger's work on quantum statistics of ideal gases (and also about Planck's), see Hanle (1977).

[127] Schrödinger (1926b).

that Planck presented on his behalf to the Prussian Academy on July 23, Schrödinger recognized that the compatibility of Bose–Einstein's distribution with Nernst's theorem was an important point in favor of the new theory.[128] In this paper, Schrödinger analyzed different entropy functions which had been used in the past or were being used at the moment.

Einstein himself argued in favor of his theory appealing to the third paper in a letter, with which he answered some of Schrödinger's criticism. Schrödinger's letter, on the other hand, showed that he had not understood the new way of counting which was implicit in Bose's statistics.[129] In his response Einstein had to point out:

> In Bose's statistics, which I use, the quanta or molecules are regarded as *not independent of each other*. [...] I failed to emphasize clearly the fact that here a new kind of statistics is employed, which for the time being is justified by nothing but its success.[130]

And about the third, non-combinatorial paper, he wrote:

> In a third paper, which is currently in press, I lay out considerations that are independent of statistics and that are analogous to the derivation of Wien's displacement law. These latter results have convinced me completely of the correctness of the road to follow.[131]

Once again, Einstein tried to underline the independence of statistics of the arguments in his paper. We will see in the following section that this was also the way he presented them to Ehrenfest.

As far as we have been able to determine, none of the major journals contain papers that called attention to the last installment of Einstein's new theory of the quantum ideal gas, not even in *Zeitschrift für Physik*, where many of the most relevant papers of theoretical physics of those days were published. We think one should bear in mind Jordan's verdict about those days: The statistical treatment of the ideal gas was not anything that particularly worried the physicists.[132] A superficial consultation of other journals seems to confirm this statement.

Neither was there a presentation especially devoted to quantum statistics during the fifth Solvay conference in 1927 (Fermi-Dirac statistics had been born the previous year).[133] In fact, as we will discuss below, it was Einstein who had been asked by Lorentz to give a talk on that subject but he declined the invitation a few months

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[128] Schrödinger (1925).

[129] See Schrödinger to Einstein, 5 February 1925 (AEA 22-001).

[130] "In der von mir verwendeten Bose'schen Statistik werden die Quanten bzw. Moleküle nicht als *voneinander unabhängig* behandelt. [...] Ich verabsäumte es, deutlich hervorzuheben, dass hier eine besondere Statistik angewendet ist, die durch nichts anderes als durch den Erfolg vorläufig begründet werden kann". Einstein to Schrödinger, 28 February 1925 (AEA 22-002). For a French translation of this letter, see Balibar et al. (1992, p. 194).

[131] "In einer dritten Arbeit, die gegenwärtig im Druck ist, werden Betrachtungen gegeben, die von der Statistik unabhängig sind und der Abl. des Wienschen Verschiebungsgesetzes analog sind. Diese letzten Ergebnisse haben mich von der Richtigkeit des eingeschlagenen Weges fest überzeugt" (Ibid.).

[132] See footnote 119.

[133] NN (1928), for an account of the 1927 conference, see Bacciagaluppi and Valentini (2009).

before. Einstein's third paper on quantum ideal gas theory did not have any effect. Nor did the papers that preceded it and that even today constitute the most known and celebrated part of his theory cause an immediate avalanche of reactions.

7 Einstein, Ehrenfest, and the Bose–Einstein statistics

Let us now look at Ehrenfest's role for Einstein's non-combinatorial paper. There are different reasons that make it worthwhile to investigate it. The reference to Ehrenfest in the second paper indicates that both colleagues had discussed the new theory after the publication of its first installment, in July 1924.[134] This reference is not surprising, because in 1924 Einstein and Ehrenfest had a very close relation, both professionally and personally; in fact, since 1920 Einstein had been an official visitor staying in Leiden, coming from time to time to Leiden as a teacher.[135] Moreover, many of the questions Einstein's theory put on the table had been and still were subject of interest to Ehrenfest.

As we have already said, Ehrenfest had penetrated into the analysis of the implicit statistics in Planck's radiation law, comparing it with that underlying in Wien's.[136] Iuri A. Krutkow, one of Ehrenfest's students from his Petersburg years, had elucidated this contraposition, during one of his stays in Leiden together with Ehrenfest, even more in a polemic he maintained in *Physikalische Zeitschrift* with the Polish physicist Mieczysław Wolfke.[137] The contraposition presented by Einstein in 1925 between Boltzmann's and Bose's statistics strongly recalls these papers of the Russian physicist.

In general, it was Ehrenfest who had extracted more information from Wien's displacement law in his quantum researches than anyone else. It has been observed that it was precisely the analysis of Wien's law that had led him to the adiabatic hypothesis.[138] In Einstein's third paper the main character is Wien's displacement law.

In addition, in 1905 Ehrenfest maintained the polemic with Jeans on the dimensional derivation of the displacement law we have analyzed in Sect. 5.2, which inspired Einstein's own derivation in 1909. Hanle suggests, commenting on the statistical works of Schrödinger prior to the formulation of wave mechanics, that what we are calling here Einstein's third paper might be interpreted as a response specifically designed to convince Ehrenfest of the suitability of the new theory. Although Hanle maintains that Ehrenfest's attitude should be taken as representative of that of other physicists, the third paper would be constituted, according to this interpretation, by a new series of arguments put together in order to convince Ehrenfest of the plausibility of the obtained results. This opinion is supported by documentary evidence in some letters.[139]

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[134] See footnote 37.

[135] See Klein (1985) and van Delft (2006) and the Introduction to Kormos Buchwald et al. (2006, pp. xlii–xlvi).

[136] See Sect. 5 above.

[137] Krutkow (1914a,b).

[138] Klein (1985) and Navarro and Pérez (2004, 2006).

[139] See footnote 58.

Not any less important is the talk Ehrenfest gave in Göttingen at the beginning of the summer of 1925. Among other things, he spoke about the new statistics of Bose and Einstein. According to Jordan, Ehrenfest showed himself to be skeptic of the new method.[140] His presence—presumably during June—left its mark in more than one physicist. Max Born referred to it in a letter to Einstein:

> …your brain, heaven knows, looks much neater: its products are clear, simple, and to the point. With luck, we may come to understand them in a few years' time. This is what happened in the case of your and Bose's gas degeneracy statistics. Fortunately, Ehrenfest turned up here and cast some light on it. Then I read Louis de Broglie's paper, and gradually saw what they were up to. I now believe that the wave theory of matter could be of very importance.[141]

In a note in a well-known paper of 1926, in which Born together with Jordan and Heisenberg developed the matrix mechanics formulation of quantum theory, the authors also refer to this talk: "P. Ehrenfest, Lecture in the Göttingen seminar on the Structure of Matter, Summer 1925. The contents of this lecture were of great assistance to our present considerations."[142] According to the context in which this footnote appears, we can assume that Ehrenfest presented the fluctuation analysis he published a few months later.[143]

Nevertheless, we can see in their correspondence that both Einstein and Ehrenfest also rejected the proposal by Bohr, Kramers and Slater. On 9 January 1925, Ehrenfest wrote to his friend:

> If Bothe–Geiger should find "statistical independence" of electrons and scattered light quantum, it would prove nothing. But if they find dependence, then it is a triumph of Einstein over Bohr. This time I believe (but only this time!) firmly in you, that is I would be glad if dependence would be made evident.[144]

Two days later, Einstein responded to a previous letter by Ehrenfest, commenting on the fluctuation analysis of a vibrating string with which Ehrenfest had discussed the dual nature of the radiation suggested first by Einstein in 1909[145]:

> I forgot in my letter to express my agreement with the statistical consideration about the fluctuations of the energy of the subvolume according to the

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[140] See footnte 119.

[141] "Dein Gehirn sieht, weiss der Himmel, reinlicher aus. Seine Produkte sind klar, einfach und treffen die Sache. Wir kapieren es dann zur Not ein paar Jahre später. So ist es uns auch mit Deiner Gasentartung gegangen. Glücklicherweise erschien Ehrenfest hier und hat uns ein Licht aufgesteckt. Darauf habe ich die Arbeit von Louis de Broglie gelesen und bin allmählich auch hinter Deine Schliche gekommen. Jetzt glaube ich, dass die 'Wellentheorie der Materie' eine sehr gewichtige Sache werden kann". Born to Einstein, 15 July 1925 (AEA 8-177). English translation in Born (2005, p. 83).

[142] Born et al. (1926). English translation in van der Waerden (1967); the quote is on p. 380, note 2.

[143] Ehrenfest (1925).

[144] "Falls Bothe–Geiger „statistische Unabhängigkeit" von Elektron und gestreutem Lichtquant finden beweist es *nichts*. Falls sie aber *Abhängigkeit* finden ist es ein Triumph von Einstein über Bohr.—Diesmal glaube ich (ausnahmsweise) fest an Dich, würde mich also freuen wenn Abhängigkeit evident gemacht würde." Ehrenfest to Einstein, 9 January 1925 (AEA 10-100).

[145] Ehrenfest (1925).

> understanding of standing waves. It would probably be good to publish this at some point.[146]

Ehrenfest followed his friend's advice and sent it for publication in August. As mentioned above, its content must have been the core of the talk he gave in Göttingen that summer.

In this paper, Ehrenfest calculated, in different ways, the energy fluctuations of the simple system of a string held fixed in its two ends. In all cases, he used the normal modes with which he had analyzed the black-body radiating cavity more than 10 years before. Thus, he showed and demonstrated a conclusion to which Leonard Ornstein and Frits Zernike had already come earlier: Einstein had supposed that the entropy was an extensive quantity, which is incompatible with a pure wave treatment (because of overlapping of the waves). We will not analyze Ehrenfest's paper here (he already referred to "Bose–Einstein's statistics" and also alluded to the concept—but not the name—of a phonon), but we will refer to recent works that have put it in direct relation to a later analysis by Jordan in which many historians place the origin of quantum electrodynamics.[147] The contradiction demonstrated by Ehrenfest turned, in the hands of Jordan and his quantum mechanical approach, into one of the first demonstrations of complementarity. Both terms in the fluctuation expression, which Einstein had attributed in 1909 to corpuscular and undulatory components respectively, were shown to be necessary consequences of the new mechanics.

In Ehrenfest's paper we see what remained of the old project of publishing a note with Krutkow and Bursian. It is only a footnote:

> The words of the paper by S.N. Bose, Planck's Law and the Light Quantum Hypothesis [ref.], readily create the impression as though Planck's radiation law could be derived from the assumption of *independent* light corpuscles. But this is not the case. Independent light corpuscles would correspond to Wien's radiation law.[148]

It seems that Ehrenfest's influence on Einstein's research during those days was not very significant. From the available evidence we cannot exclude the possibility of additional meetings before the presentation of the second paper, but also in this case it would not appear that there existed a very close collaboration between the two friends. To confirm this impression, we have consulted the Paul Ehrenfest Archives, particularly his correspondence and notebooks.

We have found no evidence of Ehrenfest's concern with the problem of the quantum ideal gas in those months of 1924 and 1925. In his notebooks there are scarcely any annotations on this subject. There are many notes on what appears to be the

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[146] "Ich vergaß, Dir in meinem Briefe zuzustimmen zu der statistischen Betrachtung über die Schwankungen der Energie des Teilraumes nach der Auffassung der stehenden Schwingungen. Es wäre wohl gut, dies einmal zu publizieren". Einstein to Ehrenfest, 11 January 1925 (AEA 10-102).

[147] Duncan and Janssen (2008).

[148] "Der Text der Arbeit von S.N. Bose, Plancks Gesetz und Lichtquantenhypothese [ref.] erweckt leicht den Eindruck, als ob sich das Plancksche Strahlungsgesetz aus der Vorstellung *unabhängiger* Lichtkorpuskeln ableiten ließe. Aber das ist nicht der Fall. Unabhängige Lichtkorpuskeln würden dem Strahlungsgesetz von W. Wien entsprechen" (Ehrenfest 1925, p. 364, note 1). Ehrenfest's emphasis.

calculations for his paper of 1925 on fluctuations.[149] These series of annotations date back to mid-December 1924. Among them we find references to "Einstein's fluctuations" and to the comments of Tatiana to which he referred in the paper.

In the lists of points that indicate something like topics to be treated next we can find references to light quanta, e.g., in this one:

> …
> $h\nu$-corpuscles
> $\delta Q/T$ in Quantumth.[eory]
> …
> Radiat.[ion] Fluct.[uations]
> $1/N! \leftrightarrow$ Gibbs Paradox
> $\rightarrow$ Bose
> …,[150]

In any case, there is not an alluvium of annotations related to the new way of counting introduced by Bose. Certainly, there are isolated annotations on Bothe's works or on Gibbs's paradox and the $N!$-factor, but nothing more.

Let us recall again that the combinatoric observations that Einstein did in his second paper on gas theory did not need any extensive of sophisticated calculations, at least for Ehrenfest, who was deeply convinced that only some kind of dependence among quanta might lead to Planck's law. We would not be surprised if the way, in which Einstein demonstrated the peculiarities of the new statistics was suggested to him by Ehrenfest. But we have no evidence for this possibility.

On the contrary, nothing seems to indicate that Ehrenfest collaborated closely with Einstein in the months between the arrival of Bose's letter and the publication of the third paper.[151] According to him, in those days:

> About my scientific things, all goes so incredibly bad, that I would be very happy if I could already retire![152]

(Ehrenfest was 46 years old). The density of annotations in his notebooks is indeed not very high; but then annotations could have been done in notebooks that no longer exist, and Ehrenfest's tendency to underestimate both his capacities and his achievements is notorious.

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[149] See ENB:1–28 and ENB:1–29, from April 1923 to December 1926. In EHA, microfilms AHQP/EHR-4 and AHQP/EHR-5.

[150] ENB:1-29, probably around 24 December. In EHA, microfilm AHQP/EHR-5.

[151] In a letter he wrote in May 1927, Ehrenfest asked Einstein for offprints of subsequent papers to the second one of the theory of the quantum ideal gas. The non-statistical paper is then the first one he had no offprint of. However, we do not think this coincidence is significant. Ehrenfest to Einstein, 16 May 1927 (AEA 10-164).

[152] Ehrenfest to Joffé, 16 February 1925. In Moskovchenko and Frenkel (1990, p. 186).

8 A rightfully forgotten paper?

This question has two opposite answers, depending on whether one refers it to the reception that Einstein's work had in the months immediately after its publication, or to the attention it has received in later years by historians of quantum physics.

In the first case the oblivion seems understandable. The practically immediate appearance of the revolutionary contributions of 1925 to quantum theory eclipsed any possible interest of Einstein's paper. The arguments it contains only concern the ideal gas from a thermodynamic perspective. But, what is more important, it includes hypotheses that were in open contradiction with the course quantum researches had taken. Many physicists had rejected already the laws of mechanics, and Einstein assumed their validity for describing the motions of the gas molecules.

The papers of the twenties that refer to Einstein's theory usually mention all three installments. This indicates that, in spite of the almost complete lack of comments on it, its existence was known. We are inclined to think that it simply was not of any interest to Einstein's colleagues. Einstein justified the considerations of the non-statistical paper with the deep dissatisfaction over the statistical route by which he had arrived at the new distribution function. However, the problem was not whether his colleagues saw Bose's statistics favorably, but that in the following months the physicists' ideas around the quantum issues changed substantially. Bose's statistics, in spite of implying a way of counting that was incompatible with classical statistics, led to an already accepted result. This was much more than could be said of other attempts of explaining, for example, the Zeeman effect or the multielectronic spectra. This state of affairs appears to be what Niels Bohr was referring to in a postscript he added to a paper, after learning about the result of the Bothe–Geiger experiments, in July 1925:

> The renunciation of space-time pictures is characteristic of the formal treatment of problems of the radiation theory and of the mechanical theory of heat attempted in recent papers by de Broglie and Einstein. Especially in consideration of the perspectives opened up by these papers, I have thought that the discussion presented in the preceding paper might be of some interest, and I have therefore decided to publish the paper without change, although the endeavor underlying it may now seem hopeless.[153]

Although the Bothe–Geiger results supported the light quanta hypothesis before the BKS theory, Bohr insisted on the necessity of giving up the "space–time" pictures. As an example, he gave precisely Einstein's theory of the quantum ideal gas. But Bohr's attitude toward Einstein's quantum theory was biased. He mentioned de Broglie's dissertation and only the first two papers of Einstein's theory. This omission might be deliberate, since the third paper does not fit in that "renunciation" that Bohr alluded to. Einstein's paper begins as follows:

> Motivated by a derivation of PLANCK's radiation formula, which was given by BOSE and which is based stringently on the hypothesis of light quanta, I

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[153] Bohr (1925). English translation in Stolzenburg (1984, p. 206).

> recently formulated a theory of the ideal gas. This theory appears justified, if one proceeds on the assumption that a light quantum differs (apart from its property of polarization) from a monatomic molecule essentially only by the vanishingly small rest mass of the quantum.[154]

As we have seen, Einstein also assumed the validity of Hamilton's equations for the mechanical motion of the gas molecules. Therefore, Einstein took as a starting point what the Danish physicist propagated to "renunciate."

In retrospect, Einstein's initial suspicion about Bose's statistics will turn into one of the first symptoms of his later distancing himself from quantum mechanics. For this reason we find no justification for the neglect of Einstein's paper by historians of physics. Perhaps we are dealing here with Einstein's last attempt to contribute positively to the construction of the quantum theory, for which he had done so much. In addition, this paper closed the circle he initiated in 1905 with the hypothesis of energy quanta. First, the analogy was going one way, now, finally, it was also going the other way. The statistical dependence among light quanta which had limited the analogy with an ideal gas now was found also among molecules. Hence, for the first time the analogy was complete.

In the months before the fifth Solvay conference, which was devoted to photons and electrons, Einstein declined Lorenz's invitation to give a talk on quantum statistics. This happened a bit more than 2 years after his trilogy on the ideal quantum gases was published. These are Einstein's words:

> I recall having committed myself to you to give a report on quantum statistics at the Solvay congress. After much reflection back and forth, I come to the conviction that I am not competent [to give] such a report in a way that really corresponds to the state of things. The reason is that I have not been able to participate as intensively in the modern developments of the quantum theory as would be necessary for this purpose. This is in part because I have on the whole too little receptive talent for fully following the stormy developments, in part also because I do not approve of the purely statistical way of thinking on which the new theories are founded.[155]

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[154] "Angeregt durch eine von BOSE herrührende Ableitung der PLANCKschen Strahlungsformel, welche sich konsequent auf die Lichtquantenhypothese stützt, habe ich neulich eine Quantentheorie des idealen Gases aufgestellt. Diese Theorie erscheint dann als berechtigt, wenn man von der Überzeugung ausgeht, daß ein Lichtquant (abgesehen von seiner Polarisationseigenschaft) sich von einem einatomigen Molekül im wesentlichen nur dadurch unterschiede, daß die Ruhemasse des Quants verschwindend klein ist" (Einstein 1925b, p. 18).

[155] "Ich erinnere mich, dass ich Ihnen gegenüber die Verpflichtung übernommen habe, am Solvay-Kongress ein Referat zu halten über Quanten-Statistik. Nach vielem Hin- und Her-Überlegen komme ich aber zu der Überzeugung, dass ich nicht fähig bin zu einem solchen Referat, das wirklich dem Stande der Dinge entspricht. Der Grund liegt darin, dass ich die moderne Entwicklung der Quantentheorie nicht so intensiv habe mitmachen können, wie es hiezu nötig wäre. Das kommt teilweise daher, dass ich überhaupt receptiv zu wenig begabt bin, um der stürmischen Entwicklung völlig zu folgen, teilweise auch daher, weil ich innerlich die rein statistische Denkweise, auf denen die neuen Theorien beruhen, nicht billige." Einstein to Lorentz, 17 June 1927 (AEA 71-153). In Pais (1982, pp. 431–432).

In that last year Born had proposed the probabilistic interpretation of the wave function. Surely Einstein was thinking of that result, but arguably he must also bear in mind that the only possible characterization of the quantum ideal gas was still statistical.

Ehrenfest shared this rejection. He had noticed several years ago what now appeared clearly in Einstein's theory: If the particles were treated as statistically independent ones the law observed and confirmed in the laboratory could never be derived. But if anything appears with clarity after examining the correspondence between the two friends, and also their publications, it is that not for a glimpse they conceived anything similar to the *indistinguishability* of the particles. That is to say, they always thought in terms of a certain "statistical dependence." What did not even cross their minds was to think that the way of counting introduced by Bose—and, in a certain way, already by Planck—could be, in fact, a new way of counting.

This is more noticeable if we remember the thesis argued by Don Howard.[156] According to him, Einstein was also aware, since 1909, that statistically independent quanta would never lead to Planck's radiation law. Until he received Bose's letter and manuscript, he had never applied the analogy from quanta to molecules. Therefore, indistinguishability was far from being born in 1924. Furthermore, Howard claims that it was entanglement which mainly worried Einstein in the new mechanics, not probability. Expressions used by Einstein, like "incriminated statistics" or "purely statistical way of thinking" as well as the goal of the non-statistical paper we have analyzed support this claim.

However, Einstein became more and more convinced of the good sense of his approach to the quantum ideal gas. He was interested in new experimental results to test the quantum corrections.[157] Only the statistical side deserved contemptuous comments by his author. As he told to Ehrenfest, he tried to ensure the macroscopic (thermodynamic) facts in order to build—or to have an intuition of—the mechanics behind them. Only a new mechanics would square with an ideal gas with such odd properties.

But Einstein's paper also displayed an ambiguity, which also would contribute to his colleagues' lack of interest in his third paper on the subject. The ambiguity comes to the fore in his questioning the very concept of ideal gas, and this questioning was precisely the idea under analysis. For instance, in the introduction to the paper, Einstein announced he would not assume that collisions between molecules are governed by mechanics. In fact, what he did in the paper is, to neglect them, as corresponds to an ideal gas. But neither Einstein nor Ehrenfest appear to have given up the expectation that Bose's counting could conceal some kind of "quantum influence," which prevented one from talking properly of an ideal gas; Einstein considered some kind of "thermal forces."[158] The waves, and particularly the way in which de Broglie introduced them in the quantum treatments, might allow a recomposition of the puzzle into which the ideal quantum gas had turned. Einstein's initial preference for

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[156] Howard (1990).

[157] See Einstein to Kamerlingh Onnes, 4 November 1924; Kamerlingh Onnes to Einstein, 13 November 1924 (AEA 14-384, 14-386).

[158] See footnote 56.

Schrödinger's wave mechanics, in opposition to the matrix mechanics of Heisenberg, Born and Jordan, is as much known as understandable.

The last "positive contribution" of Einstein to statistical physics includes a paper in which he offered arguments independent of the "incriminated statistics," because what nowadays is called Bose–Einstein's statistics was not more, according to its creator, than a calculatory artifice absolutely devoid of any physical meaning. It was simply a consequence of using the wrong mechanics or of not considering some kind of interaction. As Einstein explained to Halpern, it "cannot be considered as giving a true theoretical basis to Planck's law."

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