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Max Planck and the 'Constants of Nature'

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Summary

When at the end of the 1900s Planck introduced the constant h into the black-body radiation law together with constant k, he provided no explanation of either its meaning or why it had that particular value. He simply introduced it. In reality the history of the constant was far from straightforward. Planck was confident enough to introduce it like this because he had been working on the question for over a year. In this paper we reconstruct the process that began with the first two constants (c' and C) introduced by Wien in 1896, continued with the constants a and b obtained by Planck in 1899 and was finally concluded with the constants h and k used by Planck in 1900. The questions that we shall try to answer are as follows.

(1) What is the relationship between these three pairs of constants?
(2) Why, at a certain point in his intellectual development, did Planck decide to introduce new constants with new names and what new meaning did these constants have?
(3) How far and in what way did Planck's considerations on the constants influence the formulation of his famous law?

An historical analysis of this type shows that, despite the simple numerical relationship between the three pairs of constants, the conceptual differences between them were so profound as to require different names even though the value in the case of one constant was the same. We also show how his analysis of the constants pointed Planck in the direction of 'Boltzmann's trend of ideas', allowing him to solve the black-body problem and, at the same time, to arrive at a general definition of entropy.

Contents

It is not we who create the outside world because it is convenient, but the outside world which imposes itself on us with a primal violence. We must insist

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> on this in our positivism-impregnated age. When in the study of any natural phenomenon we move from that which is particular, conventional and causal to that which is general, objective and necessary, all we do is look for the independent behind the dependent, the absolute behind the relative, the perennial behind the transitory. (Planck, 'Von Relativen zum Absoluten', *Physikalische Abhandlungen und Vorträge*, III (Braunschweig, 1958) 157.)

1. Introduction

The origin of quantum theory and the theoretical work of Max Planck are without doubt some of the most quoted episodes in the published histories of quantum physics, for the obvious reason that they are the point of departure of all these histories but, paradoxically, specific studies on Planck and the *annus mirabilis* of 1900 are relatively few and far between[1] as well as differing on a number of points. In our opinion this is linked to the hermetic nature of certain passages in Planck's writings, particularly in the key works of October and December 1900. Faced with these hermetic passages, a number of historians have preferred to offer an exhaustive analysis of the milestones along Planck's path, often resorting to retrospective reconstructions rather than trying to give a general overview of Planck's contribution.

This has often reduced Planck's entire contribution to the black-body problem to the introduction of the 'quantum of energy'. Planck seems to have expressed his opinion on the matter in no uncertain terms, as in his letter of 7 October 1931 to Robert Wood:[2]

> In short I can characterise the entire episode as an 'act of desperation' because I am by nature pacific and unwilling to embark on dubious enterprises. But by then I'd been fighting with the problem of the equilibrium between radiation and matter for six years (from about 1894) without obtaining a result. I was aware that the problem was of fundamental importance for physics and knew the formula for normal spectrum energy distribution. A theoretical explanation had be found at any cost, no matter how high.

These affirmations have sometimes been used as the basis for a number of standard theses on Planck's intervention, including that he found the solution to the black-body problem by interpolating experimental data, purely formal hypotheses or a proved formal analogy between the kinetic theory of gas and the theory of radiation. What we shall attempt to point out here is that a close analysis of the specifics of Planck's research programme shows that his 'act of desperation' was not merely a question of taking a semiempirical formula or formal analogy and working on it, but of making much more profound theoretical choices (like the generalization of the original Boltzmann formula) based on far more general criteria.

This paper attempts to recreate Planck's train of thought between 1899 and 1900

[1] L. Rosenfeld, 'La premiere phase de l'evolution de la theorie des quanta', *Osiris*, 2 (1936), 149–96; M. J. Klein, 'Max Planck and the beginnings of quantum theory', *Archive for History of Exact Sciences*, 1 (1962), 459–479; 'Thermodynamics and Quanta in Planck's Work', *Physics Today*, 19 (11) (1966), 23–32; H. Kangro, *Early History of Planck's Radiation Law* (London, 1976); A. Hermann, *The Genesis of Quantum Theory* (Cambridge, 1969); T. S. Kuhn, *Blackbody Theory and the Quantum Discontinuity 1894–1912* (Oxford, 1978); 'Revisiting Planck', *Historical Studies in the Physical and Biological Science*, 14 (2) (1984) 231–52; J. Mehra and H. Rechenberg, *The Historical Development of Quantum Theory*, 1 (1) (New York, 1982); O. Darrigol, *From c-numbers to q-numbers* (Berkeley, 1992); M. Jammer, *The Conceptual Development of Quantum Mechanics* (New York, 1966).

[2] Planck to Robert Wood, 7 October 1931 (Sources for the History of Quantum Physics).

from a textual analysis of what he actually wrote in the period, trying to interpret the most hermetic passages in his various papers and also focusing particular attention on the footnotes. An analysis of this kind shows that Planck's work has a profound internal unity throughout the entire period (culminating in the discovery of the 'element of energy') and contains everything needed to understand his reasoning and results. One of the keys to interpreting Planck's work and shedding light on the relationships between the various parts involved is, in our opinion, represented by Planck's interest in universal constants. This interest was based on the fact that universal constants provide the whole theory with a 'real physical meaning';[3] moreover they can be used to build a universal system of units of measurement.

The origin of Planck's focus on universal constants is, in our opinion, linked to his personal quest for the 'absolute' in physics. For Planck 'absolute' meant liberating physical concepts from human characteristics and subjective experiences, and this aim is considered by Planck like a fundamental tendency of the development of physics.[4]

We shall also show that Planck's approach to the black-body problem featured a series of pairs of constants. The presence of these pairs of constants in the black-body radiation distribution law was a key criterion for Planck. So much so that it must also have played a leading role in what has been defined as the most difficult step, the decision to use the probabilistic definition of entropy.

The concept of entropy was the cornerstone of Planck's entire theoretical framework. We shall attempt to demonstrate the role played by the resonator entropy condition that Planck derived from Wien's displacement law. Suitably reviewed and reinterpreted, this law provided Planck with a relationship between energy and frequency, justifying the introduction of constant h and its meaning. Furthermore, once the probabilistic definition of entropy *à la* Boltzmann had been defined, Planck showed its applicability and successfully obtained a 'universal' meaning for it which was, as he himself observed, independent of all human practice.

We are aware that parts of this paper can be found in the extensive literature on the subject, but they are needed to present the story coherently.

2. Planck and the quest for the absolute

Before entering into our analysis proper, a brief reconstruction of Planck's concept of scientific research in general and physics in particular is perhaps appropriate. It is in the framework of the latter that the quest for universal constants finds its most profound justification. An eloquent example of what Planck thought the aim of science to be is found at the start of his *Scientific Autobiography*:[5]

> The decision to dedicate myself to science was the direct result of a discovery which has not ceased to fill me with enthusiasm from my early youth. The laws

[3] M. Planck, 'Die Entstehung und bisheringe Entwicklung der Quantentheorie', *Physikalische Abhandlungen und Vorträge*, III (Braunschweig, 1958), 126.

[4] In support of his thesis, Planck recalled past developments in physics research: 'In conclusion we can say that up to now theoretical physics shows a marked tendency towards a unitary system, liberating itself from anthropomorphic elements and sensorial criteria in particular. This conscious renunciation of its fundamental precepts may surprise us and even appear paradoxical, when we remember the importance of sensations as the starting point for every physical study. But despite this, there is no more evident fact in the development of physics' (M. Planck, 'Die Einheit der physikalische Weltbild', *Physikalische Abhandlungen und Vorträge*, III (Braunschweig, 1958), 9).

[5] M. Planck, 'Wissenschaftliche Selbstbiographie', *Physikalische Abhandlungen und Vorträge*, III (Braunschweig, 1958), 374.

> of human thought coincide with the laws which regulate the succession of impressions we receive from the world around us. Similarly, pure logic allows us to penetrate the mechanism of the latter. Which means it is of fundamental importance that the outside world be independent and absolute. The quest for the laws which govern this absolute seem to me to be the most important scientific mission of my life....

This interest encouraged Planck, as he himself recalls, to examine the black-body problem from 1894. Indeed, later in the *Scientific Autobiography*, Planck told of his first contacts with the German Physical–Technical Institute:[6]

> Otto Lummer and Ernst Pringsheim's measurements made at the German Physical–Technical Institute during their studies of the thermal spectrum drew my attention to Kirchhoff's law, which states that in an empty cavity enclosed by completely reflecting walls and containing any number of substances which emit and absorb radiation, a state is reached over time in which all the bodies have the same temperature. And the radiation, with all its properties, including the spectral energy distribution, depends not on the nature of the bodies, but simply and exclusively on the temperature. With the result that this 'normal' spectral energy distribution represents something absolute. And because I always considered the quest for the absolute as the highest of all scientific activities, I set myself actively to work.

Planck's work, as we shall see later, took the form of a research programme which culminated in December 1900 in the law which bears his name. Even if the path followed was tortuous, his programme maintained its original inspiration in the quest for an 'absolute' meaning for entropy.[7] Indeed, Planck was not satisfied with the classical definition of entropy. As he wrote retrospectively in 1908:[8]

> According to Clausius' original definition, entropy is measured by a reversible process, and the weak point of the definition lies in the fact that similar processes can never be reproduced exactly. It could be objected at this point with a certain justification that it is not a question of real processes or even of a physicist in flesh and blood, but an ideal process, of imaginary experiments performed by an ideal physicist handling all the experimental methods with absolute precision.

However, Planck asked himself: 'How far can we take these ideal measurements of ideal physicist?' If they are closely analysed, according to Planck, some appeared 'very doubtful' and others 'surprising', but none was completely free of doubts as to their 'real possibility of execution'.

The solution therefore proposed by Planck was to find a definition of entropy free of any aspects which depended on human experience and therefore above all suspicion. Planck found this solution, as we shall see, in 1900 with the adoption of Boltzmann's probabilistic definition and generalizing it.

This tendency towards the absolute and the complete elimination of all anthropomorphic features from physical concepts (not just from the concept of entropy) therefore represented the underlying guideline for Planck's programme, as

[6] *Ibid.*, 389–90.

[7] On the manner in which, in the concrete, this 'absolute meaning for entropy' was developed see Kuhn (note 1) and Darrigol (note 1).

[8] Planck (note 4), 18.

well as the basis for his philosophy of science. The starting point for the latter lay in the criticism of positivistic concepts and Mach in particular, as is amply documented in the bibliography in the note. In his first popular paper of 1908 Planck wrote:[9]

> Is our physical image of the world exclusively a more or less arbitrary creation of our spirit, or does it reflect real, natural phenomena which are absolutely independent of us? In more concrete terms: can we reasonably believe that the principle of energy conservation was already valid in nature when there were no people to think about it and that the heavenly bodies will continue to move according to the laws of gravity when our Earth was disintegrated with all its inhabitants? ... I answer this question affirmatively, even though I realise I am in disagreement with a certain tendency in natural philosophy deriving from Ernst Mach and which today enjoys wide acceptance in scientific circles. According to this theory there is no other reality outside our sensations, and all natural science, in the final analysis, is nothing but an economic adaptation of our thought, in which direction our fight for survival pushes us. The limit between physical and psychic is exclusively practical and conventional, but the real and only elements of the world are sensations.

Planck therefore reproaches the positivism and philosophy of Mach in particular with having imposed a physical image of the world excessively dependent on human sensations and wills. This conduct, in that it is exempt from 'intimate contradictions', was extraneous to 'the essence of the natural sciences'. He therefore proposed '*the complete detachment of the physical image of the world from the individuality of the mind that creates it*', commenting that 'this is a more precise and better formed definition of which above I have referred to as emancipation from anthropomorphic elements'.[10]

The attempt to liberate science from its anthropomorphic roots can also be seen when Planck approaches the problem of the units of measurement to adopt. In 1899, as we shall see, he proposed for the first time a system of units of measurement free from human interference and particularity which require the use of universal constants contained in its law of radiation. In 1908, Planck wrote:[11]

> So far as the laws of thermal irradiation in the free ether are concerned, it is particularly interesting that their constants, like the gravitation constant, are universal in character and independent of reference to any special substances or bodies. We can therefore use them to establish units of length, time, mass and temperature which necessarily maintain their meaning for all times and for all cultures, even for extra-terrestrial or non-human life forms. This cannot be said of the units in our usual systems of measurement. While they are usually defined as absolute units of measurement, they are in fact too linked to the special conditions of our actual civilisation on Earth.

By the way we can note that a similar position had already been assumed by Stoney in 1874 and by Drude a few years before Planck.

In an article significantly entitled 'On the physical units of Nature',[12] Stoney proposed the need to identify a new system of units of measurement which took

[9] *Ibid.*, 25.
[10] *Ibid.*, 27.
[11] *Ibid.*, 21.
[12] G. J. Stoney, 'On the physical units of Nature', Report of the British Association, Forty-fourth Meeting (1874), published in *Philosophical Magazine*, 11 (1881), 381–90.

account of 'nature as it really is'. To do this in Stoney's view, it was necessary to identify three 'universal constants' and derive from them 'natural' units of measurement for length, mass and time. It was in this quest for 'universal constants' that Stoney gave a new interpretation of the laws of electrolysis (in the light of the theory of valency) and discovered 'a definite quantity of electricity', which Stoney subsequently called the 'electron', according to which the atoms seemed to combine chemically with each other.

This 'definite quantity of electricity'[13] was considered by Stoney to be a 'universal constant', like the *two universal constants* already known, namely c (the speed of light in a vacuum) and G (the universal gravitational constant), and such as to permit the construction of a 'new system of units of measurement'.

Likewise Drude, in a 1897 paper, expressed his hope for the creation of a universal system of units of measurement which in his opinion should be based on the properties of the ether. This is how he expressed the need to liberate units of measurement from human interference:[14]

> There is also the hope that a true system of absolute measurement can be created, which no longer depends on the particularities of our Earth or on the choice of a particular substance, but is related to the universal properties of the ether. The mean free path by an atom of ether could, for example, provide the measure of length, while time could be measured according to the speed of light.

There appear to be no direct links between Stoney, Drude and Planck; however, it is possible to find a common characteristic of these three contributions, that is a general aspiration to liberate science from subjective aspects, also in connection with the problem of the units of measurement to adopt.

However, these attempts limited themselves to choosing the units of measurement, without questioning the adoption of the three mechanical quantities of length, mass and time as base quantities even if, in the same years, this adoption was questioned (above all by Mach and Wilhelm Ostwald).[15] It must also be pointed out that towards the end of the nineteenth century there was also debate, starting with Gauss around 1830,[16] on various practical aspects connected with measurement process, that is on the choice of units common to different nations, on the adoption of units which facilitate calculations and on the shape and material to use for standards.[17] Inevitably these problems also involved the question of the precision of physical measurements.[18] The debate continued along different lines in different countries for the entire nineteenth century.[19] However, both Drude and Planck, and to a certain degree

[13] For which Stoney obtained the value of $e = 10^{-20}$ A (i.e. 10^{-10} esu).

[14] P. Drude, 'Über Fernewirkungen', *Annalen der Physik*, 62 (1897), XLIX.

[15] The latter in particular proposed using energy (e), length (l) and time (t) as base quantities. It is interesting to note that the resulting mass was expressed in $e \times l^{-2} \times t^2$ (W. Ostwald, 'Studien zur Energetik', *Zeitschrift für Physikalische Chemie*, 9 (1891), 563–78).

[16] On this argument see C. Jungnickel and R. McCormmach, *Intellectual Mastery of Nature*, I (Chicago, 1986), 70–1.

[17] See for example Jungnickel and McCormmach (note 16).

[18] On this subject see S. Schaffer, 'Accurate measurement is an English science', *The Values of Precision*, edited by N. Wise (Princeton, 1993), 135–72; K M. Olesko, 'Precision, tolerance and consensus: local cultures in German and British resistance standards', *Archimedes* (1996) 117–56; 'The meaning of precision: the exact sensibility in early nineteenth-century Germany', *The Values of Precision*, edited by N. Wise (Princeton, 1993), 103–34.

[19] A reconstruction of the debate in England has been given by S. Schaffer, 'Late Victorian metrology and its instrumentation: a manufactory of ohms', *Invisible Connections*, edited by R. Bud and S. E. Cozzens (Bellingham, 1991), 23–56; B. J. Hunt, 'The ohm is where the art is: British telegraph engineers and the development of electrical standards', *Osiris*, 9 (1994), 48–63; in Germany and Europe in general

Stoney as well, were not directly involved in this type of problem, and exclusively concerned with guaranteeing that the units chosen obeyed the criterion of 'absoluteness'.[20]

3. A new natural system

The first appearance of the problem of 'natural units' in Planck's work can be traced back to a paper presented to the German Physical Society on 18 May 1899[21] entitled 'On the irreversible processes of radiation'. In it, Planck for the first time gave a theoretical derivation of the black-body law.

It is not our intention here to reconstruct the theoretical and experimental background[22] of the black-body law because the question has been comprehensively studied, as shown in the bibliography cited in the introduction. At this juncture it is sufficient to remember that the first important step to finding the black-body law was the Stefan–Boltzmann law of 1884:[23]

$$\int_0^\infty e_\lambda \, d\lambda = \text{constant} \times T^4, \tag{1}$$

where T is the temperature and e_λ is the distribution of radiation intensity at a given wavelength λ.[24]

In 1893, Wien[25] successfully explained the link between λ and T. In particular he proved that there is a transformation of radiation in a cavity for which initially 'black' radiation remains so and for which the wavelengths change in inverse proportion to the temperature, so obtaining his famous 'displacement law':

$$\lambda T = \text{constant}. \tag{2}$$

In 1896, Wien[26] used the 'displacement law', a special gas model and highly arbitrary assumptions on the behaviour of gases to obtain the distribution law in the form

$$e_\lambda \, d\lambda = \frac{C\lambda^{-5}}{\exp(c'/\lambda T)} d\lambda, \tag{3}$$

where C and c' are two constants which Wien did not calculate.

This law, when it was proposed by Wien, represented the best approximation of

it has been comprehensively analysed by Jungnickel and McCormmach (note 16); D. Cahan, *An Institute for an Empire* (Cambridge, 1989); D. Cahan, 'The Zeiss Werke and ultramicroscope: the creation of a scientific instrument in context', *Archimedes* (1996), 67–116.

20 As suggested to us by a referee, Planck's attitude with regard to the practical aspects of standards and the ideal of absolute measurement respectively should be distinguished. As we have pointed out, Planck was not much involved in the former (although he was interested in the black-body measurements related to an absolute standard for high-temperature measurement), but he was certainly aware of the latter, because the notion of absolute measurement was a central component of any physics teaching programme in Germany and in Great Britain at that time.

21 M. Planck, 'Über irreversible Strahlungvorgänge. 5. Mitteilung', *Sitzungsberichte der Preussischen Akademie der Wissenschaften* (1899), 440–80; *Physikalische Abhandlungen und Vorträge*, I (Braunschweig, 1958), 560–600.

22 On this subject see for example Kangro (note 1) and Kuhn (note 1).

23 L. Boltzmann, 'Ableitung des Stefan'schen Gesetzes betreffend die Abhängigkeit der Wärmestrahlung von Temperatur aus der elektromagnetischen Lichttheorie', *Annalen der Physik*, 22 (1884), 291–4.

24 The intensity differs from the more common emissive power by a factor of π^{-1}

25 W. Wien, 'Eine neue Beziehung der Strahlung schwarzer Körper zum zweiten Hauptsatz der Wärmetheorie', *Sitzungsberichte der Preussischen Akademie der Wissenschaften* (1893), 55–62.

26 W. Wien, 'Über die Energievertheilung im Emissionsspektrum eines schwarzen Körpers', *Annalen der Physik*, 58 (1896), 662–9.

the experimental data available at the time. Again, in 1896, Paschen[27] obtained a law similar to equation (3), independently of Wien and on the basis of his own experimental data. In this expression the exponent of λ was left indeterminate and the value of the constant c' was estimated as 1.455 °C cm s^{-1}

In the paper of 1899 referred to above,[28] Planck set himself the goal of obtaining a theoretically rigorous derivation of equation (3).

Planck based his theory on two starting points.[29] The first was that the black-body distribution law was intended as a *universal law* in which 'two universal constants' appeared. The second was that the 'two universal constants' should appear in the expression which describes the entropy of the independent oscillators when placed within a cavity with perfectly reflecting walls.

The first of Planck's two statements can be traced back to Kirchhoff's statement of 1860[30], according to which the relationship between the emissive power and the absorbing power at a certain wavelength λ and at a certain temperature T 'is independent of the shape and other particularities of the body'.[31] In the case of the black body, this implied that the emissive power, and therefore the intensity, was a 'universal function'. As such, according to Planck's postulates, it contained only 'universal constants'. If the distribution law, in which the two constants c' and C appear as proposed by Wien (equation (3)), is accepted as valid, there should therefore be two constants involved which should be considered 'universal constants'.

The second assumption on the presence of universal constants in the entropy expression had its origin in Planck's project to obtain the law of energy distribution in the black-body spectrum as follows:

(1) 'the fundamental equation of the electromagnetic theory of radiation' given by

$$u_\nu = \frac{8\pi\nu^2}{c^3}\bar{U}_\nu, \tag{4}$$

where c is the speed of light, obtained by Planck himself in the same paper (in a state of equilibrium, this expression linked the energy density distribution of the radiation in a cavity u_ν, and therefore the intensity e_λ, to the average energy $\bar{U}_\nu$ (hereafter indicated by U) of the resonators placed in the cavity at temperature T);[32]

(2) using the following thermodynamic relationship (valid at constant volume) to calculate U:

$$\frac{\partial S}{\partial U} = \frac{1}{T}, \tag{5}$$

where S represents the entropy of the resonator.

[27] F. Paschen, 'Über Gesetzmässigkeiten in den Spektren fester Körper', *Annalen der Physik*, 58 (1896), 455–92.

[28] Planck (note 21).

[29] As amply shown by the work of Klein (note 1) and of Kuhn (note 1), Planck's programme was based on an electromagnetic understanding of irreversibility and entropy law. Darrigol (note 1) also showed how subsequently, because in particular of the comparison with Boltzmann's work, Planck's programme moved to the research of closer formal analogies between radiation theory and gas theory. These considerations, however, do not contradict our thesis because they represent a general context of Planck's programme.

[30] G. Kirchhoff, 'Über des Verhältnis zwischen dem Emissionsvermögen und dem Absorptionsvermögen der Körper für Wärme und Licht', *Annalen der Physik*, 109 (1860), 275–301.

[31] Kirchhoff (note 20), 292.

[32] The intensity e_λ is linked to u_ν by $e_\lambda d\lambda = (\lambda^2/4\pi)u_\nu d\nu$. From the definition $\nu = c/\lambda$ it follows that $d\nu = -(c/\lambda^2)d\lambda$, from which $u_\nu d\nu = u_\lambda(c/\lambda^2)d\lambda$. Since $u_\lambda = (4\pi/c)e_\lambda$, one obtains $u_\nu d\nu = (4\pi/\lambda^2)e_\lambda d\lambda$.

From this viewpoint the 'two universal constants' should therefore be contained in the entropy expression for the resonator, which in this context became a fundamental character.

In the 18 May 1899 paper being discussed here,[33] Planck proposed the following definition of entropy for a resonator with energy U and frequency ν:

$$S = -\frac{U}{a\nu}\log\left(\frac{U}{eb\nu}\right), \tag{6}$$

which contains two 'universal constants' a and b, and e, the base of the natural logarithms.[34]

Deriving equation (6) with respect to U, one obtains

$$\frac{\partial S}{\partial U} = -\frac{1}{a\nu}\log\left(\frac{U}{b\nu}\right). \tag{7}$$

By setting, on the basis of equation (5),

$$\frac{1}{T} = -\frac{1}{a\nu}\log\left(\frac{U}{b\nu}\right) \tag{8}$$

and applying the exponential function, Planck obtained the energy U of the resonator as follows:

$$U = b\nu\exp\left(-\frac{a\nu}{T}\right). \tag{9}$$

Substituting this expression into equation (4), he arrived at the following distribution law:

$$u_\nu \mathrm{d}\nu = \frac{8\pi\nu^3}{c^3} b\exp\left(-\frac{a\nu}{T}\right)\mathrm{d}\nu \tag{10}$$

or the equivalent in terms of intensity:[35]

$$e_\lambda \mathrm{d}\lambda = \frac{2c^2 b}{\lambda^5}\exp\left(-\frac{ac}{\lambda T}\right)\mathrm{d}\lambda. \tag{11}$$

In this expression, which is similar to Wien's version (3), the constants c' and C were replaced by the new constants a and b respectively. This clearly gave

$$C = 2c^2 b, \qquad c' = ac. \tag{12}$$

However, unlike Wien, Planck attempted to define the value of the two 'universal constants' a and b. By introducing equation (11) into the Stefan–Boltzmann law (1) and using a series of experimental results obtained by Kurlbaum in 1898 regarding

[33] Planck (note 21).

[34] This definition was not motivated by Planck when he introduced it. However, as Klein (note 1) and Darrigol (note 1) observed, Planck most likely was guided by equation (3) and partially by Boltzmann's *H* function.

[35] For convenience, in the following, we have used only the intensity of energy at the wavelength λ or the density of energy at the frequency ν. For these two quantities we have always used the symbols e_λ and u_ν respectively, even if the various researchers used different notation.

'the total energy of black bodies',[36] Planck obtained the following value for the ratio b/a^4:

$$\frac{b}{a^4} = 1.278 \times 10^{15} \text{ erg s}^{-3} \, {}^\circ\text{C}^{-4}. \tag{13}$$

Now, using the value of exponent c' in equation (3) as calculated by Paschen (see above), we have

$$c' = ac = 1.4455 \, {}^\circ\text{C cm}. \tag{14}$$

In conclusion, Planck obtained the following values for his two 'universal constants':

$$a = 0.4818 \times 10^{-10} \text{ s } {}^\circ\text{C}, \qquad b = 6.885 \times 10^{-27} \text{ erg s}. \tag{15}$$

As can be seen from equations (15), the 'universal constant' b in 1899 had the same value as the more famous 'universal constant' h in 1900, while the 'universal constant' a was to become, again in 1900, part of the constant k ($k = b/a$).

After obtaining this new derivation of Wien's law and making the value of the universal constants that appear in it explicit, Planck concluded his 1899 article with a paragraph dedicated to 'natural units of measurement':[37]

> All the systems of physical measurement adopted so far, including the so-called c.g.s. absolute system, are based on a coincidence of random circumstances, as the choice of units…is not generalised for any place and any time, but is founded in the particular requirements of our culture on Earth. Therefore, for example, the units of length and time have been obtained from the actual dimensions and actual motion of our planet… It would therefore be perfectly imaginable that at a certain point, in a different situation, all systems of units of measurement so far adopted would lose either partially or completely their original natural meaning.

To remedy this limitation, Planck proposed creating a new system of units of measurement, this time based on quantities independent of all contingencies. The constants a and b were of fundamental importance for this purpose. According to Planck they were to be considered 'universal constants', on a par with the two universally recognized constants c (speed of light) and G (gravitational constant) and were such as to identify, together with c and G, a new 'natural' system of units of measurement.

Planck wrote:

> It cannot be without interest to note that constants a and b…provide the possibility of identifying the new units of length, mass, time and temperature, which, independently of specific bodies or particular circumstances, necessarily maintain their meaning at all times and for all cultures, even for extra-terrestrial or non-human life forms, and can therefore be considered as 'natural units of measurement'.

At this point, Planck had paved the way to creating this system of natural units of measurement, for which it was sufficient to choose as 'natural units' those deduced by the four universal constants a, b, c and G.

[36] F. Kurlbaum, 'Über eine Methode zur Bestimmung der Strahlung in absoluten Mass und die Strahlung des schwarzen Körpers zwischen 0 und 100 Grad', *Annalen der Physik*, 65 (1898), 746–60.

[37] Planck (note 21), 599.

A few simple mathematical steps and Planck obtained the following quantities as 'natural units':

$$\text{unit of length} = \left(\frac{bG}{c^3}\right)^{1/2} = 4.13 \times 10^{-33}\ \text{cm},$$

$$\text{unit of mass} = \left(\frac{bc}{G}\right)^{1/2} = 5.56 \times 10^{-5}\ \text{g},$$

$$\text{unit of time} = \left(\frac{bG}{c^5}\right)^{1/2} = 1.38 \times 10^{-43}\ \text{s},$$

$$\text{unit of temperature} = a\left(\frac{c^5}{bG}\right)^{1/2} = 3.5 \times 10^{32}\ {}^\circ\text{C}.$$

Planck concluded:[38]

> These quantities will retain their natural meaning for as long as the laws of gravity, the propagation of light in vacuum and the two principles of the theory of heat hold, and, even if measured by different intelligences and using different methods, must always remain the same.

4. Thiesen and the 'universal' constants

Just a few weeks after Planck's announcement, Max Thiesen,[39] a theoretical physicist in Berlin and a colleague of Planck, took up the challenge of obtaining a new distribution law for black-body radiation.[40]

The reason behind the project lay in the new measurements of Lummer and Pringsheim, performed at the Physical–Technical Institute,[41] which deviated from Wien's law at low frequencies (they were not yet published but Thiesen was aware of them).

As a first step, Thiesen attempted to establish 'the minimum conditions' that had to be satisfied by the distribution law. Combining Wien's displacement law (2) with the Stefan–Boltzmann law (1), he obtained the following expression for e_λ:

$$e_\lambda = T^5\psi[\lambda T], \tag{16}$$

where the function ψ was to be defined.

Indeed equation (16), which added nothing to Wien's law and the Stefan–Boltzmann law, had already been proposed by Rayleigh in 1898[42] without raising any interest. However, it deserves a number of comments. In the first instance, and this was also pointed out by Thiesen, equation (16) represented the most general form in which the 'displacement law' formulated by Wien could be expressed (it must be remembered that Wien never wrote it in this form).[43] In the second place it showed

[38] *Ibid.*, 600.

[39] M. Thiesen, 'Über das Gesetz der schwarzen Strahlung', *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 2 (1900), 65–70.

[40] Kuhn (note 1), 94–5, has already pointed out the importance of a number of aspects of Thiesen's work in the development of Planck's theory. However, like Kangro (note 1), 194–205, he did not emphasize, in our opinion, with sufficient force the considerations of Thiesen himself on the universal constants, which subsequently had repercussions, as we shall see, on Planck's path.

[41] On this measurement and more in general on the interest for the black-body problem at the Physical-Technical Institute see Cahan (note 19).

[42] J. W. Strutt (Lord Rayleigh), 'Note on the pressure of radiation showing an apparent failure of the usual electromagnetic theory', *Philosophical Magazine*, 5 (45) (1898), 522–5.

[43] It is interesting to note, as pointed out by one of the referees, that Wien expressed this law in words. In 1896, Wien (note 25) wrote: 'If therefore we imagine the energy at a certain temperature [ϑ] expressed as a function of wavelength, this curve would remain the same with changes of temperature, if the scale

that, like the 'displacement law' or Wien's law (3) of 1896, the distribution law could be expressed as a function of one single variable λT rather than the two variables λ and T taken separately.

Thiesen's observations, however, were not limited merely to an exposition of law (16). As he pointed out, 'the law reveals two natural constants with dimensions that depend exclusively on the unit of temperature and the three mechanical units'.[44] So far as the first constant is concerned. Thiesen reached this conclusion (which guarantees the presence of two 'natural constants' independently of the form of the distribution law) by considering the fact that 'as can easily be seen, ψ cannot be a simple power' and therefore 'there must be a natural constant in the order of argument λT'. So far as concerns the second constant, in Thiesen's opinion 'it is already given by Boltzmann's law'.

Later Thiesen also proposed a family of solutions for the function $\psi[\lambda T]$ in the form

$$\psi_{[x]} = \psi_{\mathrm{m}}\left[\frac{x_{\mathrm{m}}}{x}\exp\left(1-\frac{x_{\mathrm{m}}}{x}\right)\right]^{a}, \tag{17}$$

where x_{m} and ψ_{m} were the 'two universal constants' which, according to Thiesen, should necessarily appear in the distribution law, while the exponent a was left indeterminate. Wien's distribution law was obtained by setting $a = 5$. It was a simple matter indeed to calculate

$$e_{\lambda} = \frac{\psi_{\mathrm{m}}\, x_{\mathrm{m}}^{5}\, e^{5}}{\lambda^{5}}\exp\left(-\frac{5x_{\mathrm{m}}}{\lambda T}\right).$$

So the two constants that appear in Wien's formula were

$$C = \psi_{\mathrm{m}}\, x_{\mathrm{m}}^{5}\, e^{5} \qquad c = 5x_{\mathrm{m}}.$$

As Thiesen reminded us, both Wien and Planck tried to derive this law theoretically using different methods but, as Thiesen commented, this law was not in agreement with recent experimental results:[45]

> Mr Lummer and Mr Pringsheim have announced that their experiments confirm Wien's displacement law without any shadow of doubt..., but they reveal systematic deviations from the Wien–Planck distribution law....[[46]] Initially from the diagrams published and subsequently to a greater degree of accuracy using the original numerical values kindly transmitted to me by the gentlemen in question, I found that the experiments would have been reproduced better...if a were set to 4.5 in [equation (17)].

At the start of 1900, therefore, the form of the distribution law proposed by Wien was once more the subject of discussion. At the same time, the accumulation of uncertain experimental data, comprehensively demonstrated in the cited bibliography, created a situation of confusion and uncertainty surrounding the precise spectral characteristics of black-body radiation. However, the idea that there should be two universal constants in the distribution law was not put in doubt, but on the contrary confirmed.

were altered in such a way as to decrease the ordinates in a ratio of $1/\vartheta^{4}$ and increase the abscissa in a ratio of ϑ.'

[44] Thiesen (note 39), 66.

[45] *Ibid.*, 68.

[46] See Wien's formula (3).

The question of the constants was re-examined by Thiesen in a subsequent paper[47] presented to the German Physical Society in June the same year. Thiesen began the paper by recalling Planck's considerations on the demise of the 1899 communication:[48]

> Mr Planck has pointed out that Wien's radiation law gives two natural constants which, together with the speed of light and the gravitational constant, are sufficient to express mechanical quantities and temperature in natural units, independently of the quality of a particular body.

However, the point that Thiesen was most interested in was that the two constants are 'independent of the particular form of the law of radiation [and] follow on from the black-body laws presented by Boltzmann and Wien'. This guaranteed two universal constants to create a system of natural units of measurement, independently of whether or not Wien's law was valid. As we have just seen, Thiesen had already proposed an expression for the law of radiation requiring two universal constants. It must be pointed out that Thiesen's analysis was to be developed in Planck's next paper both in regard to the formulation of Wien's 'displacement law' and the observations on the presence of two universal constants in the distribution law.

5. From constants *a* and *b* to constants α and *B*

Following the publication of the experimental data of Lummer and Pringsheim[49] (see above) and more recent data from Rubens and Kurlbaum,[50] on 19 October 1900, Planck[51] presented a brief paper to the German Physical Society in which he proposed a new formula for the distribution law, differing from Wien's 1896 formula in terms of the denominator (-1):

$$e_\lambda = \frac{C\lambda^{-5}}{\exp(c'/\lambda T) - 1}, \tag{18}$$

where C and c' were the same constants as in Wien's law (3), both in name and in value, and e was the intensity distribution.

To arrive at this 'radiation formula with two constants' (in Planck's words), Planck used an expression for entropy as his starting point as he did in 1899. He did not write the expression explicitly but, as he remarked, 'we obtain [it] if we set

$$\frac{d^2S}{dU^2} = \frac{\alpha}{U(\beta + U)}\text{'}, \tag{19}$$

where, at this level of analysis, α and β are two indeterminate constants (it must be remembered that β is necessarily an energy). As is emphasized in the bibliography

[47] M. Thiesen, 'Über allgemeine Naturcostanten', *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 2 (1900), 116–21.

[48] *Ibid*., 116.

[49] O. Lummer and E. Pringsheim, 'Die Vertheilung der Energie im spektrum des schwarzen Körpers', *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 1 (1899), 23–41.

[50] H. Rubens and F. Kurlbaum, 'Über die Emission langwelliger Wärmestrahlen durch den schwarzen Körper bei verschiedenen Temperaturen', *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 2 (1900), 929–41.

[51] M. Planck, 'Über eine Verbesserung der Wienschen Spektralgleichung', *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 2 (1900), 687–9 (*Physikalische Abhandlungen and Vorträge*, I (Braunschweig, 1958) 687–9); English translation of *Planck's Original Papers in Quantum Physics*, edited by H. Kangro (London, 1972).

quoted in the introduction, the choice of equation (19) was justified by the need both to preserve the validity of Wien's law in the high-frequency range and to interpret the recent experimental deviations at low frequencies.[52]

The entropy expression derived from equation (19) which Planck now used was

$$S = \alpha\left[\left(1+\frac{U}{\beta}\right)\log\left(1+\frac{U}{\beta}\right)-\frac{U}{\beta}\log\left(\frac{U}{\beta}\right)\right]. \tag{20}$$

It is interesting to note that Planck considered equation (19) as 'by far the simplest of all the expressions that lead to S as a logarithmic function of U (as suggested by probability considerations)',[53] already adumbrating the path that he would subsequently take, namely the adoption of the probabilistic definition of entropy.

At this point, Planck's article becomes extremely synthetic. He states that using the relation $\partial S/\partial U = 1/T$ (equation (5)) and Wien's displacement law in the form that Planck had already been aware of since 1899, namely

$$S = f\left(\frac{U}{\nu}\right), \tag{21}$$

he obtained the distribution law given by equation (18).

The reason why Wien's 'displacement law' could be written in the form of equation (21) is deferred to 'another occasion' as he commented in a note. This occasion was provided by the article published in *Annalen der Physik* of 1901[54] in which, as we shall see, Planck's reasoning is given in full.

Here we attempt to reconstruct the route followed by Planck to arrive at equation (18).[55] By integrating equation (19) with respect to the energy U and using equation (5) we have

$$\frac{\mathrm{d}S}{\mathrm{d}U} = \frac{1}{T} = \frac{\alpha}{\beta}\log\left(\frac{U}{\beta+U}\right), \tag{22}$$

from which, passing from logarithmic to exponential form,

$$U = \frac{\beta \exp(\beta/\alpha T)}{1-\exp(\beta/\alpha T)}. \tag{23}$$

After obtaining a formula for the energy of the resonator, Planck could use the 'fundamental equation of the electromagnetic theory of radiation' (equation (4)) to determine the expression for energy density u_ν, which is as follows:

$$u_\nu = \frac{8\pi\nu^2}{c^3}\beta\frac{1}{\exp(\beta/\alpha T)-1}. \tag{24}$$

At this point Wien's 'displacement law', expressed in the form $S = f(U/\nu)$ (equation (21)), must be used to obtain equation (18). As equation (21) shows, the entropy had to be a function of U/ν. Therefore the expression adopted for entropy and expressed in equation (20) also had to be a function of U/ν. This presupposes that β had to be proportional to the frequency ν, that is

$$\beta = \text{constant} \times \nu. \tag{25}$$

[52] With regard to Planck's interest in the second derivative of entropy and its links to Planck's electromagnetic H theorem see Kuhn (note 1) and Darrigol (note 1).

[53] Planck (note 51), English translation of *Planck's Original Papers in Quantum Physics*, 36.

[54] M. Planck, 'Über das Gesetz der Energieverteilung im Normalspektrum', *Annalen der Physik*, 4 (4) (1901), 553–63.

[55] This reconstruction of Planck's reasoning is made by nobody but Darrigol. However, Darrigol does not emphasize both equation (25) and the link between Planck's and Wien's constants.

In this paper, Planck did not write equation (25) but, to arrive at the black-body distribution law (18) he necessarily encountered this formula. We would like to emphasize that this expression told Planck that the entropy formula for a resonator contained an energy β of constant value and proportional to the frequency ν by means of a constant. The physical meaning of this result was pointed out in December 1900 when β was replaced by the 'element of energy' ε.[56] The main differences between this and known interpretations such as that of Klein and Kuhn can now be clarified. In our opinion these last interpretations contain two basic elements: firstly, the universal constants and absolute units of measurement are basically presented as a corroborating consequence of the theory and, secondly, Planck's conversion to Boltzmann's probabilistic theory was for theoretical reasons. In particular, Planck started with a semiempirically discovered distribution law and then, working backwards, derived the relationship for the entropy of the resonator. Only then, noting the formal similarity with Boltzmann's definition for entropy, did he decide in favour of the probabilistic theory, requiring energy quantization as a consequence. What, on the other hand, we are suggesting is, firstly, that the universal constants represented a valuable point of reference from the start, by way of Kirchhoff's law, and, secondly, that Planck decided to move towards Boltzmann's probabilistic theory for reasons linked to the universal constants. Indeed, his starting point was the relation for the second derivative of entropy with respect to energy and, developing it, he derived the aforementioned expression for constant quantity of energy β. This faced him with the fact that the resonator had to interact with a constant quantity of energy proportional to the frequency and that the latter was not simply an artifice of calculation but had to have a physical meaning because the proportionality was guaranteed by a universal constant. At this point, only the probabilistic theory was in a position to interpret this definite quantity of energy. In our view, therefore, the presence of a constant quantity of energy drove Planck to adopt Boltzmann's probabilistic theory and not vice versa. This may also underpin the fact that Planck, as already noted by Darrigol[1], attempted to interpret Boltzmann's probabilistic theory in a deterministic sense.

We can also observe the close analogy between equation (25) and the more famous 1900 expression $\varepsilon = h\nu$!

If the constant in equation (25) is called B, equation (24) becomes

$$u_\nu = \frac{8\pi\nu^3}{c^3} B \frac{1}{\exp(B\nu/\alpha T) - 1}, \tag{26}$$

and therefore the intensity e_λ of radiation is given by

$$e_\lambda = \frac{2c^2 B}{\lambda^5} \frac{1}{\exp(Bc/\alpha\lambda T) - 1}. \tag{27}$$

In the October article, however, Planck does not write e_λ according to equation

[56] What we have just described could be seen to contradict a passage of a letter that Planck wrote to Lummer on 26 October 1900 (quoted by C. Jungnickel and R. McCormmach, *Intellectual Mastery of Nature*, II (Chicago, 1986), 261–2) indicated to us by a referee. It seems that, in this letter, Planck needed only the resonator theory to define a connection between entropy and probability. This contradiction disappears if one considers our claim that, in Planck's derivation, universal constants did not play an exclusive role but only acted as a privileged point of reference. In fact, at the end of this letter, Planck wrote that derivation of the radiation law 'would then also give us the physical significance of [Wien's] constants c and C'.

(27) where the still undetermined constants α and B appear. Planck's problem is, on the one hand, comparison with experimental data and, on the other hand, how to maintain the validity of Wien's law at short wavelengths. As a result, Planck presents his law in the aforementioned form (18):

$$e_\lambda = \frac{C\lambda^{-5}}{\exp(c'/\lambda T) - 1}, \tag{18}$$

where the two constants have a precise value that coincides with the value assigned to Wien's 1896 constants. This is how Planck concluded his article:[57]

> As far as I can see at the moment, [this law] fits the observational data published up to now as satisfactorily as the best equation put forward for the spectrum. ... [This was demonstrated by some numerical examples.] I should therefore be permitted to draw your attention to this new formula which I consider to be the simplest possible apart from Wien's expression from the point of view of the electromagnetic theory of radiation.

We have reported the previous calculation to show that writing equation (18) with C and c' as assigned constants cannot be considered, as is usually stated in the bibliography, as the result of interpolating experimental data. As we have attempted to prove, and this is a novelty, proposing equation (18) concerned a series of operations involving the following:

(1) the acceptance that the entropy S of the resonator was a logarithmic expression of the type given in equation (20), with constants α and β (complete unknowns at this point), one of which multiplied the logarithm (this could offer to Planck a possible solution to the entropy definition problem);
(2) the interpretation of β as a constant quantity of energy proportional to the frequency by applying a constant B (this could suggest a possible theoretical framework for his new entropy definition).

A consequence of these operations was that there are precise relationships between the values of constants α and β (or rather α and B) and the values of Wien's constants C and c'. These relationships, obtained by comparing equations (18) and (27), are

$$C = 2c^2B, \qquad c' = \frac{Bc}{\alpha}. \tag{28}$$

Once these links were established, determining the value of the new constants α and B was straightforward. We do not know whether or not Planck performed this calculation. However, if he had, he would have found two constants, one, namely α, completely new, equal to 1.34×10^{-16} erg °C^{-1} (which 2 months later was to become the constant k) and the other, namely B (the proportionality constant between energy and frequency), identical with constant b introduced in 1899, to which he had attributed the value 6.55×10^{-27} erg s and which was to become the constant h.

The points that Planck had to focus his attention on at the end of October 1900 if he wanted to give a physical meaning to his deductions therefore seem clear. In his Nobel lecture of 1920 he recalled:[58]

57 Planck (note 51), English translation of *Planck's Original Papers in Quantum Physics*, 37.
58 Planck (note 3), 125.

> I busied myself, from then on, that is from the day of its establishment with the task of elucidating a true physical character for the formula… until after some weeks of the most strenuous work of my life light came into the darkness and a new, undreamed-of perspective opened up before me.

This 'undreamed-of perspective' was described by Planck in a subsequent announcement in December 1900 and, in more systematic form, in the next article that he submitted to *Annalen der Physik* in January 1901, where equation (18) was presented in terms of the 'universal constants h and k'.[59]

6. From constants α and B to constants h and k

In his December 1900 paper, Planck did not specify the route that he had taken to obtain the black-body law in the form now known. He wrote:[60]

> Elsewhere I will soon give a detailed account of the considerations I have only hinted at here, as well as a retrospective look at the development of the theory so far.

These calculations and considerations were presented in a series of articles published in 1901 and 1902 to which we shall refer directly. What Planck in any case does in his article of December 1900 is to sketch out the route that he took and the results that he achieved.

It is interesting, however, to note the importance given here by Planck himself to natural constants. He wrote:

> What interests me today… is to demonstrate in the clearest manner possible the true central point, and this is best achieved by describing here a new and completely elementary procedure by which, without knowing anything at all about a spectral formula or even any theory, it is possible to calculate in numeric form the distribution of a given quantity of energy into the individual colours of the normal spectrum with the help of a single natural constant and then, with the help of a second constant, also the temperature of this radiant energy.

As we shall see, these two constants were the constant h and the constant k respectively. The first 'natural' constant multiplied by the frequency of the resonator defined the 'element of energy' ε and the second natural constant appeared instead in the entropy expression.[61]

Returning to the path followed by Planck to arrive at the distribution law, we must first point out that Planck's main problem was to derive an expression for entropy of the type in equation (20), in which β, as we have seen, was an energy of constant value proportional to the frequency ν and at the same time to guarantee that it contained two universal constants.

In our opinion the two problems were intertwined and in part reciprocally solved when Planck decided to follow 'Boltzmann's trend of ideas', linking the entropy of

[59] Planck (note 51).

[60] M. Planck, 'Zur Theorie des Gesetzes der Energievertielung im Normalspektrum', *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 2 (1900), 237–45 (*Physikalische Abhandlungen und Vorträge*, I (Braunschweig, 1958), 704).

[61] Indeed, the relationship $dS/dU = 1/T$ allowed Planck to obtain the expression for U using the usual procedure.

a set of resonators in a stationary state to the probability of this state. Boltzmann[62] was the first (in 1877) to propose a probabilistic definition for entropy. The case that he examined on that occasion was that of a mole of ideal monoatomic gas. He proposed the following expression for the entropy S' of this system:

$$S' = \int \frac{dQ}{E_k} = \tfrac{2}{3}\Omega, \tag{29}$$

where E_k was the kinetic energy of a gas molecule, Q the quantity of heat and Ω the logarithm of thermodynamic probability $\mathscr{B}$ of the state considered, that is the number of complexions compatible with that state.[63] This expression of entropy, written as a function of temperature as was Planck's habit, became for a mole of monatomic gas[64]

$$S = \frac{R}{N}\log \mathscr{B} + \text{constant}, \tag{30}$$

with R the known absolute constant of gases.

As can be seen from equation (30), Boltzmann's route gave Planck the threefold advantage of

(1) guaranteeing the presence of a multiplication constant for the logarithm which, owing to how entropy was written, had the same dimension as required by Thiesen's analysis,

[62] L. Boltzmann, 'Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht', *Wiener Berichte*, 76 (II) (1877), 373–435.

[63] Boltzmann obtained this expression by writing the first principle of thermodynamics and the fundamental law of ideal gases respectively as

$$dQ = N\,dE_k + p\,dV,$$

$$pV = \tfrac{2}{3}NE_k,$$

where N is the ratio of the gram-molecular mass to the mass of a molecule or, in current terms, the inverse of Avogadro's number, p is the pressure and V is the volume of the gas. Starting from these relations he could express entropy as a function of E_k in the form

$$\int \frac{dQ}{E_k} = \int \frac{2N}{3pV}(N\,dE_k + p\,dV),$$

from which, by means of a series of steps, he obtained

$$\int \frac{dQ}{E_k} = \tfrac{2}{3}N\log(VE_k^{3/2}). \tag{a}$$

Boltzmann had previously obtained the following expression for Ω:

$$\Omega = \tfrac{3}{2}N + N\log\left[V\left(\frac{4\pi E_k}{3m}\right)^{3/2}\right] - N\log N,$$

where m is the mass of a gas molecule, from which, multiplying both sides by $\tfrac{2}{3}$ and grouping the constants, he obtained

$$\tfrac{2}{3}\Omega = \tfrac{2}{3}N\log(VE_k^{3/2}) + \text{constant}. \tag{b}$$

By setting (a) equal to (b), Boltzmann arrived at equation (29).

[64] Indeed, as the relationship

$$E_k = \frac{3}{2}\frac{R}{N}T$$

exists between kinetic energy and temperature, substituting it in equation (29) is sufficient to obtain equation (30).

(2) giving a way to justify the introduction of a definite quantity of energy β or ε by means of the theory of probability and
(3) providing a logarithmic expression for entropy as required by his previous analysis.

In order to apply equation (30) to a set of resonators (i.e. to the case that Planck had to examine), Planck generalized[65] and rewrote it in the following form (which was to become famous):

$$S = k \log \mathscr{P} + \text{constant}, \tag{31}$$

where k was a new constant.

At this point the main problem to solve was the calculation of $\mathscr{P}$, the number of complexions for the set of N oscillators, in thermal equilibrium and at a given energy.

It is not our intention here to enter into the details of Planck's statistical calculation of $\mathscr{P}$ (already examined in an extensive bibliography).[66] We only wish to point out that this calculus required the total energy of identical resonators not to be a continuum but is made up of 'a fixed number of equal and finite parts'. Planck performed this by considering the total energy of a set of N identical resonators at the same frequency as being composed of these elements, and therefore distributing this energy between N resonators. In this way, we would like to note that the existence of a definite quantity of energy β found in October 1900 could be justified as becoming the more famous element of energy ε.

Then, if we allow the total energy of a set of identical resonators with the same frequency to be divided into energy elements ε, the application of equation (31) gives the following formula for the entropy of a resonator:

$$S = k\left[\left(1+\frac{U}{\varepsilon}\right)\log\left(1+\frac{U}{\varepsilon}\right)-\frac{U}{\varepsilon}\log\left(\frac{U}{\varepsilon}\right)\right], \tag{32}$$

where U represented its average energy (where ε replaces the constant β in equation (2), giving it a precise meaning).

This expression, as Planck commented, could be written in the more general form

$$S = kf\left(\frac{U}{\varepsilon}\right). \tag{33}$$

In this way, Planck successfully obtained an expression for entropy similar to that required in his October 1900 paper (where ε corresponds to the previous constant β) and at the same time managed to guarantee the presence of one (k) of the two 'universal constants' that he was looking for, with particular reference to the constant whose dimension depends on temperature.

This left the problem of identifying the 'second universal constant', which necessarily had to appear in the black-body radiation formula. This second constant (h) was obtained by Planck more directly, with brief considerations[67] on Wien's 'displacement law'.

As we saw, Planck had already used Wien's 'displacement law' in a special form without explaining from where it was derived. Here Planck provided the theoretical justification.

[65] Planck (note 54).
[66] Klein (note 1); Kuhn (note 1).
[67] Planck (note 54).

On the basis of Thiesen's formulation of this law (see equation (16)), that is

$$e_\lambda \, d\lambda = T^5 \psi(\lambda T) \, d\lambda, \tag{34}$$

passing to energy density u_ν and on the basis of the Kirchhoff–Clausius law, according to which the energy emitted by a 'black body' in a diathermal medium (per unit of surface in a unit of time) is proportional to $1/c^2$, Planck obtained

$$u_\nu = \frac{\nu^3}{c^3} \psi\left(\frac{T}{\nu}\right).$$

By backtracking along his previous route, that is passing from u_ν to U, to $1/T$ and finally to dS/dU, Planck deduced the following general expression for the entropy of the oscillator, which was already used in October 1900;

$$S = f\left(\frac{U}{\nu}\right). \tag{35}$$

Planck commented as follows:[68]

> The entropy of a resonator ... is a function of a single variable (U/ν) and apart from this contains only universal constants. This is the simplest version I know of Wien's displacement law.

Starting, on the one hand, from the probabilistic definition of entropy and, on the other hand, from Wien's displacement law, Planck obtained two different conditions for the entropy of the oscillator, given respectively by equations (33) and (35).

At this point[69] the condition for both expressions to be simultaneously satisfied was to assume that ε was proportional to the frequency ν of the oscillator (analogously to the article of October 1900). The constant linking the two quantities, with dimensions of energy × time, was included in the expression of oscillator entropy and as such was acknowledged as a 'universal constant'. All this was condensed by Planck in the famous expression

$$\varepsilon = h\nu, \tag{36}$$

where the new universal constant was indicated with the symbol h. It is interesting to note in this regard that Planck introduced this expression without comment, calling it simply the 'element of energy' ε.

Substituting this expression in equation (32) provided the following expression for entropy

$$S = k\left[\left(1+\frac{U}{h\nu}\right)\log\left(1+\frac{U}{h\nu}\right)-\frac{U}{h\nu}\log\left(\frac{U}{h\nu}\right)\right]. \tag{37}$$

Following the reasoning applied in 1899, and presumably used again in the October 1900 paper, with the average energy of the resonator derived from the entropy expression and substituted into 'the fundamental equation of the electromagnetic theory of radiation', Planck arrived at the distribution law in terms of energy density:

$$u_\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{\exp(h\nu/kT)-1}. \tag{38}$$

[68] *Ibid.*, 725.

[69] This procedure has been indicated by Planck (note 54).

In order to complete his derivation, Planck moved on to calculate the new 'universal constants' h and k. The procedure used is conceptually similar to the 1899 procedure, when the constants in play were a and b. First, equation (38) was introduced into the Stefan–Boltzmann law (1) and Kurlbaum's 1889 results were used to determine the ratio

$$\frac{k^4}{h^3} = 1.1682 \times 10^{15} \text{ erg s}^{-3} \text{ °C}^{-4}. \quad (39)$$

Secondly, and this was an innovation,[70] Planck used the new measurements of $\lambda_m T$ (the product of the maximum wavelength and the temperature) made by Lummer and Pringsheim to obtain

$$\frac{h}{k} = 4.866 \times 10^{-11} \text{ s °C}. \quad (40)$$

Combining the data provided by equations (39) and (40) enabled Planck to determine the values of h and k, with the following results:

$$h = 6.55 \times 10^{-27} \text{ erg s}, \quad (41)$$

$$k = 1.346 \times 10^{-16} \text{ erg °C}^{-1}. \quad (42)$$

It is interesting to observe that these two values correspond to the two values of B and α respectively which, as we have seen in §5, Planck was able to calculate in October 1900.

This analysis enabled Planck to 'flesh out with physical meaning' the law proposed in October 1900 and to establish the value of the constants without recourse to the empirical values in Wien's formula.

Doing this had, however, raised other and no less problematic questions. These included the fundamental question as to the validity of the probabilistic definition of entropy for a set of resonators. This definition could be interpreted as an unjustified generalization of the definition proposed by Boltzmann for a completely different case, that is the ideal monatomic gas.[71] The problem was therefore that of verifying whether these two definitions were equivalent or whether, in the final analysis, the multiplication constants in the two cases had the same value.

This question was examined by Planck at the end of the December 1901 article.[72] He first adapted the definition given by Boltzmann for a gas of molecules, rewriting Boltzmann's expression as

$$S' = \omega R \log \mathscr{B}, \quad (43)$$

where R is the 'gas constant' and ω is 'the ratio (equal for all substances) of the mass of a molecule to the gram-molecular mass', that is, in current terms, the inverse of Avogadro's number.

He therefore considered a system formed of a gas and of a set of radiating resonators. Adopting a probabilistic interpretation of entropy '*à la* Boltzmann', the entropy of this system should be 'proportional to the logarithm of the total number

[70] The calculus has been reported both by Planck (notes 60 and 54).

[71] The analogy between Boltzmann's kinetic theory of gas and theory of radiation is comprehensively covered by Darrigol (note 1).

[72] This question was discussed by M. Planck, 'Über die Elementarquanta der Materie und der Elektrizität', *Annalen der Physik*, 4 (1901), 564–66 (*Physikalische Abhandlungen und Vorträge*, I (Braunschweig, 1958), 728–30); 'Über die Verteilung der Energie zwischen Äether und Materie', *Annalen der Physik*, 9 (1902), 629–41 (*Physikalische Abhandlungen und Vorträge*, I (Braunschweig, 1958), 731–43).

of all the possible complexions'. If we indicate this number for the gas and the resonators as $\mathscr{B}$ and $\mathscr{P}$ respectively, since they are independent, the total number of complexions 'is simply equal to the product' $\mathscr{P}\mathscr{B}$. If we call the proportionality factor f, we have

$$f \log(\mathscr{P}\mathscr{B}) = f \log \mathscr{B} + f \log \mathscr{P}, \tag{44}$$

where the first term on the right-hand side was the entropy of the gas and the second that of the resonators. If Planck's formula for the entropy of resonators (equation (31)) was correct, f should be

$$f = k = \omega R. \tag{45}$$

By substituting the previously calculated value for k and the 'known gas constant' R (8.31×10^7 erg mol K), Planck obtained the value of 1.62×10^{-24} for ω or

$$\frac{1}{\omega} = 6.175 \times 10^{23}.$$

Planck concluded:[73]

> Mr O. E. Meyer[74] gives for this number 640×10^{21} which agrees closely (to the previous value).

This seemed to prove the validity of the proposed definition of entropy, and with it part of the deduction of the black-body law. On this point, however, Planck was to return very soon, proposing a more generalized and detailed exposition of these ideas.[75]

The link found by Planck through equation (46) between k and R deserves more consideration.[76] The fact that the same universal constant appeared in the entropy for a set of gas molecules as well as in the entropy for a set of resonators shows that gas and radiation phenomena had been unified, as Planck repeatedly pointed out during his life.

By following this path Planck also finally managed to achieve a definition of entropy which met the requirements at the foundation of Planck's research, that is to liberate physics from all human interference. In 1908, Planck wrote:[77]

> The merit goes to Ludwig Boltzmann for having completed … the emancipation of the concept of entropy from human experimental technique and so of having elevated the second principle to the dignity of a real principle. This was obtained, in brief, by reconnecting the principle of entropy with the probability concept. This gives a more precise meaning … to when I said that Nature shows a 'preference' for a given state. Nature prefers a more probable state to a less probable one, in the sense that it performs only moves in the direction of greater probability.[78]

In this way, Planck recognized that Boltzmann had introduced a revolutionary change in the concept of entropy, reserving for himself the merit of continuing along the same path, developing Boltzmann's definition of entropy beyond all the limits of

[73] Planck (note 60), English translation of *Planck's Original Papers in Quantum Physics*, 44.
[74] O. Meyer, *Die kinetische Theorie der Gase* (Breslau, 1899).
[75] Planck (note 72).
[76] This point has been dealt with by Kuhn (note 1), 110–3, with particular regard to the electromagnetic interpretation of k and by Klein (note 1), 27–8.
[77] Planck (note 8), 19.
[78] This phrase seems to confirm Darrigol's thesis according to which Planck made every attempt to interpret Boltzmann's probabilistic theory of entropy in a deterministic sense. Indeed, he supports the view here that evolution towards a more probable state is not due solely to the probability of this state (and therefore subject to statistical fluctuations), but to a more profound natural requirement.

the theory of gases and enlarging it to include any physical system. In fact, already in 1902, in the article 'On the distribution of energy between ether and matter', he gave the following generalized formulation of Boltzmann's definition:[79]

> The entropy of a system in a certain state depends only on the probability of that state.

7. From constants *h* and *k* to constants *a* and *b*

The new derivation of the black-body radiation law enabled Planck to identify two 'universal constants' h and k, in a similar manner to the analysis of 1899.

What was the link between these constants and the previously introduced a and b? A reply was given by Planck only in 1902[80] in an article published in *Annalen der Physik*, according to which the validity of the constants a and b remained unchanged.

These constants were also used by Planck to obtain and confirm the numerical values attributed to constants h and k by another route.

To carry out this task, Planck began with the definition of entropy given by equation (37), in which $h\nu$ was substituted for ε:

$$S = k\left[\left(1+\frac{U}{h\nu}\right)\log\left(1+\frac{U}{h\nu}\right)-\frac{U}{h\nu}\log\left(\frac{U}{h\nu}\right)\right]. \tag{37}$$

In order to compare this expression with the previous definition of entropy (equation (6)) which, as he was to recall, led to Wien's law and therefore was valid only at high frequencies, Planck calculated the limit of S for $U/\nu \to 0$, that is for $\nu \to \infty$, obtaining

$$S = -\frac{kU}{h\nu}\log\left(\frac{U}{eh\nu}\right). \tag{46}$$

As Planck observed, in this high-frequency range Wien's original law held true, as did the previous entropy equation (6) based on Wien's law and introduced in 1899:

$$S = -\frac{U}{a\nu}\log\left(\frac{U}{eb\nu}\right). \tag{6}$$

By comparing this expression with equation (46), Planck obtained the following relations between the four constants a, b, h and k:

$$b = h, \qquad \frac{b}{a} = k. \tag{47}$$

Using the values of a and b obtained in 1899, Planck could recalculate values h and k. The result was the following:

$$h = 6.885\times10^{-27}\text{ erg s}, \qquad k = 1.429\times10^{-16}\text{ erg }°\text{C}^{-1},$$

which appeared to be in good agreement with the values calculated in 1900:

$$h = 6.55\times10^{-27}\text{ erg s}, \qquad k = 1.346\times10^{-16}\text{ erg }°\text{C}^{-1}.$$

Planck observed that the small divergence between the two sets of values could be ascribed to 'deviations between the measurements of the various experiments'[81] and therefore cast no doubt on the correctness of the reasoning followed in 1900.

It was with this numerical agreement that Planck concluded the discourse he

[79] Planck (note 72), 741.
[80] M. Planck, 'Über irreversible Strahlungsvorgänge. Nachtrag', *Annalen der Physik*, 4, 6 (1902), 818–831.
[81] Planck (note 80), 749.

began in 1899, demonstrating the underlying continuity between the two laws of distribution. Despite their being defined at different times and using profoundly different procedures, they were linked by a common thread, represented by the presence of two 'universal constants'.

However, what about the 'system of natural units of measurement' that seemed so dear to Planck in 1899? Planck re-examined the problem in 1906[82] in the volume *Vorlesungen über die Theorie der Wärmestrahlung*, when this theory had begun to be accepted. A whole paragraph (§159), 'The natural units of measurement', was dedicated to the question. In it, Planck re-proposed the system of units of measurement put forward in 1899 for the same reasons and even in the same words, with the difference that the constant h was now substituted for b and k for a. Obviously the 'natural units' were different:

$$\text{unit of length} = \left(\frac{Gh}{c^3}\right)^{1/2} = 4.03 \times 10^{-33}\ \text{cm},$$

$$\text{unit of mass} = \left(\frac{ch}{G}\right)^{1/2} = 5.42 \times 10^{-5}\ \text{g},$$

$$\text{unit of time} = \left(\frac{Gh}{c^5}\right)^{1/2} = 1.34 \times 10^{-43}\ \text{s},$$

$$\text{unit of temperature} = \frac{1}{k}\left(\frac{c^3h}{G}\right)^{1/2} = 3.63 \times 10^{32}\ {}^\circ\text{C}.$$

This renewed 'natural' system was reiterated by Planck in all subsequent editions of the book as if to emphasize the importance of the 'universal constants'.

8. Conclusion

In this historical analysis we have tried to describe the process by which Wien's two constants C and c', followed by Planck's first set of constants a and b and second set of constants α and B finally gave rise to the constants h and k. An analysis of this type has enabled us to bring together the various aspects of Planck's work that put him on the right track to solving the black-body problem. It was anything but easy. As we have seen, it involved a series of highly complex operations that threw doubt on consolidated semiempirical laws, including Wien's distribution law. This required a special re-interpretation of Wien's 'displacement law', first by Thiesen and then by Planck, the introduction of a new dependence of a definite quantity of energy on frequency, the interpretation of this definite quantity as the famous 'element of energy' $h\nu$ and, finally, the extension of the probabilistic concept of entropy (beyond pure thermodynamics) to the Hertzian resonators.

At the end of these operations it was possible to identify the two 'constants of nature', which must be present in the black-body law with the constants h and k and so to give the definitive solution of the black-body problem. However, the constants h and k that finally emerged, even if they were indissolubly linked to the previous values by a precise numerical ratio, formed part of a completely different theoretical context. Consequently their name changed too, despite the fact that their numerical values remained the same, as in the case of b and h. Indeed, the two constants a and b in Planck's first law were initially just two 'universal constants' introduced *ad hoc* into the entropy definition. However, in 1900 the two constants h and k in Planck's

[82] M. Planck, *Vorlesungen über die Theorie der Wärmestrahlung* (Leipzig, 1906).

second law represented the 'universal constant' that characterized the energy component and guaranteed that energy and frequency were proportional, and the 'universal constant' which ensured that the entropy of a state was proportional to its probability respectively. When the proportional quantities linked by these universal constants had been defined, it gave a physical context in which to look for the meaning of these constants. As we know, this was attempted immediately in the years that followed, generating a wide-ranging debate on the various meanings of the two constants and making a fundamental contribution to opening the way to quantum and statistical mechanics—but that is another story.

What we would like instead to emphasize here is the new definition of entropy arising from the route followed by Planck starting in 1899. As Planck himself realized, entropy successfully achieved the status of universality that he had been searching for for so long. In 1908, crowning his efforts, Planck wrote retrospectively:[83]

> The relationship between the probability of a system and its entropy is based simply on the postulate that the probability of two independent systems is equal to the product of the individual probabilities ($W = W_1 W_2$), while entropy is equal to the sum of the individual entropies ($S = S_1 + S_2$). Entropy is therefore proportional to the logarithm of the probability ($S = k \log W$). This theorem opened the way to a new method, far superior to those used in common thermodynamics, to calculate the entropy of a system in a given state. Indeed, the definition of entropy is not limited here to states of equilibrium, like those which are almost exclusively taken into consideration in usual thermodynamics, but extends to any dynamic state. And to calculate the entropy it is no longer necessary to have recourse, as Clausius does, to a reversible process which is always more or less problematic to realise, but is completely independent of all the artifices of human techniques. To sum up, the anthropomorphic character is completely eliminated and in this way the second principle, like the first, rests on a real base.

As a last consideration, we might ask ourselves what happened to the 'natural system of units of measurement' proposed by Planck back in 1899 and reiterated in 1906? The answer can be found in modern high-energy physics and cosmology manuals. After initial lack of interest, Planck's idea was resuscitated and reworked. In particular from the 1930s onwards, with the development of theory of general relativity and quantum mechanics.[84] Today Planck's 'units of measurement' (using $\hbar$ instead of h) have the following values:

$$m_P = \left(\frac{\hbar c}{G}\right)^{1/2} = 2.18 \times 10^{-5}\ \text{g},$$

$$t_P = \left(\frac{\hbar G}{c^5}\right)^{1/2} = 5.31 \times 10^{-44}\ \text{s},$$

$$l_P = \left(\frac{\hbar G}{c^3}\right)^{1/2} = 1.62 \times 10^{-35}\ \text{m},$$

and they bear the historically appropriate name of 'Planck values'.

83 Planck (note 8), 20–1.

84 This argument has been dealt with by G. Gorelik, 'The first step of quantum gravity and the Planck values', *Studies in the History of General Relativity*, edited by J. Eisenstraedt and A. Kox (Boston, 1992) if only briefly and in a different context. Gorelik's aim is to show that Planck's system of units was re-evaluated starting from the 1930s to build a new theory of Quantum Gravity.

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