

OF WEIGHTING AND COUNTING: STATISTICS AND ONTOLOGY IN THE OLD QUANTUM THEORY

Massimiliano Badino

University of Verona

Forthcoming in: Bacciagaluppi, G., Darrigol, O., Freire Jr, O., Hartz, T., Joas, C., Kojevnikov, A. (eds.), *Oxford Handbook of the History of Interpretations and Foundations of Quantum Mechanics*. Oxford: Oxford University Press (expected publication: late 2021).

1. Introduction: Philosophical Preliminaries

“Degrees of freedom should be weighted, not counted.”¹ With this witty paraphrase of Schiller, who was in turn paraphrasing an old Yiddish saying,² Arnold Sommerfeld summarized a fundamental conceptual tension of statistical mechanics. Sommerfeld was discussing the problem of specific heats in gases, one of the “clouds of nineteenth-century physics,” as William Thomson famously dubbed it. In his quip, he was putting his finger on the fact that not always what one counts statistically makes automatically sense from a dynamical point of view.

This tension traverses the entire history of quantum statistics, and this article tries to unfold the main fracture lines. It is often stated that quantum statistics deals with indistinguishable particles or, alternatively, it abandons the notion of an individual particle. It is important for our story to keep these concepts separate. The complex relation between distinguishability and individual identity goes back to Leibniz’s principle of indiscernibles³ and depends essentially on which properties must be considered intrinsic. In general, objects are distinguished by virtue of properties such as mass, color, shape, and so on. However, even if two objects have exactly the same intrinsic properties (say, for example, two identical coins), they still are two distinct individuals. Hence, the

¹ (Sommerfeld 1911 p. 1061).

² In his play *Demetrius*, Schiller referred to votes, while the Yiddish saying referred to words.

³ For a discussion of this point see (French 1989; French & Krause 2006 pp. 15–17). For an overview on the problem of individuality in science see (Dorato & Morganti 2013).

central ontological question is: What confers identity to physical objects? For brevity's sake, let's call the criteria to determine the individual identity an ontology. Thus, an ontology is a way to single out the furniture of the universe.

Classical statistical mechanics rests on the delicate equilibrium between two different ontologies. First, there is the ontology of dynamics or D-ontology for short. According to D-ontology, identity is the unifying element of a continuous dynamical story. Two particles, albeit similar in their intrinsic properties, are two different individuals because they belong to two uninterrupted spatio-temporal trajectories.⁴ Hence, each particle is labeled by a dynamical story whose uniqueness is sanctioned by the Hamiltonian equations of motion. Moreover, the continuity of this story is a necessary condition to ensure individual identity.

In statistics, however, individuals are entities whose permutation generates a new countable event. In other words, individuals are difference-makers: if one swaps them, the ensuing state is statistically different from the original one and must be accordingly counted. While D-ontology rests on the continuity of trajectories, the ontology of statistics or S-ontology rests on the equiprobability of elementary states: states generated by permuting individuals have the same probability. Thus, while the dynamic identity is conferred by persistence over a continuous spatio-temporal trajectory, the statistical identity is ensured by countability under equiprobable events.

This article discusses how this tension panned out in the history of quantum statistics. It is organized as follows. In section 2, I summarize the basics of Boltzmann's statistics and in section 3, I discuss Planck's peculiar use of combinatorics in his radiation theory. I argue that Planck's reluctance to take an ontological commitment toward microscopic particles combined with his opportunistic use of statistics contributed to make the conceptual tension between D-ontology and S-ontology even more problematic. In sections 4 and 5, I analyze how the tension developed in radiation theory and in gas theory in the 1910s. During these developments, it became increasingly clear that Planck's statistics introduced a form of interdependence, but opinions were split whether it had to be interpreted dynamically or statistically. In the epilogue, I briefly discuss the transition to Bose-Einstein statistics.

⁴ (French & Krause 2006 pp. 40–51).

2. Prologue: Boltzmann's Statistics

The name of Ludwig Boltzmann is inextricably linked to the birth of modern statistical mechanics. Although he was not the first one to apply statistics to thermodynamics, he was certainly the first to use combinatorial arguments most notably in his famous 1877 article. To be sure, he had briefly touched upon similar issues at the end of another paper, back in 1868.⁵ On that occasion, Boltzmann calculates the marginal probability for a gas particle to have a certain energy. He assumes that the total energy of a n -particle system can be divided into p elements of magnitude ε . The probability that the energy of an arbitrary particle lies in the interval between $i\varepsilon$ and $(1+i)\varepsilon$ depends on the number of ways in which the remaining energy can be distributed among the remaining particles or, which is the same, the number of ways in which the particles can be distributed over the corresponding energy intervals. In this model, both the particles and the energy intervals are individuals, i.e., a permutation of particles is a countable event. In the general case, the number of ways in which one can distribute n individual particles over p individual boxes amounts to:

$$(1) \quad J(n, p) = \frac{(n+p-1)!}{(n-1)!(p-1)!}$$

Bear in mind this number because it will play a key role in our story.⁶

From an early stage Boltzmann was convinced that statistics and mechanics were tightly interwoven and must play an equal role in the explanation of thermal equilibrium. In the 1870s, he explored multiple strategies and, even when he was not using statistics explicitly, one could see it lurking behind purely mechanical analyses.⁷ But it is in the 1877 paper that combinatorics feature prominently.⁸ While conceived to investigate the relations between the second principle of thermodynamics and probability calculus, this article is historically important because of the role it would play in Planck's blackbody

⁵ (Boltzmann 1868, 1909 p. I, 92–96); for a discussion of this argument see (Badino 2011 pp. 359–360).

⁶ (Boltzmann 1909 p. I, 85). For the details of Boltzmann's combinatorial calculation see (Badino 2009 pp. 83–85; Costantini *et al.* 1996 pp. 284–288; Uffink 2007 pp. 955–956).

⁷ See (Badino 2011). It should be noted that this reading is at odds with the common wisdom according to which Boltzmann followed a purely kinetic approach to thermal equilibrium until he was convinced by his colleague Josep Loschmidt that statistics was inevitable. For the classical interpretation see (Klein 1973; Brown *et al.* 2009). For a general analysis of Boltzmann's works in statistical mechanics see (Darrigol 2018a).

⁸ (Boltzmann 1877, 1909 p. II, 164–223).

theory of December 1900. To fully appreciate this role, it is necessary to dive into the intricacies of Boltzmann's combinatorial models.

In 1877 Boltzmann developed not less than three different combinatorial models whose relations are very revealing of the connections between statistics and ontology. The first and by far most famous model is described through an analogy with tickets drawing from an urn.⁹ Let us assume the total energy of a system of n particles be divided up into p elements of fixed magnitude ε . Let us also assume to have an urn with countless tickets each of which carries a number between 0 and p . Imagine now to make n drawings and at each drawing the corresponding number of elements is attributed to a certain particle and then reintroduced in the urn. After n drawings, one obtains an allocation of energy elements over the particles, which Boltzmann calls a *complexion*. Likely, the sum total of the energies will be larger or smaller than the total energy of the system. In that case, we repeat the entire procedure until we have a large number of acceptable complexions.

Now, Boltzmann notices that, while a permutation of energies between two particles gives a different complexion, it leaves untouched the distribution of energy, thus, assuming that all complexions are equiprobable, the probability of a distribution is proportional to the number of complexions corresponding to it, that is the number of permutations of a complexion. As for the normalization factor, this is the total number of ways of distributing $p + 1$ individual tickets¹⁰ over n individual particles or, which is the same, n individual particles into $p + 1$ individual boxes. This is precisely number (1) above, hence the probability of a distribution is:

$$(2) \quad P = \frac{1}{J(n,p+1)} \frac{n!}{n_0! \dots n_p!}$$

where n_i is the i -th occupation number, that is the number of particles with i elements of energy. By maximizing the probability and letting ε go to zero, Boltzmann finds Maxwell's distribution.

But Boltzmann isn't through with combinatorics. First he toys shortly with a provisional model, which must be rejected because it does not satisfy exchangeability.¹¹ Much later in

⁹ (Boltzmann 1909 p. II, 167–186).

¹⁰ Differently from the 1868 model, here 0 energy is a possible value.

¹¹ (Boltzmann 1909 p. II, 171–172); for a discussion of this model see (Costantini *et al.* 1996 pp. 288–292).

the paper, however, he introduces a third and more interesting urn model.¹² Contrary to the first procedure, he now supposes to make p drawings (with reintroduction) from an urn containing the n particles suitable labelled. At the end of the p drawings, each particle is assigned a number of energy elements equal to the number of times it was drawn. This urn model automatically satisfies the energy constraint, but this is perhaps the least interesting of its features. Although the final result is again a complexion this urn model is statistically very different. At each step, one allocates a single energy element over a certain particle, but the energy elements are statistically non-individual because swapping two drawings does not change the final result. As one makes p drawings, the model consists in distributing p non-individual energy elements over n individual particles. Boltzmann calculates the total number of complexions generated by this model, which turns out to be:

$$(3) \quad J'(n, p) = \frac{(n+p-1)!}{(n-1)!p!} = J(n, p+1)$$

In other words, the total number of ways of distributing n individual particles over $p+1$ individual energy levels is equal to the total number of ways of distributing p non-individual energy elements over n individual particles.

Boltzmann wasn't too moved by what he probably considered a formal coincidence. In hindsight, an argument can be made that Boltzmann is here switching between two different statistics. In the first urn model, individual particles are allocated over *individual energy levels* and each such configuration is equiprobable: the model is ruled by a classical Maxwell-Boltzmann statistics. The third model behaves differently. An elementary configuration is *the number* of energy elements go over individual particles. Hence, a countable event is the permutation of groups of energy elements, which means that they follow a Bose-Einstein statistics. This difference might appear purely formal (after all, the energy levels in the first model are defined by the number of energy elements) and certainly Boltzmann never invites to consider energy elements as distinguishable. However, some writers discussed the possibility that Boltzmann was in fact anticipating the Bose-Einstein statistics.¹³ For Boltzmann, the abundance of formal models was not a philosophical problem, because his statistical mechanics was firmly rooted in the classical D-ontology. There is no doubt that he thought of particles as identifiable by their

¹² (Boltzmann 1909 p. II, 211–214).

¹³ See, for example, (Bach 1987, 1990; Costantini & Garibaldi 1997).

continuous spatio-temporal history. At times he compares molecules to macroscopic individuals,¹⁴ and in the introduction to his *Lectures on the Principles of Mechanics* he states explicitly the continuity principle and declares that “it only allows us to recognize the same material point at different times.”¹⁵ A robust D-ontology constrains the S-ontology and allows Boltzmann to tell apart genuine combinatorial models from formal artifacts. In the next sections we shall see how this natural coupling between the two ontologies was disrupted in Planck’s radiation theory and how physicists at the beginning of the 20th century laboriously searched to restore it in a new form.

3. Enter the Quantum

3.1. Planck’s Program

With few exceptions, Boltzmann himself never made use of his complicated combinatorial model after 1877. He probably regarded it more as an ingenious illustration of the statistical nature of irreversibility than a physically workable instrument. One of the reasons why this model is so famous is that it made a surprising comeback in a completely unrelated ambit: Max Planck’s theory of blackbody radiation.¹⁶

When Planck entered the problem of blackbody, in the late 1890s, it seemed to be a moribund, if not dead, horse. Introduced by Gustav Kirchhoff in 1860 as a formal tool to investigate thermal radiation, a blackbody was conceived as a physical system able to absorb all the radiation impinging on it.¹⁷ As Kirchhoff proved by means of the second law of thermodynamics, the energy distribution of a blackbody is particularly simple because it is a universal function of temperature only. This theorem led not only to construct experimental approximations of a blackbody, but also to find theoretical constraints on the energy distribution such as the Stefan-Boltzmann law and Wien’s displacement law. Increasingly accurate measurements in the mid-1880s showed that the energy distribution was characteristically bell-shaped, which suggested that the radiation law contained an exponential function of the energy and temperature. By cunningly

¹⁴ This analogy, which was customary for Maxwell too, is stated at the beginning of his famous 1872 paper on the Boltzmann equation (Boltzmann 1872, 1909 p. I, 316–402).

¹⁵ (Boltzmann 1897 p. 9).

¹⁶ On the connection between Boltzmann’s combinatorics and Planck’s theory see (Hoyer 1980; Darrigol 1988).

¹⁷ The standard reference on the experimental background of Planck’s theory is (Kangro 1970).

combining thermodynamic, kinetic, and electromagnetic arguments, Wilhelm Wien reached in 1896 an expression for the energy distribution that, apparently, fitted well the existing observations.

Thus, when Planck started to work on the theory of the blackbody, the problem in itself did not offer a theoretical challenge. Planck, however, was aiming at a much larger target. A fierce opponent of Boltzmann's statistical view of irreversibility, he was determined to show that, under certain conditions, a conservative system behaves in a strictly irreversible way. The blackbody was ruled by the reversible Maxwell equations, but, at the same time, it had the traits of an irreversible thermodynamic process. In addition, it was a perfect case for three reasons. First, it was theoretically simple and fairly well-known. Second, the thermal features of the blackbody radiation were independent of the kind of matter-radiation interaction occurring within the cavity. Third, being a purely electromagnetic phenomenon, Planck could eschew all the quandaries related to molecular collisions.

Planck supposed a spherical cavity filled up with radiation and a Hertzian resonator at its center.¹⁸ It is important to notice that the resonator interacts only with the field component nearly at the same characteristic frequency, therefore is not able to change the energy distribution of the cavity. What it does, however, is to make the radiation more spatially uniform by absorbing a plane wave and re-emitting a spherical wave. Hence, at this stage Planck is interested only in the isotropy of the blackbody radiation. By using Maxwell's equations, the resonator equations and reasonable boundary conditions, Planck calculates the field-resonator interaction and its time-reversal to show that the latter does not fulfil the boundary conditions. As the time-reversal is not a physically acceptable solution of the electromagnetic problem, Planck concludes that the field-resonator interaction is a strictly irreversible process.¹⁹

Unsurprisingly, Boltzmann opposed this conclusion. He realized that Planck's argument was embarrassingly flawed, as he summarized in a letter to Felix Klein:

Herr Planck has reversed the exciting wave for a specific case, but he has completely forgotten that the wave prior emitted by the resonator must be reversed

¹⁸ On the details of Planck's theory of radiation see (Kuhn 1978 pp. 72–91; Darrigol 1992 pp. 29–50; Badino 2015 pp. 41–80; Duncan & Janssen 2019 pp. 51–64).

¹⁹ (Planck 1898a, 1958 p. I, 508–531).

as well. From the circumstances that he has obtained a totally counterintuitive formula, he has not concluded that he was wrong, but rather that he had found out a process whose reversal is not possible. I have sent him directly my considerations, a move that will not necessarily shorten the dispute; I'm curious to hear his response.²⁰

Boltzmann also proved that if the time-reversal is calculated correctly, then it is necessarily a physically acceptable solution of Planck's electromagnetic problem. Planck had no choice but to abandon his original project and try to find an alternative route to irreversibility. His new argument, which he developed in 1898 and 1899, hinged on two main pillars.

3.2 Natural Radiation and Entropy

Although badly hit by Boltzmann's criticism, Planck did not give up his thermodynamics-inspired approach to radiation theory. This approach rested on a sharp distinction between physically meaningful macroscopic quantities and the mysterious microscopic world. The former are empirically measurable, slow-varying quantities such as the field intensity and the resonator energy, while the latter is a physically inaccessible and ontologically suspicious realm. More precisely, Planck regarded macroscopic quantities as the time averages of innumerable fast-changing monochromatic field vibrations, which have no independent physical meaning on their own. The statement that the microscopic field vibrations change so rapidly and disorderly that, for the purpose of radiation theory, they can be safely ignored and replaced by their averages is the hypothesis of natural radiation, Planck's first pillar.²¹

To appreciate the ontological role played by natural radiation is instructive to contrast it with kinetic theory. Microscopic field quantities correspond to individual molecular quantities such as position and velocity, while macroscopic quantities are averages such as total energy. Natural radiation is tantamount to stating that molecular dynamics is so complicated and uncontrollable that one might as well black-box much of what is

²⁰ Boltzmann to Felix Klein, 12 February 1898, (Höflechner 1994 sec. 462).

²¹ The hypothesis of natural radiation is first introduced in (Planck 1898b, 1958 p. I, 532–559). For a discussion see (Kuhn 1978 pp. 80–82; Badino 2015 pp. 60–71).

happening at that microscopic level and confine the calculations to macroscopic, measurable quantities.

The second pillar of Planck's theory is the definition of entropy.²² After Boltzmann's radical rebuttal of his first argument, Planck resorted to his opponent's favorite strategy: to show that a certain state function existed, which increases monotonically over time. In order to define electromagnetic entropy, Planck proceeded backwards. He knew that the maximum of that entropy must give Wien's law, which holds at equilibrium. He then worked out an entropy formula that fitted such a requirement and showed that, given natural radiation, the entropy calculated for the combination of the free field and the field-resonator interaction was a monotonically increasing function.²³

3.3 Resorting to Combinatorics

As we have seen, Planck's general argument for irreversibility was tightly related with the fate of Wien's law. At the beginning of 1900, however, Wien's law was being challenged from several quarters. Already in March Otto Lummer and Ernst Pringsheim argued that, at temperature as high as 1800 K and in the region of wavelengths between 12 and 18 μ "the Wien-Planck spectral equation does not represent the black radiation measured by us."²⁴ The situation deteriorated further in October when Heinrich Rubens and Ferdinand Kurlbaum found a marked failure of Wien's law at wavelengths equal to 51.2 μ . Planck was informed in advance and could work out a new energy distribution formula by interpolation,²⁵ but the new law was incompatible with his previous entropy formula. It was at this point that Planck resorted to Boltzmann's 1877 model.²⁶ Much ink has been spilled over Planck's combinatorial argument in December 1900. Here I want merely to recapitulate the key differences with Boltzmann's original procedure.

To find the equilibrium distribution between resonators and free field, Planck assumes the energy divided into quanta of fixed magnitude $h\nu$, so that the total energy to be allocated over the resonators with natural frequency ν_i can be written as $E_i = P_i h \nu_i =$

²² (Planck 1899, 1958 p. I, 560–600).

²³ Because of the formal similarity between Planck's electromagnetic entropy and Boltzmann's H -function, several authors speak of an electromagnetic H -theorem (Kuhn 1978 pp. 72–91; Darrigol 1992 pp. 45–50).

²⁴ (Lummer & Pringsheim 1900 p. 171).

²⁵ (Planck 1900b, 1958 p. I, 687–689).

²⁶ (Planck 1900c, 1958 p. I, 698–706).

$P \varepsilon_i$. If there are N_i resonators with that frequency, the number of ways of distributing the energy quanta is:

$$(4) \quad J(N_i, P_i) = \frac{(N_i + P_i - 1)!}{(N_i - 1)! P_i!}$$

By using (4) as the equilibrium probability and plunging it into the so-called Boltzmann's principle that entropy is proportional to the logarithm of the state probability, Planck arrives at the correct energy distribution law.²⁷

There are two important points to notice about Planck's combinatorial procedure. First, historians have been discussing for years the status that Planck ascribed to the quantum in 1900. While Martin Klein argued that Planck considered the energy elements as discrete indistinguishable units to be allocated individually on resonators, Thomas Kuhn countered that the energy elements can play the same role as continuous and distinguishable energy intervals.²⁸ To be sure, statistics, with some cautions, supports both claims. Remembering equation (3), Planck's equations (4) can be interpreted as the total number of ways of distributing N_i individual resonators over $P_i + 1$ individual energy intervals or P_i non-individual energy elements over N_i individual resonators. The formal ambiguity that worked for Boltzmann's 1877 model, works here as well. Planck was aware of this ambiguity²⁹ and, after all, it fitted perfectly with his thermodynamic approach. As we have seen, Planck's general strategy was to black-box the microscopic part of his theory, so it was just a fortunate coincidence that statistics allowed him to maintain a noncommittal position about the ontology of resonators and quanta.

However, one could argue that, where statistics fails, physics comes to the rescue. In Planck's combinatorial model, the resonators play the role of molecules, so they might be granted individuality: the D-ontology can be applied to them. By contrast, energy elements are not localized, so they cannot be labelled. This brings me to my second point. There is a fundamental ontological fracture between the two parts of Planck's theory and the statistical underdetermination only makes it worse. Clearly, the combinatorial part relies on the analogy between resonators and molecules: it is this analogy that enables Planck to deploy Boltzmann's procedure. But in the radiation part, the elementary entities are the field monochromatic components. In a paper written in March 1900, Planck

²⁷ For the details of Planck's combinatorial calculations see (Badino 2015 pp. 94–98).

²⁸ (Klein 1962; Kuhn 1978, 1984). For a survey of the debate see (Badino 2009; Gearhart 2002).

²⁹ Much later, in a passage of his *Lectures on the Heat Radiation*, Planck makes an explicit reference to the twofold models underlying his combinatorial calculations (Planck 1906 pp. 151–152).

himself warns the reader against a quick analogy between resonators and molecules, for the same reasons above.³⁰ Hence, both the S-ontology and the D-ontology of Planck's theory are ultimately confused and unstable. This instability, as we shall see, is the original sin of Planck's theory.

4. Ehrenfest, Einstein, and the Riddle of Radiation Theory

It is difficult to tell the story of the emergence of quantum statistics. It consists of several seemingly unrelated research lines, exotic ideas, and obscure arguments. It comes as no surprise that, in describing this episode, some writers used the term 'serendipity' to signal the absence of a coherent development.³¹ If we focus on the tension between D-ontology and S-ontology, we can, with a good measure of approximation, single out three reactions to it. First, Ehrenfest and his disciples insisted that Planck's combinatorics called for a radical change in the classical S-ontology. Second, Einstein, albeit in agreement with Ehrenfest's diagnosis, thought that a way out of the impasse was to modify the D-ontology by means of the wave-particle duality. Lastly, Planck shifted his attention from radiation theory back to thermodynamics and tried to justify the new S-ontology as the result of the application of the quantum hypothesis to the ideal gas.

From the very beginning, it was clear that the problem of Planck's theory lied in the mix of combinatorics and quanta. As for the resonator, it seemed to play only a marginal role. Lord Rayleigh, James Jeans, and Hendrick Antoon Lorentz showed that they could be effectively replaced by normal modes of vibration in the free field. Paul Ehrenfest even reinforced this conclusion by showing that Planck's mechanism of resonator-field interaction could not ensure an entropy increase.³² To muddle the situation even more, in 1905 Einstein published a landmark article where he proposed a daring analogy between gas and radiation. By comparing the entropy variations of an ideal gas and a cavity radiation in the Wien regime, Einstein concluded that radiation behaved as if it consisted of corpuscles of energy $E = nh\nu$.³³ Although the idea that the quanta existed in empty

³⁰ (Planck 1900a, 1958 p. I, 668–686); see especially 673-674.

³¹ See, for instance (Delbruck 1980; Bergia 1987). Some writers have described this story as the thermodynamic route to quantum mechanics as opposed to the traditional atomic route (Darrigol 1991, 2002; Desalvo 1992).

³² (Ehrenfest 1905). Ehrenfest's criticism was in fact a bit unfair. Planck's mechanism was not meant as a way to redistribute energy among frequencies, but rather as a spatial equilibrator, a point Ehrenfest would later acknowledge.

³³ (Einstein 1905).

space was too unorthodox to be accepted, Einstein's theory had the merit to give a statistical backdrop to Wien's law and thus rapidly became a useful term of comparison. In particular, understanding the statistical difference between Einstein's and Planck's quanta, became Paul Ehrenfest's main research theme. A loyal follower of Boltzmann and the guardian of the sacred fire of the Boltzmannian statistical mechanics, Ehrenfest pursued this goal with his characteristically obsessive devotion. In 1906, he set out to clarify once and for all what made it possible to obtain the correct radiation law.³⁴ He considered a cavity full of radiation (without resonators) and defined a tridimensional distribution function for the normal modes in terms of their frequency, amplitude, and momentum. He then calculated the maximum entropy for the cavity radiation under the constraints of normalization and total energy. Unsurprisingly, the calculation yielded the Rayleigh-Jeans law, whose validity is limited to the low-frequency regime. Ehrenfest then investigated how the argument could be modified in order to get Planck's law in its stead and concluded that the fixed magnitude of the energy quanta was the key additional constraint. This general analysis convinced Ehrenfest that the quantization was a purely formal device, which somehow had to play a role in the statistical part of the theory. In other words, while quantization of energy was a sufficient condition for Planck's law, Einstein's corpuscularization was not. For Ehrenfest, it was a matter of finding the correct S-ontology implicit in Planck's combinatorics, while the D-ontology was secondary.

In the meantime, Einstein was working in a different direction. He also realized that quantization was a sufficient condition, but insisted that the solution of the mystery lied in the physics. These thoughts led him to formulate a hypothesis possibly even more destabilizing than the light quantum. In 1909, Einstein argued that if we calculate the fluctuation of the cavity radiation using Planck's law, the resulting formula is made of two parts: a classical expression for the interference of waves and the fluctuation generated by a system of independent particles.³⁵ To Einstein, this weird cohabitation meant that classical D-ontology underlying statistical mechanics had to be supplemented with some interaction mechanism between the particles whose deep nature was hidden in their undulatory features. Convinced of the corpuscular structure of radiation, Einstein argued

³⁴ (Ehrenfest 1906); for a discussion see (Navarro & Pérez 2004 pp. 101–102).

³⁵ (Einstein 1909). On Einstein's work in radiation theory see (Duncan & Janssen 2019 pp. 94–107).

that quanta were physical individuals, but their individuality had to be negotiated with a wave aspect.³⁶

Ehrenfest thought differently. During the late 1900s, he worked intensely on the problem of radiation trying to understand why Planck got the right answer although his combinatorics was incompatible with Boltzmann's.³⁷ The breakthrough happened in 1911, when he proved that quantization was not only sufficient for Planck's law, but it was in fact necessary.³⁸ Near the end of the article and almost in passing, Ehrenfest finally hit the nail on the head. The key difference between Einstein's and Planck's quanta was that the former were independent, while the latter manifested an non-classical statistical interdependence. Planck's peculiar twofold derivation of the radiation law (see section 3.3) had masked the fact that quanta are statistically very different from gas molecules. To clarify this point, Ehrenfest argues, it suffices the following consideration. In Einstein's combinatorics, if a particle has, say, n quanta of energy, this is the result of receiving one quantum in n independent attributions. By contrast, if a resonator has n quanta, they have been allocated together so that the individual quanta making up the total energy are interdependent. This is of course reminiscent of Boltzmann's third model, but the fact that the quanta do not vanish makes the key difference. Ehrenfest realizes that this simple fact changes the S-ontology radically because it introduces a new countable event: a permutation of an entire bunch of quanta changes the state. This point is best formulated in an article authored with Kamerlingh-Onnes: "The real object which is counted remains the number of all the different distributions of N resonators over the energy grades $0, \varepsilon, 2\varepsilon, \dots$ with a given total P ."³⁹

Thus, the discussion on Planck's radiation theory generated two research paths, which, albeit closely related, were often seen as competing. Some scholars such as Ehrenfest and Władysław Natanson⁴⁰ focused primarily on unearthing the S-ontology hidden in the ambiguities of Planck's combinatorial procedure. By contrast, for other physicists like

³⁶ The commitment toward an enlarged D-ontology marked Einstein's work in radiation theory, see for example his 1916-17 theory of emission and absorption in which he attributes a momentum to light quanta (Einstein 1917).

³⁷ Ehrenfest's research notebooks registered his strenuous efforts to cope with the statistical puzzle. Particularly in note 843, written on 21 March 1911 (of the Russian Calendar), he expresses all his frustration that Planck's procedure "must be wrong", and still leads to the correct result ("but how", double underscore). See (Navarro & Pérez 2004 p. 119).

³⁸ (Ehrenfest 1911). For a detailed analysis see (Klein 1970 pp. 245–251; Navarro & Pérez 2004 pp. 110–118).

³⁹ (Ehrenfest & Kamerlingh Onnes 1915 p. 873).

⁴⁰ (Natanson 1911); on Natanson's very interesting analysis see (Kokowski 2019).

Einstein understanding the D-ontology was much more illuminating. An illustration of how detached these two paths could become is given by the short dispute between Mieczyslaw Wolfke and Georg Krutkow. A follower of Einstein, Wolfke published two short communications in which he proposed to treat Einstein's light quanta as "light atoms" that can be dynamically labelled and combinatorially treated in order to obtain Planck's law. Krutkow, who was a student of Ehrenfest, replied that Einstein's light quanta were independent and, as such, could not be correctly treated by Planck's combinatorics. Taken by surprise, Wolfke argued that Einstein's quanta were *existentially* independent, but *spatially* interdependent, that is, they, presumably, were individuals connected by some sort of physical interaction.⁴¹ Krutkow did not pursue the discussion further, because it was obvious that they saw the ontological problem from two very different perspectives.

5. The Issue of Entropy Extensivity

5.1 Early Attempts at Gas Quantization

During the 1910s, the quantum was applied to atoms in two circumstances. One was, famously, the construction of atomic models by Bohr and Sommerfeld. The other was the much less famous, but not less important attempt at formulating a quantum theory of the ideal gas. To understand the contest of this attempt, a little detour into physical chemistry is necessary.

The most important quantity for calculating equilibrium in chemical reactions is the so-called equilibrium constant, which is the ratio between forward and backward rates. At the end of 19th century, by applying thermodynamics to chemistry, Jacobus Henricus van 't Hoff and Josiah Willard Gibbs managed to find connections between the equilibrium constant, temperature, and maximum work, but failed to give a direct method to measure it from calorimetric data.⁴² The problem was that classical thermodynamics provided no tools to determine integration constants. A breakthrough happened in 1906 with Walther Nernst's heat theorem which entailed a zero value for the integration constant of entropy. Unfortunately, Nernst's arguments cannot be applied to gases, thus a workaround had to be found. Nernst noticed that the van 't Hoff equation for a gas could be solved by

⁴¹ (Krutkow 1914; Wolfke 1913a, 1913b).

⁴² For a survey on the problem of chemical equilibrium and its relation with thermodynamics see (Badino & Friedrich 2013 pp. 299–302).

exploiting a relation between its integration constant and the Clausius-Clapeyron equation, which gives the pressure of a gas in equilibrium with a condensate. The integration constant of the van 't Hoft equation was dubbed by Nernst the chemical constant.

While this further change of constant set a different experimental problem, it did not necessarily ease the experimenter's task because it was difficult to measure chemical constants at temperatures low enough to have an equilibrium with a condensate. Somewhat unexpectedly, help came from quantum theory. In the third edition of his *Lectures on Thermodynamics*, Planck stressed that, in combination with Nernst's heat theorem, quantum theory entailed that it was possible to express the entropy constant in terms of universal quantities.⁴³ This hint was picked up by Otto Sackur, who spotted a theoretical relation between the chemical constant of a gas and its entropy constant.⁴⁴ The problem was thus reduced to find a quantum expression of the entropy of a gas. From a theoretical standpoint, however, the application of the quantum hypothesis to the ideal gas is far from trivial, the reason being that quantization requires a natural frequency, while there is no such thing for gas molecules. Sackur circumvented the obstacle exploiting another of Planck's hints. In the *Heat Radiation*, Planck had noticed that the fixed magnitude of the energy element entailed a partition of the phase space of a resonator into 'elementary regions'. Sackur's simple but brilliant idea was to transfer this procedure to the phase space of a gas and then apply Boltzmann's combinatorial approach to arrive at an entropy formula.⁴⁵ It worked surprisingly well and Sackur managed to find an expression for the entropy constant of a monatomic ideal gas, but there was a small problem with extensivity. The nature of this problem is deeply entrenched with the tension between D-ontology and S-ontology.

It is well known from thermodynamics that entropy is additive (i.e., the entropy of a system is equal to the sum of the entropies of its subsystems) and extensive (i.e., it depends on the quantity of the system, for instance the number of gas molecules). Occasionally, these two properties lead to a phenomenon called the Gibbs paradox.⁴⁶ Let's assume a container divided by a partition into two equal volumes filled up with a gas.

⁴³ (Planck 1911 pp. 268–269).

⁴⁴ On Sackur's life and work see (Badino & Friedrich 2013).

⁴⁵ (Sackur 1911, 1912).

⁴⁶ On the physical definition and the philosophical consequences of the Gibbs paradox see (Pešić 1991; Dieks 2018; Saunders 2018); on its history see (Darrigol 2018b).

Let's now remove the partition and let the two amounts of gas mix. Two things can happen. If the gases in both volumes are chemically indistinguishable, the removal of the partition can be performed reversibly and the final entropy is the sum of the initial entropies. By contrast, if the gases in the volumes are different, the mixing process is irreversible, and leads to an additional entropy term, called mixing entropy. The paradoxical aspect of the entire process lies in the fact that the mixing entropy is nonzero even for infinitesimally different gases, but disappears suddenly when they become indistinguishable, a behavior that apparently contradicts the fact that entropy is a state function. In fact, this discontinuous behavior is a consequence of the clear-cut distinction between reversible and irreversible processes. Gas molecules on either side of the partition are *D*-ontologically, and therefore *S*-ontologically, distinguishable regardless of their chemical similarity and their swap counts as a different microstate. This means that some statistical adjustment is necessary to safeguard entropy extensivity in those cases in which, from a thermodynamic standpoint, no mixing entropy is produced. Gibbs solved the issue by introducing a distinction between two notions of statistical description or, in his parlance, phase.⁴⁷ Although a permutation of molecules makes a difference in *specific* (microscopic) phases, it does not change the *generic* (macroscopic) phase.⁴⁸ Sackur's method to save extensivity was more cumbersome, but consequential nonetheless. He supposed to divide the volume V of the gas into N/n independent sub-volumes v , N being the total number of molecules and n the molecules contained in each sub-volume. As the sub-volumes are arbitrary, Sackur is in fact introducing an interdependence between the size of the elementary regions and the number of molecules.

In one of those odd coincidences that occasionally occur in history of science, the seventeen-year old Hugo Tetrode published, almost at the same time, an alternative approach to the same problem.⁴⁹ Tetrode's solution was much more in the spirit of Gibbs' statistical mechanics, although his language was still largely Boltzmannian. Contrary to Sackur, Tetrode works directly with probability and notices that, if the particles are similar and "exchangeable", the definition of probability must be accordingly modified by cancelling out the permutations originated by exchanging similar particles. This entails that the Boltzmannian probability must be corrected by a division by $N!$, where N is the

⁴⁷ (Willard Gibbs 1902 p. 187).

⁴⁸ On the importance of the concept of generic phase for indistinguishability see (Saunders 2020).

⁴⁹ (Tetrode 1912b); see also (Tetrode 1912a)}. On Tetrode's life and work see (Dieks & Slooten 1986).

number of particles. This ‘corrected Boltzmann counting’ as we call it today, is introduced by Tetrode as a straightforward consequence of Gibbs’ distinction between specific and generic phases.

The duality in gas theory reminds the duality we already observed in radiation theory. Once again, physicists were split between focusing on the S-ontological side of the problem or rather looking for a D-ontological solution in terms of definition of physical identity.

5.3 Planck’s Quantum Theory of the Ideal Gas

In the second edition of the *Heat Radiation*, Planck had stressed that the fixed size of the phase space cell and the absolute meaning of entropy were the distinctive features of quantum theory.⁵⁰ Thus, when Sackur’s published his idea of an interdependence between elementary regions and number of molecules, Planck received it sympathetically. In particular, he saw Sackur’s idea hinging upon a point which was very important for him: the disanalogy between resonators and gas molecules. He first elaborated on this idea in a lecture delivered at the Wolfskehl conference in April 1913. Resonators, Planck argued, occupy a fixed place and they only interact with the free field. Thus, each resonator can be easily identified in space and time. This is not the case for gas molecules, which move and interact with each other by elastic collisions. According to Planck, this entails a difference in the structure of the elementary regions of the corresponding phase spaces. While regions representing the state of resonators are individual ellipses, the elementary regions of each molecule should somewhat depend on the state of the other molecules. This holistic interdependence was the physical reason for Sackur’s correction to attain extensivity.⁵¹

Planck’s argument was indeed sketchy and, unsurprisingly, did not pass the test of Hendrik Antoon Lorentz: it seemed to invoke a mutual determination in position and momenta of the molecules, which was inconsistent both with usual statistical assumptions and with the physical nature of an ideal gas.⁵² These points were well received and Planck refined his approach. He accepted that extensivity could be reached

⁵⁰ See (Planck 1912 sec. 125).

⁵¹ (Planck 1914 pp. 7–8, 1958 p. II, 320–321); on Planck’s quantum theory of monatomic ideal gas see (Badino 2010).

⁵² See (Lorentz 1915).

by dividing the number of complexions by $N!$, but could not force himself to regard this as a mere formal trick. On the contrary, he was convinced that a modification in the S-ontology called for some change in the D-ontology of the gas molecules. In the ensuing years, he concentrated his efforts on the study of the structure of the phase space, a research that brought him very close to the program pursued by Arnold Sommerfeld in atomic theory.

By introducing the partition function, Planck was able to show that the calculation of the most important thermodynamic functions boils down to the computation of the accessible states, which, in turns, depends on how one partitionates the phase spaces into elementary regions.⁵³ In classical statistical mechanics, the elementary regions are infinitesimal in size and are defined by the integrals of motion, but in quantum physics the constant h determines a finite size of the regions. So far, Planck's procedure simply generalized to an arbitrary mechanical system the argument developed for resonator in 1906. But now comes a new step. We need to distinguish, Planck argued, between two formal spaces: one describing the individual state of the system and one describing the physically meaningful states. This difference is introduced to account for a combinatorial fact:

[I]f groups of similar atoms are present in the body (...) a more or less large number of physically equivalent points of the phase space will be ascribed to a certain physical state of the body, because a given point of the phase space of a single individual atom depends on determined coordinates and velocity. As many permutations of the similar atoms are possible, so many phase points will correspond to a given physical state. Therefore, to clarify the expression, I will distinguish between "phase point" [Phasenpunkt] and "state point" [Zustandpunkt].⁵⁴

Sackur's idea of dividing up the formal space into two different ways makes here a second and more sophisticated appearance. Planck states that while the phase space accounts for the individuality of atoms in terms of their Hamiltonian properties of position and momenta, we still need to account for their physical indistinguishability. As this is combinatorially dealt with by cancelling out a corresponding number of complexions, Planck introduces a new formal space, whose elementary regions—or state-regions as he calls them—correspond to an N -dependent cluster of phase regions. Planck's move sounds

⁵³ See (Planck 1916b, 1958 p. II, 420–434) see also (Planck 1916a, 1958 p. II, 386–419).

⁵⁴ (Planck 1916b p. 661, 1958 p. II, 428).

familiar. In his 1899 radiation theory he had affirmed that individual oscillations in the electromagnetic field had no independent physical meaning as opposed to macroscopic quantities. Here, again, Planck expresses a physical difference in terms of individuality and physical meaning.

The conceptual similarities between Planck's radiation theory and his quantum theory of gas did not escape the attention of Ehrenfest. In an article written with Viktor Trkal, Ehrenfest insisted that Planck's absolute entropy approach was wrongheaded. Using Boltzmann's theory of dissociation, they showed that extensivity could be easily recovered as a property of entropy differences rather than entropy itself.⁵⁵ Hence, Planck's abstract distinction between phase- and state-space was unwarranted. One needs to stay with old good thermodynamics and refer entropy to corresponding reversible processes. Extensivity would then come out as a natural output of Boltzmann's theory.

Planck replied almost immediately with an article and, very tellingly, with a brand new section of the fourth edition of his *Heat Radiation*.⁵⁶ As in the Wolfskehl lecture, he moved from statistics back to dynamics and, once again, he exploited the disanalogy between resonators and gas molecules. The former are fixed in space and cannot interact, while the latter are in continuous interaction. This generates an *Austauschmöglichkeit* (exchange possibility), i.e., molecules can be exchanged without altering the macroscopic state. It is important to stress that the physical reason of the *Austauschmöglichkeit* is the series of correlations and symmetries originated by the molecular interaction: “[in the case of gas] we have no system of separate molecules, but a single structure arranged by symmetries and these symmetries consist in the fact that there is no physical mark that allows to single out a certain atom if one considers the gas first in one state and then in the other.”

⁵⁷ Despite the obscure language, it is not difficult to grasp what Planck is after. The correction of the traditional Boltzmann counting entails a sort of D-ontological interdependence between particles that Planck interpreted, much like 1899, as a feature of the mysterious microdynamics of the system. Although he is not explicit about this point, Planck arguably regarded the $N!$ division and the *Austauschmöglichkeit* on a par with the hypothesis of natural radiation: a simplifying assumption to account for the complex microscopic interactions.

⁵⁵ (Ehrenfest & Trkal 1921).

⁵⁶ (Planck 1921a, 1958 p. II, 527–534, 1921b sec. V).

⁵⁷ (Planck 1921b p. 209).

6. Epilogue

Famously, the breakthrough eventually happened in radiation theory. In 1924, Satyendra Nath Bose, an obscure Indian physicist, sent to Einstein a short article in which he proposed a new derivation of Planck's law. Bose's simple yet effective idea was to start with a new definition of countable event, i.e., a distribution of quanta (treated as particle) over cells, and then recast this event in an apparently classical formula:⁵⁸

$$(5) \quad W = \prod_s \frac{A_s!}{P_0^{s_0} P_1^{s_1} \dots}$$

where W is the number of ways of distributing A^i cells over N^j quanta and P_i^s is the occupancy number, i.e., the number of cells containing i quanta. In this way, Bose scaled up the statistical description to a new definition of countable event and a new analogue of the distribution in Boltzmann's statistics. In Bose's S-ontology the cells and not the quanta were statistically independent. Einstein, who arranged the publication, immediately realized the potential of Bose's derivation and applied it to gas theory. He found the Sackur-Tetrode entropy as well as the behavior predicted by Nernst's theorem at low temperature and even a new condensation phenomenon.⁵⁹

Ehrenfest reacted immediately pointing out that the statistical interdependence displayed by the quanta was not new: one could see it at work in Planck's radiation and gas theory all along. Einstein agreed and acknowledged that his new gas theory "expresses indirectly an implicit hypothesis about the mutual influence of the molecules of a totally new and mysterious kind." Now that the S-ontology was more or less clear, it remained to understand the D-ontology, and this was no easy task. Einstein came back to his idea that the mysterious influence could be due to the wave features of the particles. The wave-particle duality had recently found a new support with de Broglie's theory of matter waves. Eventually, the man who put all these strands together was Erwin Schrödinger. An expert of thermodynamics and statistical mechanics, in 1926 Schrödinger treated quantized matter waves like Debye's normal modes thus inaugurating a new undulatory version of quantum mechanics. After the developments in 1924-1926, classical statistics was definitely overcome. Quantum mechanics brought in a new conceptual arsenal made

⁵⁸ (Bose 1924).

⁵⁹ (Einstein 1924, 1925). On Bose's statistics and Einstein's application to the gas see (Monaldi 2009; Pérez & Sauer 2010).

of wave function, eigenvalues, degeneracy, and even a third type of statistics. The search for a new alignment between S-ontology and D-ontology lasted for some more years, but this is another story.

References

- Bach, A. (1987). Indistinguishability or Distinguishability of the Particles of Maxwell-Boltzmann Statistics. *Physics Letters A*, **125**(9), 447–450.
- Bach, A. (1990). Boltzmann's Probability Distribution of 1877. *Archive for History of Exact Sciences*, **41**(1), 1–40.
- Badino, M. (2009). The Odd Couple: Boltzmann, Planck and the Application of Statistics to Physics (1900-1913). *Annalen Der Physik*, **18**(2–3), 81–101.
- Badino, M. (2010). Das Verfolgen einer Idee: Plancks Theorie idealer Gase. In D. Hoffmann, ed., *Max Planck und die moderne Physik*, Berlin: Springer, pp. 135–148.
- Badino, M. (2011). Mechanistic Slumber vs. Statistical Insomnia: The Early Phase of Boltzmann's H-theorem (1868-1877). *European Physical Journal H*, **36**, 353–378.
- Badino, M. (2015). *The Bumpy Road. Max Planck from Radiation Theory to the Quantum (1896-1906)*, New York: Springer.
- Badino, M., & Friedrich, B. (2013). Much Polyphony but Little Harmony: Otto Sackur's Groping for a Quantum Theory of Gases. *Physics in Perspective*, **15**(3), 295–319.
- Bergia, S. (1987). Who Discovered the Bose-Einstein Statistics. In M. G. Doncel, A. Hermann, L. Michel, & A. Pais, eds., *Symmetry in Physics (1600–1980)*, Bellaterra: Universitat Autònoma de Barcelona, pp. 221–248.
- Boltzmann, L. (1868). Studien über das Gleichgewicht der lebendigen Kraft zwischen bewegten materiellen Punkten. *Sitzungsberichte Der Akademie Der Wissenschaften Zu Wien*, **58**, 517–560.
- Boltzmann, L. (1872). Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen. *Sitzungsberichte Der Akademie Der Wissenschaften Zu Wien*, **66**, 275–370.
- Boltzmann, L. (1877). Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respective den Sätzen über das Wärmegleichgewicht. *Sitzungsberichte Der Akademie Der Wissenschaften Zu Wien*, **76**, 373–435.
- Boltzmann, L. (1897). *Vorlesungen über die Principe der Mechanik*, Vol. 1, Leipzig: Barth.
- Boltzmann, L. (1909). *Wissenschaftliche Abhandlungen*, Vols. 1–3, Leipzig: Barth.
- Bose, S. N. (1924). Planck's Gesetz und Lichtquantenhypothese. *Zeitschrift Für Physik*, **26**, 178–181.
- Brown, H. R., Myrvold, W., & Uffink, J. (2009). Boltzmann's H-theorem, its Discontents, and the Birth of Statistical Mechanics. *Studies in History and Philosophy of Modern*

- Physics*, **40**, 174–191.
- Costantini, D., & Garibaldi, U. (1997). A Probabilistic Foundation of Elementary Particle Statistics. Part I. *Studies in History and Philosophy of Modern Physics*, **28**, 483–506.
- Costantini, D., Garibaldi, U., & Penco, M. A. (1996). Ludwig Boltzmann alla nascita della meccanica statistica. *Statistica*, **3**, 279–300.
- Darrigol, O. (1988). Statistics and Combinatorics in Early Quantum Theory. *Historical Studies in the Physical Science*, **19**, 18–80.
- Darrigol, O. (1991). Statistics and Combinatorics in Early Quantum Theory, II: Early Symptoma of Indistinguishability and Holism. *Historical Studies in the Physical Science*, **21**, 237–298.
- Darrigol, O. (1992). *From c-numbers to q-numbers. The Classical Analogy in the History of Quantum Theory*, Berkeley, CA: University of California Press.
- Darrigol, O. (2002). Quantum Theory and Atomic Structure, 1900–1927. In M. J. Nye, ed., *The Cambridge History of Science: Volume 5: The Modern Physical and Mathematical Sciences*, Vol. 5, Cambridge: Cambridge University Press, pp. 329–349.
- Darrigol, O. (2018a). *Atoms, Mechanics, and Probability. Ludwig Boltzmann's Statistico-Mechanical Writings - An Exegesis*, Oxford: Oxford University Press.
- Darrigol, O. (2018b). The Gibbs Paradox: Early History and Solutions. *Entropy*, **20**(6), 443–497.
- Delbruck, M. (1980). Was Bose-Einstein Statistics Arrived at by Serendipity? *Journal of Chemical Education*, **57**(7), 467–470.
- Desalvo, A. (1992). From the Chemical Constant to Quantum Statistics: A Thermodynamic Route to Quantum Mechanics. *Physica*, **29**, 465–537.
- Dieks, D. (2018). The Gibbs Paradox and Particle Individuality. *Entropy*, **20**(6), 466–481.
- Dieks, D., & Slooten, W. J. (1986). Historic Papers in Physics - The Case of Hugo Martin Tetrode, 1895-1931. *Czechoslovak Journal of Physics*, **36**, 39–42.
- Dorato, M., & Morganti, M. (2013). Grades of Individuality. A Pluralistic View of Identity in Quantum Mechanics and in the Sciences. *Philosophical Studies*, **163**(3), 591–610.
- Duncan, A., & Janssen, M. (2019). *Constructing Quantum Mechanics: Volume 1: The Scaffold: 1900-1923*, Oxford: Oxford University Press.
- Ehrenfest, P. (1905). Über die physikalischen Voraussetzungen der Planck'schen Theorie der irreversiblen Strahlungsvorgänge. *Sitzungsberichte Der Akademie Der Wissenschaften Zu Wien*, **114**, 1301–1314.
- Ehrenfest, P. (1906). Zur Planckschen Strahlungstheorie. *Physikalische Zeitschrift*, **7**,

528–532.

- Ehrenfest, P. (1911). Welche Züge der Lichtquantenhypothese spielen in der Theorie der Wärmestrahlung eine wesentliche Rolle? *Annalen Der Physik*, **36**, 91–118.
- Ehrenfest, P., & Kamerlingh Onnes, H. (1915). Vereinfachte Ableitung der kombinatorischen Formel, welche der Planckschen Strahlungstheorie zugrunde liegt. *Annalen Der Physik*, **46**, 1021–1024.
- Ehrenfest, P., & Trkal, V. (1921). Ableitung des Dissociationgleichgewichts aus der Quantentheorie und darauf beruhende Berechnung chemischer Konstanten. *Annalen Der Physik*, **65**, 609–628.
- Einstein, A. (1905). Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt. *Annalen Der Physik*, **17**, 132–148.
- Einstein, A. (1909). Zur gegenwärtigen Stand des Strahlungsproblems. *Physikalische Zeitschrift*, **10**, 185–193.
- Einstein, A. (1917). Zur Quantentheorie der Strahlung. *Physikalische Zeitschrift*, **18**, 121–128.
- Einstein, A. (1924). Quantentheorie des einatomigen idealen Gases I. *Sitzungsberichte Der Preussischen Akademie Der Wissenschaft*, 261–267.
- Einstein, A. (1925). Quantentheorie des einatomigen idealen Gases II. *Sitzungsberichte Der Preussischen Akademie Der Wissenschaft*, 3–14.
- French, S. (1989). Why the Principle of the Identity of Indiscernibles is not Contingently True Either. *Synthese*, **78**(2), 141–166.
- French, S., & Krause, D. (2006). *Identity in Physics: A Historical, Philosophical, and Formal Analysis*, Oxford: Oxford University Press.
- Gearhart, C. (2002). Planck, the Quantum, and the Historians. *Physics in Perspective*, **4**, 170–215.
- Höflechner, W. (1994). *Ludwig Boltzmann. Leben und Briefe*, Graz: Akademische Druck und Verlaganstalt.
- Hoyer, U. (1980). Von Boltzmann zu Planck. *Archive for History of Exact Sciences*, **23**, 47–86.
- Kangro, H. (1970). *Vorgeschichte des Planckschen Strahlungsgesetzes*, Wiesbaden: Steiner.
- Klein, M. J. (1962). Max Planck and the Beginnings of the Quantum Theory. *Archive for History of Exact Sciences*, **1**, 459–479.
- Klein, M. J. (1970). *Paul Ehrenfest*, Vol. 1. The Making of a Theoretical Physicist, Amsterdam: North Holland.
- Klein, M. J. (1973). The Development of Boltzmann's Statistical Ideas. *Acta Physica*

- Austriaca, Supplementum*, **10**, 53–106.
- Kokowski, M. (2019). The Divergent Histories of Bose-Einstein Statistics and the Forgotten Achievements of Władysław Natanson (1864–1937). *Studia Historiae Scientiarum*, **18**, 327–464.
- Krutkow, G. (1914). Aus der Annahme unabhängiger Licht-quanten folgt die Wiensche Strahlungsformel. *Physikalische Zeitschrift*, **15**, 133–136.
- Kuhn, T. S. (1978). *Black-Body Theory and the Quantum Discontinuity, 1894-1912*, Oxford: Oxford University Press.
- Kuhn, T. S. (1984). Revisiting Planck. *Historical Studies in the Physical Science*, **14**, 232–252.
- Lorentz, H. A. (1915). Some remarks on the theory of monoatomic gases. *Proceedings Koninklijke Akademie van Wetenschappen Te Amsterdam*, **19**, 737–751.
- Lummer, O., & Pringsheim, E. (1900). Über die Strahlung des schwarzen Körpers für lange Wellen. *Verhandlungen Der Deutschen Physikalische Gesellschaft*, **2**(12), 163–180.
- Monaldi, D. (2009). A Note on the Prehistory of Indistinguishable Particles. *Studies in History and Philosophy of Modern Physics*, **40**(4), 383–394.
- Natanson, L. (1911). Über die statistische Theorie der Strahlung. *Physikalische Zeitschrift*, **12**, 659–666.
- Navarro, L., & Pérez, E. (2004). Paul Ehrenfest on the Necessity of Quanta (1911): Discontinuity, Quantization, Corpuscularity, and Adiabatic Invariance. *Archive for History of Exact Sciences*, **58**(2), 97–141.
- Pérez, E., & Sauer, T. (2010). Einstein's Quantum Theory of the Monatomic Ideal Gas: Non-statistical Arguments for a New Statistics. *Archive for History of Exact Sciences*, **64**(5), 561–612.
- Pešić, P. D. (1991). The Principle of Identity and the Foundations of Quantum Theory. I. The Gibbs Paradox. *American Journal of Physics*, **59**(11), 971–974.
- Planck, M. (1898a). Über irreversible Strahlungsvorgänge. 3. Mitteilung. *Sitzungsberichte Der Preussischen Akademie Der Wissenschaften*, **1**, 1122–1145.
- Planck, M. (1898b). Über irreversible Strahlungsvorgänge. 4. Mitteilung. *Sitzungsberichte Der Preussischen Akademie Der Wissenschaften*, **2**, 449–476.
- Planck, M. (1899). Über irreversible Strahlungsvorgänge. 5. Mitteilung. *Sitzungsberichte Der Preussischen Akademie Der Wissenschaften*, **1**, 440–480.
- Planck, M. (1900a). Entropie und Temperatur strahlender Wärme. *Annalen Der Physik*, **4**, 719–737.

- Planck, M. (1900b). Über eine Verbesserung der Wienschen Spektralgleichung. *Verhandlungen Der Deutschen Physikalische Gesellschaft*, **2**, 202–204.
- Planck, M. (1900c). Zur Theorie des Gesetzes der Energieverteilung im Normalspektrum. *Verhandlungen Der Deutschen Physikalische Gesellschaft*, **2**, 237–245.
- Planck, M. (1906). *Vorlesungen über die Theorie der Wärmestrahlung*, Barth.
- Planck, M. (1911). *Vorlesungen über Thermodynamik*, 3rd edn, Leipzig: Barth.
- Planck, M. (1912). *Vorlesungen über die Theorie der Wärmestrahlung*, 2nd edn, Leipzig: Barth.
- Planck, M. (1914). Die gegenwärtige Bedeutung der Quantenhypothese für die kinetische Gastheorie. In D. Hilbert, ed., *Vorträge über die kinetische Theorie der Materie und der Elektrizität*, Göttingen: Teubner, pp. 3–16.
- Planck, M. (1916a). Die physikalische Struktur des Phasenraumes. *Annalen Der Physik*, **50**, 385–418.
- Planck, M. (1916b). Über die absolute Entropie einatomiger Körper. *Sitzungsberichte Der Preussischen Akademie Der Wissenschaft*, 653–667.
- Planck, M. (1921a). Absolute Entropie und chemische Konstante. *Annalen Der Physik*, **66**, 365–372.
- Planck, M. (1921b). *Vorlesungen über die Theorie der Wärmestrahlung*, 4th edn, Leipzig: Barth.
- Planck, M. (1958). *Physikalische Abhandlungen und Vorträge*. (M. Von Laue, Ed.), Vols. 1–3, Vieweg u. Sohn.
- Sackur, O. (1911). Die Anwendung der kinetischen Theorie der Gase auf chemische Probleme. *Annalen Der Physik*, **36**, 958–980.
- Sackur, O. (1912). Die universelle Bedeutung des sogenannten elementaren Wirkungsquantums. *Annalen Der Physik*, **40**, 67–86.
- Saunders, S. (2018). The Gibbs Paradox. *Entropy*, **20**(8), 552–576.
- Saunders, S. (2020). The Concept ‘Indistinguishable.’ *Studies in History and Philosophy of Modern Physics*, **71**, 37–59.
- Sommerfeld, A. (1911). Das Plancksche Wirkungsquantum und seine allgemeine Bedeutung für die Molekularphysik. *Physikalische Zeitschrift*, **12**, 1057–1069.
- Tetrode, H. M. (1912a). Berichtigung zu meiner Arbeit: ‘Die chemische Konstante der Gase und das elementare Wirkungsquantum’. *Annalen Der Physik*, **39**, 255–256.
- Tetrode, H. M. (1912b). Die chemische Konstante der Gase und das elementare Wirkungsquantum. *Annalen Der Physik*, **38**, 434–442.

- Uffink, J. (2007). Compendium of the Foundations of Classical Statistical Mechanics. In J. Butterfield & J. Earman, eds., *Philosophy of Physics*, Vol. 2, Amsterdam: North Holland, pp. 923–1074.
- Willard Gibbs, J. (1902). *Elementary Principles in Statistical Mechanics*, Woodbridge: Ox Bow Press.
- Wolfke, M. (1913a). Zur Quantentheorie. Zweite vorläufige Mitteilung. *Verhandlungen Der Deutschen Physikalischen Gesellschaft*, **15**, 1215–1218.
- Wolfke, M. (1913b). Zur Quantentheorie. Vorläufige Mitteilung. *Verhandlungen Der Deutschen Physikalischen Gesellschaft*, **15**(21), 1123–1129.