

# On the Law of Distribution of Energy in the Normal Spectrum

Max Planck

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[Transcriber's Note: Where an equation is numbered and NOT part of an image, I have used a pound (#) sign to indicate a numbered equation. Due to the formatting, I would not want some to think that a numerical factor was being used in the equation. J.P.]

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The recent spectral measurements made by O. Lummer and E. Pringsheim<sup>1</sup>, and even more notable those by H. Rubens and F. Kurlbaum<sup>2</sup>, which together confirmed an earlier result obtained by H. Beckmann,<sup>3</sup> show that the law of energy distribution in the normal spectrum, first derived by W. Wien from molecular-kinetic considerations and later by me from the theory of electromagnetic radiation, is not valid generally.

In any case the theory requires a correction, and I shall attempt in the following to accomplish this on the basis of the theory of electromagnetic radiation which I developed. For this purpose it will be necessary first to find in the set of conditions leading to Wien's energy distribution law that term which can be changed; thereafter it will be a matter of removing this term from the set and making an appropriate substitution for it.

In my last article<sup>4</sup> I showed that the physical foundations of the electromagnetic radiation theory, including the hypothesis of "natural radiation," withstand the most severe criticism; and since to my knowledge there are no errors in the calculations, the principle persists that the law of energy distribution in the normal spectrum is completely determined when one succeeds in calculating the entropy  $S$  of an irradiated, monochromatic, vibrating resonator as a function of its vibrational energy  $U$ . Since one then obtains, from the relationship  $dS/dU = 1/q$ , the dependence of the energy  $U$  on the temperature  $q$ , and since the energy is also related to the density of radiation at the corresponding frequency by a simple relation,<sup>5</sup> one also obtains the dependence of this density of radiation on the temperature. The normal energy distribution is then the one in which the radiation densities of all different frequencies have the same temperature.

Consequently, the entire problem is reduced to determining  $S$  as a function of  $U$ , and it is to this task that the most essential part of the following analysis is devoted. In my first treatment of this subject I had expressed  $S$ , by definition, as a simple function of  $U$  without further foundation, and I was satisfied to show that this form of entropy meets all the requirements imposed on it by thermodynamics. At that time I believed that this was the only possible expression and that consequently Wien's law, which follows from it, necessarily had general validity. In a later, closer analysis,<sup>6</sup> however, it appeared to me that there must be other expressions which yield the same result, and that in any case one needs another condition in order to be able to calculate  $S$  uniquely. I believed I had found such a condition in the principle, which at the time seemed to me perfectly plausible, that in an infinitely small irreversible change in a system, near thermal equilibrium, of  $N$  identical resonators in the same stationary radiation field, the increase in the total entropy  $S_N = NS$  with which it is associated depends only on its total energy  $U_N = NU$  and the changes in this quantity, but not on the energy  $U$  of individual resonators. This theorem leads again to Wien's energy distribution law. But since the latter is not confirmed by experience one is forced to conclude that even this principle cannot be generally valid and thus must be eliminated from the theory.<sup>7</sup>

Thus another condition must now be introduced which will allow the calculation of  $S$ , and to accomplish this it is necessary to look more deeply into the meaning of the concept of entropy. Consideration of the untenability of the hypothesis made formerly will help to orient our thoughts in the direction indicated by the above discussion. In the following a method will be described which yields a new, simpler expression for entropy and thus provides also a new radiation equation which does not seem to conflict with any facts so far determined.

## **I. CALCULATIONS OF THE ENTROPY OF A RESONATOR AS A FUNCTION OF ITS ENERGY**

§1. Entropy depends on disorder and this disorder, according to the electromagnetic theory of radiation for the monochromatic vibrations of a resonator when situated in a permanent stationary radiation field, depends on the irregularity with which it constantly changes its amplitude and phase, provided one considers time intervals large compared to the time of one vibration but small compared to the duration of a measurement. If amplitude and phase both remained absolutely constant, which means completely homogeneous vibrations, no entropy could exist and the vibrational energy would have to be completely free to be converted into work. The constant energy  $U$  of a single stationary vibrating resonator accordingly is to be taken as time average, or what is the same thing, as a simultaneous average of the

energies of a large number  $N$  of identical resonators, situated in the same stationary radiation field, and which are sufficiently separated so as not to influence each other directly. It is in this sense that we shall refer to the average energy  $U$  of a single resonator. Then to the total energy

$$\text{(Equation \#1)} \quad U_N = NU$$

of such a system of  $N$  resonators there corresponds a certain total entropy

$$\text{(\#2)} \quad S_N = NS$$

of the same system, where  $S$  represents the average entropy of a single resonator and the entropy  $S_N$  depends on the disorder with which the total energy  $U_N$  is distributed among the individual resonators.

Â§2. We now set the entropy  $S_N$  of the system proportional to the logarithm of its probability  $W$ , within an arbitrary additive constant, so that the  $N$  resonators together have the energy  $E_N$ :

$$\text{(\#3)} \quad S_N = k \log W + \text{constant}$$

In my opinion this actually serves as a definition of the probability  $W$ , since in the basic assumptions of electromagnetic theory there is no definite evidence for such a probability. The suitability of this expression is evident from the outset, in view of its simplicity and close connection with a theorem from kinetic gas theory.<sup>8</sup>

Â§3. It is now a matter of finding the probability  $W$  so that the  $N$  resonators together possess the vibrational energy  $U_N$ . Moreover, it is necessary to interpret  $U_N$  not as a continuous, infinitely divisible quantity, but as a discrete quantity composed of an integral number of finite equal parts. Let us call each such part the energy element  $e$ ; consequently we must set

$$\text{(\#4)} \quad U_N = Pe$$

where  $P$  represents a large integer generally, while the value of  $e$  is yet uncertain.

[The above paragraph in the original German](#)

Now it is evident that any distribution of the  $P$  energy elements among the  $N$  resonators can result only in a finite, integral, definite number. Every such form of distribution we call, after an expression used by L. Boltzmann for a similar idea, a "complex." If one denotes the resonators by the numbers 1, 2, 3,

... N, and writes these side by side, and if one sets under each resonator the number of energy elements assigned to it by some arbitrary distribution, then one obtains for every complex a pattern of the following form:

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

Here we assume  $N = 10$ ,  $P = 100$ . The number  $R$  of all possible complexes is obviously equal to the number of arrangements that one can obtain in this fashion for the lower row, for a given  $N$  and  $P$ . For the sake of clarity we should note that two complexes must be considered different if the corresponding number patterns contain the same numbers but in a different order.

From combination theory one obtains the number of all possible complexes as:

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

Now according to Stirling's theorem, we have in the first approximation:

$$N! = N^N$$

Consequently, the corresponding approximation is:

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

§4. The hypothesis which we want to establish as the basis for further calculation proceeds as follows: in order for the  $N$  resonators to possess collectively the vibrational energy  $U_N$ , the probability  $W$  must be proportional to the number  $R$  of all possible complexes formed by distribution of the energy  $U_N$  among the  $N$  resonators; or in other words, any given complex is just as probable as any other. Whether this actually occurs in nature one can, in the last analysis, prove only by experience. But should experience finally decide in its favor it will be possible to draw further conclusions from the validity of this hypothesis about the particular nature of resonator vibrations; namely in the interpretation put forth by J. v. Kries<sup>9</sup> regarding the character of the "original amplitudes, comparable in magnitude but independent of each other." As the

matter now stands, further development along these lines would appear to be premature.

Â§5. According to the hypothesis introduced in connection with equation (3), the entropy of the system of resonators under consideration is, after suitable determination of the additive constant:

$$\begin{aligned} (\#5) \quad S_N &= k \log R \\ &= k \{ (N + P) \log (N + P) - N \log N - P \log P \} \end{aligned}$$

and by considering (4) and (1):

$$S^N = kN \left\{ \left( 1 + \frac{U}{\epsilon} \right) \log \left( 1 + \frac{U}{\epsilon} \right) - \frac{U}{\epsilon} \log \frac{U}{\epsilon} \right\}$$

Thus, according to equation (2) the entropy  $S$  of a resonator as a function of its energy  $U$  is given by:

$$(6) \quad S = k \left\{ \left( 1 + \frac{U}{\epsilon} \right) \log \left( 1 + \frac{U}{\epsilon} \right) - \frac{U}{\epsilon} \log \frac{U}{\epsilon} \right\}$$

## II. Introduction of Wien's Displacement Law

Â§6. Next to Kirchoff's theorem of the proportionality of emissive and absorptive power, the so-called displacement law, discovered by and named after W. Wien,<sup>10</sup> which includes as a special case the Stefan-Boltzmann law of dependence of total radiation on temperature, provides the most valuable contribution to the firmly established foundation of the theory of heat radiation, In the form given by M. Thiesen<sup>11</sup> it reads as follows:

$$E \cdot dl = q^5 y(lq) \cdot dl$$

where  $l$  is the wavelength,  $E \cdot dl$  represents the volume density of the "black-body" radiation<sup>12</sup> within the spectral region  $l$  to  $l + dl$ ,  $q$  represents temperature and  $y(x)$  represents a certain function of the argument  $x$  only.

Â§7. We now want to examine what Wien's displacement law states about the dependence of the entropy  $S$  of our resonator on its energy  $U$  and its characteristic period, particularly in the general case where the resonator is situated in an arbitrary diathermic medium. For this purpose we next generalize Thiesen's form of the law for the radiation in an arbitrary diathermic

medium with the velocity of light  $c$ . Since we do not have to consider the total radiation, but only the monochromatic radiation, it becomes necessary in order to compare different diathermic media to introduce the frequency  $n$  instead of the wavelength  $l$ .

Thus, let us denote by  $u \, dn$  the volume density of the radiation energy belonging to the spectral region  $n$  to  $n + dn$ ; then we write:  $u \, dn$  instead of  $E \, dl$ ;  $c / n$  instead of  $l$ , and  $cdn / n^2$  instead of  $dl$ . From which we obtain

$$u = \theta^5 \frac{c}{v^2} \cdot \psi\left(\frac{c\theta}{v}\right)$$

Now according to the well-known Kirchoff-Clausius law, the energy emitted per unit time at the frequency  $n$  and temperature  $q$  from a black surface in a diathermic medium is inversely proportional to the square of the velocity of propagation  $c^2$ ; hence the energy density  $U$  is inversely proportional to  $c^3$  and we have:

$$u = \frac{\theta^5}{v^2 c^3} \cdot f\left(\frac{\theta}{v}\right)$$

where the constants associated with the function  $f$  are independent of  $c$ .

In place of this, if  $f$  represents a new function of a single argument, we can write:

$$(7) \quad u = \frac{v^3}{c^3} \cdot f\left(\frac{\theta}{v}\right)$$

and from this we see, among other things, that as is well known, the radiant energy  $u \cdot l^3$  at a given temperature and frequency is the same for all diathermic media.

Â§8. In order to go from the energy density  $u$  to the energy  $U$  of a stationary resonator situated in the radiation field and vibrating with the same frequency  $n$ , we use the relation expressed in equation (34) of my paper on irreversible radiation processes<sup>13</sup>:

$$K = \frac{n^2}{c^2} U$$

(  $K$  is the intensity of a monochromatic linearly, polarized ray), which together with the well-known equation:

$$u = \frac{8\pi K}{c}$$

yields the relation:

$$(\#8) \quad u = \frac{8\pi n^2}{c^3} U$$

From this and from equation (7) follows:

$$U = v \cdot f\left(\frac{\theta}{v}\right)$$

where now  $c$  does not appear at all. In place of this we may also write:

$$\theta = v \cdot f\left(\frac{U}{v}\right)$$

Â§9. Finally, we introduce the entropy  $S$  of the resonator by setting

$$(9) \quad \frac{1}{\theta} = \frac{dS}{dU}$$

We then obtain:

$$\frac{dS}{dU} = \frac{1}{v} \cdot f\left(\frac{U}{v}\right)$$

and integrated:

$$(10) \quad S = f\left(\frac{U}{v}\right)$$

that is, the entropy of a resonator vibrating in an arbitrary diathermic medium depends only on the variable  $U/v$ , containing besides this only universal constants. This is the simplest form of Wien's displacement law known to me.

Â§10. If we apply Wien's displacement law in the latter form to equation (6) for the entropy  $S$ , we then find that the energy element  $e$  must be proportional to the frequency  $\nu$ , thus:

$$e = h\nu$$

and consequently:

$$S = k \left\{ \left( 1 + \frac{U}{h\nu} \right) \log \left( 1 + \frac{U}{h\nu} \right) - \frac{U}{h\nu} \log \frac{U}{h\nu} \right\}$$

here  $h$  and  $k$  are universal constants.

By substitution into equation (9) one obtains:

$$(11) \quad \frac{1}{\theta} = \frac{k}{h\nu} \log \left( 1 + \frac{h\nu}{U} \right)$$

$$U = \frac{h\nu}{e^{h\nu/k\theta} - 1}$$

and from equation (8) there then follows the energy distribution law sought for:

$$(12) \quad u = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/k\theta} - 1}$$

or by introducing the substitutions given in Â§7, in terms of wavelength  $\lambda$  instead of the frequency:

$$(13) \quad E = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{ch/k\lambda\theta} - 1}$$

I plan to derive elsewhere the expressions for the intensity and entropy of radiation progressing in a diathermic medium, as well as the theorem for the increase of total entropy in nonstationary radiation processes.

### III. Numerical Values

§11. The values of both universal constants  $h$  and  $k$  may be calculated rather precisely with the aid of available measurements. F. Kurlbaum,<sup>14</sup> designating the total energy radiating into air from 1 sq cm of a black body at temperature  $t^\circ\text{C}$  in 1 sec by  $S_t$ , found that:

$$S_{100} - S_0 = 0.0731 \text{ watt/cm}^2 = 7.31 \times 10^5 \text{ erg/cm}^2 \cdot \text{sec}$$

From this one can obtain the energy density of the total radiation energy in air at the absolute temperature 1:

$$\frac{4 \cdot 7.31 \cdot 10^5}{3 \cdot 10^{10}(373^4 - 273^4)} = 7.061 \cdot 10^{-15} \text{ erg/cm}^3 \cdot \text{deg}^4$$

On the other hand, according to equation (12) the energy density of the total radiant energy for  $q = 1$  is:

$$\begin{aligned} u^* &= \int_0^\infty u dv = \frac{8\pi h}{c^3} \int_0^\infty \frac{v^3 dv}{e^{hv/k} - 1} \\ &= \frac{8\pi h}{c^3} \int_0^\infty v^3 (e^{-hv/k} + e^{-2hv/k} + e^{-3hv/k} + \dots) dv \end{aligned}$$

and by termwise integration:

$$\begin{aligned} u^* &= \frac{8\pi h}{c^3} \cdot 6 \left( \frac{k}{h} \right)^4 \left( 1 + \frac{1}{24} + \frac{1}{34} + \frac{1}{44} + \dots \right) \\ &= \frac{48\pi k^4}{c^3 h^3} \cdot 1.0823 \end{aligned}$$

If we set this equal to  $7.061 \cdot 10^{-15}$ , then, since  $c = 3 \cdot 10^{10}$  cm/sec, we

obtain:

$$(\#14) \frac{k^4}{h^3} = 1.1682 \cdot 10^{15}$$

Â§12. O. Lummer and E. Pringswim<sup>15</sup> determined the product  $l_m q$ , where  $l_m$  is the wavelength of maximum energy in air at temperature  $\theta$ , to be 2940 micron  $\cdot$  degree. Thus, in absolute measure:

$$l_m = 0.294 \text{ cm} \cdot \text{deg}$$

On the other hand, it follows from equation (13), when one sets the derivative of E with respect to  $q$  equal to zero, thereby finding  $l = l_m$

$$\left( 1 - \frac{ch}{5k\lambda_m\theta} \right) \cdot e^{ch/k\lambda_m\theta} = 1$$

and from this transcendental equation:

$$l_m q = ch / 4.9651k$$

consequently:

$$h / k = (4.9561 \cdot 0.294) / 3 \cdot 10^{10} = 4.866 \cdot 10 \hat{\text{A}}^{-11}$$

From this and from equation (14) the values for the universal constants become:

$$(\#15) h = 6.55 \cdot 10 \hat{\text{A}}^{-27} \text{ erg} \cdot \text{sec}$$

$$(\#16) k = 1.346 \cdot 10 \hat{\text{A}}^{-16} \text{ erg/deg}$$

These are the same number that I indicated in my earlier communication.

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## Citations

<sup>1</sup> O. Lummer and E. Pringsheim, *Transactions of the German Physical Society* 2 (1900), p. 163

<sup>2</sup> H. Rubens and F. Kurlbaum, *Proceedings of the Imperial Academy of Science*, Berlin, October 25,

1900, p. 929.

<sup>3</sup> H. Beckmann, *Inaugural dissertation*, Tübingen 1898. See also H. Rubens, *Weid. Ann.* 69 (1899) p. 582.

<sup>4</sup> M. Planck, *Ann. d. Phys.* 1 (1900), p. 719.

<sup>5</sup> Compare with equation (8).

<sup>6</sup> M. Planck, *loc. cit.*, pp. 730 ff.

<sup>7</sup> Moreover one should compare the critiques previously made of this theorem by W. Wien (*Report of the Paris Congress 2*, 1900, p. 40) and by O. Lummer (*loc. cit.*, 1900, p.92.).

<sup>8</sup> L. Boltzmann, *Proceedings of the Imperial Academy of Science*, Vienna, (II) 76 (1877 ), p. 428.

<sup>9</sup> Joh. v. Kries, *The Principles of Probability Calculation* (Freiburg, 1886), p. 36.

<sup>10</sup> W. Wien, *Proceedings of the Imperial Academy of Science*, Berlin, February 9, 1893, p. 55.

<sup>11</sup> M. Thiesen, *Transactions of the German Physical Society 2* (1900), p. 66.

<sup>12</sup> Perhaps one should speak more appropriately of a "white" radiation, to generalize what one already understands by total white light.

<sup>13</sup> M. Planck, *Ann. D. Phys.* 1 (1900), p. 99.

<sup>14</sup> F. Kurlbaum, *Wied. Ann.* 65 (1898), p. 759.

<sup>15</sup> O. Lummer and Pringsheim, *Transactions of the German Physical Society 2* (1900), p. 176.