

# The overcoming of the mechanistic world view in Planck's research around 1900: a comparison with the contributions of Boltzmann, Wien, Rayleigh, Einstein

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**Abstract.** The studies on the spectrum of the cavity radiation around 1900 are analyzed. The originality of Planck's approach is discussed, related to the overcoming of the mechanistic world view, and in contrast with Boltzmann's ideas. It is discussed how Rayleigh and Jeans researches were mainly related with the equipartition theorem, did not search for an expression of the spectrum of radiation, and had no influence on Planck's thought. Finally, the relationship between Planck' and Einstein's contribution is briefly considered.

**Sumario.** Se analizan los estudios sobre el espectro de la radiación de cavidad alrededor del año 1900. Se discute la originalidad de los trabajos de Planck en relación con la superación del enfoque mecanicista, y en contraste con las ideas de Boltzmann. Se subraya que los estudios de Rayleigh y Jeans se desarrollaron con relación al problema de la validez del teorema de equipartición, no buscaron una expresión del espectro de la radiación, y no influenciaron el pensamiento de Planck. Se subraya en fin brevemente la relación entre las contribuciones de Planck y las de Einstein.

**Key words** History of Science, 01.65.+g ; blackbody radiation 44.40.+a

## 1 Introduction

Max Planck is acknowledged for the introduction of the quantization of energy in his usually cited paper of 1900<sup>1</sup>. A faithful analysis of his contribution, in the context of his physical worldview and his line of research since the end of the 19<sup>th</sup> century, shows that such a claim is unjustified. Planck has however the, probably higher, scientific merit of having overcome the mechanistic view and method in physics.

In order to approach this problem, it seems useful to start from the history of Planck's radiation law repeated in every textbook of physics, i.e. that in the year 1900:

- Rayleigh proposed an expression for the spectrum of the cavity radiation based on the equipartition theorem for the normal modes.

- in response to the failure of this formula, Planck introduced a statistical approach based on the quantum of energy.

Both these assertions are actually false. In fact:

- Rayleigh did not propose the expression known as "Rayleigh formula", but merely modified Wien's heuristic exponential law, preserving its exponential behaviour;
- in fact, Planck not even mentioned Rayleigh's paper;
- in 1900 Planck actually published *two papers*, not merely one, in which he derived his law: the **first one** contains a *purely thermodynamic* inference of his formula, while only in the **second one** he adopted a *discretization procedure* (very usual at that time) in order to perform a statistical counting, although he had opposed till then Boltzmann's statistical approach to the second

law.

This paper will be limited to these aspects: the points of view that we will discuss have been extensively developed in previous studies.<sup>2,3,4,5,6,7</sup> The expansion of the electrical industry as the nineteenth century drew to a close was an important context for the prominent role of electrodynamics and its increasingly sophisticated experimental technique. It was only the robustness of knowledge founded in practical experience that made for the explosive power of borderline problems of classical physics.

## 2 Rayleigh, 1900

At the end of the 19<sup>th</sup> century the generally acknowledged law for the spectrum of the cavity radiation was a heuristic expression proposed by Wien in 1896<sup>8</sup>

$$u(\lambda, T) \cdot d\lambda = \gamma \lambda^{-5} e^{-\delta/\lambda T} \cdot d\lambda \quad (1)$$

In his paper in 1900<sup>9</sup>, Rayleigh actually limited himself to propose an empirical modification of Wien's expression (1), preserving its exponential behaviour

$$u(\lambda, T) \cdot d\lambda = \gamma \lambda^{-4} T \cdot e^{-\delta/\lambda T} \cdot d\lambda \quad (2)$$

In fact, on the basis of phenomenological considerations, he concludes that the density of normal modes should be have the behavior

$$T \lambda^{-4} \cdot d\lambda$$

In Rayleigh's words:

«There are reasons to suppose that [this] expression can be more suitable than  $\lambda^{-5} \cdot d\lambda$ , obtained from (1) when  $\lambda T$  is large. »

He concluded that:

«I cannot say if (2) reproduces the observed data as well as (1). »

It is important to add that Rayleigh's main interest was not represented by the radiation field, or the cavity radiation, but instead by the problem of the validity of the equipartition theorem, as we will see at the end of our discussion.

## 3 Planck against Boltzmann: thermodynamics vs. probability

In order to appreciate Planck's research program, one has to recall that at the end of the 19<sup>th</sup> century he opposed Boltzmann's statistical approach. Boltzmann tried to solve the conflict between mechanics and thermodynamics by giving the second law a statistical meaning, while Planck first pinned his hopes on electrodynamics. Has he recalls in his *Scientific Autobiography*<sup>10</sup>:

«Boltzmann knew that my point of view was fundamentally different from his one. He was especially upset for the fact that I was not only indifferent, but in a certain sense *hostile towards atomic theory*, which was at the basis of all his researches. The reason was that, in that moment, *I considered the principle of entropy in-*

*crease as no less immutably valid of the principle itself of the conservation of energy*, while Boltzmann treated it simply as a law of probability. [...] Boltzmann answered the young Zermelo in a tone of bitter sarcasm, that obviously was in part directed to me, since Zermelo's paper had been published with my approval. This was the reason of that malevolent tone that, in other occasion too, Boltzmann kept on showing me, both in publications and in our personal correspondence. It was only in the years of his life, when I informed him of the atomistic basis of my radiation law, that he assumed a more friendly attitude. »

In what concerns his studies on radiation, Planck thought he had found an irreversible elementary process in the absorption and emission of radiation by an electrical resonator, but he had met difficulties, and had finally acknowledged that:

«I had no other alternative than to resume the problem from the beginning, this time from the opposite point of view, from *the side of thermodynamics*: here I felt on my own ground. »

We could conclude, therefore, that before 1900 Planck had already considered, rejected and overcome an approach based on the atomic statistical theory. For him, the search for the thermal radiation law thus took on a central role. Originally Planck had tried to derive a law of Wilhelm Wien for the energy distribution among the different colours of heat radiation from the laws of thermodynamics and electrodynamics. When he needed an additional assumption in his derivation of Wien's law – just like Lorentz had to introduce one when confronting the result of the Michelson-Morley experiment – he found it in a soon-to-be-controversial expression for the entropy of a resonator

$$\left( \frac{\partial^2 s}{\partial \varepsilon^2} \right)^{-1}, \quad (3)$$

where  $s$  and  $\varepsilon$  are, in Planck's absolute conception of thermodynamics, respectively the entropy and energy of a resonator. We will discuss later on the deep physical content of this function. Planck's resonators are simply a specific type of the matter that is supposed to be in thermal equilibrium with heat radiation. There were good reasons to expect that this specification by and large would not affect his argument. In the following we must pay attention to the dates: the experimental results on the spectrum of the cavity radiation were communicated in October of 1900.

## 4 Planck, february 1900: justification of Wien's law

In February of 1900 Planck was able to establish a connection between Wien's formula (1) and the analytic expression of the thermodynamic function (3), i.e. the following expression<sup>11</sup>

$$\left(\frac{\partial^2 s}{\partial \varepsilon^2}\right)^{-1} = -a\varepsilon \quad (4)$$

In fact, integrating with respect to energy gives

$$\partial s / \partial \varepsilon = -1/\alpha \cdot \ln(\varepsilon / \beta),$$

whence, since  $\partial s / \partial \varepsilon = 1/T$ , one gets the energy of the material oscillator

$$\varepsilon = \beta \cdot \exp(-\alpha/T)$$

and consequently the expression of the spectral density

$$u(\nu, T) d\nu = 8\pi\beta / c^3 \nu^3 e^{-\alpha(\nu/T)} d\nu, \quad (1\text{-bis})$$

which coincides with Wien's law (1).

This paper represents a non mechanistic, purely thermodynamic approach to the study of the properties of the radiation field: in fact, it allowed Planck to reach the first derivation of his radiation law eight months later.

## 5 The first paper deducing Planck's law, october 1900

When the experimental results on the spectrum of the cavity radiation showed that the expressions (1), or (1-bis), are incorrect, Planck was well prepared to study a more complicated expression than (4). In the first of the two papers in which he obtained his law<sup>12</sup>, he simply assumed the following expression

$$\left(\frac{\partial^2 s}{\partial \varepsilon^2}\right)^{-1} = -a(\varepsilon^2 + \gamma\varepsilon) \quad (5)$$

whence, by integration

$$1/T \equiv \partial s / \partial \varepsilon = (\alpha/\gamma) \cdot \ln \frac{\gamma + \varepsilon}{\varepsilon} = \frac{\alpha}{\gamma} \cdot \ln \left(1 + \frac{\gamma}{\varepsilon}\right) \quad (6)$$

and finally

$$\varepsilon = \frac{\gamma}{\exp(\alpha/\gamma T) - 1} \Rightarrow u(\nu, T) = \frac{A\nu^3}{e^{B\nu/T} - 1},$$

where the general Wien's law requires for the constants  $\gamma = A\nu$  and  $\alpha/\gamma = B\nu$ .

Planck then concludes:

«...at last I reached the point of constructing an absolutely arbitrary expression for entropy which, though more complicated than Wien's expression, seems to satisfy with the same perfection every requirement of the thermodynamic and electromagnetic theories».

As he recalls in his *Scientific Autobiography*:

«The following morning I received a visit from Rubens. He told me that after the meeting, the same night, he had compared my formula with the results of his measurements and had found good agreement in every point. Lummer and Pringsheim too.»

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## 6 A remark: potential implications of Planck's parameterization

It seems interesting to add some comments on this paper. As we have discussed, Planck rejected the statistical interpretation of entropy, in favour of an absolute interpretation: as a consequence, he could not have paid attention to the fluctuations of the energy of the oscillators. To be sure, statistical mechanics had not yet been introduced in 1900. Nevertheless, had Planck considered this fact, he would have anticipated the wave-particle duality, introduced by Einstein in 1909, precisely on the basis of the fluctuations of the electromagnetic field. In fact, the thermodynamic function (3) has a very important physical meaning in statistical mechanics, since

$$\overline{(\varepsilon - \bar{\varepsilon})^2} = \frac{\int_0^\infty (\varepsilon - \bar{\varepsilon})^2 \cdot W(\varepsilon)}{\int_0^\infty W(\varepsilon)} = -k_B \left(\frac{\partial^2 s}{\partial \varepsilon^2}\right)^{-1}$$

Planck's assumption (5) implies then

$$\overline{(\varepsilon - \bar{\varepsilon})^2} = -A\varepsilon - B\varepsilon^2 \quad (5\text{bis})$$

i.e. the simultaneous presence of a wave and a particle contribution. With this insight, which Einstein published only in 1909 but probably had before 1905, the wave-particle dualism was born, and would determine the subsequent development of quantum theory: Einstein advanced it further in connection with another model, involving a mirror exposed to heat radiation, which executes Brownian motion due to radiation pressure.

In eq. (5bis) the linear term corresponds to the exponential Wien's formula, while the quadratic one leads to the so-called "Rayleigh's formula" (although nobody had introduced it!). Eq. (5) could then be interpreted, *a posteriori*, as an interpolation between Wien's and "Rayleigh's" formulae.

## 7 The second paper on Planck's law in 1900

Let us discuss now Planck's second paper, the unique that is usually cited, in which he tried to give an explanation of his previous result, one that he called an "act of despair" in his Nobel lecture, i.e. to provide a sounder foundation for «the very simple logarithmic expression for the dependence of the entropy of the radiant oscillator, vibrating in a monochromatic way, on its vibration energy». [Eq. (6)]

One could remark that he seems to assign a more fundamental meaning to the thermodynamic parameterisation (6), than to the final law he had obtained. After attempts to derive the mean energy distribution of the resonators by purely thermodynamic arguments had failed, Planck resorted to a statistical method taken over from Boltzmann

$$S = k \cdot \ln W \quad (7)$$

which he adapted in such a way that the mean energy distribution followed first for the resonators and then for

the heat radiation and trying to calculate the different ways of distributing the energy on the material oscillators of different frequencies.

*«In the procedure that follows, it will seem to you that there is something arbitrary and complicated»*

One central element of his paper consists in the introduction of a discretization procedure, in order to calculate the number of different partitions of energy on the material oscillators: that assumption which has been interpreted as the early introduction of energy quantum

«We have now to divide energy over the oscillators of each kind, in the first place the energy E among the  $z_v$  oscillators of frequency  $\nu$ . If we consider E as a magnitude infinitely divisible, the division is possible in an infinity of ways. We however – and this is the most essential point in all the calculation – will consider E as composed of a determined number of equal finite parts, and use then the physical constant  $h = 6,55 \cdot 10^{-27}$  erg·s. This constant, multiplied by the common frequency  $\nu$  of the resonators, gives us the energy element  $\epsilon_0$  in erg; dividing E by  $\epsilon_0$ , we get the number  $n_v$  of the energy elements which must be divided over the  $z_v$  resonators. *When the ratio thus calculated is not an integer, we take for  $n_v$  an integer in the neighbourhood.*»

We have put in italics the last sentence, since it clearly shows that the “energy element” did not have for Planck any physical meaning: although one must justify the fact that at the end he did not let this “energy element” tend to zero. In fact, Planck himself did not imagine a quantum structure of radiation and did not doubt the classical radiation theory.

There is however a second aspect of Planck’s work which must be underlined. Boltzmann’s formula (7) was in fact interpreted at that time together with the expression of probability,  $W = N! / \prod_i n_i!$ . Planck assumed instead the following expression

$$W = \prod_{\nu=1}^k \frac{(n_\nu + z_\nu)!}{n_\nu! z_\nu!}, \quad (8)$$

which had to be interpreted only 24 years later as an approximation of Bose-Einstein statistics.<sup>13</sup>

From (7) and (8) one easily gets

$$\begin{aligned} s_\nu &= \frac{S_\nu}{z_\nu} = \frac{k_B \ln W_\nu}{z_\nu} = \frac{k_B}{z_\nu} \ln \frac{(z_\nu + n_\nu)^{(z_\nu + n_\nu)}}{z_\nu^{z_\nu} \cdot n_\nu^{n_\nu}} \\ &= k_B \left[ \left( \frac{n_\nu + 1}{z_\nu} \right) \cdot \ln \left( \frac{n_\nu + 1}{z_\nu} \right) - \frac{n_\nu}{z_\nu} \cdot \ln \frac{n_\nu}{z_\nu} \right] \\ &= k_B \left[ \left( \frac{\bar{\epsilon}}{\epsilon_0} + 1 \right) \cdot \ln \left( \frac{\bar{\epsilon}}{\epsilon_0} + 1 \right) - \frac{\bar{\epsilon}}{\epsilon_0} \cdot \ln \frac{\bar{\epsilon}}{\epsilon_0} \right] \end{aligned}$$

Deriving this expression with respect to the energy  $\epsilon$  of the oscillator, one gets

$$\frac{1}{T} = \frac{\partial s_\nu}{\partial \bar{\epsilon}} = \frac{k_B}{\epsilon_0} \cdot \ln \left( 1 + \frac{\epsilon_0}{\bar{\epsilon}} \right).$$

that is, just “*the very simple logarithmic expression*” eq. (2). Here he could stop: it was then not necessary to impose the limit  $\epsilon_0 \rightarrow 0$ , although Planck did not add any comment on this.

## 8 The end of the story of “Rayleigh’s formula”: Rayleigh and Jeans, 1905

It may be interesting to complete the story of the so-called “Rayleigh’s formula”. In fact, it appeared in 1905, but with very different physical meanings than usually assumed.

**Rayleigh, 1905.** In fact, Rayleigh published a paper<sup>14</sup> on his research line on the validity of the equipartition theorem. At that time the scientific community was aware of the success of Planck’s law for the cavity radiation. This fact led Rayleigh to remark that

*«For some reason the high modes cannot impose.»*

Deriving the expression of the distribution for the low modes, Rayleigh calculated the density of the normal modes, but made a mistake of a numerical factor 8, since he did not divide for the number of quadrants. Apart from this error, this seems the first appearance of “Rayleigh’s formula”, but it was never conceived as the possible expression of the full spectrum Rayleigh wrote in fact

$$u(\lambda, T) \cdot d\lambda = 128\pi \cdot \lambda^{-4} \epsilon_\nu \cdot d\lambda \quad (9)$$

which, with  $\epsilon_\nu = \frac{1}{2}kT$ , becomes

$$u(\lambda, T) \cdot d\lambda = 64\pi \cdot \lambda^{-4} kT \cdot d\lambda$$

As Rayleigh concluded:

«My result is 8 times higher than Planck’s one» «It seems that we must admit the failure of the equipartition law in these extreme cases»

**Jeans, 1905.** In this paper<sup>15</sup> Jeans corrected the factor 8 in Rayleigh’s result, writing correctly

$$u(\lambda, T) \cdot d\lambda = 8\pi \cdot RT\lambda^{-4} \cdot d\lambda$$

It seems more relevant, however, the very different interpretation that Jeans proposed for this result. He held in fact an opposite view than Rayleigh’s, i.e. that equipartition holds at equilibrium, but equilibrium is not reached (Boltzmann’s 1896 hint). Jeans referred in fact to a hypothesis proposed by Boltzmann in 1896, in order to justify the fact that the internal degrees of freedom do not contribute to the specific heats: Boltzmann had supposed in fact that the exchange of energy between the internal degrees of freedom and the thermal bath is so slow that it never happens in practice. In Jeans’ words:

*«It is obvious that this law [eq. (9)] cannot be the true law of partition of radiant energy which really occurs in nature. The law is obtained from the hypothesis of having reached the statistical equilibrium between the energies of the different wavelengths and matter; the inference that has to be made from the failure of this law to represent natural radiation, is that in natural radiation*

*this equilibrium state is not reached. A similar situation is met in gas theory. Along with the equipartition theorem, the energy of a gas is almost completely absorbed by the internal vibration modes of its molecules, while it is known that in nature only a very small fraction of energy is held by these internal vibrations. We arrive then to suppose that there is not an equilibrium state between the internal vibrations of molecules and their energy of translation; we find that the transference of energy from the translational to the vibrational degrees of freedom is so slow, that the latter never acquire the part of energy that corresponds to them from the theorem of equipartition, since the energy of these vibrations is dissipated as rapidly as it is received from the translational energy of molecules. A similar explanation is suggested from the case of the partition of radiant energy. [...] The radiant energy acquired from the ether, both of short and long wavelengths, is reabsorbed by other bodies, or is irradiated in space, so that the partition of energy really present in ether in every instant is completely different from that predicted from the law of equipartition.*

*From this view, the true radiation law can be obtained only from a study of the process of transference of energy from matter to ether. »*

## 9 From Planck to Einstein and the 1900 revolution

While the knowledge about the energy distribution of heat radiation was firmly rooted in precision measurements combined with laws of classical physics, Planck's statistical arguments could not be anchored in an equally well-established area of classical physics. They owed their substantiation not least to the fact that they gave the correct result: the known law of heat radiation. Planck's radiation formula solved this special problem at the border between electrodynamics and thermodynamics, however this veiled a foundational crisis: the classical picture of a continuum of waves of all possible energies could not be reconciled with Planck's radiation formula. Instead it turned out that totally new, non-classical concepts were necessary to find a physical interpretation for the energy distribution of radiation in thermal equilibrium, as described by this formula. Even the most outstanding results of the masters of classical physics did not yet represent the breakthrough to modern physics: Planck's derivation of the radiation law in particular had as little to do with the beginning of the quantum theory as Lorentz's derivation of his transformation equations can be considered as a first result of relativity theory.

Every attempt to understand the origin of the 1905 revolution will fall short if it does not take this pattern into account. Only against this background does it become clear which specific perspective ever made Einstein concentrate on these borderline problems and

perceive them as challenges. Evidently there were also other points of view, which simply made these look like special problems, presenting no questions of principle about the compatibility of concepts between different subfields of classical physics. For example, Max Planck regarded the problem of heat radiation essentially as a special problem in the theory of heat; Ludwig Boltzmann regarded fluctuation phenomena, like Brownian motion, as problems in mechanics; and for Hendrik Antoon Lorentz the electrodynamics of moving bodies was of concern just to electrodynamics, and not to the foundations of mechanics. Lorentz would be – and also would not be – the initiator of the theory of relativity, Planck would be the father of quantum theory, and Boltzmann the originator of statistical physics, just as Galileo was at the same time a late representative of Aristotelianism and a pioneer of classical mechanics.

It was apparently no accident that the scientific revolution kindled by Einstein in 1905 ignited on the very borderline problems we have discussed. Namely, these borderline problems concern not just any single question, but the overlap zones between the continents of classical physics, where highly integrated systems of knowledge collided. The solutions to the borderline problems of classical physics found by Lorentz, Boltzmann and Planck remained in the conceptual framework of classical physics, even if several of their assumptions and constructions could not really be interpreted in this framework. In contrast, the solutions suggested by Einstein in his revolutionary papers of 1905 broke out of this frame and replaced it with a completely new one, at least in the case of the special theory of relativity.

Einstein's later theory is based on the assumption that, contrary to classical physics, the energy of a single resonator can take on only discrete values. Although the speculative idea of the young Einstein did not anticipate such a break with classical physics, it provides a model whose details could later be made to agree with such new insights. What is more important for our story is that this idea also provided the framework for Einstein's critique of Planck's radiation theory. In fact, soon after formulating his idea Einstein began to have doubts whether resonators with fixed period and damping can bring about the energy exchange in thermal equilibrium. But the first encounter with Planck had placed just that aspect of the problem of radiation at the center of Einstein's attention that was to become one of the germs for the later conceptual innovation: the relationship between heat radiation in equilibrium and the law of equipartition of Energy. The first part of Einstein's light quantum paper shows with the aid of the equipartition theorem of energy that a classical theory of radiation is impossible because it leads to the ultraviolet catastrophe.

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