

The following two papers of Planck represent only a very small part of the historical development of our knowledge about the spectral energy distribution of electromagnetic radiation. They are the result of a long series of investigations undertaken not only by Planck (in his work on irreversible processes since 1878, and—stimulated by Maxwell's theory as developed especially by H. Hertz—on the application of thermodynamics to electromagnetic processes, from about 1891) but also by many other scientists who contributed to these experimentally and theoretically in the 19th century or earlier. Planck did not work in a vacuum. On the theoretical side, his formulations were most directly preceded by the theoretical research of Wilhelm Wien, who not only introduced the entropy of (resonator-free) radiation in 1894, but also in 1893 and 1894 discovered several regularities governing the form of the black-body radiation function introduced in 1860 by Gustav Robert Kirchhoff; in 1896 Wien found, simultaneously and independently with Friedrich Paschen, what is now called Wien's distribution law. But Planck also drew on J. H. Poynting's theorem on energy flux, as well as on the law for total radiation obtained by Josef Stefan in 1879 from measurements of earlier authors and derived theoretically in 1884 by L. Boltzmann. Indeed, Planck may have retained as "youthful memories" his intense preoccupation, in his 19th year, with John Tyndall's works on heat radiation.

On the other hand the results, as they become evident in these two papers, are only the initial steps in the direction of the quantum theory to be developed later. In the years 1900 and 1901 Planck still had no conception of an essentially new hypothesis, later known as the quantum hypothesis. In 1900 in more than one regard he still relied strictly on Boltzmann's statistics of discrete kinetic energies and had no inkling, for example, of a "Bose statistics". He saw his radiation function—known to contemporaries as the "Wien-Planck" equation—as only a suggestion, which needed to be experimentally tested. This testing, undertaken in the long-wave region especially by Heinrich Rubens, would take two more decades. Such signs of incompleteness of the theory itself and of its relation to experiment affect in general, by the way, every physical problem.

In the history of physics these two papers are considered "milestones", since in the 20th century it has turned out that

they opened up a new field of physics—one field among others that were becoming important around this time (e.g. the nature of the electron, X-rays, relativity theory and nuclear radiation).

Sources of information in which the individual thought-steps of Planck toward the radiation equation and its statistical foundation can be found are almost non-existent. The collection of Planck's manuscripts in Berlin was almost completely burned in the second World War. Thus one is limited essentially to a careful study of the publications of Planck and his contemporaries and predecessors as well as of reports of meetings. If one takes proper account also of the writings of the experimenters and does not neglect to check numerical values, one can construct at least a rough picture of the possibilities, up to and around 1900, which physicists had for obtaining knowledge and confirming it. This picture comes close to the actual events. Later retrospective accounts of Planck and other authors do not—it is demonstrable—in general possess this validity.

6. On an improvement of Wien's equation for the spectrum¹

by M. Planck

(read at the meeting of 19 October 1900)

(cf. above p. 181)^{1a}

The interesting results of long wave length spectral energy measurements which were communicated by Mr. Kurlbaum at today's meeting,² and which were obtained by him and Mr. Rubens, confirm the statement by Mr. Lummer and Mr. Pringsheim, which was based on their observations that Wien's energy distribution law is not as generally valid as many have supposed up to now,³ but that this law at most has the character of a limiting case,⁴ the exceedingly simple form of which was due only to a restriction to short wave lengths and low temperatures.* Since I myself even in this Society have expressed the opinion that Wien's law must be necessarily true,⁵ I may perhaps be permitted to explain briefly the relationship between the electromagnetic radiation theory developed by me and the experimental data.

The energy distribution law is according to this theory determined as soon as the entropy S of a linear⁶ resonator which interacts with the radiation is known as a function of its vibrational energy⁷ U . I have, however, already in my last paper on this subject[†] stated that the law of increase of entropy is by itself not yet sufficient to determine this function completely;⁸ my view that Wien's law would be of general validity, was brought about rather by special considerations, namely by the evaluation of an infinitesimal increase of the entropy of a system of n identical resonators in a stationary radiation field by two different methods which led to the equation[‡]

$$dU_n \cdot \Delta U_n \cdot f(U_n) = n dU \cdot \Delta U \cdot f(U),$$

where $U_n = nU$ and $f(U) = -\frac{3}{5} \frac{d^2 S}{dU^2}$.

* Mr. Paschen has written to me that he also has recently found appreciable deviations from Wien's law.

† M. Planck, *Ann. Phys.* **1** [=306], 730 (1900).

‡ l.c.p. 732.

From this equation Wien's law follows in the form⁹

$$\frac{d^2S}{dU^2} = \frac{\text{const}}{U}.$$

The expression on the right-hand side of this functional equation is certainly the above-mentioned change in entropy since n identical processes occur independently, the entropy changes of which must simply add up. However, I could consider the possibility, even if it would not be easily understandable and in any case would still be difficult to prove, that the expression on the left-hand side would not have the general meaning which I attributed to it earlier, in other words: that the values of U_n , dU_n and ΔU_n are not by themselves sufficient to determine the change of entropy under consideration, but that U itself must also be known for this.¹⁰ Following this suggestion I have finally started to construct completely arbitrary expressions for the entropy which although they are more complicated than Wien's expression still seem to satisfy just as completely all requirements of the thermodynamic and electromagnetic theory.

I was especially attracted by one of the expressions thus constructed which is nearly as simple as Wien's expression¹¹ and which would deserve to be investigated since Wien's expression is not sufficient to cover all observations. We get this expression by putting*

$$\frac{d^2S}{dU^2} = \frac{\alpha}{U(\beta + U)} \quad ^{12}$$

It is by far the simplest of all expressions which lead to S as a logarithmic function of U —which is suggested from probability considerations¹⁴—and which moreover for small values of U reduces to Wien's expression mentioned above. Using the relation

$$\frac{dS}{dU} = \frac{1}{T}$$

and Wien's "displacement" law† one gets a radiation formula with two constants:^{15, 16}

* I use the second derivative of S with respect to U since this quantity has a simple physical meaning¹³ (l.c.p. 731).

† The expression of Wien's displacement law is simply¹⁹ $S=f(U/\nu)$, where ν is the frequency of the resonator, as I shall show elsewhere.

$$E = \frac{C\lambda^{-5}}{e^{c/\lambda T} - 1},$$

which, as far as I can see at the moment, fits the observational data, published up to now, as satisfactorily as the best equations put forward for the spectrum, namely those of Thiesen,*¹⁷ Lummer-Jahnke,† and Lummer-Pringsheim.‡ (This was demonstrated by some numerical examples.¹⁸) 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.

* M. Thiesen, *Verh. Deutsch. Phys. Ges.* **2**, 67 (1900).

One can see there that Mr. Thiesen had put forward his formula before Mr. Lummer and Mr. Pringsheim had extended their measurements to longer wave lengths. I emphasise this point as I have made a somewhat different statement before this paper was published. (M. Planck, *Ann. Phys.* **1** [= 306], 719 (1900).)

† O. Lummer and E. Jahnke, *Ann. Phys.* **3** [= 308], 288 (1900).

‡ O. Lummer and E. Pringsheim, *Verh. Deutsch. Phys. Ges.* **2**, 174 (1900).

7. On the theory of the Energy Distribution Law of the Normal Spectrum²⁰

by M. Planck

(read at the meeting of 14 December 1900)

(cf. above p. 235)^{20a}

Gentlemen: when some weeks ago I had the honour to draw your attention to a new formula which seemed to me to be suited to express the law of the distribution of radiation energy over the whole range of the normal spectrum,* I mentioned already then that in my opinion the usefulness of this equation was not based only on the apparently close agreement of the few numbers, which I could then communicate to you, with the available experimental data,† but mainly on the simple²¹ structure of the formula and especially on the fact that it gave a very simple logarithmic expression²² for the dependence of the entropy of an irradiated monochromatic vibrating resonator on its vibrational energy. This formula seemed to promise in any case the possibility of a general interpretation much better than other equations which have been proposed, apart from Wien's formula which, however, was not confirmed by experiment.

Entropy means disorder, and I thought that one should find this disorder in the irregularity with which even in a completely stationary radiation field the vibrations of the resonator change their amplitude and phase, as long as one considers time intervals long compared to the period of one vibration, but short compared to the duration of a measurement. The constant energy of the stationary vibrating resonator can thus only be considered to be a time average,²⁴ or, put differently, to be an instantaneous average of the energies of a large number of identical resonators which are in the same stationary radiation field, but far enough from one another not to influence each other directly. Since the entropy of a resonator is thus determined by the way in which the energy is distributed at one time over many resonators, I suspected that one should evaluate

* M. Planck, *Verh. D. Phys. Ges.* 2, 202 (1900).

† In the meantime Mr. H. Rubens and Mr. F. Kurlbaum have given a direct confirmation for very long wave lengths. (*S.B. Königl. Preuss. Akad. Wiss.* of 25 October, p. 929 (1900).)²³

this quantity by introducing probability considerations into the electromagnetic theory²⁵ of radiation, the importance of which for the second law of thermodynamics was originally discovered by Mr. L. Boltzmann.* This suspicion has been confirmed; I have been able to derive deductively an expression for the entropy of a monochromatically vibrating resonator and thus for the energy distribution in a stationary radiation state, that is, in the normal spectrum. To do this it was only necessary to extend somewhat the interpretation of the hypothesis of "natural"²⁶ radiation" which has been introduced by me into electromagnetic theory. Apart from this I have obtained other relations which seem to me to be of considerable importance for other branches of physics and also of chemistry.

I do not wish to give today this deduction—which is based on the laws of electromagnetic radiation, thermodynamics and probability calculus—systematically in all details, but rather to explain to you as clearly as possible the real core of the theory. This can probably be done most easily by describing to you a new, completely elementary treatment through which one can evaluate—without knowing anything about a spectral formula or about any theory—the distribution of a given amount of energy over the different colours of the normal spectrum using one constant of nature only and after that also the value of the temperature of this energy radiation using a second constant of nature. You will find many points in the treatment to be presented arbitrary and complicated, but as I said a moment ago I do not want to pay attention to a proof of the necessity and the possibility to perform it easily and practically, but to the clarity and uniqueness of the given prescriptions for the solution of the problem.

Let us consider a large number of linear, monochromatically vibrating resonators— N of frequency ν (per second),²⁸ N' of frequency ν' , N'' of frequency ν'' , ..., with all N large numbers—which are properly separated and are enclosed in a diathermic²⁷ medium with light velocity c and bounded by reflecting walls. Let the system contain a certain amount of energy, the total energy E_t (erg) which is present partly in the medium as travelling radiation and partly in the resonators as vibrational

* L. Boltzmann, especially *S.B. Kais. Ak. Wiss. Wien II*, 76, p. 373 (1877 [= 1878]).

energy. The question is how in a stationary state this energy is distributed over the vibrations of the resonators and over the various colours of the radiation present in the medium, and what will be the temperature of the total system.

To answer this question we first of all consider the vibrations of the resonators²⁹ and try to assign to them certain arbitrary energies, for instance, an energy E to the N resonators ν , E' to the N' resonators ν' , The sum

$$E + E' + E'' + \dots = E_0$$

must, of course, be less than E_t . The remainder $E_t - E_0$ pertains then to the radiation present in the medium. We must now give the distribution of the energy over the separate resonators of each group, first of all the distribution of the energy E over the N resonators of frequency ν . If E is considered to be a continuously divisible quantity, this distribution is possible in infinitely many ways. We consider, however—this is the most essential point of the whole calculation— E to be composed of a well-defined number of equal parts and use thereto the constant of nature $h = 6.55 \times 10^{-27}$ erg sec.³⁰ This constant multiplied by the common frequency ν of the resonators gives us the energy element³¹ ϵ in erg, and dividing E by ϵ we get the number P of energy elements which must be divided over the N resonators. If the ratio thus calculated is not an integer, we take for P an integer in the neighbourhood.³²

It is clear that the distribution of P energy elements over N resonators can only take place in a finite, well-defined number of ways. Each of these ways of distribution we call a “complexion”,³³ using an expression introduced by Mr. Boltzmann for a similar concept. If we denote the resonators by the numbers 1, 2, 3, ..., N , and write these in a row, and if we under each resonator put the number of its energy elements, we get for each complexion a symbol of the following form

$$\begin{array}{cccccccccc} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 & 10 \\ \hline 7 & 38 & 11 & 0 & 9 & 2 & 20 & 4 & 4 & 5 \end{array}$$

We have taken here $N = 10$, $P = 100$. The number of all possible complexions is clearly equal to the number of all possible sets of numbers which one can obtain in this way for the lower sequence for given N and P . To exclude all misunderstandings, we remark that two complexions must be considered to be

different if the corresponding sequences contain the same numbers, but in different order. From the theory of permutations we get for the number of all possible complexions

$$\frac{N(N+1) \cdot (N+2) \dots (N+P-1)}{1 \cdot 2 \cdot 3 \dots P} = \frac{(N+P-1)!}{(N-1)!P!}$$

or to a sufficient approximation,³⁴

$$= \frac{(N+P)^{N+P}}{N^N P^P}.$$

We perform the same calculation for the resonators of the other groups, by determining for each group of resonators the number of possible complexions for the energy given to the group. The multiplication of all numbers obtained in this way gives us then the total number R of all possible complexions for the arbitrarily assigned energy distribution over all resonators.

In the same way any other arbitrarily chosen energy distribution³⁵ E, E', E'', \dots will correspond to the number R of all possible complexions which must be evaluated in the above manner. Among all energy distributions which are possible for a constant $E_0 = E + E' + E'' + \dots$ there is one well-defined one for which the number of possible complexions R_0 is larger than for any other distribution. We then look for this energy distribution, if necessary by trial, since this will just be the distribution taken up by the resonators in the stationary radiation field, if they together possess the energy E_0 . The quantities E, E', E'', \dots can then be expressed in terms of one single quantity E_0 . Dividing E by N, E' by N', \dots we obtain the stationary value of the energy $U_\nu, U_\nu', U_\nu'', \dots$ of a single resonator³⁶ of each group, and thus also the spatial density of the corresponding radiation energy in a diathermic medium in the spectral range ν to $\nu + d\nu$,³⁷

$$u_\nu d\nu = \frac{8\pi\nu^2}{c^3} \cdot U_\nu d\nu,$$

so that the energy of the medium is also determined.

Of all quantities which occur only E_0 seems now still to be arbitrary. One sees easily, however, how one can finally evaluate E_0 from the given total energy E_t , since if the chosen value of E_0 leads, for instance, to too large a value of E_t , we must decrease it appropriately, and the other way round.³⁸

After the stationary energy distribution is thus determined using a constant h , we can find the corresponding temperature ϑ in degrees absolute* using a second constant of nature $k = 1.346 \times 10^{-16}$ erg degree $^{-1}$ through the equation

$$\frac{1}{\vartheta} = k \frac{d \ln R_0}{dE_0}.$$

The product $k \ln R_0$ is the entropy³⁹ of the system of resonators; it is the sum of the entropy of all separate resonators.

It would, to be sure, be very complicated to perform explicitly the above-mentioned calculations, although it would not be without some interest to test the truth of the attainable degree of approximation in a simple case. A more general calculation which is performed very simply, using exactly the above prescriptions shows much more directly⁴⁰ that the normal energy distribution determined in this way for a medium containing radiation is given by the expression⁴¹

$$u_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/k\vartheta} - 1},$$

which corresponds exactly to the spectral formula which I gave earlier

$$E_\lambda d\lambda = \frac{c_1 \lambda^{-5}}{e^{c_2/\lambda\vartheta} - 1} d\lambda.$$

The formal differences are due to the differences in the definitions of u_ν and E_λ . The first formula is somewhat more general inasfar as it is valid for an entirely arbitrary diathermic medium with light velocity c . I calculated the numerical values of h and k which I mentioned from that formula using the measurements by F. Kurlbaum and by O. Lummer and E. Pringsheim.†

I shall now make a few short remarks about the question of the necessity of the above given deduction. The fact that the chosen energy element ϵ for a given group of resonators must be proportional to the frequency ν follows immediately from

* The original states "degrees centigrade" which is clearly a slip [D. t. H.].

† F. Kurlbaum (*Ann. Phys.* **65** [=301], 759 (1898)) gives $S_{100} - S_0 = 0.0731$ Watt cm $^{-2}$, while O. Lummer and E. Pringsheim (*Verh. Deutsch. Physik Ges.* **2**, 176 (1900)) give $\lambda_m \vartheta = 2940 \mu$ degree.

the extremely important so called Wien displacement law.⁴² The relation between u and U is one of the basic equations of the electromagnetic theory of radiation. Apart from that, the whole deduction is based upon the single theorem that the entropy of a system of resonators with given energy is proportional to the logarithm of the total number of possible complexions for the given energy. This theorem can be split into two other theorems: (1) The entropy of the system in a given state is proportional to the logarithm of the probability of that state, and (2) The probability of any state is proportional to the number of corresponding complexions, or, in other words, any given complexion is equally probable as any other given complexion. The first theorem is, as far as radiative phenomena are concerned, just a definition of the probability of the state, insofar as we have for energy radiation no other *a priori* way to define the probability than the determination of its entropy. We have here one of the distinctions⁴³ from the corresponding situation in the kinetic theory of gases. The second theorem is the core of the whole of the theory presented here: in the last resort its proof can only be given empirically. It can also be understood as a more detailed definition of the hypothesis of natural radiation which I have introduced. This hypothesis I have expressed before only in the form that the energy of the radiation is completely "randomly" distributed over the various partial vibrations present in the radiation.* I plan to communicate elsewhere in detail the considerations, which have only been sketched here, with all calculations and with a survey of the development of the theory up to the present.

* M. Planck, *Ann. Phys.* **1** [=306], 73 (1900). When Mr. W. Wien in his Paris report (Rapports II, p. 38, 1900) about the theoretical radiation laws did not find my theory on the irreversible radiation phenomena satisfactory since it did not give the proof that the hypothesis of natural radiation is the only one which leads to irreversibility, he surely demanded, in my opinion, too much of this hypothesis. If one could prove the hypothesis, it would no longer be a hypothesis, and one did not have to formulate it at all. However, one could then not derive anything essentially new from it. From the same point of view one should also declare the kinetic theory of gases to be unsatisfactory since nobody has yet proved that the atomistic hypothesis is the only one which explains irreversibility. A similar objection could with more or less justice be raised against all inductively obtained theories.

To conclude I may point to an important consequence of this theory which at the same time makes possible a further test of its admissibility. Mr. Boltzmann* has shown that the entropy of a monatomic gas in equilibrium is equal to $\omega R \ln P_0$, where P_0 is the number of possible complexions (the "permutability") corresponding to the most probable velocity distribution, R being the well known gas constant (8.31×10^7 for $O=16$), ω the ratio of the mass of a real molecule to the mass of a mole, which is the same for all substances. If there are any radiating resonators present in the gas, the entropy of the total system must according to the theory developed here be proportional to the logarithm of the number of all possible complexions, including both velocities and radiation. Since, however, according to the electromagnetic theory of radiation the velocities of the atoms are completely independent of the distribution of the radiation energy, the total numbers of complexions is simply equal to the product of the numbers relating to the velocities and the number relating to the radiation. For the total entropy we have thus

$$f \ln (P_0 R_0) = f \ln P_0 + f \ln R_0,$$

where f is a factor of proportionality. The first part of the sum is the kinetic, the second part the radiation entropy. Comparing this with the earlier expressions we find

$$f = \omega R = k,$$

or
$$\omega = \frac{k}{R} = 1.62 \times 10^{-24},$$

that is, a real molecule is 1.62×10^{-24} of a mole, or, a hydrogen atom weighs⁴⁴ 1.64×10^{-24} g, since $H=1.01$, or, in a mole of any substance there are $1/\omega = 6.175 \times 10^{23}$ real molecules.⁴⁵ Mr. O. E. Meyer† gives for this number 640×10^{21} which agrees closely.⁴⁵

Loschmidt's number L , that is, the number of gas molecules in 1 cm^3 at 0°C and 1 atm is⁴⁶

$$L = \frac{1\ 013\ 200}{R \cdot 273 \cdot \omega} = 2.76 \times 10^{19}.$$

Mr. Drude‡ finds $L = 2.1 \times 10^{19}$.

* L. Boltzmann, *S.B. Kais. Akad. Wiss. Wien II*, **76**, 428 (1877 [= 1878]).

† O. E. Meyer, "Die kinetische Theorie der Gase" 2nd ed., p. 337 (1899).

‡ P. Drude, *Ann. Phys.* **1** [= **306**], 578 (1900).

The Boltzmann-Drude constant α , that is, the average kinetic energy of an atom at the absolute temperature l is

$$\alpha = \frac{3}{2}\omega R = \frac{3}{2}k = 2.02 \times 10^{-16}.$$

Mr. Drude* finds $\alpha = 2.65 \times 10^{-16}$.

The elementary quantum of electricity e , that is, the electrical charge of a positive monovalent ion or of an electron is, if ϵ is the known charge of a monovalent mole,⁴⁷

$$e = \epsilon\omega = 4.69 \times 10^{-10} \text{ e.s.u.}$$

Mr. F. Richarz† finds 1.29×10^{-10} and Mr. J. J. Thomson‡ recently 6.5×10^{-10} .

If the theory is at all correct, all these relations should be not approximately, but absolutely, valid.⁴⁸ The accuracy of the calculated numbers is thus essentially the same as that of the relatively worst known, the radiation constant k , and is thus much better than all determinations of those quantities up to now. To test it by more direct methods should be both an important and a necessary task for further research.

* loc. cit.

† F. Richarz, *Ann. Phys.* **52** [=288], 397 (1894).

‡ J. J. Thomson, *Phil. Mag.* (5)**46**, 528 (1898).

8. Notes

1. In June 1896, Wilhelm Wien proposed for the energy-distribution function the equation

$$\varphi_{\lambda} = C\lambda^{-5} \exp\left(-\frac{c}{\lambda\vartheta}\right).$$

In deriving this equation he used the transformation equation obtained from the Doppler principle,

$$\vartheta\lambda = \vartheta_0\lambda_0$$

(where ϑ , ϑ_0 are temperatures and λ , λ_0 are wavelengths) and the Stefan-Boltzmann law for the total radiation (Wien 1896). Planck, by systematic consideration of the energy of a Hertzian resonator and of the energy and entropy of the radiation field, gave Wien's function the alternative form

$$u = \frac{8\pi b\nu^3}{c^3} \exp\left(-\frac{a\nu}{\vartheta}\right)$$

(u =energy density, ν =frequency, c =speed of light, a , b =radiation constants) (Planck 1899, p. 471).

Independently of Wien, Friedrich Paschen in June 1896 obtained from experimental data an equation similar to the first one mentioned above,

$$\varphi_{\lambda} = c_1\lambda^{-\alpha} \exp\left(-\frac{c_2}{\lambda T}\right)$$

(T =temperature, $\alpha=5.660$). These and other energy distribution functions obtained before 1896 by W. A. Michelson (1887), H. F. Weber (1888), and R. von Kövesligethy (1890) have been discussed by H. Kangro (1970).

1a. Reference to the first notice in this Journal on Planck's speech of 19 October 1900.

2. Ferdinand Kurlbaum presented the results of measurements by himself and Heinrich Rubens of the radiation energy of a black body by spectral decomposition through "Reststrahlen" (residual rays) of fluorspar ($\lambda=24\ \mu$ and $31.6\ \mu$) and of rock salt ($\lambda=51.2\ \mu$) (soon afterwards also of quartz, $\lambda=8.5\ \mu$). Rubens had already communicated these results verbally to Planck on 7 October 1900. By the evening of the

very same day Planck found the new equation characteristic of the beginning of the quantum hypothesis. One or two days later Rubens reconfirmed its agreement with the results of his observations. On that 7 October, Rubens told Planck, "that for the longest waves measured by him the law recently proposed by Lord Rayleigh ... is valid" (G. Hettner 1922, p. 1036).

Later, after W. Nernst and Th. Wulf (1919) doubted the validity of the Planck radiation law, Rubens acknowledged that in 1900 he was pretty satisfied that the test was successful to within a few percent. (Rubens and Michel 1921, p. 577) Rubens made more exact measurements in 1920. It seems to be the sign of an historical process that knowledge must be gained in steps, if one does not wish to be drowned in the flood of new phenomena.

3. Lummer and Pringsheim 1900 (*circa* September), 163–180; both speak simply of an invalidity of the Wien law, not of a partial validity. Therefore they suggest a new form, most probably influenced by knowledge of the Rayleigh equation:

$$E = CT\lambda^{-4} \exp\left(-\frac{c}{(\lambda T)^\nu}\right), \quad 1.2 \leq \nu \leq 1.3$$

In the preceding year, despite systematic deviations of the measured values of c from each other and from the theoretical value, they still did not dare to make this decision. (Lummer & Pringsheim 1899, February and November) History teaches above all the important principle that a problem consists in distinguishing between errors of measurement and real disagreement of experimental results and valid theories.

4. Planck speaks here of Wien's law as a "limiting law". Lummer and Pringsheim had recently conceded that even for the energies measured by them at long wavelengths ($12 \mu \leq \lambda \leq 18 \mu$) for low temperature the "Wien formula can still represent our observations" (Lummer & Pringsheim 1900, pp. 179–80; cf. 1899, p. 224).

5. Date unknown.

6. I.e., one-dimensional oscillator (Planck 1895, p. 290).

7. U is more precisely the energy in the vicinity of the resonator out to distances that are "infinite" compared to the size of the resonator (Planck 1896, p. 161).

8. Planck knew very well in 1899 and March 1900 that he could make only the *negative* assertion: he said he did not find any other function (other than Wien's) which would satisfy his entropy equation (Planck 1899, p. 476; 1900, p. 730).

$$9. \quad n dU \cdot n \Delta U \cdot f(U_n) = n \cdot dU \Delta U f(U) \\ (1) \quad nf(nU) = f(U).$$

Differentiating this functional equation with respect to n gives:

$$U \frac{df(nU)}{d(nU)} = -\frac{1}{n^2} f(U);$$

using (1),

$$\frac{f'(nU)}{f(nU)} = -\frac{1}{nU}$$

and integrating,

$$f(nU) = \frac{\text{const}}{nU}$$

from (1) again:

$$f(U) = \frac{\text{const}}{U} \Rightarrow \frac{d^2 S}{dU^2} = -\frac{\alpha}{U}$$

$$\frac{dS}{dU} = -\alpha \{\ln U + C\}, \quad C = (\ln \beta + 1)$$

$$\frac{1}{\vartheta} = -\alpha \{\ln (\beta e U)\}; \quad \frac{1}{\vartheta} \equiv \frac{dS}{dU}$$

since α , β must be, according to W. Wien, functions of λ , which again depends on the velocity of Maxwell's distribution (Planck 1900, 732; Wien, *Ann. Phys.* 1896, **294**, 665), Planck got with $\alpha = (av)^{-1}$ and $\beta = (ebv)^{-1}$:

$$\frac{1}{\vartheta} = -\frac{1}{av} \left\{ \ln \frac{U}{bv} \right\}$$

$$U = bv \cdot \exp \left(-\frac{av}{\vartheta} \right)$$

(Planck 1900, p. 732-3. See note 19.)

10. This discerning remark was justified in 1906 (Planck 1906, p. 218):

$$(S_t, \Sigma_t \text{ total entropy})$$

for one resonator:

$$dS_t = -\frac{3}{5}k \frac{dU \cdot \Delta U}{U(U+h\nu)}$$

for n resonators:

$$d\Sigma_t = -\frac{3}{5}k \frac{dU_n \cdot \Delta U_n}{U_n \left(\frac{U_n}{n} + h\nu \right)}$$

and with $d\Sigma_t = \frac{3}{5} dU_n \cdot \Delta U_n \cdot \frac{d^2 S_n}{dU_n^2}$ (Planck 1906)

$$\Rightarrow \frac{d^2 S_n}{dU_n^2} = -\frac{nk}{U_n(U_n + nh\nu)}$$

$$n \frac{d^2 S_n}{dU_n^2} = -\frac{nk}{U_n(U+h\nu)} = -\frac{k}{U(U+h\nu)}$$

(assumed in 1900) $nf(U_n, U) = f(U)$

(1901, 555) $nf(U_n, n) = f(U)$

Planck acknowledged in 1901 that he had already called attention to the problem at the Physics Congress at the beginning of August 1900 in Paris, where Otto Lummer and Wilhelm Wien had criticized his conclusion for n resonators based on a single resonator (Planck 1901, p. 554–5; cf. Kangro 1970, p. 220).

11. The principle of “simplicity” is for Planck an important support for his argument; cf. his remarks at the end of the first paper and beginning of the second paper.

12. For small β the expression obviously reduces to

$$\frac{d^2 S}{dU^2} = +\frac{\alpha}{U^2}.$$

This corresponds to the case of large values of λT and becomes:

$$\frac{dS}{dU} = -\frac{\alpha}{U} (+ \text{const.})$$

$$\equiv \frac{1}{T}$$

$$\Rightarrow U \sim T$$

For large values $\beta \gg U$ we have:

$$\frac{d^2S}{dU^2} = \frac{\alpha}{U(\beta+U)}$$

$$\approx \frac{\alpha}{\beta} \frac{1}{U}$$

which is equivalent to Wien's law.

In December 1900 Planck changed, in consequence of his statistics, the sign:

$$\frac{d^2S}{dU^2} = -\frac{\alpha}{U(\beta+U)} \quad (\text{cf. notes 16 and 41})$$

13. d^2S/dU^2 is the change in entropy increase. Only to the latter did Planck ascribe a physical meaning (March 1900): "the numerical measure of the irreversibility of the process or for the uncompensated transformation of work into heat" (Planck 1900, p. 731). The entropy itself, however—he argued—has no physical meaning.

14. By the time of publication of this paper (October 1900) Planck thus had clearly made the connection with the probability concept, as he confirmed in December (second paragraph of the second paper). Perhaps he never lost sight of this concept, he who is known to have remained in communication with Boltzmann every year previously, for example at the Naturforschertagung in Munich in September 1899.

Already in 1898 Planck had obtained, for the entropy of a resonator vibrating with frequency ν_0 , the equation

$$S = \ln U_0$$

(Planck 1898, p. 472). Yet this equation had not appeared again. It would have led to the "Rayleigh term":

$$\frac{d^2S}{dU^2} \sim \frac{1}{U_0^2}$$

Apart from this, logarithmic expressions for the entropy in terms of the variables (T , V) were already common in thermodynamics as was familiar to Planck.

15. The fact that there are two constants (corresponding to the two variables λ and T) was emphasized by Planck especially in his December paper and even earlier, 1898, when he viewed the damping constant σ and the resonator proper frequency ν_0 as characteristic in the expression for the resonator energy (Planck 1898, p. 474).

$$16. \quad \frac{dS}{dU} = \frac{\alpha}{\beta} \{ \ln U - \ln (\beta + U) \}$$

$$\equiv \frac{1}{T}$$

$$\Rightarrow \quad U = \beta \left\{ \exp \left(-\frac{\beta}{\alpha T} \right) - 1 \right\}^{-1}.$$

Planck can apply his 1899 expressions for the energy-radiation of the field in any direction:

$$K = 2 \int_0^{\infty} \bar{K} \, d\nu = \int_0^{\infty} E_{\lambda} \, d\lambda$$

$$\Rightarrow \quad E_{\lambda} = \frac{2c}{\lambda^2} \cdot \bar{K}$$

where \bar{K} = intensity per unit frequency interval of monochromatic polarized radiation in one direction, E_{λ} = intensity per unit wavelength of monochromatic polarized radiation in one direction, $d\nu \sim (c/\lambda^2) \, d\lambda$.

On the other hand, \bar{K} is connected in the stationary state with the energy U of one resonator by the equation

$$\bar{K} = (\nu^2/c^2)U = U/\lambda^2.$$

Since according to the relation $S = f(U/\nu) = \alpha f_1(U/\beta)$ we have

$$\beta \sim \nu = c/\lambda$$

it follows that

$$E_{\lambda} \sim (2c^2/\lambda^5) \frac{1}{e^{-\beta/\alpha T} - 1} \quad (c = \text{speed of light})$$

and by analogy to the 1899 theory [$E_{\lambda} = (2c^2b/\lambda^5) \exp(-ac/\lambda T)$]:

$$E_{\lambda} = (2c^2b/\lambda^5) \frac{1}{e^{-bc/\alpha T\lambda} - 1}$$

$$= C\lambda^{-5} \{ \exp(\bar{c}/\lambda T) - 1 \}^{-1}. \quad (\bar{c} = \text{radiation constant})$$

The total energy density (taking all resonances together) would be (1899):

$$\bar{E} = (4\pi/c) \cdot E_\lambda \\ = \frac{8\pi cb}{\lambda^5} \frac{1}{e^{-bc/\alpha T\lambda} - 1}$$

(Planck 1899, p. 458, 461, 475; cf. 1901, p. 561).

17. Max Thiesen first modified the Wien distribution equation on the basis of deviations which the values measured up to that date had given (February 1900):

$$E_1 = c_1' \sqrt{\lambda T} \lambda^{-5} \exp(-c_2'/\lambda T).$$

If one retrospectively combines the Wien form (E_2) with the form first proposed in June 1900 by Lord Rayleigh,

$$[E_3] = \bar{c}_1 \cdot \lambda^{-4} \exp(-\bar{c}_2/\lambda T)$$

by taking the geometric mean, then one obtains (including the various constants c_1 , c_2 , c_1' , c_2' , \bar{c}_1 , \bar{c}_2 as determined by the Stefan-Boltzmann law and the displacement law) exactly:

$$E_1 = \sqrt{E_2 E_3}.$$

For this reason Planck, Lummer and Pringsheim as well as Rubens emphasized correctly the relatively good agreement of Thiesen's formula with the observed values in the intermediate region.

18. Not yet discovered.

19. With the help of this form (derivation: Planck 1901, pp. 559-61) of the so-called displacement law Planck could make the comparison $\beta \sim \nu$. The name "displacement law" [*Verschiebungsgesetz*] was introduced for the first time in 1899 by Lummer and Pringsheim, but the law itself is older. In 1887 W. A. Michelson first attempted to give a form $\lambda_m^2 \vartheta = \text{constant}$ ($\vartheta = \text{temperature}$); in 1888 H. F. Weber wrote $\lambda_m = 1/bT$ (where b in general depends on the nature of the substance). W. Wien appealed to this law in his derivation of the transformation formula

$$\vartheta \lambda = \vartheta_0 \lambda_0$$

(1893; and 1894, without assuming equal distribution). Earlier (1890) R. v. Kövesligethy had already published such a form.

Planck's original form,

$$E d\lambda = T^5 \psi(\lambda T) d\lambda$$

(Planck 1901, p. 559) can first be found in a paper of Lord Rayleigh (1898), and then, independently, in a paper of Max Thiesen (1900). Both emphasize that in it ψ depends only on the single variable λT (Rayleigh 1898, p. 522). The form $I \cdot \lambda^5 = \varphi(\lambda T)$ appeared first in October 1900 in a paper of Joseph Larmor (cf. Kangro 1970, *passim*).

20. By "Normalspectrum" Planck means the blackbody spectrum; this must be distinguished from the term "normales Spectrum" then also in use, to mean the graph of the energy of a spectrum as a function of the wavelength.

20a. Reference to the announcement in this journal of Planck's speech on December 14, 1900.

21. Cf. note 11. The principle of simplicity can be traced throughout the entire history of physics. Thus for example Lord Rayleigh in 1889 gave on the ground of simplicity the energy distribution function of H. F. Weber preference over other functions (Rayleigh 1889, p. 460). Also J. P. Joule in 1848 used this principle to justify his hypothesis of the rectilinear movement of "atoms", R. E. Clausius in 1879 to support the one fluid hypothesis in electricity.

22. This refers to the equation

$$S = \alpha \cdot f_1(U/\beta) = \alpha \left\{ \frac{U}{\beta} \ln \frac{U}{\beta} - \left(1 + \frac{U}{\beta}\right) \ln \left(1 + \frac{U}{\beta}\right) \right\}$$

October 1900 derived from:

$$\frac{d^2 S}{dU^2} = \frac{\alpha}{U(\beta + U)}.$$

23. The detailed report on the results of measurements of the energy of very long wave radiation contained of course the values already communicated orally to Planck by Rubens on 7 October (note 2).

24. In the 1897 theory for radiation intensity in the medium Planck introduced the average values—in reference to W. Wien—arguing that only these are accessible to physical measurements (Planck 1897, p. 1130). Already in 1898 he

used the time average of the energy U in the neighborhood of a resonator (Planck 1898, p. 459). In 1899, J. Königsberger attempted to save W. Wien's statistics of the velocities of many molecules agitated by radiation against objections by replacing these statistics in the same way by the time-average for a single molecule (Königsberger 1899, pp. 249–50).

25. Several (N) resonators of the same vibration frequency are treated statistically later (see below).

26. Planck called the radiation "natural" since—as he argued—the phenomena of absorption and emission of heat rays indicate that the exciting waves of the radiation field in *nature* are not without connection with the energy U of the resonators. Mathematically this connection will not be guaranteed since certain coefficients of the partial vibrations in the Fourier decomposition of the resonator energy as a function of the field intensity are unknown. So the partial vibrations—as many as possible—(of small amplitude) ought to be reduced on the average to zero. The field radiation should therefore not be considered "synchronized with the resonator", but rather disordered (Planck 1898, p. 469; 1897, pp. 1132–3). "Nature", a favorite concept of Planck, demonstrates the existence of irreversible processes. Nature, he said, decides which connection between the properties (wavelength, amplitude, phase) of the exciting wave and of the "secondary conductor" (=Hertzian resonator) exist (Planck 1895, p. 295).

27. Penetrable by heat.

28. Planck, like earlier theoreticians (e.g. E. Lommel, 1871) but unlike the experimentalists, uses the frequency instead of the wavelength (cf. also J. Stoney, 1871).

29. I.e., without considering the energy in the "medium of the propagating radiation".

30. Modern value: $h = 6.626 \times 10^{-27}$ erg sec.

Planck's calculation: The difference between the two measured values S_{t_1} , S_{t_2} of the energy radiated per second into the air by the same cubic centimeter of a black body at two different temperatures, say $t_2 = 100^\circ$ and $t_1 = 0^\circ$, is compared with the total energy density in space,

$$\int_0^{\infty} u_{\nu} d\nu = \int_0^{\infty} \frac{8\pi h\nu^3}{c^3} \frac{d\nu}{e^{h\nu/kT} - 1}$$

which gives:

$$(1) \quad \frac{4(S_{100} - S_0)}{c(T_2^4 - T_1^4)} = \frac{48\pi k^4}{c^3 h^3} \sum_1^{\infty} \frac{1}{\nu^4}$$

(c = speed of light).

From the transcendental equation obtained by calculating the energy u at the wavelength where it is a maximum, he finds

$$(2) \quad \lambda_m = \frac{ch}{Tk\beta}$$

where $\beta = 4.9651 \dots$. From (1) and (2) and from a measured value of λT there follows:

$$h = 6.55 \times 10^{-27} \text{ erg sec}$$

$$k = 1.346 \times 10^{-16} \text{ erg/deg}$$

(Planck 1901, pp. 561–63). The modern value of k is 1.3805×10^{-16} erg/deg.

Theoretically one must have—contrary to Planck's lifelong opinion (first stated in 1901, pp. 822–23)—

$$h \neq b \quad \text{and} \quad k \neq b/a$$

(cf. Kangro 1970, pp. 144–47; for b , a see note 1).

31. This states in words the equation:

$$\epsilon = h\nu.$$

The expression “energy quantum” for ϵ was first coined by Einstein (1905). Planck first spoke of a quantum of action h in 1906, yet there was still no mention of a “quantum hypothesis” even at this time, to say nothing of a “quantum theory”. In the following years Planck, referring to the phase space of J. W. Gibbs, emphasized the quantity of action, whereas Einstein preferred to speak of energy.

32. This postulate was never used again. L. Boltzmann had suggested a similar approximation in 1877 in order to approximate a continuum by the statistics of a set of discrete energy values (L. Boltzmann 1878, pp. 393–94).

He used discrete energy values as early as 1872 and pointed explicitly to the fact that the method of approximating continuous quantities by discrete quantities is based on a

well-established tradition (Lagrange, Stefan, and Riemann) (Boltzmann 1909, vol. 1, p. 347; for English translation see S. G. Brush, "Kinetic Theory", Oxford, 1966, vol. 2, pp. 117-132). The idea is even older; it is found for example in the geometric derivation of the law of gravity by Isaac Beeckman (1618).

33. "Complexion", according to Boltzmann, is a method of distributing integer multiples p of the energy ϵ which belong to a given total energy $E = \lambda\epsilon$ among n molecules. Boltzmann considered the distribution of energy elements $\epsilon, 2\epsilon \dots p\epsilon$ in such a way that $w_0 \dots w_p$ molecules have $0 \dots p\epsilon$ energy. A particular distribution k has

$$P_k = \frac{n!}{(w_0)!(w_1)! \dots}$$

permutations. For *this* distribution of states the probability is defined by Boltzmann as P_k/J , where J is the sum $\sum_k P_k$ of all possible distributions:

$$J = \frac{(\lambda + n - 1)!}{(n - 1)! \lambda!}. \quad (\text{Boltzmann})$$

In contrast to Boltzmann, Planck left out the first step and defined at once the number of complexions of *all* state distributions as the "number of all possible complexions":

$$\frac{(N + P - 1)!}{(N - 1)! P!}$$

this expression corresponding to Boltzmann's J (cf. Klein 1962, p. 473).

34. Planck applied Stirling's formula in first approximation. If one wished to take account of e^{-n} as well as $n^{1/2}$, then under the assumption $N \gg P$ there would be no change in Planck's approximation. $N > P$ is valid for $\lambda T < 20760 \mu \text{ deg}$, and thus even for all the energies of quartz residual rays measured by Rubens and Kurlbaum ($\lambda = 8.5 \mu, T < 1800^\circ \text{K}$). However, Boltzmann himself used a simplification to calculate his J just for the opposite assumption, namely $\lambda \gg n$ (Boltzmann 1878, 399).

35. After the distribution of the *other* E_k among the individual groups of resonators k with frequency ν_k , the statistics must be, according to Planck's idea, determined anew for each group of resonators.

36. Therefore he did not—as later, in 1901—average the total energy of all resonators but only that of each group of resonators.

37. See note 16; according to this set

$$u = \frac{4\pi K}{c}$$

$$= \int_0^\infty \bar{u} \, d\nu$$

38. Thus the energy of the radiation field is included as part of the energy U in the neighbourhood of the resonator and is “analyzed” by the resonator (Planck 1898, p. 461).

39. Boltzmann writes the entropy, which he defines as $\int dQ/T$ (where “ T is the average kinetic energy of a gas molecule”), in the form

$$\int \frac{dQ}{T} = \frac{2}{3} \Omega$$

where Ω , the measure of permutability, is proportional to the logarithm of the permutability P (essentially to its denominator), and therefore to

$$-\sum_{a,b,c,\dots} w_{abc\dots} \ln w_{abc\dots}$$

Planck reduces it to the entropy as he has defined it:

$$\int \frac{dQ}{T} = \frac{2}{3} \ln P$$

$$\int \frac{dQ}{\vartheta} = R\omega \ln P = k \ln P$$

where $T = \frac{3}{2} R\vartheta\omega$, ϑ = temperature, $\omega = m_{\text{atom}}/M_{\text{gram-atom}}$ (Planck 1901, p. 564–65).

40. Avoiding the procedure of maximization.

41. This expression for u , dv has probably been obtained from the form statistically calculated for U before (cf. 1901, 556–558):

$$\text{Using } R \approx \frac{(N+P)^{N+P}}{N^N \cdot P^P} \quad \text{and} \quad U_n = P\epsilon = NU$$

the equation $S_N = k \ln R$ leads to:

$$S_N = kN \left\{ \left(1 + \frac{U}{\epsilon}\right) \ln \left(1 + \frac{U}{\epsilon}\right) - \frac{U}{\epsilon} \ln \frac{U}{\epsilon} \right\},$$

which implies:

$$S = \frac{S_N}{N} \quad (\epsilon = h\nu)$$

$$\frac{dS}{dU} \equiv \frac{1}{\vartheta}$$

$$U = h\nu \{ \exp(h\nu/k\vartheta) - 1 \}^{-1}$$

(Planck 1901, p. 561). Thus it is certain that Planck knew U in December 1900; in October, however, he knew it only up to a constant factor k (and h).

42. Therefore known already in October to Planck (see note 19).

43. Not until 1913 did Planck refer back again to Boltzmann's logarithm of the denominator of the permutation number, i.e. to the quantity which Boltzmann essentially had equated to the entropy

$$-\sum w_n \ln w_n,$$

in order to compute from it by two *different* constraints first the Maxwell velocity distribution, then the radiation energy distribution function:

Constraints:

1. Gas and radiation

$$\sum_1^{\infty} \delta w_n = 0$$

2. Ideal gas:

$$\sum_1^{\infty} E_{\text{kin}}^{(n)} \delta w_n = 0$$

Radiation:

$$\sum_1^{\infty} \left(n - \frac{1}{2}\right) \delta w_n = 0$$

(Boltzmann 1878, p. 402, 427–8; Planck 1919, pp. 122–3, 127 139).

44. Modern value (1971): $m_{H^+} = 1.67 \times 10^{-24}$ g.

45. Modern value (1971): 6.022×10^{23} mol⁻¹. Planck interpreted Meyer's results incorrectly. For Meyer spoke of "640 trillion molecules per mg" of hydrogen. This number, however, corresponds to

$$\begin{aligned} N &= 640 \times 10^{18} \times 10^3 \times 2.016 \\ &= 1.29 \times 10^{24} \text{ molecules mol}^{-1}. \end{aligned}$$

Others in Meyers' time also used such nearly doubled values for the molecule number.

$$\begin{aligned} 46. \quad N &= \frac{p}{RT} \frac{1}{\omega} \\ &= \frac{p}{RT} \frac{M}{m} \\ &= \frac{n}{V} \end{aligned}$$

$$\begin{aligned} p &= l_{\text{Hg}} \cdot \rho_{\text{Hg}} \\ &= 76 \cdot 13.595 \cdot 981 \text{ gcm}^{-1} \text{ s}^{-2} \\ &= 1\,013\,500 \text{ gcm}^{-1} \text{ s}^{-2} \end{aligned}$$

where $\omega = m/M$ (see above), $pV = RT$, V = molar volume, n = number of molecules in a mol, $p = 1$ at. of pressure at 0°C, l_{Hg} = length of the corresponding mercury column, ρ_{Hg} = specific gravity (= $d_{\text{Hg}} \cdot g$), g acceleration of gravity at earth's surface.

47. ϵ (Faraday's constant) = 1.29×10^{10} c.g.s. (Richarz and Thomson)

$$[= 96,100 \text{ coulombs mol}^{-1}]$$

Modern value (1971): 96,487 coulombs mol⁻¹.

The modern value (1971) for e is 4.803×10^{10} c.g.s.; thus Planck's value was by far the most accurate one known up to 1900.

48. Planck referred to the mass of the hydrogen atom m and the elementary quantum of electricity e by the collective names "elementary quanta of matter and electricity" (1901).

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(See pp. 30–31, “Quellen”, for full titles of German-language articles)

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