

Teoretická fyzika – Proč kvantová mechanika?

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1. Záření černého tělesa

1.1 Rayleigh 1900

Termín Rayleighův – Jeansův zákon je všeobecně užíván, vede však k nesprávnému závěru, že Lord Rayleigh a Sir James uvažovali jen dlouhovlnnou část spektra. Základním článkem k problematice je Rayleighova stručná poznámka, uveřejněná v *Philosophical Magazine* (5. serie) **49** (1900), 539 – 540.

Remarks upon the Law of Complete Radiation

By complete radiation I mean the radiation from an ideally black body, which according to Stewart* and Kirchoff is a definite function of the absolute temperature θ and the wavelength λ . Arguments of (in my opinion[†]) considerable weight have been brought forward by Boltzmann and W. Wien leading to the conclusion that the function is of the form

$$\theta \phi(\theta \lambda) \lambda \quad (1)$$

expressive of the energy in that part of the spectrum which lies between λ and $\lambda + \Delta\lambda$. A further specialization by determining the form of the function ϕ was attempted later[‡]. Wien concludes that the actual law is

$$c_1 \lambda^{-5} e^{-c_2 / \lambda \theta} \quad (2)$$

in which c_1 and c_2 are constants, but viewed from the theoretical side the result appears to me to be little more than a conjecture. It is, however, supported upon general thermodynamic grounds by Planck[§].

Upon the experimental side, Wien's law (2) has met with important confirmation. Paschen finds that his observations are well represented, if he takes

$$c_2 = 1.4328 \text{ cm}^\circ\text{K}$$

θ being measured in centigrade degrees and λ in thousandths of a millimetre (μ). Nevertheless, the law seems rather difficult of acceptance, especially the implication that as the temperature is raised, the radiation of given wavelength approaches a limit. It is true that for visible rays the limit is out of range. But if we take $\lambda = 60 \mu$, as (according to the remarkable researches of Rubens) for the rays selected by reflexion at surfaces of Sylvian, we see that for temperatures over 1000° (absolute) there would be but little further increase of radiation.

The question is one to be settled by experiment; but in the meantime I venture to suggest a modification of (2), which appears to me more probable *à priori*. Speculation upon this subject is hampered by the difficulties which attend the Boltzmann – Maxwell doctrine of the partition of energy. According to this doctrine every mode of vibration should be alike favoured ; and although for some reason not yet explained the doctrine fails in general, it seems possible that it may apply to the graver modes. Let us consider in illustration the case of a stretched string vibrating transversely. According to the Boltzmann – Maxwell law the energy should be equally divided among all the modes, whose frequencies are as 1, 2, 3, Hence if k be the reciprocal of λ , representing the frequency, the energy between the limits k and $k+dk$ is (when k is large enough) represented by dk simply.

When we pass from one dimension to three dimensions, and consider for example the vibrations of a cubical mass of air, we have ('Theory of Sound', §267) as the equation for k^2 ,

$$k^2 = p^2 + q^2 + r^2$$

where p, q, r are integers representing the number of subdivisions in the three directions. If we regard p, q, r as the coordinates of points forming a cubic array, k is the distance of any point from the origin. Accordingly the number of points for which k lies between k and $k+dk$, proportional to the volume of the corresponding spherical shell, may be represented by $k^2 dk$, and this expresses the distribution of energy according to the Boltzmann – Maxwell law, so far as regards the wave-length or frequency. If we apply this result to radiation, we shall have, since the energy in each mode is proportional to θ ,

$$\theta k^2 dk \tag{3}$$

or, if we prefer it,

$$\theta \lambda^{-3} d\lambda \tag{4}$$

It may be regarded as some confirmation of the suitability of (4) that it is of the prescribed form (1).

The suggestion is that (4) rather than, as according to (2)

$$\theta \lambda^{-2} d\lambda \tag{5}$$

may be the proper form when $\lambda\theta$ is great*. If we introduce the exponential factor, the complete expression will be

$$c_1 \theta \lambda^{-3} e^{-\lambda\theta} d\lambda \tag{6}$$

If, as is probably to be preferred, we make k the independent variable, (6) becomes

$$c_1 \theta^{-5} u_{\lambda} \quad (7)$$

Whether (6) represents the facts of observation as well as (2) I am not in a position to say. It is to be hoped that the question may soon receive an answer at the hands of the distinguished experimenters who have been occupied with this subject.

* Stewart's work appears to be insufficiently recognized upon the Continent. [See *Phil.Mag.* i. p. 98, 1901; p. 494 below.]

† *Phil. Mag.* Vol. XLV. p. 522 (1898).

‡ *Wied. Ann.* Vol. LVIII. p. 662 (1896).

§ *Wied. Ann.* Vol. i. p. 74 (1900).

*[1902. This is what I intended to emphasize. Very shortly afterwards the anticipation above expressed was confirmed by the important researches of Rubens and Kurlbaum (*Drude Ann.* iv. p. 649, 1901), who operated with exceptionally long waves. The formula of Planck, given about the same time, seems best to meet the observations. According to this modification of Wien's formula, $e^{-\frac{c_2}{\lambda\theta}}$ in (2) is replaced by $1 - \frac{c_2}{\lambda\theta}$. When $\lambda\theta$ is great, this becomes $\lambda\theta/c_2$, and the complete expression reduces to (4).]

1.2 Planck 1901

Model, který přesně popisuje spektrální hustotu v celém frekvenčním rozsahu publikoval Max Planck jako “Über das Gesetz der Energieverteilung im Normalspektrum” v *Annalen der Physik* (4. serie) 4 (1901), 553 – 563. Uvádím anglický překlad, originální článek je snadno dostupný.

On the Law of Distribution of Energy in the Normal Spectrum

Introduction.

The recent spectral measurements made by O. Lummer and E. Pringsheim¹, and even more notable those by H. Rubens and F. Kurlbaum², which together confirmed an earlier result obtained by H. Beckmann³, 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.

¹ O.Lummer, E.Pringsheim, *Verhandl. Der. Deutschg. Physikal. Gesellsch.* 2. p.163. 1900.

² H.Rubens, F.Kurlbaum, *Sitzungsber. D. k. Akad. D. Wissensch. Zu Berlin* vom 25. October 1900, p.929.

³ H. Beckmann, *Inaug.-Dissertation*, Tübingen 1898. Vgl. Auch H.Rubens, *Wied. Ann.* 69. p.582. 1899.

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 article⁴ 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 $dS/dU = 1/\theta$, the dependence of the energy U on the temperature θ , and since the energy is also related to the density of radiation at the corresponding frequency by a simple relation⁵, 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 analysis⁶, 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

⁴ M. Planck, Ann. D. Phys. 1. p.719. 1900.

⁵ See Eq. (8) below.

⁶ M. Planck, loc. cit., p. 730 ff.

that even this principle cannot be generally valid and thus must be eliminated from the theory⁷.

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

$$(1) \quad U_N =$$

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

$$(2) \quad S_N =$$

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.

§ 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 U_N

⁷ 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).

$$(3) \quad S_N = \dots +$$

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 theory⁸.

§ 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 ε ; consequently we must set

$$(4) \quad U_N =$$

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

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” (v originálu “Complexion”). 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:

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

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:

$$\mathfrak{R} = \frac{N!}{1! \cdot 2! \cdot 3! \cdot \dots \cdot P!} = \frac{N!}{P!}$$

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

$$N! =$$

⁸ L.Boltzmann, Sitzungsber. D. k. Akad. D. Wissensch. Zu Wien (II) **76**. p.428, 1877.

And consequently, the corresponding approximation is:

$$\mathfrak{R} = \frac{N^M}{N^N P^P}$$

§ 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. Kries⁹ 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.

§ 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:

$$(5) \quad S_N = \mathfrak{R} + \dots + \dots - \dots - \dots$$

and by considering (4) and (1):

$$S_N = \left\{ \left(\dots \right) \left(\dots \right) \right\}$$

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

$$(6) \quad S = \left\{ \left(\dots \right) \left(\dots \right) \right\}$$

II. Introduction of Wien’s displacement law.

§ 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. Wien¹⁰ which includes as a special case the Stefan – Boltzmann law of dependence of total radiation on temperature,

⁹ Joh. V. Kries, Die Principien der Wahrscheinlichkeitsrechnung p.36. Freiburg 1886.
¹⁰ W. Wien, Sitzungsber. D. k. Akad. D. Wissensch. Zu Berlin vom 9. Febr. 1893. p.55.

provides the most valuable contribution to the firmly established foundation of the theory of heat radiation, In the form given by M. Thiesen¹¹ it reads as follows:

$$E \cdot d\lambda = \theta \psi(\lambda)$$

where λ is the wavelength, $E \cdot d\lambda$ represents the volume density of the “black-body” radiation¹² within the spectral region λ to $\lambda + d\lambda$, θ represents temperature and $\psi(x)$ represents a certain function of the argument x only.

§ 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 ν instead of the wavelength λ .

Thus, let us denote by $u \cdot d\nu$ the volume density of the radiation energy belonging to the spectral region ν to $\nu + d\nu$; then we write: $u \cdot d\nu$ instead of $E \cdot d\lambda$; c/ν instead of λ , and $c \cdot d\nu/\nu^2$ instead of $d\lambda$. From which we obtain

$$u = \frac{1}{\nu^2} \left(\dots \right)$$

Now according to the well-known Kirchoff – Clausius law, the energy emitted per unit time at the frequency ν and temperature θ 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:

$$u = \frac{1}{c^3} \left(\dots \right)$$

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:

$$(7) \quad u = \frac{1}{c^3} \left(\dots \right)$$

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

¹¹ M. Thiesen, Verhandl. D. Deutsch. Phys. Gesellsch. 2. p.66. 1900.

¹² Perhaps one should speak more appropriately of a „white“ radiation, to generalize what one already understands by total white light.

§ 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 ν , we use the relation expressed in equation (34) of my paper on irreversible radiation processes¹³:

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

(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:

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

From this and from equation (7) follows:

$$U = \left(\frac{1}{\theta} \right)$$

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

$$\theta = \left(\frac{1}{\nu} \right)$$

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

$$(9) \quad \frac{1}{\theta} = \frac{1}{\nu} e^{S/c}$$

We then obtain:

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

and integrated:

$$(10) \quad S = \left(\frac{1}{\nu} \right) \ln U$$

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

¹³ M. Planck, Ann. D. Phys. 1. p.99 1900.

§ 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 ε must be proportional to the frequency ν , thus:

$$\varepsilon =$$

and consequently:

$$S = \left\{ \left(\frac{h\nu}{k\theta} \right) \left(\frac{h\nu}{k\theta} \right) \right\}$$

here h and k are universal constants.

By substitution into equation (9) one obtains:

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

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

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

$$(12) \quad u = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{k\theta} - 1}$$

or by introducing the substitutions given in § 7, in terms of wavelength λ instead of the frequency:

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

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. Kurlbaum¹⁴, designating the total energy radiating into air from 1 sq cm of a black body at temperature t °C in 1 sec by S_t , found that:

$$S_{100} = \frac{W_{100}}{\text{cm}^2 \text{ sec}} = \frac{\text{erg}}{\text{cm}^2 \text{ sec}}$$

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

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

$$\frac{4.7,31.10^5}{3.10^{10} \cdot 373^4} = \gamma \frac{\text{erg}}{\text{cm}^3 \text{grad}^4}$$

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

$$u = \int_0^\infty u \cdot \dots = \int_0^\infty \dots$$

and by termwise integration:

$$u = \frac{1}{c} \left(\dots \right)$$

If we set this equal to $7,061 \cdot 10^{-15}$, then, since $c = 3.10^{10}$ cm/sec, we obtain:

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

§ 12. O. Lummer and E. Pringsheim¹⁵ determined the product $\lambda_m \theta$, where λ_m is the wavelength of maximum E in air at temperature θ , to be 2940 $\mu \cdot \text{grad}$. Thus, in absolute measure:

$$\lambda_m \theta = \dots \text{ n.grad}$$

On the other hand, it follows from equation (13), when one sets the derivative of E with respect to θ equal to zero, thereby finding $\lambda = \lambda_m$

$$\left(\dots \right)$$

and from this transcendental equation:

$$\lambda_m \theta = \frac{\dots}{4,9651 \cdot k}$$

Consequently:

$$\frac{h}{k} = \frac{4,9651 \cdot 10^{15}}{3.10^{10}} = \dots$$

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

$$(15) \quad h = \dots \text{ erg.sec}$$

¹⁵ O.Lummer, E.Pringsheim, Verhandl. Der Deutschen Physikal. Gesellsch. 2 p.176. 1900.

(16) $k = \dots \frac{\text{mg}}{\text{grad}}$.

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