

On the Law of the Energy Distribution in the Normal Spectrum

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Preface

The recent spectral measurements of O. Lummer and E. Pringsheim¹ and even more striking those of H. Rubens and F. Kurlbaum², both confirming more recent results obtained by H. Beckmann³, would discover that the law of the energy distribution in the normal spectrum first stated by W. Wien from the molecular-kinetic consideration and later by me from the theory of electromagnetic radiation is not universally correct.

In any case an improvement on the theory is needed and I shall further try to carry through basing on the theory of electromagnetic radiation developed by me. First of all there is necessary for it to find an alterable link in the chain of reasons resulting in the Wien's energy distribution law. So one handles to remove this link from the chain and create a suitable substitute.

The fact that the physical ground of the electromagnetic radiation theory including the hypothesis of the "natural radiation", resists destructive criticism, is shown in my recent work⁴; and since the calculations are known to be error free, so the statement remains to be held that the energy distribution law of the normal spectrum is totally defined if one succeeds in calculation of

¹O. Lummer, E. Pringsheim. Verhandl. Deutsch. Phys. Ges., 1900, **2**, 163.

²H. Rubens, F. Kurlbaum. Sitzungsber. Akad. Wiss. Berlin, 1900, 929.

³H. Beckmann. Inaug-Dissert. Tübingen, 1898, see also: H. Rubens. Wied. Ann., 1899, **69**, 582.

⁴M. Planck. Ann. Phys., 1900, **1**, 719.

entropy S of irradiated monochromatic vibrating resonator as a function of its vibrational energy. So then from the relation $dS/dU = 1/\vartheta$ one keeps the temperature ϑ dependence on energy U , and since the energy U , on the other hand, is simply related⁵ with a radiation density of appropriate number of vibrations, so the temperature dependence on this radiation density is also obtained. So the normal distribution of energy is one for which the radiation densities of any different numbers of vibrations have the same temperature.

Thus the total problem is self reduced to that of definition S as a function of U , and the essential part of the following research is devoted to the solution of this problem. In the first my work on this problem I have entered S directly by defining with no further substantiation, as the simple function of U , and have limited by showing that such form for the entropy satisfies to all requirements of the thermodynamics. Then I considered that it is alone possible and therefore the Wien's law, from it flowing out, necessarily is the universal one. In later, more particular research⁶ it seemed to me, however, that it should be expressions, doing the same, and that in any case therefore one more condition is needed for anyone being able to calculate S uniquely. It seemed to me that I have found one such condition in the form of statement, immediately then considered by me as plausible, that by the infinitesimal irreversible alteration of the near thermal equilibrium being system of N uniform, just in stationary radiation field placed resonators, the bound up with it alteration of the total entropy $S_N = NS$ depends only on their total energy $U_N = NU$ and their alteration but not on the energy U of particular resonators. This statement leads again with necessity to the Wien's energy distribution law. But now however the later is not confirmed by experience, so the conclusion is forced that this statement in its universality also cannot be right and so from the theory is to be removed⁷.

Therefore yet another condition should be entered which enables the calculation of S , and for its realization the more detailed consideration of the entropy concept is needed. The direction of these deliberate thoughts is indicated by the consideration of the fragility of early made supposition. The path is below described, in which the new simple expression for entropy as well as the new formula for radiation are self found, both contradicting no fact established till now.

⁵See below equation (8)

⁶M. Planck. Ann. Phys., 1900, **1**, 730.

⁷One compares besides the criticism, to which this statement is exposed yet: W. Wien. Rapport für den Pariser Congress, 1900, **2**, 40; O. Lummer. Loc. cit., p. 92.

I. The calculation of entropy of any resonator as a function of its energy

§ 1

An entropy is conditioned by disorder, and this disorder in accordance with electro-magnetic theory of radiation is based on monochromatic vibrations of any resonator if although it remains in a stable stationary field of radiation, on non-regularity by which it permanently changes its amplitude and its phase, since one clocks time intervals which are long compared with a time of vibration, but short compared with a measurement time. If the amplitude and the phase both are absolutely constant as well as vibrations are quite homogeneous, no entropy could exist and the vibrational energy should be quite free convertible into the work. A constant energy U of alone stationary vibrating resonator is therefore as an average by time to be perceived or what turns to quite the same result, as a simultaneous average of energies of large number N of uniform resonators, just into stationary radiation field placed, sufficiently removed from one another to have no affect to each other directly. In this sense in future we will speak about an average energy U of a separate resonator. Then a total energy

$$U_N = NU \quad (1)$$

of such system of N resonators is corresponded to certain total entropy

$$S_N = NS \quad (2)$$

of the same system where an average entropy of any separate resonator is represented by S , and this entropy S_N is based on a disorder with which the total energy U_N is distributed among particular resonators.

§ 2

Now we suppose an entropy S_N of a system with an arbitrary remaining additive constant to be proportional to logarithm of the probability W with which N resonators altogether possess an energy U_N ; therefore:

$$S_N = k \ln W + \text{const.} \quad (3)$$

In my opinion this supposition originates from the base of the definition of the probability W mentioned whereas in the premise, put on the ground of the electromagnetic theory of radiation, we have not any support, enabling to speak about such probability in a definite sense. For the expedience of so aimed supposition its simplicity as well as its neighbourhood with that of the kinetic theory of gases are standing for ⁸.

§ 3

Now it is worth reminding to find the probability W of N resonators altogether having a vibrational energy U_N . It is necessary for it to imagine U_N not as a continuous unlimited divided value, but as a discrete one, composed of integer number of finite equal parts. If we give a name energy element ε to such part, so one can suppose that

$$U_N = P \cdot \varepsilon, \quad (4)$$

where P is an integer, in general, large number, whereas the value for ε is till to be defined.

Now it is clear that the distribution P of energy elements among N resonators can happen by some limited quite definite number of manners. We give a name “complexion” to every such manner of distribution following L. Boltzmann who had used this name for an expression with a similar idea. Having numbered resonators by $1, 2, 3, \dots, N$, one writes them in a row each to another and under each resonator places a number of energy elements fallen to it in some arbitrary distribution, so for each complexion one obtains a symbol of the following form:

1	2	3	4	5	6	7	8	9	10
7	38	11	0	9	2	20	4	4	5

Here $N = 10$, $P = 100$ are considered. The number \mathfrak{R} of all possible complexions is obviously equal to one of all possible digital images which can be obtained in this manner for the lower row with definite N and P . For intelligibility it should be mentioned that two complexions are considered as different if corresponding digital images have the same numbers but in a different order.

⁸L. Boltzmann. Sitzungsber d. k. Akad. d. Wissensch. zu Wien (I), 1877, **76**, 428.

Following combinatory, the number of all possible complexions is

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

Here is in a first approximation according to Stirling offer:

$$N! = N^N;$$

therefore in appropriate approximation

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

§ 4

The hypothesis, we now wish to put into the base of further calculation, is as follows: the probability of that N resonators altogether possess vibrational energy U_N is proportional to the number \mathfrak{R} of all possible complexions with energy U_N distributed among N resonators, or by other words: each certain complexion is as probable as either another one. It should in last line only by experience be proved whether this hypothesis virtually hit into nature. Instead however an opposite one should be possible: once an experience should judge in its favor, the validity of hypothesis will result in the further conclusions on the special nature of resonator's vibrations, namely on the character of meanwhile appearing "indifferent and in their value compared primary game spaces" by expression manner of J. v. Kries⁹. In a modern state of this question a further promotion of this idea should certainly appear as premature.

§ 5

According to hypothesis introduced in relation with the equation (3), the entropy of considered system of resonators with suitable definition of additive constant is:

$$S_N = k \ln \mathfrak{R} = k \{(N + P) \ln (N + P) - N \ln N - P \ln P\}, \quad (5)$$

⁹Joh. v. Kries. Die Principien der Wahrscheinlichkeitsrechnung. Freiburg, 1886, p. 36.

and accepting (4) and (1):

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

Therefore according to (2), entropy S of a resonator as a function of its energy U is:

$$S = k \left\{ \left(1 + \frac{U}{\varepsilon}\right) \ln \left(1 + \frac{U}{\varepsilon}\right) - \frac{U}{\varepsilon} \ln \frac{U}{\varepsilon} \right\}. \quad (6)$$

II. The deduction of the Wien's displacement law

§ 6

Following a Kirchhoff's law of proportionality of both emission- and absorbability, discovered by W. Wien¹⁰ and called by his name so-called the displacement law, including, as a particular case, the law of Stefan–Boltzmann of full emittance dependence on temperature, builds the most valuable constituent in the well grounded foundation of the theory of heat radiation. In a fashion, given by M. Thiesen¹¹, it announces:

$$E \cdot d\lambda = \vartheta^5 \psi(\lambda\vartheta) \cdot d\lambda,$$

where λ is a wavelength, $E d\lambda$ is a volume density of a spectral slice between λ and $\lambda + d\lambda$ belonging to “black” radiation¹², ϑ is a temperature and $\psi(x)$ is a known function of a single argument x .

§ 7

Now we are coming to investigate what Wien's displacement law says about our resonator's entropy S dependence on its energy and its own period, that is in those general case that resonator itself is in an arbitrary

¹⁰W. Wien. Sitzungsber. Acad. Wissensch. Berlin, 1893, 55.

¹¹M. Thiesen. Verhandl. Deutsch. Phys. Ges., 1900, 2, 66.

¹²One should perhaps more conveniently speak about “white” radiation, whose proper generalization is now understood as a “quite white light”.

diathermal medium. For this aim first of all let us generalize the Thiesen's form of the law on the radiation in an arbitrary diathermal medium with the velocity of light propagation c . Since we have to consider not a total radiation but monochromatic one, so when comparing different diathermal media, the number of vibrations ν should necessarily be introduced instead of wavelength λ .

Thus the volume density of a spectral slice between ν and $\nu + d\nu$, belonging to energy of radiation, is to be denoted as $\mathbf{u}d\nu$, so one should write: $\mathbf{u}d\nu$ instead of $E d\nu$, c/ν instead of λ and $cd\nu/\nu^2$ instead of $d\lambda$. This results in:

$$\mathbf{u} = \vartheta^5 \cdot \frac{c}{\nu^2} \cdot \psi \left(\frac{c\vartheta}{\nu} \right).$$

Now according to known Kirchhoff-Clausius's law, the energy, emitted by black surface in a time unit into a diathermal medium, for defined temperature ϑ and defined number of vibrations ν is reverse proportional to the square of the velocity of propagation c^2 ; thus the volume energy density \mathbf{u} is reverse proportional to c^3 , and we obtain:

$$\mathbf{u} = \frac{\vartheta^5}{\nu^2 c^3} f \left(\frac{\vartheta}{\nu} \right),$$

where constants of the function f do not depend on c .

Instead of it we could also write when f every time, as in following, means a new function of a single argument:

$$\mathbf{u} = \frac{\nu^3}{c^3} f \left(\frac{\vartheta}{\nu} \right) \quad (7)$$

and by the way see that in a cube of a wavelength size a contained radiation energy with a certain temperature as well as a number of vibrations is known to be: $\mathbf{u}\lambda^3$, the same for all diathermal media.

§ 8

In order to pass from the volume density of radiation \mathbf{u} to the energy U of the resonator being in the radiation field and stationary vibrating with the same number of vibrations ν , we shall use the relation, published in equation (34) of my work on non-reversible processes of radiation¹³:

$$\mathfrak{R} = \frac{\nu^2}{c^2} \cdot U$$

¹³M. Planck. Ann. Phys., 1900, **1**, 99.

(\mathfrak{R} is the intensity of monochromatic line-polarized beam), which together with the known equation

$$\mathbf{u} = \frac{8\pi\mathfrak{R}}{c}$$

yields the relation:

$$\mathbf{u} = \frac{8\pi\nu^2}{c^3} U. \quad (8)$$

From here and (7) it follows:

$$U = \nu f\left(\frac{\vartheta}{\nu}\right),$$

where now c is not at all present. Instead of it we should also write:

$$\vartheta = \nu f\left(\frac{U}{\nu}\right).$$

§ 9

Finally introducing yet more the entropy of resonator S , we assign:

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

Then it turns out:

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

and integrating, one obtains:

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

i.e. the entropy of resonator, vibrating in an arbitrary diathermal medium, depends only on the single variable U/ν and besides keeps only the universal constants. This, as I know, is the simplest representation of the Wien's displacement law.

§ 10

Applying the Wien's displacement law in its latter representation to the expression (6) for the entropy S , one can realize that the energy element ε should be proportional to the number of vibrations ν , so:

$$\varepsilon = h \cdot \nu$$

and therefore:

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

Here h and k are the universal constants.

By substitution into (9) one obtains:

$$\frac{1}{\vartheta} = \frac{k}{h\nu} \ln \left(1 + \frac{h\nu}{U}\right), \quad (11)$$

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

and the energy distribution law searched then follows from (8):

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

or also if one with in § 7 shown substitutions instead of the number of vibrations ν introduces again the wavelength λ , that is:

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

I suppose to show in the other place the expression for the intensity and one for the entropy of the in diathermal medium propagating radiation as well as the law of the increase of the total entropy in unstationary radiating process.

III. The numeral values

§ 11

The values of both natural constants h and k may be calculated well precisely with a help of measurements available. F. Kurlbaum¹⁴ has found that if one designates by S_t the total energy, radiating into an air in 1 sec from the 1 cm² surface of the black body exposed with t° , then it is:

$$S_{100} - S_0 = 0.0731 \frac{Watt}{cm^2} = 7.31 \cdot 10^5 \frac{erg}{cm^2 \cdot sec}.$$

From here the volume density of the total radiation energy in the air for the absolute temperature of 1 turns out:

$$\frac{4 \cdot 7.31 \cdot 10^5}{3 \cdot 10^{10} \cdot (373^4 - 273^4)} = 7.061 \cdot 10^{-15} \frac{erg}{cm^2 \cdot grad^4}.$$

From the other hand, according to (12), the volume density of the total radiation energy for $\vartheta = 1$ is as follows:

$$\begin{aligned} u &= \int_0^\infty \mathbf{u} d\nu = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{e^{\frac{h\nu}{k}} - 1} \\ &= \frac{8\pi h}{c^3} \int_0^\infty \nu^3 \left(e^{-\frac{h\nu}{k}} + e^{-\frac{2h\nu}{k}} + e^{-\frac{3h\nu}{k}} + \dots \right) d\nu \end{aligned}$$

and by all terms integration it yields:

$$u = \frac{8\pi h}{c^3} \cdot 6 \left(\frac{k}{h} \right)^4 \left(1 + \frac{1}{2^4} + \frac{1}{3^4} + \frac{1}{4^4} + \dots \right) = \frac{48\pi k^4}{c^3 h^3} \cdot 1.0823.$$

Assuming it to be equal to $7.061 \cdot 10^{-15}$, one obtains, since $c = 3 \cdot 10^{10}$,

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

¹⁴F. Kurlbaum. Wied. Ann., 1898, **65**, 759.

§ 12

O. Lummer and E. Pringsheim¹⁵ have determined the product $\lambda_m \vartheta$, where λ_m is the wavelength of the maximum of E in the air for the temperature ϑ , having value up to 2940 μ ·grad.

So in absolute units that is

$$\lambda_m \vartheta = 0.294 \text{ cm} \cdot \text{grad.}$$

From the other hand, if one assumes the partial derivative of E in respect to λ to be equal to zero, so that $\lambda = \lambda_m$, then it follows from (13):

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

and from this transcendental equation one obtains:

$$\lambda_m \vartheta = \frac{ch}{4.9651 \cdot k}.$$

Therefore:

$$\frac{h}{k} = \frac{4.9651 \cdot 0.294}{3 \cdot 10^{10}} = 4.866 \cdot 10^{-11}.$$

From here and from (14) the values for the universal constants turn out:

$$h = 6.55 \cdot 10^{-27} \text{ erg} \cdot \text{sec}, \quad (15)$$

$$k = 1.346 \cdot 10^{-16} \text{ erg/grad.} \quad (16)$$

These are just the same values that I have presented in my recent communication.

¹⁵O. Lummer, E. Pringsheim. Verhandl. Deutsch. Phys. Ges., 1900, **2**, 176.