

PART ONE. Chapter I

PLANCK:

die Wahrscheinlichkeit zu finden, dass die N Resonatoren insgesamt Schwingungsenergie U_N besitzen, U_N nicht als eine unbeschränkt teilbare, sondern als eine ganzen Zahl von endlichen gleichen Teilen aufzufassen
...

(Planck: To find the probability that N oscillators have a total energy U_N , it is necessary to suppose that U_N is not continuously divisible, but is an integral multiple of finite equal parts. ... We call such a part an energy-quantum ϵ . (Ann. d. Phys. 4, 553 (1901); see our **Paper I-4**.)

§I-1. Introduction.

Planck's discovery of the Quantum of Action 'h' in November 1900 [1] is an archetype of scientific revolutions, but Planck was more a Marx than a Lenin, and certainly no Stalin. He himself never pursued the meaning or significance of his parametrization. When he introduced the new fundamental constant 'h' – known forevermore as 'Planck's constant' – to fit the wavelength and temperature dependence of the universal energy spectrum of the radiant heat emitted by hot 'black' bodies, his success was greeted by a resounding silence. Even the few participants who had been involved in the intense controversy over this central subject for the preceding five years were – after a brief flurry of bickering from Wien [2] – silenced by the precision of Planck's result. The subject vanished almost completely from the pages of the *Annalen der Physik*. For four years no further mention of the word 'quantum' can be found in the pages of this premier journal where Planck had first introduced it, and no speculations on its implications, until Einstein's revelations of March 1905 [3].

In fact, for most it was something even less than business as usual after January

1901. Wien – after his initial objections – seems to have ignored the subject and shifted his interests to other areas. Planck himself spent a year tidying up his preliminary work on the application of the Second Law to radiation using his new result for the energy distribution [4], but he meticulously avoided use of the word ‘quantum’ in doing so. With amazing prescience falling just short of an Olympian vision, in a treatise on the nature of white light, Planck [5] did take the Fourier analysis of incoherent classical electromagnetic fields to the very edge of a semi-classical description of the photon field. He introduced the expression ‘partial wave’ in a sense different from what we use today, effectively to describe the field of an individual uncorrelated photon; he used the concept of ‘ray bundles’, again effectively to describe coherent photons; he described light rays from the point of view of emission and of detection; he emphasized the analogy “... the partial waves can be compared with the motion of molecules ... the principal difference being the molecules of the gas are individual, whose mass and other properties have no variation, whereas the partial waves have not only their amplitude and phase, but also their period”; and most of all “the energies (square of the amplitudes) ... of the individual partial waves into which the light wave can be decomposed, can be interpreted in the sense of probability theory”; and finally “... the nature of the light of the spectral lines is the most difficult and complicated problem which now faces Optics and Electrodynamics.” And never a mention of the word ‘quantum’.

In the midst of this uncertainty, confusion, competition, and conflict, Planck had the purest insight to introduce the quantum of energy, but not the insight to develop the idea any further. We now explore in depth Planck’s great achievement recorded in his three classic papers in *Annalen der Physik* of 1900 and 1901.

§I-2. Blackbody Radiation.

The Planck Spectrum of Blackbody Radiation is the primary cornerstone of modern physics and its importance cannot be overstated. Its manifestations range from the phonons of solid state physics, to the photons of the cosmic background radiation, from the Bose-Einstein condensation of supercooled atoms to the elusive phase transition in the quark-gluon plasma, with many fascinating and important variants in between. It was the motivating force in the development of quantum

statistics which has become the subject matter of every undergraduate text on modern physics. By the introduction of the quantum of energy hf it was directly responsible for Einstein's elucidation of the photon, for the Bohr atom, for de Broglie's postulate of the wave nature of matter, and for the eventual development of quantum mechanics in all its glory. Our purpose here is to take our streamlined and sophisticated understanding of Planck's result and go back from this modern vantage point to understand as best we can, in as deep and intimate a way as possible, the steps that led Planck to the quantum.

It is clearly incorrect – but nonetheless tempting – to undervalue Planck's accomplishment as somehow a lucky trick that worked, something that fell to him by chance as one of many fiddling about to parametrize the data. And even with the hindsight of 43 years, reflecting on his discovery at age 85 in wartime Berlin [6], Planck could barely explain his insight more deeply than at the first instant. It was done, he tells us, as a necessary first stratagem to define an entropy for the radiation field in terms of the probability of thermodynamic states, as dictated by Boltzmann. Probabilities, he decided, can be calculated only for discrete and countable alternatives.

Planck's Blackbody Energy Spectrum is the energy density \mathcal{U} of the radiant heat in the 'Hohlraum' or cavity of a furnace, as a function of the frequency f or the wavelength $\lambda = c/f$ of the radiation and of the equilibrium temperature T of the furnace walls (assumed emitting and absorbing at all wavelengths), the heating element, and the radiation, all monitored through a peep-hole and measured by bolometers. The result we all know (in terms of $\hbar = h/2\pi$, the photon energy E and momentum p with $E = cp = \hbar\omega = hf$) is:

$$\mathcal{U} = \frac{2}{(2\pi)^3} \int 4\pi p^2 dp \frac{hf}{\exp(hf/kT) - 1} \equiv \int_0^\infty df u_f(T) \text{ or } \int_0^\infty d\lambda u_\lambda(T), \quad (1)$$

where the spectral densities are defined as

$$u_f(T) = \frac{8\pi h}{c^3} \frac{f^3}{e^{hf/kT} - 1} \quad \text{and} \quad u_\lambda(T) = \frac{8\pi h}{c^2 \lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}, \quad (2)$$

which involve Planck's constant h , Boltzmann's constant k , and the speed of light

c. The integral gives Stefan's Law

$$\mathcal{U} = \sigma T^4 \quad \text{with} \quad \sigma = \frac{8\pi^5 k^4}{15h^3 c^3}. \quad (3)$$

The peak in the energy distribution $u_f(T)$ occurs at f_m with

$$\frac{hf_m}{kT} = 2.8214,$$

and that in $u_\lambda(T)$ at λ_m with

$$\frac{hc}{\lambda_m kT} = 4.9651.$$

At frequencies large compared to f_m , the exponential term in the spectral density dominates and Planck's distribution reduces to Wien's speculated result:

$$u_f(T)_{f \gg f_m} \rightarrow \frac{8\pi h f^3}{c} e^{-hf/kT}.$$

Einstein was to explain this [3] as the result of high energy photons undergoing only quasi-elastic scattering at low temperatures, and retaining their existence almost unchanged, like a classical gas of material molecules.

In the opposite limit, Rayleigh's result from classical electrodynamics and equipartition is obtained:

$$u_f(T)_{f \ll f_m} \rightarrow \frac{8\pi f^2}{c} kT.$$

Here the thermal energies kT are so much larger than the quantum energies hf that the quanta are produced almost without energy constraints and the classical wave theory is adequate.

Today we have the powerful machinery of quantum statistical mechanics [7] to derive the Planck distribution – from which, in fact, it originated. The Grand Partition Function, or equivalently the density matrix, defined as the sum of Boltzmann factors over all possible states κ is simply

$$\mathcal{Q} = \sum_{\kappa} e^{-\beta E_{\kappa}},$$

with $\beta = 1/kT$. We apply this to a cell of momentum \vec{p} and polarization $\hat{\epsilon}$ and all possible number $n(\vec{p}, \hat{\epsilon})$ of photons, as an open system in thermodynamic equilibrium with a reservoir at temperature T . We are instructed to count each state $n(\vec{p}, \hat{\epsilon}) = 1, 2, \dots$ once, with weight unity. Then, in what has become a ritual,

$$Q = \sum_{\vec{p}} \sum_{\hat{\epsilon}} Q(\vec{p}, \hat{\epsilon}),$$

the grand partition function for an individual cell is

$$Q(\vec{p}, \hat{\epsilon}) = e^{-\beta E_p} + e^{-2\beta E_p} + e^{-3\beta E_p} + \dots = \frac{1}{e^{\beta E_p} - 1}.$$

From the standard formalism, the average occupation number of a cell of momentum \vec{p} (including both polarization states $\hat{\epsilon} = \pm 1$) is

$$\langle n_{\vec{p}} \rangle = -\frac{1}{\beta} \frac{\partial}{\partial E_{\vec{p}}} \log Q = \frac{2}{e^{\beta E_p} - 1}; \quad (4)$$

and the internal energy density is

$$U = -\frac{\partial}{\partial \beta} \log Q = \sum_{\vec{p}} E_p \langle n_{\vec{p}} \rangle, \quad (5)$$

which reduces to the above integral over Planck's spectral density $u_f(T)$ with $E_p = \hbar\omega_p = hf_p$.

So we understand the Planck distribution from today's vantage point. We now turn to a detailed scrutiny of Planck's original discovery.

§I-3. Planck's Discovery of the Blackbody Formula.

For 20 years Planck had struggled to understand the full implications of the Second Law of Thermodynamics [6]. For four years he had tried to understand the equilibrium between radiant heat – tentatively recognized as electromagnetic radiation – and its sources – idealized as an array of simple harmonic oscillators radiating at all frequencies. As a devoted student of thermodynamics, Planck set himself the task to understand the equilibrium state of radiant heat and its sources as a problem akin to chemical equilibrium. The radical departure was the idea to apply thermodynamics to empty space! Spurred on by Wien's exponential

fit to the observed spectrum [8], Planck [9] was able to 'define' an entropy for an individual oscillator of frequency f and energy U , which he extended to an entropy for the radiation field of the same frequency and of intensity \mathcal{R} . He then defined an equilibrium temperature T the same for all frequencies by requiring the entropy to be a minimum, and from his postulated form of the entropy to derive the Wien distribution.

The successes of the Wien spectrum were impressive. Already with it, Planck was able to deduce values for what would become the fundamental constants k and h , which even without the impending correction to the spectrum could have led him to definitive values for Avogadro's number, the atomic mass unit, and the electron charge.

Wien criticized Planck's assumption of thermodynamic equilibrium as requiring a reversibility of fundamental radiative processes which was ruled out by examples of coherent processes which he conjured up. This objection is answered finally in Planck's 1943 *Reflections* by invoking a sort of molecular disorder for the radiation field as well as for the oscillators. But even after all these years, Planck never acknowledged the contribution of Gibbs who resolved all such paradoxes by invoking the Gibbs' ensemble [10] – a distribution in phase space, not a single point – as the fundamental physical state to which thermodynamic arguments apply.

Wien's exponential spectral density was soon put to a severe test by experiments at long wavelengths in the classical Rayleigh regime, and found to fail completely. The first somewhat tentative reports of discrepancies came from Lummer and Pringsheim [11] and from Paschen [12], but these were controversial. Then – as Planck recalled the exact chronology in his 1943 *Reflections* – Rubens and Kurlbaum, at the Deutschen Physikalischen Gesellschaft meeting of 19 October 1900, reported measurements of almost incredible precision [13] which showed spectral densities at long wavelengths increasing linearly with the temperature, in complete disagreement with Wien's spectrum. Planck had been told about the result a few days before Kurlbaum's lecture and had some time to prepare his response.

Planck's first step was to set $U = C \cdot T$ and from

$$\frac{\partial S}{\partial U} \equiv \frac{1}{T}, \quad (6)$$

then $S = C \cdot \log U$ and

$$\frac{\partial^2 S}{\partial U^2} = -\frac{C}{U^2} \quad (7)$$

valid for large U . From the entropy previously constructed to give Wien's distribution

$$S_W = -\frac{U}{af} \log \frac{U}{ebf}, \quad (8)$$

on the other hand, we get

$$\frac{\partial^2 S_W}{\partial U^2} = -\frac{1}{afU} \quad (9)$$

valid for small U . Planck combined these in a simple heuristic way to give

$$\frac{\partial^2 S}{\partial U^2} = -\frac{1}{afU + U^2/C}, \quad (10)$$

valid in both limits. By integration

$$\frac{\partial S}{\partial U} \equiv \frac{1}{T} = \frac{1}{af} \log \left(1 + \frac{aCf}{U} \right), \quad (11)$$

which we can solve for [14]

$$\mathcal{R}_f = \frac{f^2}{c^2} U = \frac{hf^3}{c^2} \frac{1}{e^{hf/kT} - 1}, \quad (12)$$

after comparison with Planck's earlier derivation [9] of the Wien distribution.

This was the basis of the distribution put forward by Planck in the 'lively' discussion following Kurlbaum's lecture. Rubens immediately verified that this form was in complete agreement with their results, as he reported to Planck the next morning [6].

Planck's preliminary work of 19 October 1900 was completed and reported first on 14 December 1900, and submitted for publication in *Annalen der Physik* on 7 January 1901. His path to the derivation is recalled very briefly and modestly in his 1943 *Reflections*. The formal derivation of the Planck spectrum which

actually appears in his published result makes no mention of the heuristic result he says in his *Reflections* to have been cobbled together in response to Rubens and Kurlbaum's lecture. On the contrary, the formal derivation makes full use of the necessity of the countability of the states of the radiation in order to define the entropy. In his 1901 paper, Planck states "... the theory (Note added: of 1900, see **Papers I-1,2,3**) requires revision ... the whole question is to find S as a function of U ... I had written down S directly ... without foundation ... it cannot be true"; and "... another condition must be introduced to make the entropy calculable ... necessary to have a more fundamental conception of the idea of entropy."

From his *Reflections*: "Boltzmann ... had the deepest understanding of entropy ... a measure of the probability of that state ..." Planck had ignored this directive because he believed any calculation of probability involved assumptions and he "firmly believed ... the Second Law was free of assumptions." But then, "that a similar fundamental hypothesis about the radiation is just as necessary and plays exactly the same role there as that of molecular disorder in the theory of gases, occurred to me at once with perfect clarity."

Again in 1901: "... set the entropy proportional to the logarithm of the probability W ... In fact we have ... no criterion to speak of such a probability ... the prescription is suggested by its simplicity ... it is necessary to suppose that U_N is ... a discrete, even an integral, multiple of finite equal parts ... We call such a part an energy-quantum ..."

And in his *Reflections*: "Since such a probability-like quantity can only be found by counting, then it was necessary for the energy U_N to be expressible as a sum of discrete identical energy elements ϵ ."

In his 1901 discovery paper, Planck made almost no comment about the deeper significance of the energy-quantum. One remark does appear in a note immediately following on 9 January 1901 [15]. Here Planck applies his new theory to derive values of unprecedented precision for the electron charge, the hydrogen atomic weight, and Avogadro's number among others. With this supporting evidence he does declare that the theory must be correct in general, and with absolute validity. In a longer paper almost a year later [4], Planck showed – following his first paper

of the same title – that the new energy distribution was stationary, but made no further interpretation or even any specific mention of the quantum. And again in 1902 [5] in a long discussion of the nature of white light, although he emphasized the outstanding problem of the interpretation of the nature of spectral lines, he made no mention of the energy-quantum.

In 1943: “... there arose the all-important problem, to assign this remarkable constant a physical meaning. ... But the nature of the energy-quantum remained unclear.” And finally: “For many years I continued to do further research, trying somehow to fit the action quantum into the system of classical physics. But it seems to me that this is not possible.”

§I-4. Planck’s Discovery as Prolog.

In the remainder of this book we collect and discuss principal landmark contributions to the discoveries of quantum theory which sprang directly – if at first slowly and reluctantly – from Planck’s invention of the energy quantum. We have chosen to follow a fundamental but rather narrow path leading from Planck to Einstein, Bohr, and de Broglie; then to the formulations of quantum mechanics due to Heisenberg, Born and Jordan, and to Schrödinger, and to Dirac. Then we enter into the interpretation of quantum mechanics, again following original contributions, here of Born, Heisenberg, and Bohr. Then we vault forward to contemporary contributions from Bell and Aspect and others, originating in the Einstein-Podolsky-Rosen paradox.

We complete our account of the first one hundred years of Planck’s h-quantum with an introduction to recent advances in the theory of measurement and decoherence. We conclude with brief speculations on the next one hundred years and what remains to be achieved within the limited but fundamental context of non-relativistic quantum mechanics.

We now commend to you the original papers in which Max Planck first developed his ideas and then reported his discovery of the Blackbody Spectrum.

Footnotes and References:

- 1) M. Planck, *Ann. d. Phys.* **4**, 553 (1901); **4**, 564 (1901) (here as **Papers I-4,5**).

- 2) W. Wien, *Ann. d. Phys.* **4**, 422 (1901) (here as **Paper I-3**).
- 3) A. Einstein, *Ann. d. Phys.* **17**, 17 (1905) (here as **Paper II-1**).
- 4) M. Planck, *Ann. d. Phys.* **6**, 818 (1901).
- 5) M. Planck, *Ann. d. Phys.* **7**, 390 (1902).
- 6) M. Planck, *Die Naturwissenschaften* **14/15**, 153 (1943) (here as **Paper I-6**).
- 7) K. Huang, *Statistical Mechanics*, John Wiley & Sons, New York (1987), p.280.
- 8) W. Wien, *Wied. Ann.* **58**, 69 (1900).
- 9) M. Planck, *Ann. d. Phys.* **1**, 69 (1900); **1**, 719 (1900) (here as **Papers I-1,2**).
- 10) e.g., R.C. Tolman, *The Principles of Statistical Mechanics* (Oxford, London 1942), Pp.70, 325. This is an endlessly quarrelsome subject.
- 11) O. Lummer and E. Pringsheim, *Verhandl. d. Deutsch. Physikal. Gesellsch.* **1**, p.31 (1900); **2**, p.163 (1900); **3**, p.37 (1900); *Ann. d. Phys.* **4**, 225 (1901).
- 12) F. Paschen, *Ann. d. Phys.* **4**, 277 (1901); **6**, 646 (1901).
- 13) H. Rubens and F. Kurlbaum, *Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin* **41**, 928 (1900); *Ann. d. Phys.* **4**, 649 (1901) (from which many references can be traced).
- 14) The relation $\mathcal{R}_f = f^2 U / c^2$ can be understood on dimensional grounds. Planck expends great effort to establish this connection between the equilibrium energy of the charged dipole oscillator U and the energy flux \mathcal{R}_f of the equilibrium field by equating the emission rate $\sim fU$ and the absorption rate $\sim c^2 \mathcal{R}_f / f$. We forgo this lengthy discussion in Paper I-1.
- 15) M. Planck, *Ann. d. Phys.* **4**, 564 (1901) (here as **Paper I-5**).

Biographical Note on Planck.

Max Karl Ernst Ludwig Planck (1858-1947) – From the London Times 6OCT47 we learn about Planck's long, distinguished and much documented life. Planck was the son of a Professor of Constitutional Law at Kiel and Göttingen, distinguished as joint author of the Prussian Civil Code. Planck studied physics and mathematics, but especially thermodynamics, under Helmholtz, Kirchoff and Weierstrauss and in 1879 obtained his doctorate *summa cum laude* from Munich for his studies on the Second Law of Thermodynamics. In 1884 he became Professor in Kiel, in 1889 Professor Extraordinarius in Berlin, and in 1892 succeeded Kirchoff there in the chair of Experimental Physics. He became Permanent Secretary to the Prussian Academy of Science (1912), Rector of the University of Berlin (1913-14), Nobel Laureate (1918), President (1920) of the Kaiser Wilhelm Society (now the Max Planck Society). He climbed the Jungfrau at age 72. Planck's Berlin villa was destroyed by bombs in WWII, so what his circumstances were when he wrote his

1943 *Reflections* is an interesting question. His son Erwin was executed by the Gestapo for his part in the July 1944 attempted assassination of Hitler.

Yourgrau and Mandelstam [†] describe the extreme irony of Planck's personal views and his scientific discovery of the h -quantum, which he himself was first to recognize as the 'elementary quantum of action'. Planck was in a quandary "Can it be that the astonishing simplicity of ... [the Principle of Least Action] ... rests ... on chance? It is ... difficult to believe this. On the contrary ... Leibniz's Principle of Least Action ... [leads] ... to a deeper understanding of the quantum of action." They characterize Planck's arguments as "... metaphysical ... put forward with zeal and persistence." Yourgrau and Mandelstam recommend instead Born's attitude "... I do not like this metaphysics ... that there is a definite goal to be reached and often claims to have reached it. Metaphysical systematization means formalization and petrification ... there *are* metaphysical problems ... they are 'beyond physics' indeed and demand an act of faith. We have to accept this fact to be honest."

These comments are almost fifty years old, and it is interesting to compare them to what we believe today in light of our efforts to forecast the next 100 Years of Planck's h Quantum.

Yourgrau and Mandelstam express equal regard for the action and for the equations of motion, on the grounds that Sturm-Liouville differential equations of motion are equivalent to a variation principle. This was at a time (1955~1963) when S-matrix theory was in, and quantum field theory out of fashion. The revolution of the Standard Model restored full faith in field theory based on an Action Principle constructed to express profound invariance properties, symmetries both full and broken, and renormalizability. The only conceivable access to the construction of such theories, and then to calculation with them is via the Action Principle. The equations of motion are available but not of primary interest. As Born feared, it seems that there *is* a definite goal, there *are* frequent claims to have reached it, and the hope of systematization, formalization, and we suppose the remote specter of ultimate petrification. Then this remote, ultimate, intricate 'reality' and all its elements will require an existential - possibly only metaphysical - understanding.

† - W. Yourgrau and S. Mandelstam, *Variational Principles in Dynamics and Quantum Theory* (Pitman, London, 1960), Pp.146, 160.

Paper I-1: Excerpt from *Annalen der Physik* 1, 69 (1900).

On Irreversible Radiation Processes

von **Max Planck**

(Nach den Sitzungsbr. d. k. Akad. d. Wissensch. zu Berlin vom 4. Februar 1897, 8. Juli 1897, 16. December 1897, 7. Juli 1898, 18. Mai 1899 and from a lecture given at the 71st Natural-Philosophy Meeting in Munich, edited for the *Annalen der Physik* by the author.)

The following is an exposition of the principal results of my investigations into the meaning of the Second Law of Thermodynamics as applied to radiant heat considered from the standpoint of electromagnetic theory.

That even radiant heat must respect the requirements of this fundamental Law – for example, the balance of radiation between bodies of different temperature is always in the direction to equalize their temperatures – is generally undisputed. The electromagnetic nature of radiant heat makes it a most urgent problem to understand and even to prove the Second Law of Thermodynamics as applied to heat radiated purely electromagnetically. The prerequisite to this is that one should understand the emission and absorption of radiant heat as an electromagnetic process; that one consider the emission of radiant heat as the emission of electromagnetic waves by elementary oscillators which have some connection with the actual atoms of the radiating matter; and further, that one consider the absorption not as the result of an electrical resistance or some kind of friction, but as a resonance phenomenon, in which the oscillators not only emit waves, but also are stimulated into vibrations by incident waves.

Chapter One: Emission and Absorption of Electromagnetic Radiation by an Oscillator.

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Note added in translation: We cannot follow every strand back to its beginning but must accept some results as being “obvious” although

they are by no means trivial or uninteresting. Planck's oscillator was an electric dipole with a natural frequency f ; its energy U was electric and magnetic energy related to the square of its amplitude. On average, the oscillator energy decreases due to 'spontaneous' radiation at a rate proportional to fU and increases due to absorption of the incident flux \mathcal{R}_f of radiant energy at the resonant frequency. On dimensional grounds the rate of absorption must be proportional to $c^2\mathcal{R}_f/f$. Planck establishes the equality at equilibrium, $\mathcal{R}_f = f^2U/c^2$.

Chapter Two: Conservation of Energy and Increase of Entropy.

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§17. Definition of the Electromagnetic Entropy.

By analogy to the total energy of the system U , we define a new quantity, the *total electromagnetic entropy* of the system:

$$S_t = \sum S + \int s dr.$$

The sum is over all the oscillators, the integration over all volume elements dr occupied by the fields. S is the entropy of an individual oscillator and s the entropy density at a point in the fields.

The entropy S of an oscillator of frequency f and energy U we *define* as follows:

$$S = -\frac{U}{af} \log \frac{U}{ebf}, \tag{41}$$

where a and b are two universal positive constants \dots ; and $e = 2.71 \dots$ is included for later convenience. $\dots\dots$.

Planck's choice for the entropy of an oscillator mimics the Boltzmann H function as a function of U , chosen as the only available characteristic of the oscillator. The factors af and bf could be arbitrary positive functions of frequency in this state of the theory, but are

chosen linear anticipating Wien's fit to the data. Planck's choice for the field entropy – which eventually has to be modified by the quantum hypothesis – is understood when we recognize that the field energy per unit volume for an unpolarized, isotropic distribution is

$$U_F \equiv \int \frac{d^3 f}{c^3} \mathcal{U}_f = \int \frac{2 \cdot 4\pi}{c^3} f^2 df \frac{c^2}{f^2} \mathcal{R}_f.$$

The factor 2 comes from the sum over the polarizations and the factor $4\pi f^2 df/c^3$ from the integration over the wave-number $\vec{k} = f\vec{c}$.

The equality of Eqn49 $\mathcal{R}_f = f^2 U/c^2$ which originated from the energy equilibrium of the oscillator-field system, is now a result of the entropy maximum with the above definitions of the entropy.

We ... define the entropy of a monochromatic linearly polarized beam of intensity \mathcal{R} by:

$$\mathcal{L} = -\frac{\mathcal{R}}{af} \log \frac{c^2 \mathcal{R}}{ebf^3}. \tag{43}$$

..... In the special case that the radiation through the point is unpolarized and independent of direction, the entropy density is ...

$$s = \frac{8\pi}{c} \cdot \int_0^\infty df \cdot \mathcal{L}. \tag{45}$$

§19. Requirements on the Stationary State.

That state of the system which corresponds to the maximum total entropy, is referred to as the stationary state; from the Law of Increase of Entropy, it is no longer possible for it to undergo further changes, so long as there are no interactions from outside the system. Another necessary condition for the stationary state is that the total entropy itself no longer changes with the time, so that all the inequalities of the preceding paragraphs become equalities. This condition is fulfilled, as can easily be shown, when at every point and for every direction of propagation and polarization

$$\mathcal{R} = \frac{f^2}{c^2} U. \tag{49}$$

The total radiation of each frequency is assumed unpolarized and isotropic.

But the conditions necessary for the absolute maximum of the total entropy go still further. For each infinitesimally small virtual change of state of the system, the change in the total entropy S_t must vanish. If we imagine a virtual change in which an infinitesimal amount of energy of an oscillator with frequency f_1 is transferred to another oscillator of frequency f_2 , while everything else remains unchanged, then we must have

$$\delta S_t = \delta S_1 + \delta S_2 = 0 \quad \text{and} \quad \delta U_1 + \delta U_2 = 0.$$

These equations with Eqn41 give:

$$-\frac{1}{af_1} \log \frac{U_1}{bf_1} = -\frac{1}{af_2} \log \frac{U_2}{bf_2};$$

If we abbreviate

$$-\frac{1}{af_1} \log \frac{U_1}{bf_1} \equiv \frac{1}{T}, \quad (50)$$

then it follows, since f_1 and f_2 are completely independent, that the value of T in the stationary state must be the same for all oscillators in the system. Since the value of U determines that of \mathcal{R} by Eqn49, then the stationary state of the whole system in all its parts depends only on the single parameter T .

We can now express the value of all quantities in the stationary state in terms of the parameter T . First, from Eqn50, the energy of an oscillator of frequency f :

$$U = bfe^{-af/T},$$

and from Eqn49, the intensity of a linearly polarized beam of frequency f :

$$\mathcal{R} = \frac{bf^3}{c^2} e^{-af/T}, \quad (51)$$

and from Eqn25 for the total intensity of radiation in a given direction:

$$K = 2 \int_0^\infty \mathcal{R} df = \frac{12bT^4}{c^2 a^4} \quad (52)$$

and from Eqn28 for the energy density of the field:

$$u = \frac{4\pi K}{c} = \frac{48\pi bT^4}{c^3 a^4}. \quad (53)$$

This energy density consists of the sum of the energy densities $U(f)$ of the individual frequencies in the following way:

$$u = \int_0^{\infty} U(f)df, \text{ with } U(f) = \frac{8\pi\mathcal{R}}{c} = \frac{8\pi bf^3}{c^3} e^{-af/T}.$$

From Eqns41 and 50, the entropy of an oscillator of frequency f is:

$$S = b \left(\frac{f}{T} + \frac{1}{a} \right) e^{-af/T},$$

and from Eqns43 and 50, that of the radiation of frequency f in a given direction is:

$$\mathcal{L} = \frac{bf^2}{c^2} \left(\frac{f}{T} + \frac{1}{a} \right) e^{-af/T}.$$

The total intensity of the radiation entropy in a given direction is, from Eqn43:

$$L = 2 \int_0^{\infty} \mathcal{L}df = \frac{16bT^3}{c^2 a^4},$$

and finally the total density of the field entropy from Eqn45:

$$s = \frac{4\pi L}{c} = \frac{64\pi bT^3}{c^3 a^4}, \quad (54)$$

which follows from the entropy density $\mathcal{S}(f)$ of a single frequency:

$$s = \int_0^{\infty} \mathcal{S}(f)df, \text{ with } \mathcal{S}(f) = \frac{8\pi\mathcal{L}}{c} = \frac{8\pi bf^2}{c^3} \left(\frac{f}{T} + \frac{1}{a} \right) e^{-af/T}.$$

That the total entropy S_t actually has its maximum value can easily be shown from the first and second variations.

Chapter Three: Thermodynamic Conclusions.

§20. Thermodynamic Entropy of The Radiation.

If one accepts the electrodynamic nature of light and radiant heat, one gets the stationary radiation states of the above chapter. These have a fundamental thermodynamic significance. According to a law derived by Kirchoff and used in this context by Wien [1], the heat radiation, which is surrounded by equal temperature matter completely containing it, is independent of the nature of the

matter, and completely determined by a single parameter: the temperature. The radiation is the same as if the surrounding matter was completely “black”.

The same law holds when the walls of the vacuum are perfectly reflecting and when the matter is distributed in any manner in the vacuum. One does have to assume that at least some finite part of the matter’s radiation is emitted into each spectral interval. If this condition is not met, then an essentially unstable radiation state can occur in which a single color is completely missing.

According to the known laws the amount and the particular nature of the emitting and absorbing matter is completely irrelevant to the equilibrium state of the radiation, so one is forced to the conclusion *that the stationary radiation state of the vacuum fulfills all the conditions of the radiation of black bodies, completely without regard to the question whether or not the assumed electromagnetic oscillators are the actual sources of heat radiation in any particular matter.*

This conclusion leads to a somewhat different point of view: The Second Law of Thermodynamics requires that not only the ambient heat, but also the radiant heat must correspond to a definite entropy; when a body loses heat by radiation its entropy decreases, and – according to the Principle of Increasing Entropy – there must occur somewhere a compensating entropy increase, which in this case can only be in the resulting heat radiation. If thermal and electromagnetic radiation are identical, then nothing is left for the thermal radiation entropy, which must be determined solely by the state of the radiation, except to be identified with the electromagnetic entropy. When we do this, we arrive at the further conclusion that the absolute maximum of the entropy corresponding to the stationary radiation state or equivalently to the equilibrium state of the heat radiation, gives the blackbody radiation.

From the identification of thermodynamic and electromagnetic entropy there follows a number of connections between thermal and electrical quantities, whose significance is pointed out in the following paragraphs.

§21. Electromagnetic Definition of Temperature.

From the entropy of a system in thermodynamic equilibrium its temperature

is also defined, because the absolute temperature is the ratio of an infinitesimal amount of heat added to the system to the resulting change in the entropy, provided the system is kept in thermodynamic equilibrium during the change of state. If we assume a unit volume of the vacuum filled with the stationary radiation and hold the volume constant and the radiation at equilibrium, then the infinitesimal change in the energy u of the system is equal to the infinitesimal amount of heat added dQ , and from Eqn53:

$$dQ = du = \frac{192\pi b T^3}{c^3 a^4} dT = T ds,$$

where the resulting change of the entropy s of the system is ds , and the absolute temperature is T . Defined in this way, the absolute temperature of the stationary radiation state in the vacuum is identical to the purely electromagnetically defined parameter T previously introduced, which determines all properties of these states in the above way. From Eqn51 the inverse temperature of a linearly polarized monochromatic beam of frequency f and intensity \mathcal{R} is:

$$\frac{1}{T} = \frac{1}{af} \log \frac{bf^3}{c^2 \mathcal{R}}.$$

When the conditions for the stationary state are not met, but when other radiation behavior occurs in the vacuum, then one can no longer speak of the temperature at a particular place, or of the temperature of the radiation in a given direction, but one must ascribe a separate temperature to each individual linearly polarized monochromatic beam, which is determined by its intensity and its frequency according to the above equation [2]. The beam retains its temperature during propagation with its intensity unchanged – except, for example, if it passes through a focal point – until it is either divided or absorbed.

On the other hand each oscillator has a given temperature completely determined by Eqn50. The stationary radiation state can therefore be characterized as all oscillators and all monochromatic rays having the same temperature.

§22. Dependence of the Total Radiation on the Temperature.

The total intensity of the radiant energy in any given direction is given by the expression for K in Eqn52, which is proportional to the fourth power of the tem-

perature and expresses the well-known Stefan-Boltzmann Law, whose validity was established by Boltzmann [3] from thermodynamics and recently in the investigations of Lummer and Pringsheim [4], at least within the temperature interval from $T = 290K$ to $T = 1560K$, has received a remarkable experimental confirmation.

§23. Distribution of Energy in the Normal Spectrum.

The Law by which the total stationary radiation intensity K is distributed among the radiation intensities \mathcal{R} of individual frequencies f , is given by Eqn51. This Law is usually expressed in terms of the wavelength λ rather than the frequency f , so from Eqn52:

$$K = 2 \int_0^{\infty} \mathcal{R} df \equiv \int_0^{\infty} E_{\lambda} d\lambda.$$

With $\lambda = c/f$, we have

$$E_{\lambda} = 2\mathcal{R} \left| \frac{df}{d\lambda} \right| = \frac{2c\mathcal{R}}{\lambda^2}, \text{ or from Eqn51: } E_{\lambda} = \frac{2c^2b}{\lambda^5} \cdot e^{-ac/\lambda T}.$$

This is just Wien's Energy Distribution Law [5], whose at least approximate validity has recently been demonstrated in the experiments of Paschen [6], Paschen and Wanner [7], and Lummer and Pringsheim [8].

Wien derived his Law on the basis of certain assumptions about the number of radiating oscillators per unit volume and about the details of their motion; in the theory developed here these quantities play no role, but the Law appears as a necessary result of the definition developed in §17 of the electromagnetic entropy of the radiation. The question of the validity of the Law depends entirely upon the validity of that definition. *I have tried repeatedly to derive Eqn41 for the electromagnetic entropy of an oscillator - from which Eqn43 for the entropy of the radiation is determined - by modifying or generalizing it so that it has the same validity as other theoretically well established electromagnetic and thermodynamic Laws, but I have not succeeded.* (Note: Italics added.)

Thus for example one could define the entropy of an oscillator, instead of by Eqn41, in the following way:

$$S = - \frac{U}{\psi(f)} \cdot \log \frac{U}{\phi(f)},$$

where $\psi(f)$ and $\phi(f)$ are undetermined positive functions of the frequency f . Then for the electromagnetic processes discussed in §18 the Principle of Increase of Entropy is definitely fulfilled, but one gets instead of Eqn50 a different expression for the inverse temperature of the oscillators:

$$\frac{1}{T} = -\frac{1}{\psi(f)} \cdot \log \frac{eU}{\phi(f)}, \text{ and then: } U = \frac{\phi(f)}{e} \cdot e^{-\psi(f)/T}$$

and from Eqn49 an Energy Distribution Law instead of Eqn51:

$$\mathcal{R} = \frac{f^2 \phi(f)}{c^2 e} \cdot e^{-\psi(f)/T}. \quad (56)$$

This is exactly the same form as found by Wien on the basis of his special considerations. On the other hand, if one starts from some other form of the Energy Distribution Law and calculates the entropy from it, then one always gets a contradiction with the Principle of Increase of Entropy.

We must conclude that the definition of radiation entropy given in §17, and with it also Wien's Energy Distribution Law, is a necessary consequence of the application of the Principle of Increase of Entropy to the electromagnetic theory of radiation, and that the limit of the validity of these laws – if indeed such a limit exists – can only be that of the Second Law of Thermodynamics. Naturally, the further experimental test of these Laws is of the greatest fundamental interest.

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(Eingegangen 7. November 1899.)

Footnotes and References:

- 1) W. Wien, Wied. Ann. **52**, 133 (1894).
- 2) The necessity of such a generalization of the idea of temperature was noted first by E. Wiedemann, Wied. Ann. **34**, 448 (1888); see also W. Wien, loc.cit., p.132.
- 3) L. Boltzmann, Wied. Ann. **22**, 291 (1884).
- 4) O. Lummer and E. Pringsheim, Wied. Ann. **63**, 395 (1897).
- 5) W. Wien, Wied. Ann. **58**, 662 (1896).
- 6) F. Paschen, Wied. Ann. **60**, 662 (1897); Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin, p.405, p.893 (1899).
- 7) F. Paschen and H. Wanner, Sitzungsber. d. k. Wissensch. zu Berlin, p.5 (1899).
- 8) O. Lummer and E. Pringsheim, Verhandl. d. Deutsch. Physikal. Gesellsch. **1**, p.28,

p.215 (1899). Also see H. Beckmann, Inaug.-Diss., Tübingen (1898); and H. Rubens, Wied. Ann. 69, 582 (1899). These works discuss variants of Wien's Law.

Paper I:2: Excerpt from *Annalen der Physik* 1, 719 (1900).

Entropy and Temperature of Radiant Heat

von **Max Planck**

§1. Introduction and Summary.

In a recently published paper [1], I have constructed an expression for the entropy of radiant heat, which complies with all the requirements on the properties of this quantity arising on the one hand from thermodynamics, and on the other from electromagnetic theory. the result, and thus also Wien's Law, is a necessary consequence of the application of the Principle of the Increase of Entropy to the theory of electromagnetic radiation.

§6. Complete Derivation of the Entropy Function.

. . . an oscillator in its stationary radiation field . . . the energy of all the oscillators is the sum of their individual energies, $U_n = nU$, and the entropy is the sum of their individual entropies, $S_n = nS$. We set

$$\frac{d^2 S}{dU^2} = -\mathcal{F}(U), \tag{12}$$

where \mathcal{F} is a positive function of U . If one sets

$$U_n = n \cdot U \text{ everywhere, then } \mathcal{F}(nU) = \frac{1}{n} \mathcal{F}(U)$$

and the solution of this functional equation is [2]:

$$\mathcal{F}(U) = \frac{\text{const.}}{U} \text{ or from (12): } \frac{d^2 S}{dU^2} = -\frac{\alpha}{U},$$

where α can only be a positive function of the frequency f . From this expression it follows by a double integration:

$$S = -\alpha U \log(\beta U), \tag{14}$$

where β is a second positive function depending only on the frequency f . A further positive integration constant is suppressed since it can have no physical significance. Finally ... (Note: from Eqn49 of [1]) it follows that:

$$\mathcal{L} = -\frac{f^2}{c^2}\alpha U \log(\beta U) = -\alpha \mathcal{R} \log\left(\frac{\beta c^2}{f^2}\mathcal{R}\right). \quad (15)$$

If one further assumes the temperature for the oscillators T to be:

$$\frac{1}{T} = \frac{dS}{dU}, \text{ and for the radiation } \mathcal{R} \text{ to be: } \frac{1}{T} = \frac{d\mathcal{L}}{d\mathcal{R}},$$

then:

$$\frac{1}{T} = -\alpha \log(\beta e U) \text{ and } = -\alpha \log\left(\frac{\beta e c^2}{f^2}\mathcal{R}\right), \quad (16)$$

or:

$$\mathcal{R} = \frac{f^2}{\beta e c^2} e^{-1/\alpha T}$$

and this equation with the substitution:

$$\frac{1}{\alpha} = \psi(f), \quad \frac{1}{\beta} = \phi(f)$$

gives Eqn56 of my original paper. According to the thermodynamic results of Wien [2], both $\psi(f)$ and $\phi(f)$ are proportional to f , so we can set:

$$\frac{1}{\alpha} = af, \quad \frac{1}{\beta} = ebf,$$

where a and b are universal positive constants which, together with Eqns14 and 15, complete the definition of the oscillator entropy S and the radiation entropy \mathcal{L} . From Eqn16 then:

$$\frac{1}{T} = \frac{1}{af} \log\left(\frac{bf^3}{c^2\mathcal{R}}\right). \quad (17)$$

From the measurements of Kurlbaum and of Paschen, the numerical values of a and b are [3]:

$$\begin{aligned} a &= 0.4818 \times 10^{-10} [\text{sec} \times \text{deg}], \\ b &= 6.885 \times 10^{-27} [\text{erg} \times \text{sec}]. \end{aligned}$$

Berlin, März 1900.

(Eingegangen 22. März 1900.)

Footnotes and References:

- 1) M. Planck, Ann. d. Phys. **1**, 69 (1900).
- 2) W. Wien, Wied. Ann. **58**, 662 (1896).
- 3) (Note added: 1997 values are

$$a \equiv \frac{h}{k} = .47994 \times 10^{-10} [\text{sec} \times \text{deg}] \quad \text{and} \quad b \equiv h = 6.6261 \times 10^{-27} [\text{erg} \times \text{sec}].)$$

Paper I:3: Excerpt from Annalen der Physik **4**, 422 (1901).

**On the Theory of Radiation –
Comments on Planck's Criticism**

von **W. Wien**

Planck has criticized my earlier work on blackbody radiation which supports reversibility of the radiation for free propagation but asserts non-reversibility of any coherent emission processes, whereas Planck holds that such processes should also be reversible. In discussion it has been agreed that this difference of opinion is eliminated when a practical definition of an irreversible process is given. The difference of opinion arose essentially because we did not mean the same thing by an irreversible process.

If we put a radiating surface element at the center of a reflecting container, all rays will be reflected back and we can consider the reflected radiation itself as re-emitted in a larger volume and reflected from a sphere with a larger radius. This process is certainly reversible if the reflecting element is sufficiently small that all rays can be considered as radial. On the other hand, when the size of the element is not negligible, then rays strike the spherical surface at different angles and differently reflected rays will have different path lengths back and forth to the second sphere. As a result the rays will not return in phase to the first sphere. If we consider two radiation packets which traverse different length paths in their first passage, then these will only arrive in phase when the ratio of their wavelengths is

a rational number. For an extended radiation source the original state will never exactly recur. Even this process can be considered as reversible, if in a finite time the original state can recur approximately. If the time is unlimited, then there is no limit for the approximation. When one realizes that conservative processes which take place in even the greatest disorder cannot bring about irreversibility, then one is free to expand in the above sense what must be considered reversible. [2]. . .

I approve gladly that such a sharp criticism should be directed against so fundamental a problem but a renewed investigation into the question, how in this case the reversibility occurs, seems urgently desirable. I myself have not yet found a satisfactory answer.

(Eingegangen 29. December 1900.)

Note added in Proof: Jahnke, Lummer and Pringsheim [3] report a deviation from my theory [4] which essentially repeats their earlier claims. I consider it unnecessary to go into this once more. Their earlier remarks, which were prompted by my conjecture that one might expect a scaling of the radiation law, rested on a misunderstanding. I have expressly noted that deviations from the basic requirement of essential molecular disorder must occur with increasing temperature at smaller wavelengths. I have repeatedly stated that for a given wavelength, any increase in the temperature must lead to other molecular effects which for lower temperature only entered for longer wavelengths [5].

Footnotes and References:

- 1) M. Planck, Ann. d. Phys. **3**, p.764 (1900).
- 2) (Note added in translation: Here Wien embarks on a discussion of uncompensated depolarization of scattered rays, leading in his opinion to irreversibility. Planck had extended an unstated hypothesis of molecular disorder to the radiation field, cutting the Gordian knot of all such coherence effects.)
- 3) E. Jahnke, O. Lummer and E. Pringsheim, Ann. d. Phys. **4**, 225 (1900).
- 4) W. Wien, Ann. d. Phys. **3**, 530 (1900).
- 5) (Note added in translation: Here Wien reproduced the data of Jahnke, Lummer and Pringsheim which showed a small deviation at high temperature, in the direction of Planck's modification of Wien's Law.)

Paper I-4: Excerpt from *Annalen der Physik* 4, 553 (1901).

On the Energy Distribution in the Blackbody Spectrum

von **Max Planck**

(Communicated also in the Deutschen Physikalischen Gesellschaft, Sitzung vom 19. October und vom 14. December 1900, Section 2, p.202 and p.237, 1900.)

Introduction.

New spectral measurements of Lummer and Pringsheim [1] and even more remarkably those of Rubens and Kurlbaum [2], which confirm an earlier result of Beckmann [3], show that the law first derived by Wien from molecular kinetics and later by me from the theory of electromagnetic radiation, has no general validity.

In each case, the theory requires revision. In the following, I make an attempt from the basis of my previous work. It turns out, in the course of a derivation which leads to Wien's Energy Distribution Law, that one discovers a term for which a new prescription is rewarding; then it becomes a question to identify this term in the derivation and to make a suitable interpretation of it.

The physical basis of my radiation theory which includes the hypothesis of "spontaneous radiation", has strong critics with opposite views, as I have described in my recent article [4]. Nonetheless, the calculation to my knowledge contains no errors. It completely determines the Law of Energy Distribution in the Blackbody Spectrum, when one calculates the entropy S of oscillators radiating at a fixed frequency f , as a function of their vibration energy U . From the relation

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

one gets the dependence of the energy U on the temperature T . Since the energy U is simply related to the radiation density, it too is given in terms of the temperature. The Blackbody Energy Distribution is that one for which the radiation density of all different frequencies has the given temperature.

So the whole question is to find S as a function of U , and the following work describes our solution to this problem. In my first treatment of this matter, I had written down S directly by definition, without further foundation, as a simple function of U , and was content to prove that this form of the entropy satisfied all the requirements of thermodynamics. I thought then that it was unique and that Wien's Law, which necessarily follows from it, had general validity. But a later more careful investigation [5] showed there could be another derivation, which also made possible the restriction required to make S well behaved. I then saw this requirement to have been based directly on the plausible hypothesis that – for an infinitesimal irreversible change in a system of N identical oscillators almost in thermodynamic equilibrium in identical stationary radiation fields – the increase in their total entropy $S_N = NS$ only depends on the total energy $U_N = NU$ and on their changes, but not on the energy U of the individual oscillators. This hypothesis led in turn to Wien's Energy Distribution Law. But now, from recent experiments, it cannot be true. One is forced to the conclusion that even this hypothesis cannot be generally valid and must be removed from the theory [6].

Therefore another condition must be introduced to make the entropy calculable: a more fundamental conception of the idea of entropy is necessary, which does lead to a new simple expression for the entropy and thereby to a new radiation formula which appears to agree with all known facts.

I. Calculation of the Entropy of an Oscillator as a Function of its Energy.

§1. Entropy denotes disorder, and this disorder – according to the electromagnetic radiation theory of an oscillator of given frequency, in a stationary radiation field – depends on the irregularity with which changes of its amplitude and its phase occur over time-intervals large compared to the period of the oscillations, but small compared to the time of a measurement. If the amplitude and phase were absolutely constant, then the oscillations would be perfectly uniform, their entropy would be zero, and their energy would be perfectly freely transformable to work. The constant energy U of an individual oscillator is only an interrupted time-average, or equivalently a simultaneous mean value of the energies of a large

number N of identical oscillators, all in the same stationary radiation field and far enough from each other to have no direct mutual influence. In this sense, we speak of the mean energy U of individual oscillators. The total energy of the system of N oscillators is

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

corresponding to a fixed total entropy

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

where S is the mean entropy of an individual oscillator. The entropy S_N represents the disorder with which the total energy U_N is distributed among the N individual oscillators.

§2. We set the entropy S_N of the system, to within an arbitrary additive constant, proportional to the logarithm of the probability W with which the N oscillators can possess the total energy U_N , that is:

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

This prescription in my opinion is based on the definition of the probability W . In fact we have – on the assumption that electromagnetic theory is the basis of the radiation – no criterion to speak of such a probability in any definite sense. The suitability of the prescription introduced next is suggested first by its simplicity, and second by its similarity to a corresponding prescription from the kinetic theory of gases [7].

§3. *To find the probability that the N oscillators have the total energy U_N , it is necessary to suppose that U_N is not a continuous, endlessly divisible quantity, but a discrete integral multiple of finite equal parts combining to the whole. We call such a part an energy-quantum ϵ , and set*

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

where P is an integer, expected to be large, whereas the value of ϵ is as yet undecided.

Planck uses the word 'Energieelement' where we use the word 'energy-quantum'. His first and apparently only use of the word 'quantum' is in connection with the 'Elementarquantum der Electricität $e = 4.69 \cdot 10^{-10}$ esu', in his **Paper I-5** entitled "*Ueber die Elementarquanta der Materie und der Electricität*".

It is clear that the partition of P energy-quanta among N oscillators is possible in a finite exactly determined number of ways. Each individual partition we call a "complexion", following similar ideas of Boltzmann. If one labels the oscillators by the integers $1, 2, \dots, N$ in order; and the number of energy-quanta possessed by each as $\{p_1, p_2, \dots, p_N\}$ with $p_1 + p_2 + \dots + p_N = P$; then each different choice of p 's is a separate complexion. The number \mathcal{Z} of all possible complexions is equal to the number of all possible ways to distribute P identical objects (quanta) in N different cells. It should be remarked that two complexions are considered different when the same numbers p occur but in different order; so for $N = 2, P = 10$, the complexion $\{3, 7\}$ is different from $\{7, 3\}$.

From Combinatorial Theory the number \mathcal{Z} of all possible complexions for given N, P is

$$\mathcal{Z} = \frac{(N + P - 1)!}{(N - 1)!P!}.$$

Using Stirling's Approximation - $N! \approx N^N$ - we get

$$\mathcal{Z} \approx \frac{(N + P)^{N+P}}{N^N \cdot P^P}.$$

§4. The hypothesis which we use as the basis for further calculations, runs as follows: The probability W that the N oscillators have total energy U_N is proportional to the number \mathcal{Z} of all possible complexions for the partition of the energy U_N among the N oscillators; in other words, any particular complexion is just as probable as any other particular complexion. Whether this hypothesis actually corresponds to Nature, can be proved only by experiment.

§5. From Eqn3, the entropy of a system of N oscillators with energy $U_N = NU = P\epsilon$, with a suitable choice of additive constant, is:

$$S_N = k \log \mathcal{Z} = k \{ (N + P) \log (N + P) - N \log N - P \log P \}, \quad (5)$$

and using Eqns4 and 1:

$$S_N \equiv NS = kN \left\{ \left(1 + \frac{U}{\epsilon} \right) \log \left(1 + \frac{U}{\epsilon} \right) - \frac{U}{\epsilon} \log \frac{U}{\epsilon} \right\}, \quad (6)$$

expressing the entropy S of an individual oscillator in terms of its mean energy U .

II. Introduction of Wien's Displacement Law.

§6. Next to Kirchoff's Law of the equality of the emission- and absorption-strength of a radiator, Wien's Displacement Law [9] – based on a special application of the Stefan-Boltzmann Law for the temperature dependence of the total radiant energy – is the most valuable relation in the firmly established theory of radiant heat. In the form given by M. Thiesen [10], it is

$$E_\lambda \cdot d\lambda = T^5 \psi(\lambda T) \cdot d\lambda,$$

where λ is the wavelength, $E_\lambda d\lambda$ the spatial density of "black"-radiation in the interval λ to $\lambda + d\lambda$, T the temperature, and $\psi(x)$ a universal function of the single argument x .

§7. Now we investigate what Wien's Displacement Law has to say about the dependence of the entropy S of our oscillators on their energy U and their frequency f , in the general case that the oscillator is in a random thermal medium. For this purpose, we first generalize Thiesen's form of the law to radiation propagating with the speed of light c and introduce the frequency variable f instead of the wavelength λ . Introducing the spatial density of energy in the frequency interval f to $f + df$ as $\mathcal{U}df$, and the substitutions $E \cdot d\lambda \rightarrow \mathcal{U} \cdot df$, $\lambda \rightarrow c/f$, and $d\lambda \rightarrow cdf/f^2$, Thiesen's form gives

$$\mathcal{U} = T^5 \cdot \frac{c}{f^2} \cdot \psi \left(\frac{cT}{f} \right).$$

Now from the Kirchoff-Clausius Law, the rate of emission of energy by a black surface in a thermal medium, at temperature T and frequency f , is inversely

proportional to c^2 ; therefore the energy density \mathcal{U} is inversely proportional to c^3 , and we get

$$\mathcal{U} = \frac{T^5}{f^2 c^3} \xi_1 \left(\frac{T}{f} \right),$$

where the constants in the function ξ_1 are independent of c .

Thiesen's result has the thermodynamic foundation of the Stefan-Boltzmann Law $E = \sigma T^4$ combined with the empirical result of Wien's Displacement Law that

$$E_\lambda = \frac{dE}{d(\lambda \cdot T)} = \sigma T^4 \times \psi(\lambda \cdot T),$$

where $\psi(\lambda \cdot T)$ is a universal function of the single argument $x = \lambda \cdot T$. Here Planck uses these classical results to deduce that the energy-quantum must be a linear function of the frequency $\epsilon = hf$.

Instead of this we could also define a new function $\xi_2(x) \equiv x^5 \xi_1(x)$ and write

$$\mathcal{U} = \frac{f^3}{c^3} \xi_2 \left(\frac{T}{f} \right), \tag{7}$$

from which we conclude that the product $\mathcal{U} \lambda^3$ is a universal function of T/f for all media in thermodynamic equilibrium.

§8. Now to go from the spatial density of radiation \mathcal{U} , to the energy U of an oscillator with the resonant frequency f in the radiation field, we use Eqn34 of my earlier paper on irreversible radiative processes [11] to obtain the expression:

$$\mathcal{R} = \frac{f^2}{c^2} U$$

where \mathcal{R} is the intensity of monochromatic, linearly polarized radiation. Together with the known equation $\mathcal{U} = 8\pi \mathcal{R}/c$, this gives

$$\mathcal{U} = \frac{8\pi f^2}{c^3} U. \tag{8}$$

From here and from Eqn7 follows:

$$U = \frac{f}{8\pi} \xi_2 \left(\frac{T}{f} \right),$$

where c no longer occurs at all. Instead of this we can also write

$$T = f \xi_3 \left(\frac{U}{f} \right)$$

in terms of still another universal function ξ_3 .

§9. Finally we introduce the entropy per oscillator, for which we set

$$\frac{1}{T} = \frac{dS}{dU}, \tag{9}$$

which gives

$$\frac{dS}{dU} = \frac{1}{f} \xi_4 \left(\frac{U}{f} \right) \text{ and integrating } S = \xi \left(\frac{U}{f} \right), \tag{10}$$

that is, the entropy of the oscillators in a medium in thermodynamic equilibrium depends only on the single variable U/f , and on universal constants. This, to me, is the simplest way to express Wien's Displacement Law.

§10. If we apply Wien's Displacement Law in this form to Eqn5 for the entropy, then we recognize that the energy-quantum ϵ must be proportional to the frequency, that is $\epsilon = hf$, and consequently:

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

Here h and k are universal constants.

Note that this is the first use of the symbol 'h', and the first recognition of the role of this universal constant in the definition of the quantum of energy, which concept is introduced in this paper for the first time.

By substitution in Eqn9 one obtains

$$\frac{1}{T} = \frac{k}{hf} \log \left(1 + \frac{hf}{U} \right), \text{ or } U = \frac{hf}{e^{hf/kT} - 1} \tag{11}$$

and from Eqn8 the sought after energy distribution law is

$$U = \frac{8\pi h f^3}{c^3} \cdot \frac{1}{e^{hf/kT} - 1} \quad (12)$$

or also, if one uses the wavelength λ instead of the frequency f :

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

The expression for the intensity and for the entropy of the radiation propagating in the thermal medium, as well as the law of increase of the total entropy for the nonstationary radiation processes, I hope to discuss in another place.

III. Numerical Values.

§11. The value of the two universal constants h and k can be calculated exactly with the help of measurements which have already been made. F. Kurlbaum [12] has found that the total energy \mathcal{E}_t which is radiated from 1 cm² in 1 sec by a blackbody at the temperature $t^\circ\text{C}$ satisfies:

$$\mathcal{E}_{100} - \mathcal{E}_0 = 0.0731 \frac{\text{Watts}}{\text{cm}^2} = 7.31 \times 10^5 \frac{\text{ergs}}{\text{cm}^2\text{sec}}.$$

This gives the spatial density of the total radiant energy at the absolute temperature 1^oK:

$$\frac{4 \cdot 7.31 \times 10^5}{3 \times 10^{10}(373^4 - 273^4)} = 7.061 \times 10^{-15} \frac{\text{ergs}}{\text{cm}^2\text{sec}}.$$

On the other hand, from Eqn12 the spatial density of the total radiant energy for $T = 1$:

$$\begin{aligned} u &= \int_0^\infty U df = \frac{8\pi h}{c^3} \int_0^\infty \frac{f^3 df}{e^{hf/k} - 1} \\ &= \frac{8\pi h}{c^3} \int_0^\infty f^3 df \left(e^{-hf/k} + e^{-2hf/k} + e^{-3hf/k} + \dots \right). \end{aligned}$$

and by term-wise integration

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

If one sets this equal to 7.061×10^{-15} , then with $c = 3 \times 10^{10}$,

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

§12. O. Lummer and E. Pringsheim [13] have measured the product $\lambda_m T$, where λ_m is the wavelength for the maximum of E at the temperature T , to be

$$\lambda_m T = 0.2940 \text{cm} \cdot \text{deg K}.$$

By differentiating Eqn12,

$$\frac{dE}{d\lambda} = 0 \Rightarrow (1 - ch/5k\lambda_m T) \cdot e^{ch/k\lambda_m T} = 1$$

and from this transcendental equation

$$\lambda_m T = \frac{ch}{4.9651 \cdot k},$$

and

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

From this and Eqn14, the fundamental constants have the values

$$h = 6.55 \times 10^{-27} \text{erg} \cdot \text{sec}, \text{ and } k = 1.346 \times 10^{-16} \frac{\text{erg}}{\text{deg K}}. \quad (15)$$

These are the same numbers which I gave in my earlier article [14].

(Eingegangen 7. Januar 1901.)

Footnotes and References:

- 1) O. Lummer u. E. Pringsheim, Verhandl. der Deutsch. Physikal. Gesellsch. **2**, 163 (1900).
- 2) H. Rubens und F. Kurlbaum, Sitzungsber. d. k. Akad. d. Wissensch. zu Berlin vom 25 October, 1900, p.929.
- 3) H. Beckmann, Inaug.-Dissertation, Tübingen 1898. See also H. Rubens, Wied. Ann. **69**, 582 (1899).
- 4) M. Planck, Ann. d. Phys. **1**, 719 (1900). Here as **Paper I-2**.
- 5) M. Planck, l.c. p.730 ff.

- 6) One should note here the criticism that this prescription has received: by W. Wien (Report of the Paris Conference 2, 40 (1900)), and by O. Lummer (l.c. 2, 92 (1900)).
- 7) L. Boltzmann, Sitzungsber. d. k. Akad. d. Wissensch. zu Wien (II) 76, 428 (1877).
- 8) Joh. v. Kries, *Die Principien der Wahrscheinlichkeitsrechnung*, p.36, Freiburg, 1886.
- 9) W. Wien, Sitzungsber. d. k. Akad. Wissensch. zu Berlin vom 9 Februar. 1893, p.55.
- 10) M. Thiesen, Verhandl. d. Deutsch. Phys. Gesellsch. 2, 66 (1900).
- 11) M. Planck, Ann. d. Phys. 1, 69 (1900). Here as **Paper I-1**.
- 12) F. Kurlbaum, Wied. Ann. 65, 759 (1898).
- 13) O. Lummer u. E. Pringsheim, Verhandl. der Deutsch. Physikal. Gesellsch. 2, 176 (1900).
- 14) [Note added in translation: This statement is not quite accurate. The value of h/k has been increased 1% by evaluating it from the maximum of the blackbody spectrum rather than from the exponential slope of the Wien distribution; the value used for the total intensity of the blackbody spectrum between 273K and 373K has been reduced 1% but enters to the fourth power; the Planck distribution results in an 8% increase in the spectral integral at 1K; for a net reduction of $8 - 4 + 1 = 5\%$ in h from the previous value 6.886×10^{-27} (4% high) to 6.55×10^{-27} (1% low). At the same time, Boltzmann's constant has gone from 3.5% high to 2.5% low.]

Paper I-5: Excerpt from *Annalen der Physik* 4, 564 (1901).

On the Elementary Quanta of Matter and Electricity

von Max Planck

(Aus den Verhandlungen der Deutschen Physikalischen Gesellschaft, 2, p.244. 1900, mitgeteilt vom Verfasser.)

In his fundamental paper "On the Relation Between the Second Law of Thermodynamics and the Probability Basis of the Law of Thermal Equilibrium", Boltzmann [1] found the equilibrium entropy of a monatomic gas to be the logarithm of the probability of the state. He proves the relation:

$$\int \frac{dQ}{K} = \frac{2}{3} \log \mathcal{P}.$$

Here dQ is the external heat added to the system, K is the mean kinetic energy of

the atoms, and \mathcal{P} is the number of "complexions" which measures the probability of the stationary velocity distribution of the atoms.

Now if M is the mass of a gram-mole of atoms, m that of an individual atom, and $\langle v^2 \rangle$ the mean-square atomic velocity:

$$K = \frac{M}{m} \cdot \frac{1}{2} m \langle v^2 \rangle, \text{ and further: } \langle v^2 \rangle = \frac{3RT}{M},$$

where R is the gas constant (8.31×10^7 for $O = 16$), and T the temperature; so the entropy of the gas is

$$\int \frac{dQ}{T} = \frac{m}{M} R \log \mathcal{P}.$$

On the other hand, in my recently developed Electromagnetic Theory of Radiant Heat, for the entropy of a large number of linear oscillators vibrating independently in a stationary radiation field, I found the expression [2] $k \log \mathcal{R}$, where \mathcal{R} is the number of possible complexions and k is 1.346×10^{-16} [erg \times deg].

This connection between the entropy and the probability only has a physical meaning if it holds in general, not just for the atomic motion and the oscillator vibrations separately, but for both occurring together. If the oscillators in the gas are also radiating, then the entropy of the whole system must be proportional to the logarithm of the number of all possible complexions of particle velocity and radiation combined. Moreover, since according to the electromagnetic theory of radiation, the velocities of the atoms are completely independent of the distribution of the radiant energy, then the total number of complexions is simply equal to the product of the separate numbers for the motion and for the radiation, so that the total entropy is:

$$k' \log (\mathcal{P}\mathcal{R}) = k' \log \mathcal{P} + k' \log \mathcal{R}.$$

The first term is the entropy of the particle motion, the second that of the radiation. By comparison with the original expressions we get:

$$k' = \frac{m}{M} R = k, \text{ or } \frac{m}{M} = \frac{k}{R} = 1.62 \times 10^{-24},$$

that is, a single molecule is the 1.62×10^{-24} part of a gram-mole, or: one hydrogen atom weighs 1.64×10^{-24} gram, since $M_H = 1.01$ g, or a gram-mole of each substance contains $M/m = 6.175 \times 10^{23}$ molecules. Meyer [3] calculates this number

to be 6.10×10^{23} , in essential agreement. Loschmidt's Number \mathcal{N} , the number of gas molecules in one cc. at 0°C and one atmosphere pressure is:

$$\mathcal{N} = \frac{1013200}{R \cdot 273 \cdot m/M} = 2.76 \times 10^{19}.$$

Drude [4] finds $\mathcal{N} = 2.1 \times 10^{19}$.

The Boltzmann-Drude Constant α , the mean kinetic energy of an atom at the absolute temperature of 1°K , is

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

Drude [4] finds $\alpha = 2.65 \times 10^{-16}$.

The elementary quantum of electricity e , i.e. the electric charge of a positive singly charged ion or electron is, with ϵ the known charge of a gram-mole of singly charged ions:

$$e = \epsilon \frac{m}{M} = 4.69 \times 10^{-10} \text{esu}.$$

Richarz [5] finds 1.29×10^{-10} , and Thomson [6] recently found 6.5×10^{-10} .

All these relations require that the theory should be correct in general, not just approximately but with absolute validity. The precision of all the calculated constants is essentially the same as that of Boltzmann's constant k , and exceeds by far all previous determinations of these quantities. Its proof by direct methods is a necessary and important task for further research.

(Eingegangen 9. Januar 1901.)

Footnotes and References:

- 1) L. Boltzmann, Sitzungsber. d. k. Akad. d. Wissensch. zu Wien (II) **76**, Pp.373, 428 (1877).
- 2) M. Planck, see the preceding paper, Eqns5,15. Here as **Paper I-4**.
- 3) O.E. Meyer, Die kinetische Theorie der Gase, 2. Aufl. p.337 (1899).
- 4) P. Drude, Ann. d. Phys. **1**, p.578 (1900).
- 5) F. Richarz, Wied. Ann. **52**, p.397 (1898).
- 6) J.J. Thomson, Phil. Mag. (5) **46**, p.528 (1898).

Paper I-6: Excerpt from *Die Naturwissenschaften*, 14/15, 153 (1943).

Reflections on the Discovery of the Quantum of Action

von **MAX PLANCK**, Berlin.

A new epoch of physical science began with the discovery of the fundamental quantum of action. I feel the need and the obligation to record the way I arrived at the calculation of this fundamental constant, at least as it seems compressed in my memory.

I

To this end I must go back to my student years. What interested me above everything else in Physics was the great general laws which have significance for all natural processes, independent of the properties of the matter taking part in the particular process, and independent of any assumptions which one might make about its structure. This seemed to me to be particularly true of the great Laws of Thermodynamics. Whereas the First Law – the law of conservation of energy – has a very simple and easily understood meaning, and there is no reason to subject it to a particular scrutiny, the full understanding of the Second Law requires careful study. I learned this law in my last year of studies (1878, at age 20) in the lectures of R. CLAUSIUS The various attacks which lead to the CLAUSIUS proof, lead also to a deep understanding of the complete significance of his hypotheses.

In the struggle to make this point completely clear to myself, I came to a formulation of the hypothesis which seemed to me more simple and more compelling. It stated: “The process of heat conduction is ‘in no way’ ‘completely’ reversible.” With this statement the same result is derivable as from the statement of CLAU-SIUS, but without requiring a particular mechanism. One must only interpret appropriately the words ‘auf keinerlei Weise’ and ‘vollständig’. It must be understood, that in the attempts to make the process reversible, absolutely any auxiliary agent can be used – mechanical, thermal, electrical, chemical – but always with the restriction that at the end of the complete process the auxiliary agent itself must be returned to the same state that one assumed for its original use. Such a process,

which can 'in no way' be made 'completely' reversible, I called "irreversible."

But the error which one makes by a too narrow interpretation of the CLAU-SIUS statement of the Second Law, and which I have sought to correct all my life, is, it seems, still not eradicated. Even at the present time, instead of the above definition of irreversibility, I find the following: "A process is irreversible if it cannot run in the opposite direction." That is not correct. In the deeper sense of irreversibility, the Second Law holds not only for radiant heat, but also for all conceivable natural processes.

II

WIEN's Law for the normal energy distribution, derived already in 1896, was in essential agreement with all existing measurements (Mai 1899). Everything seemed to be in satisfactory order.

But soon, first by LUMMER and PRINGSHEIM, and later by PASCHEN, a deviation from WIEN's distribution law was noticed, which had been found when extending it to longer wavelengths and increasing the precision of the existing measurements. It was clear that the general validity of Eqn4 must be considered in serious doubt.

At that time a large number of prominent physicists, both on the experimental as well as on the theoretical side, turned their attention to the problem of the energy distribution in the normal spectrum. But all looked only at the result for the radiation intensity \mathcal{R}_f as a function of temperature, whereas I questioned the deeper consistency of the dependence of the entropy S on the energy U . Because the significance of the entropy had not yet found its correct mathematical expression – which concerned no one until the use of my method – I could pursue my calculations in peace and quiet without the need to fear any disturbance or competition.

Let us now take a deeper look into the properties of the entropy. First I calculated in complete generality, without making use of Eqn2 (Note added: equations referred to but omitted from the abridged text are in the footnotes.), the total entropy change when an oscillator in a stationary radiation field *absorbs* the energy dU

from the field, whose energy at the same time *increases* by a small amount ΔU . The entropy change is

$$\delta S = \frac{3}{5} \cdot \frac{d^2 S}{dU^2} \cdot \Delta U \cdot dU.$$

For any change allowed in nature, the corresponding energy changes dU and ΔU always have the opposite sign, and from the Second Law $\delta S > 0$, then it follows necessarily that

$$\frac{d^2 S}{dU^2} < 0.$$

In fact, Eqn2 for the entropy, which leads to WIEN's distribution, yields:

$$\frac{d^2 S}{dU^2} = -\frac{1}{\alpha f U}. \quad (5)$$

The remarkable simplicity of this result led me again to WIEN's distribution. . . . Thus my efforts to improve Eqn2 arrived at a dead end, and I had to abandon my idea.

Then began an event which would be a decisive turning point. In the Deutschen Physikalischen Gesellschaft meeting of 19 October 1900, KURLBAUM presented his results obtained with RUBENS on energy measurements for very long wavelengths, which among other things showed that with increasing temperature, the radiation intensity of black bodies was always approximately proportional to the temperature T , in complete contradiction to WIEN's distribution Eqn4, for which the radiation intensity must always remain finite. Since this result had already been known to me for a few days before the meeting from talking with the authors, I had time to think about its implications for my way of calculating the entropy of the corresponding oscillators.

If for high temperature T the radiation intensity \mathcal{R}_f is proportional to the temperature, then from Eqn1 the energy of the oscillators is also proportional to it,

$$U = C \cdot T, \text{ and from Eqn3 by integration: } S = C \cdot \log U.$$

Consequently

$$\frac{d^2 S}{dU^2} = -\frac{C}{U^2}. \quad (6)$$

This result should hold for large values of U , in contrast to Eqn5 which is valid for small values of U . If one seeks now a generalized relation which contains both Eqns5 and 6 as limiting cases, then the simplest suggestion would be:

$$\frac{d^2S}{dU^2} = -\frac{1}{\alpha f U + U^2/C}$$

and by integration:

$$\frac{dS}{dU} = \frac{1}{T} = \frac{1}{\alpha f} \cdot \log \left(1 + \frac{\alpha' f}{U} \right), \quad (7)$$

where $\alpha C = \alpha'$ are constants.

When one replaces U by \mathcal{R}_f using Eqn1, this is the formula for the energy distribution – expressed in wavelengths – which I proposed and tried to justify in the course of the lively discussion following KURLBAUM's lecture.

Next morning RUBENS sought me out and told me that in the Proceedings of the meeting he would include a comparison of my formula and his actual data which he had found to be in complete satisfactory agreement. Also LUMMER and PRINGSHEIM, who were the first to claim deviations, soon withdrew their objections since, as PRINGSHEIM told me, it turned out the deviations found by them were the result of a computational error. Through later measurements the formula of Eqn7 was verified repeatedly as so accurate, that it stimulated refinements of the experimental methods.

III

There remains the question of how definitively accurate the spectral energy distribution law of the Blackbody Radiation really is. However now we return to the theoretically most important problem: to give a proper foundation for this law and – what is an even greater problem – to give a theoretical derivation of the expression for the entropy of an oscillator as in Eqn7. It can be written in the following form:

$$S = \frac{\alpha'}{\alpha} \left\{ \left(\frac{U}{\alpha' f} + 1 \right) \log \left(\frac{U}{\alpha' f} + 1 \right) - \frac{U}{\alpha' f} \log \frac{U}{\alpha' f} \right\}. \quad (8)$$

In order to give this expression a physical interpretation, it was necessary to

give a completely new meaning to the concept of entropy, as applied in the domain of electrodynamics.

Among all the physicists of that time, LUDWIG BOLTZMANN was the one who had the deepest understanding of entropy. He explained that *the entropy of a physical system in a particular state is a measure of the probability of that state* and he summed up the content of the Second Law in the statement: the system during any change occurring in nature goes over into a more probable state. In fact, it was his great achievement in the kinetic theory of gases, to define a state function H which has the property that for each change of state occurring in nature, it decreases its value; it can therefore be recognized as the negative of the so-called entropy. It is possible to justify, from the proof of this famous theorem, the validity of the fundamental hypothesis that the state of the gas is “molecular disorder.” [Note added: This problem is still not resolved to everyone’s satisfaction. We appeal to Gibbs ensembles, see Ref.10 in our introductory remarks.]

I myself had not considered before then the connection between entropy and probability; it had no interest for me, since every probability calculation always involved assumptions, and I firmly believed that the validity of the Second Law was free of assumptions. That my proof of irreversibility which considered radiation processes only under the postulate of “natural radiation” could succeed, and that a similar fundamental hypothesis about the radiation is just as necessary and plays exactly the same role there as that of molecular disorder in the theory of gases, occurred to me at once with perfect clarity.

Since there now seemed to me no other way out, I tried BOLTZMANN’s method and with complete generality for a given state of a given system set:

$$S = k \cdot \log W, \quad (9)$$

where W is the probability of the particular state.

Since these relations should have truly general validity, and since the entropy is an additive quantity then the probability must be a multiplicative quantity and the constant k must be a universal number, depending only on the units. It is usually referred to as BOLTZMANN’s constant but it is fair to remark that

BOLTZMANN neither introduced it, nor to my knowledge ever even thought to ask about its numerical value. At that time it had to be multiplied by the number of effective molecules – a problem he left entirely to his colleague LOSCHMIDT. He himself always kept in sight the possibility of its calculation, but it represented only one objective of the kinetic theory of gases, and it was enough for him to stop at the molar level.

In order to apply Eqn9 to the present situation, I imagined a system consisting of a very large number N of completely similar oscillators, and set out to calculate the probability that the system should have a given energy U_N . Since a probability-like quantity can only be found by counting, then it was necessary for the energy U_N to be expressible as a sum of discrete identical energy elements ϵ , whose number likewise could be designated by a very large number P .

Therefore

$$U_N = N \cdot U = P \cdot \epsilon, \quad (10)$$

where U is the average energy of an oscillator.

A measure of the required probability W is the number of different ways in which P energy quanta can be partitioned among N oscillators: that is

$$W = \frac{(P + N)!}{P!N!}. \quad (11)$$

According to Eqn9 the entropy of the oscillator system is:

$$S_N = N \cdot S = k \cdot \log \frac{(P + N)!}{P!N!}$$

and with STIRLING's approximation:

$$S = k \cdot \left\{ \left(\frac{P}{N} + 1 \right) \log \left(\frac{P}{N} + 1 \right) - \frac{P}{N} \log \frac{P}{N} \right\}. \quad (12)$$

The similarity between Eqns8 and 12 is obvious. It only remains to make the identifications:

$$k = \frac{\alpha'}{\alpha} \quad \text{and} \quad \frac{P}{N} = \frac{U}{\alpha' f}.$$

Then it follows from Eqn10 that the magnitude of the energy element is $\epsilon = \alpha' f$. The constant α' – which I denoted as h and called the elementary quantum of

action or the action quantum, in contrast to the energy quantum hf . From the measured values of the constants α and α' the radiation law of Eqn7 gives the value of k and h :

$$k = 1.346 \times 10^{-16} \text{ ergs/degK, and } h = 6.55 \times 10^{-27} \text{ erg sec.}$$

What was of next concern was the experimental proof of this theory, which at that time was only possible in a very limited way. Before this the only constant thought of was k , for whose numerical value only the order of magnitude was known in some degree.

Now however there arose the theoretically all-important problem, to assign this remarkable constant a physical meaning. Its introduction constituted a break with the classical theory, which to many was too radical, as I had initially anticipated. So also was the way in which the entropy as a measure of the probability in the sense of BOLTZMANN was definitively determined even for the radiation. But the nature of the energy quantum remained unclear.

For many years I continued to do further research, trying somehow to fit the action quantum into the system of classical physics. But it seems to me that this is not possible. In any case, as is well known, there has been the development of the Quantum physics by the younger forces, of whom I mention here only the names EINSTEIN, BOHR, BORN, JORDAN, HEISENBERG, DE BROGLIE, SCHRÖDINGER, DIRAC,

Footnotes and References:

- 1) Eqn1: $U = \frac{c^2}{f^2} \cdot \mathcal{R}_f$.
- 2) Eqn2: $S = -\frac{U}{\alpha f} \cdot \log \frac{U}{\alpha f}$.
- 3) Eqn3: $\frac{dS}{dU} = \frac{1}{T}$.
- 4) Eqn4: $\mathcal{R}_f = \frac{bf^3}{c^2} \cdot e^{-\alpha f/T}$.

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