

ZERO-POINT ENERGY, PLANCK'S LAW AND
THE PREHISTORY OF STOCHASTIC ELECTRODYNAMICS
PART 2 : EINSTEIN AND STERN'S PAPER OF 1913

par MM. S. BERGIA, P. LUGLI, N. ZAMBONI

Istituto di Fisica dell'Università,
Istituto Nazionale di Fisica Nucleare,
Via Irnerio 46
40126 Bologna (Italie)

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Abstract : We give a commented translation of an article by Einstein and Stern, where Planck's law is derived from the hypothesis of a zero-point energy, without the need of a specific quantization postulate. The relation of this investigation with quantum mechanics and stochastic electrodynamics is analysed.

Résumé : Nous donnons une traduction commentée, en anglais, d'un article par Einstein et Stern, où la loi de Planck est dérivée en partant de l'hypothèse de l'énergie au zéro-absolu, sans qu'il soit nécessaire d'introduire un postulat indépendant de quantification. On analyse la relation entre ce résultat, la mécanique quantique et l'électrodynamique stochastique.

We recently presented ⁽¹⁾ in this journal a commented translation of a 1910 paper by Einstein and Hopf ⁽²⁾. Our work was motivated essentially by the fact that Einstein and Hopf's paper is necessary for the understanding of a subsequent paper by Einstein and Stern ⁽³⁾, of wider scope and interest, whose commented trans-

lation we similarly present here. As will be discussed later on in some detail, these writings by Einstein have their roots in earlier studies of his. Pauli ⁽⁴⁾ considered Einstein and Hopf's paper as an extension of the results obtained by Einstein for the momentum fluctuations of a mirror under the influence of a radiation field to the corresponding fluctuations of a harmonic oscillator. The motion of a delicately suspended mirror -in a Planckian radiation cavity-, as indicated in the *Autobiographical Notes* ⁽⁵⁾, had already been tackled by him in 1904, though not published at the time, and taken up again only in 1909 ⁽⁶⁾, that is the year before the paper with Hopf. It has even been pointed out by Miller ⁽⁷⁾, developing an argument formerly raised by Holton ⁽⁸⁾ and Klein ⁽⁹⁾, that this problem might have been the one which generated the three famous papers of 1905. Later on we shall argue that from the 1909 papers Einstein may have obtained the germ of the idea that led him to the paper with Stern.

If this were the common background of the two papers, the article with Stern has, however, a more immediate and specific motivation in Planck's so called second theory ⁽¹⁰⁾. As discussed by Klein ⁽¹¹⁾, this theory is due to an attempt made by Planck to retreat, at least partially, from his earlier papers on the quantum. Planck suggested in it that the absorption of electromagnetic energy by a system of oscillators was a continuous process, the emission only taking place through discrete quanta. This attempt, although "conservative" in its intentions, introduced some anticipating ideas. On the one hand, Planck had in fact assumed that the emission was subject to probabilistic laws, thus anticipating, even though the fact did not have much resonance, Einstein's paper of 1917. He had further assumed that the ratio of the probability of no emission to the probability of emission was proportional to the intensity of the incident radiation, the constant of proportionality being determined in the limiting case of radiations of great intensity, where the Rayleigh-Jeans law and classical mechanics hold valid. According to Klein ⁽¹¹⁾ and Jammer ⁽¹²⁾, this is probably the first use of what would have been later called the correspondence principle. By means of the relation linking the entropy of the system of oscillators to the probability of the occupation of the different energy states, and of the thermodynamical relation between entropy, internal energy and temperature $\left(T^{-1} = \frac{dS}{dU}\right)$, Planck obtained the expression for the mean energy of an oscillator in the form

$$\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1} + \frac{h\nu}{2} \quad [1]$$

while, for the spectral density of the black-body radiation, from the relation

$$\bar{U} = \left(\frac{c^3}{8\pi\nu^2} \rho + \frac{1}{2} \right) h\nu, \quad [2]$$

he obtained

$$\rho = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{h\nu/kT} - 1} \quad [3]$$

As is seen, for $T = 0$, one has $\rho = 0$, but $\bar{U} = \frac{h\nu}{2}$. The zero-point energy thus makes its appearance in quantum physics, even though within a controversial theory; Planck immediately connected the concept with that of the "latent energy" he had debated in his former studies on relativity ⁽¹³⁾.

In Einstein's and Hopf's paper, as we said in (1), the authors intended to free the derivation of the Rayleigh-Jeans law from the flaw of a dubious use of the equipartition theorem, thereby definitely showing that the law was a necessary consequence of classical mechanics; in this way, the inescapability of the quantum hypothesis would be demonstrated. The formulation of Planck's second theory gave rise to a new phase of studies. Einstein and Stern's paper had a two-fold aim and therefore both aspects must be commented on separately. In the first place, the authors set themselves the problem of finding experimental checks for the zero-point term. As we shall see, they thought they had found one in the rotational specific heat of hydrogen, as had been measured by Eucken (see ref. (30)). From the point of view of quantum mechanics, an incredible series of circumstances determined the fact that an unacceptable theory turns out to be in good agreement with the experiment. This point shall be discussed in detail later on; for the moment, we shall limit ourselves to point out that Einstein and Stern, to attain their result, attributed a zero-point energy to the rigid rotator. This assumption, as we shall discuss, was plausible in Planck's second theory while it is unacceptable from the quantum mechanical point of view, which associates a zero-point energy to physical systems, as a consequence of indeterminacy, only in the case of actual bound states. In the second place, Einstein and Stern introduced the hypothesis of a zero-point energy for the linear oscillator in the formalism set up by Einstein and Hopf and showed that, in this case, the formalism did not lead to the Rayleigh-Jeans formula but to Planck's result, with no assumption of discontinuities whatsoever.

The interest for a renewed discussion of Einstein and Stern's contribution arises for various reasons. In the first place, it seems interesting, from the historical point of view, to verify the existence and the consistency, of an, at least partially, alternative development which took shape in those years and was eventually relinquished from lack of a strictly scientific decisive motivation, thus suggesting once more that the growth of scientific knowledge is a far less direct process than commonly believed. Indeed, as mentioned in (1), Einstein and Stern's arguments were eventually dropped by the authors themselves. We traced out the motivation for this self-refutation in an explicit statement made by Einstein at the second Solvay Conference ⁽¹⁴⁾, in the same year Einstein and Stern's paper was published. On that occasion, in the course of the discussion following von Laue's report on "Les phénomènes d'interférence des rayons de Roentgen", Nernst intervened to ask whether, "d'une façon ou d'une autre, l'énergie au zéro absolu peut se manifester optiquement". There followed a series of comments on the matter (by Sommerfeld, Einstein, Lindemann, Wien), from which it is understood that the concept was in a considerable fluid state for everybody ; after expressing, and motivating, his "graves objections contre une énergie du point zéro consistant en vibrations élastiques", objections he linked to the discovery of superconductivity, Einstein went on : "Je dois aussi faire remarquer à ce propos que les arguments que j'ai avancés avec M. Stern en faveur de l'existence d'une énergie au zéro absolu, je ne les considère plus comme valables". This caused a reaction from Nernst, in which the polemical intention is evident : "Si vous n'admettez plus d'énergie au zéro absolu, le calcul que vous et M. Stern avez donné des chaleurs moléculaires mesurées par Eucken pour l'hydrogène aux basses températures doit évidemment être considéré comme non avénu ?". To which Einstein answered briefly : "Je dois évidemment me placer à ce point de vue que par là les considérations qui ont conduit à la formule pour l'hydrogène perdent leur fondement". This seems to have been the end of the story as far as Einstein was concerned ; and one can complain that we do not know his more detailed motivations. It was not the end, however, regarding Nernst, who took the problem up again in 1916, in a paper ⁽¹⁵⁾ of wide scope and interest. That the most strenuous defender of the idea should have been Nernst seems quite natural if one considers the strict relation between the zero-point energy and the third law of thermodynamics.

A further reason of interest for Einstein and Stern's paper arises from the fact that it took part, as suggested already in the title, in the pre-history of stochastic electrodynamics (SED), a theory which nowadays is rich of traditions and results ⁽¹⁶⁾. As was pointed out in (1), Einstein and Hopf's paper anticipates,

for certain aspects, SED ; in particular, the thermal radiation field was treated as a stochastic process. This assumption also draws its origins from Planck : it is in fact rooted in the assumption, typical of the first phase of the Planckian studies, of "natural radiation", necessary in his discussion of the achievement of equilibrium in the enclosure filled with thermal radiation. However, the interplay between oscillator and field, as far as the zero-point energy is concerned, is not the same as in SED. In the latter, in fact, the essential hypothesis is that there is a background stochastic field at zero temperature, on which Lorentz invariance prescribes an energy $h \nu/2$ for degree of freedom ; in SED, therefore, both the stochastic aspect and the zero-point energy are a prerogative of the background field. Einstein and Stern's theory and SED are thus different theories. The structure of the basic equation determining ρ is, as we shall see, different and, consequently, in SED, the solution is Eq. [3] *with the addition of a zero-point term* ; nor should it be forgotten that Einstein and Stern obtained Eq. [3] on the basis of a zero-point energy $h \nu$ instead of $h \nu/2$ ⁽¹⁷⁾. Boyer is therefore right when he stresses ⁽¹⁸⁾ the differences between his derivation ⁽¹⁹⁾ and Einstein and Stern's ; and there is no doubt that his is the convincing version. However it appears from what has been said that Einstein and Stern's theory contains, in a disguised way, some of the essential features of SED. It seems therefore that we may consider it as an instrument containing that amount of SED which permits it to obtain some of its meaningful and relevant results. From this point of view, the question concerning the hydrogen rotational specific heat can also be re-examined. While it is true that, in quantum mechanics, it does not make sense to assume a zero-point energy for the rigid rotator, it is a completely different thing to say that the rigid rotator acquires a zero-point energy in a stochastic background field ⁽²⁰⁾ ; this is actually the point of view of SED, where the property is no more linked to indeterminacy. Also concerning this problem, results qualitatively very close to the quantum mechanical ones are obtained in SED ⁽¹⁹⁾ ⁽²¹⁾ ; certainly, Boyer's treatment of the rigid rotator, based on a paper by Fokker ⁽²²⁾, is profoundly different from the Einstein and Hopf's "one-frequency" formula, inasmuch as the mean energy is determined once a Fokker-Planck equation is solved for the distribution function ; from what we have said above, however, concerning the peculiar relationship between SED and Einstein and Stern's theory, one can expect that the latter is also in fair agreement with the quantum mechanical results and the experiments.

Following the procedure of the previous paper ⁽¹⁾, we have

re-done the calculations, corrected some obvious misprints and indicated the connections between Einstein and Stern's treatment and modern views ; the fruit of this work appears in comments which follow the text of the article. Words or phrases in square brackets are additions required in the English version or original German words recalled to stress the difficulty or impossibility of an adequate English rendering. Square brackets have also been adopted for the numbering of the formulae used in the introduction and the comments. The translation itself is the work of one of the present authors (S.B.). The English rendering was improved with the help of Mrs. S. Eerdmans Gottarelli and further checked against the German text to preserve the flavour of the original language as much as possible. Finally, we want to thank G. Morandi and F. Napoli for useful discussions.

Some Arguments for the Assumptions of a Molecular Agitation at the Absolute Zero (by A. Einstein and O. Stern)

The expression for the energy of a resonator reads [lautet]

$$E = \frac{h \nu}{e^{h\nu/kT} - 1} \quad (1)$$

according to Planck's first formula and

$$E = \frac{h \nu}{e^{h\nu/kT} - 1} + \frac{h \nu}{2} \quad (2)$$

according to the second one ⁽²³⁾.

The limit-value for high temperatures becomes, if we cut the development of $e^{h\nu/kT}$ with the square term,

$$\lim_{T \rightarrow \infty} E = kT - \frac{h \nu}{2}$$

for [case] (1), and :

$$\lim_{T \rightarrow \infty} E = kT$$

for [case] (2).

The energy as a function of temperature, as presented in Fig. 1, according to formula (1), starts from zero at $T = 0$, i.e. from the value requested by the classical theory, however remains steadily smaller than that by the amount $h \nu/2$ at high temperatures.

According to formula (2), the resonator has energy $h \nu/2$ at the absolute zero, in contradiction with the classical theory, however reaches asymptotically at high temperatures the energy requested by it. Nevertheless, the derivative of the energy with respect to the temperatures, i.e. the specific heat, is equal in both cases.

For formations [Gebilde] with invariable ν these formulae are thus equivalent, whilst the theory of formations whose ν has different values for different states is substantially influenced by the assumption of a zero-point energy. The ideal case would be that of a system consisting of monochromatic formations, whose ν -value could be arbitrarily varied independently of the temperature. The dependence of the energy on the frequency at constant temperature would depend substantially on the existence of a zero-point energy. Unfortunately, experiments on a formation of this sort are not available. We know, however, for rotating molecules, of formations whose thermic motions present a fair-reaching analogy with those of monochromatic formations, and for which the mean frequency varies with the temperature. For these formations it is thus to be proved, in the first place, the rightness of the assumption of a zero-point energy ⁽²⁴⁾. In the following it will first of all be investigated to what extent we can draw conclusions for the theoretical behaviour of such formations from Planck's formula.

The specific heat of hydrogen at low temperatures.

The question is how the rotation energy of a diatomic molecule depends on the temperature. In analogy with the theory of the specific heat of solid bodies, we are authorized to assume that the mean rotational kinetic energy is independent of the fact of whether the molecule has or has not an electric moment along its symmetry axis. In the case when the molecule has such a moment, it cannot disturb the thermodynamical equilibrium between gas-molecules and radiation. From this it can be concluded that the molecule under the influence of the radiation alone must take on the same rotational kinetic energy as it would obtain through collisions with other molecules ⁽²⁵⁾. The question is thus for which value of the rotational energy a massive rigid dipole finds itself in equilibrium with radiation of definite temperature. Whatever may be the law of emission it should however be kept in mind that a rotating dipole emits twice as much energy for unit time as a one-dimensional resonator for which the amplitude of the electric and magnetic moment is equal to the electric and magnetic moment of the dipole. The same will also hold for the mean value of the absorbed energy. If we now make the further simplifying approximate assumption that at a given temperature all dipoles of our gas rotate equally rapidly,

we are led to the conclusion that at equilibrium the kinetic energy of a dipole must be twice as large as that of a one-dimensional oscillator of equal frequency ⁽²⁶⁾. By the assumptions made we can directly apply expression (1) or (2) to the calculation of the kinetic energy of a rotating gasmolecule with two degrees of freedom, where for every temperature between E and ν the equality

$$E = \frac{J}{2}(2\pi\nu)^2$$

holds (J = moment of inertia of the molecule).

One then obtains for the rotating energy per mole ⁽²⁷⁾ :

$$E = N_0 \frac{J}{2}(2\pi\nu)^2 = N_0 \frac{h \nu}{e^{\frac{h\nu}{kT}} - 1} \quad (3)$$

or

$$E = N_0 \frac{J}{2}(2\pi\nu)^2 = N_0 \left[\frac{h \nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{h \nu}{2} \right] \quad (4)$$

As ν and T are now linked through a transcendental equation, it is not possible to express dE/dT as an explicit function of T , yet one obtains if one sets $2\pi^2 J = p$, for short, as a formula for the rotation specific heat

$$C_r = \frac{dE}{dT} = \frac{dE}{d\nu} \frac{d\nu}{dT} = N_0 2p\nu \frac{\nu}{T \left(1 + \frac{kT}{p\nu^2 + h\nu} \right)} \quad (5)$$

or

$$C_r = \frac{dE}{dT} = \frac{dE}{d\nu} \frac{d\nu}{dT} = N_0 2p\nu \frac{\nu}{T \left(1 + \frac{kT}{p\nu^2 - \frac{h^2}{4p}} \right)} \quad (6)$$

where ν and T are tied by the equation

$$T = \frac{h}{k} \frac{\nu}{\ln \left(\frac{h}{p\nu} + 1 \right)} \quad (5a)$$

or

$$T = \frac{h}{k} \frac{\nu}{\ln \left(\frac{h}{p\nu - \frac{h}{2}} + 1 \right)} \quad (6a)$$

In fig. 2, curve I represents the specific heat computed on the basis of (6) and (6a), where p has the value $2.90 \cdot 10^{-40}$ ⁽²⁸⁾ ; curve II is computed from (5) and (5a) with the aid of $p = 2 \cdot 10^{-40}$. The little crosses indicate the values measured by Eucken ⁽²⁹⁾. As one can see, curve II exhibits a trend which stands in complete contradiction with the experiment while curve I, which is based on the assumption of a zero-point energy, reproduces the results of the measurements excellently. In order to establish which value is taken on by ν according to formula (4) for the limit $T = 0$, we write (4) in the following form ⁽³⁰⁾ :

$$e^{\frac{h\nu}{kT}} = \frac{h}{p\nu - \frac{h}{2}} + 1 = \frac{p\nu + \frac{h}{2}}{p\nu - \frac{h}{2}}$$

Then one sees that for $T = 0$, ν cannot become equal to zero, because then the right-hand side would converge to -1 , whilst on the left a power of e remains. Thus ν must stay finite for limit $T = 0$ (sic), and in fact the right-hand side like the left one must converge (sic) to ∞ : therefore it must be $p\nu_0 - h/2 = 0$, if we indicate with ν_0 the limit-value of ν for $T = 0$. It is thus $\nu_0 = h/2p$. In the present case, ν_0 turns out [to be] $11.3 \cdot 10^{12}$. The value of ν in the first place varies also very little with increasing temperature ; so $\nu = 11.4 \cdot 10^{12}$ at 102° abs., $\nu = 12.3 \cdot 10^{12}$ at 189° , $\nu = 14.3 \cdot 10^{12}$ at 323° . This clarifies now the reason why Eucken was still able to represent his measurements relatively well through Einstein's simple formula with ν independent of the temperature (Curve III, Fig. 2). Nevertheless one sees that this formula fails too, specifically at higher temperatures, not mentioning the fact that without the assumption of the zero-point energy the constancy of ν remains completely incomprehensible. One thus sees that the specific heat of hydrogen makes the existence of a zero-point energy probable ; and it is only a matter of proving how far the special value $h \nu/2$ is to be regarded as certified. Since in the following investigation about the radiation law the amount of the zero-point energy must be assumed as $h \nu$, we have computed the specific heat of hydrogen also for this assumption ($p = 5.60 \cdot 10^{-40}$, curve IV, fig. 2). It is apparent that at higher temperatures the curve is too steep and high. On the other hand it is to be noted that by inspection of the velocity distribution among the molecules, the curve might flatten out a little ⁽³¹⁾. Consequently it is indeed probable, though not to be excluded with certainty, that the zero-point energy has the value $h \nu$ ⁽³²⁾, ⁽³³⁾.

The derivation of the radiation law,

In the following it will be shown how Planck's radiation formula may be derived in a spontaneous, even if not completely rigorous way, and as a matter of fact without any assumption of discontinuities whatsoever. The route we shall hereto follow is essentially the same Einstein and Hopf (34) utilized in a dissertation which appeared 2 years ago. We discussed the translatory motion of a freely-moving resonator, which in some way adheres to a gas-molecule, under the influence of a disordered radiation field. At thermal equilibrium, the mean kinetic energy which the gas molecule receives must then be equal to the one it would receive through collisions with other molecules. One thus obtains the connection between the density of the black radiation and the mean kinetic energy of a gas molecule, i.e. the temperature. Einstein and Hopf found in this way the Rayleigh-Jeans law. We now want to carry out the same treatment under the assumption of a zero-point energy. The influence that the radiation exerts may be split, according to Einstein and Hopf, into two different actions. In the first place, the translatory rectilinear motion of the resonator molecule undergoes a kind of friction, occasioned through the radiation pressure on the moving oscillator. This force K is proportional to the velocity v , thus $K = -P v$, at least in the case where v is small with respect to the velocity of light. The momentum, which the resonator molecule receives in the small time τ , during which v may not change notably, is thus $-Pv\tau$. In the second place, the radiation imparts to the resonator molecule momentum fluctuations Δ , which are in first approximation independent of the motion of the molecule and the same for all directions, so that only their mean square value $\overline{\Delta^2}$ during time τ is relevant for the kinetic energy. If this is now allowed to possess the value $k(T/2)$ required by statistical mechanics (the oscillator will, for simplicity, be moving only in the x -direction and oscillate only in the z -direction) then, according to Einstein and Hopf, the following equation must hold :

$$\overline{\Delta^2} = 2 k T P \tau$$

For what concerns now the computation of P , we can assume that only the oscillations excited by the radiation itself come hereto into consideration and that one can compute them as if the zero-point energy did not exist (35). We can thus utilize the value computed by Einstein and Hopf (l.c. p.1111) :

$$P = \frac{3c\sigma}{10\pi v} \left[\rho - \frac{v}{3} \frac{d\rho}{dv} \right]$$

In order to compute now $\overline{\Delta^2}$, we set (l.c. p.1111) the momentum,

which the oscillator experiences during time τ in the x -direction

$$J = \int_0^\tau K_x dt = \int_0^\tau \frac{\partial E}{\partial x} f dt$$

where f is the [dipole] moment of the oscillator. We now want to treat in the first place the case in which the energy of the oscillations excited through the radiation is negligible with respect to the zero-point energy of the resonator, which for low enough temperatures is certainly permitted. If we indicate with f_0 the maximal [dipole] moment of the resonator, then it is

$$f = f_0 \cos \frac{2\pi n_0 t}{T}$$

where T is a very long time and $\frac{n_0}{T} = \nu_0$ is the frequency of the resonator. We approximate $\frac{\partial E}{\partial x}$ as a Fourier series :

$$\frac{\partial E}{\partial x} = \sum_n C_n \cos \left(2\pi n \frac{t}{T} - \theta_n \right)$$

Then

$$J = \int_0^\tau \sum_n C_n \cos \left(2\pi n \frac{t}{T} - \theta_n \right) f_0 \cos \left(2\pi n_0 \frac{t}{T} \right) dt$$

$$= f_0 \sum_n C_n \frac{T}{2\pi(n_0 - n)} \sin \left[\pi \frac{n_0 - n}{T} \tau \right] \cos \left(\pi \frac{n_0 - n}{T} \tau - \theta_n \right)$$

is obtained, since the term affected by $\frac{1}{(n_0 + n)}$ drops out, because $n_0 + n$ is a very large number. If one now sets $\frac{n}{T} = \nu$ and squares, then

$$\overline{J^2} = \overline{\Delta^2} = f_0^2 \overline{C_n^2} \frac{T}{8} \int_{-\infty}^{+\infty} \frac{\sin^2 \pi (\nu_0 - \nu) \tau}{[\pi (\nu_0 - \nu)]^2} d\nu$$

is obtained, or :

$$\overline{\Delta^2} = \frac{1}{8} f_0^2 \overline{C_n^2} T \cdot \tau$$

Now it is (l.c. p. 1114) :

$$\overline{C_n^2} T = \frac{64}{15} \frac{\pi^3 \nu^2}{c^2} \rho$$

Thus it is

$$\overline{\Delta^2} = \frac{8}{15} \frac{\pi^3 v^2}{c^2} \rho \tau f_0^2$$

If now the resonator possesses the zero-point energy $h\nu$ (36), it is :

$$\frac{1}{2} K f_0^2 = h\nu \quad (37) \quad \text{or} \quad f_0^2 = \frac{2h\nu}{K} = \frac{3}{8} \frac{h\sigma c^3}{\pi^4 v^2}$$

Hence it is

$$\overline{\Delta^2} = \frac{1}{5\pi} h\sigma\rho\tau$$

If one inserts this in the equation

$$\overline{\Delta^2} = 2kT\rho\tau$$

then one arrives at Wien's radiation law. Yet here we want to give up from the beginning the presupposition that the oscillation excited by the radiation is negligible. If we now assume that the energy of the oscillations imparted by the radiation to the resonator provides momentum oscillations which are independent of the oscillations corresponding to the zero-point energy, then we can sum up the mean square values of both momentum oscillations (38). We have thus still to add to the above calculated value for $\overline{\Delta^2}$ Einstein and Hopf's one to obtain :

$$\overline{\Delta^2} = \frac{1}{5\pi} h\sigma\rho\tau + \frac{c^4 \sigma \tau}{40 \pi^2 v^3} \rho^2$$

On the other hand it is

$$\overline{\Delta^2} = 2kT\rho\tau = 2kT\tau \left[\rho - \frac{v}{3} \frac{d\rho}{dv} \right]$$

As a consequence it is obtained as differential equation for ρ (39) :

$$v \left[h\rho + \frac{c^3}{8 \pi v^3} \rho^2 \right] = 3kT \left[\rho - \frac{v}{3} \frac{d\rho}{dv} \right]$$

The solution of this equation provides

$$\rho = \frac{8 \pi v^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1}$$

Planck's radiation law, [while] the energy of the resonator turns out to be (40)

$$E = \frac{h\nu}{e^{h\nu/kT} - 1} + h\nu$$

Recapitulation

1. Eucken's results for the specific heat of hydrogen make probable the existence of a zero-point energy of amount $h\nu/2$.
2. The assumption of the zero-point energy opens a way for deriving Planck's radiation formula without resorting to any discontinuities whatsoever. It appears however dubious whether the other difficulties may also be overcome without the assumption of quanta.

Note added in proof

Herr Prof. Weiss called our attention to the fact that also Curie's measurements on the paramagnetism of gaseous oxygen indicate that its energy possesses at high temperatures the value required by the classical theory and not [a value] smaller by $h\nu/2$, as would be expected without the assumption of a zero-point energy. It may be easily shown that in the latter case, due to the accuracy of Curie's measurements, deviations from Curie's law should have appeared.

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- 24) The two theories yield different expressions for $E(\nu, T)$, but give the same result for $\left. \frac{\partial E}{\partial T} \right|_{\nu}$. To discriminate between them the ideal case would be that of a physical system where frequency could be varied independently of the temperature. Since :

$$dE = \left. \frac{\partial E}{\partial \nu} \right|_T d\nu + \left. \frac{\partial E}{\partial T} \right|_{\nu} dT,$$

operating at constant T, the determination of the dependence of E upon ν in this case would give directly $\left. \frac{\partial E}{\partial \nu} \right|_T$, which is different in the two theories. The authors however knew only of systems where $E = E(\nu)$, $\nu = \nu(T)$, for which the specific heat is given by

$$\frac{dE}{dT} = \frac{dE}{d\nu} \frac{d\nu}{dT}$$

The former term on the right-hand side can be computed from the formula giving the energy as a function of frequency (which, for the case of diatomic molecules, is $E = \frac{J}{2}(2\pi\nu)^2$) and the latter term from the explicit expression, in either of Planck's theories, of $E[\nu(T)]$ as $E(\nu, T)$. It is therefore possible to compare the $\frac{dE}{dT}$ thus obtained with the experimental one. The

explicit calculation is given by the authors further on. It should be noted that this procedure had been foreseen by Nernst (see : C. Lanczos, *The Einstein Decade* (1905-1915), Elek Science, London (1974) ; the authors quote him at the end of the discussion on this point (see note n. 28).

- 25) This kind of argument is similar to the one used, in a different context, in Einstein, and Hopf's paper, and taken up again further on in this article, according to which the mean square value of the momentum of a linear oscillator in a radiation field is the same as the one the oscillator acquires, at thermal equilibrium, through collisions with the molecules of the gas which surrounds it.
- 26) A rigid dipole rotating in a plane is equivalent, from the point of view of the classical theory of radiation, to a couple of linear oscillators at right angles, each of which radiates half of the power of the dipole. A similar argument holds for the absorbed power and the kinetic energy of the rotator, These considerations presuppose that one is dealing with motion in a plane. This is correct in the interval between two collisions, since the interaction with the electromagnetic field cannot twist the rotation axis. On the other hand, it can be easily verified that in standard conditions the interval between two collisions is on the average much larger than the typical rotation period of the molecule.
- 27) Formulae (1) and (2) express the sum of the (equal) kinetic and potential energies of a linear oscillator, i.e. directly twice the oscillator's kinetic energy to be equated to the dipole's rotational energy.
- 28) Upon this Nernst first called attention ; see *Zeitschr. f. Elektroch.* 17, p. 270, 825 (1911) (Note of the authors).
- 29) If one computes the diameter of the molecule belonging to this moment of inertia, [the value] $9 \cdot 10^{-9}$ is obtained, roughly half of the value ascertained in the gas theory (Note of the authors).
- 30) A. Eucken, *Sitzungsberichte d. preuss. Akad. d. Wissenschaften*, p. 141 (1912) (Note of the authors).
- 31) As we pointed out in the introduction, from the point of view of quantum mechanics, the agreement between the values calculated by Einstein and Stern on the basis of their formula with a zero-point energy and experimental data (existing in those

times) should be attributed to an incredible series of circumstances. In the first place it does not make sense to attribute a zero-point energy to a rigid rotator. In the second place, calculating the specific heat of a rigid rotator without axial spin, whose energy levels E_j are given by

$$E_j = \frac{j(j+1)\hbar^2}{2I}$$

where I is the rotator's moment on inertia, implies using a rotational partition formula

$$\sum_{j=0}^{\infty} (2j+1) e^{-j(j+1)\frac{\theta}{T}} \quad [4]$$

where the factor $(2j+1)$ takes into account the level's degeneracy and

$$\theta = \frac{\hbar^2}{2kI}$$

Actually, it is summing over the angular momentum quantum numbers that determines the rapid drop to zero of the specific heat when T tends to zero. One has in fact (see, for instance, L.D. Landau, E.M. Lifschitz. *Statistical Physics*, Pergamon Press (1950), p. 138), for $T \ll \theta$:

$$C_{\text{rot}} = 3k \theta^2 e^{-\frac{\theta}{T}}$$

The complete calculation of C_{rot} starting from [4] may be found in Sommerfeld's treatise (*Sommerfeld, Thermodynamics and Statistical Mechanics*, Academic Press, New York (1956) ; § 34, 1 and Problem IV.6).

This is not, however, the end of the story : this calculation, in fact, cannot be applied to the hydrogen molecule (and actually it does not fit the experimental data) in so far as it is necessary to take into account the indistinguishability of the two nuclei. Correct quantum-mechanical treatment, for homonuclear molecules with odd mass number, requires wave functions antisymmetrical in the nuclei. This is obtained by combining even rotational eigenfunctions (i.e. symmetrical in the nuclei) with one of the $\frac{1}{2}(\rho-1)$ antisymmetric nuclear eigenfunctions (ρ is the spin degeneracy parameter), and the odd rotational eigenfunctions with one of the $\frac{1}{2}(\rho+1)$ symmetric nuclear eigenfunctions. The partition function for homonuclear molecules

with odd mass number is therefore :

$$r_n(T) = \frac{1}{2} \rho(\rho-1) \sum_{j=0,2,\dots}^{\infty} (2j+1) e^{-j(j+1)\theta/T}$$

$$+ \frac{1}{2} \rho(\rho+1) \sum_{j=1,3,\dots}^{\infty} (2j+1) e^{-j(j+1)\theta/T}$$

which, for the case of the hydrogen molecule ($\rho=2$) reduces to

$$\sum_{j=0,2,\dots}^{\infty} (2j+1) e^{-j(j+1)\theta/T} + 3 \sum_{j=1,3,\dots}^{\infty} (2j+1) e^{-j(j+1)\theta/T} \quad [5]$$

Partition functions of this kind were examined by Hund (Hund, Zeitschrift für Physik 42, 93 (1927) "but were found to give curves bearing no resemblance whatever to the observations" (See R. Fowler, E.A. Guggenheim, Statistical Thermodynamics, Cambridge University Press (1949), p. 83 and foll.). The correct theory was finally formulated by Dennison (Dennison, Proc. Roy. Soc. A. 115, 483 (1927)). It is based on the observation that while the possible states are correctly numbered in [5], there it is implicitly assumed that exchanges between the states may take place freely. However, in normal hydrogen gas, the exchanges between symmetric and antisymmetric states take place in a substantial way only in periods of time long in comparison with the length of an experiment. Specific heat measurements are therefore made on a gas which is not in a real equilibrium state governed by [5], but rather in a metastable equilibrium, where it behaves like a mixture of two substances, of which the one with antisymmetric spin eigenfunctions is known as para-hydrogen, while the one with symmetric spin eigenfunctions is known as ortho-hydrogen. Para-hydrogen has only symmetric rotational states and a nuclear-rotational partition function r_p given by the first term in [5]; ortho-hydrogen has only antisymmetric rotational states and a partition function $3r_0$ given by the second term in [5]. The respective molar specific heats are then given by

$$C_p^{\text{rot}} = k \frac{\partial}{\partial T} \left(T^2 \frac{\partial \log r_p(T)}{\partial T} \right)$$

and

$$C_0^{\text{rot}} = k \frac{\partial}{\partial T} \left(T^2 \frac{\partial \log 3r_0(T)}{\partial T} \right)$$

and the molar specific heat of the mixture whereby the ratio

of para-to-ortho-hydrogen is 1 to 3 is

$$C^{\text{rot}} = \frac{1}{4} C_p^{\text{rot}} + \frac{3}{4} C_0^{\text{rot}} \quad [6]$$

The figure (Fowler and Guggenheim, op. cit. ; p. 93) shows the experimental data until 1949 compared with [6] computed for

$I = 0.463 \cdot 10^{-4} \text{ g cm}^2$. The experimental data refer to the specific heat C_v , containing the contribution of the trans-

lational and rotational motion of the molecules; the data concerning C_{rot} are obtained by subtracting the constant value of the translational term ($\frac{3}{2} kT$). The data prior to 1927 are then seen to coincide with Eucken's data, as reported by Einstein and Stern.

In the figure, the curve represents a fitting to the experimental data while [6] is represented by crosses.

32) If one assumes the entropy of rotating formations [Gebilde] like that for solid bodies as zero for $T=0$ according to Nernst's theorem, the entire portion of the entropy of a mole arising from the rotation of the diatomic molecule turns out to be

$$S_r = \int_0^{TC} \frac{r}{T} dT = \frac{k}{v_0} \int_{v_0}^v \ln \frac{v+v_0}{v-v_0} dv = \frac{2pv^2}{T} + k \ln \left[\left(\frac{pv}{h} \right)^2 - \frac{1}{4} \right]$$

[which], for high temperatures, becomes

$$S_r = R \ln T + 2R + R \ln \frac{2\pi^2 Jk}{h^2}$$

According to Sackur (Nernst-Festschrift p. 414, 1912), the entropy constant of the rotation is, substantially

$$R = R \ln \frac{16\pi^3 Jk}{h^2}$$

namely in agreement with the above expression for [what concerns] expression $\frac{Jk}{h^2}$. The same result is on the other hand obtained if one inserts Formula (6) instead of Formula (5) for C_r (Note of the authors)..

33) In the first expression of S_r , two errors have been corrected. For what concerns the high temperature limit, we derive from Eq.

(2), by a development of the exponential $e^{hv/kT}$, the expression $pv^2 = kT$, i.e. $\frac{2pv^2}{T} = 2k$; by observing then that, at high tempera-

tures, $\frac{pkT}{h^2} \gg 1$, and by using the preceding relation, we may write

$$k \ln \left[\left(\frac{pv}{h} \right)^2 - \frac{1}{4} \right] = k \ln \frac{pkT}{h^2} = k \ln T + k \ln \frac{2\pi^2 Jk}{h^2}$$

- 34) A. Einstein and L. Hopf, *Annalen der Physik* 33, p. 1105-1115 (1910) (Note of the authors).
- 35) To understand the role of the zero-point energy in Einstein and Stern's calculation, one can conveniently refer to the interaction mechanism between the oscillator and the radiation field. The oscillator of proper frequency ν_0 responds to the thermal field in terms of a Lorentzian distribution about ν_0 . The amplitude A_n of these oscillations shall be linked to the field intensity and, in particular, there will be a relation between $A_{\nu_0 T}$ and $\rho(\nu_0, T)$. In the case in which the oscillator has a zero-point energy, the amplitude f_0 of its oscillation will not be linked anymore to the field but rather to this energetic term through the relation

$$\frac{1}{2} K f_0^2 = \epsilon_{z-p} = h\nu_0$$

This shall be true at low temperatures, in so far as one can neglect the energy exchanged between oscillator and field with respect to the zero-point energy.

In computing the momentum oscillations one may consider the two cases separately and compute independently the momentum fluctuations in both the limits of low temperatures, where the oscillation linked to the zero-point energy dominates, and of high temperatures, where exchanges with the field dominate.

As we argued in the introduction, Einstein may have derived the germ of this idea from his 1909 article. In that paper, considering the brownian motion of a mirror suspended in a planckian cavity, Einstein had obtained the expressions

$$\overline{\Delta^2} = 2kTP\tau \quad [7]$$

and

$$P = \frac{3}{2c} \left(\rho - \frac{1}{3} \nu \frac{\partial \rho}{\partial \nu} \right) dv \cdot f \quad [8]$$

(f is the area of the mirror) for the mean square momentum

and for the coefficient of the damping force. Formula [8] is the obvious originator of the expression computed for the case at hand by Einstein and Hopf. Substituting Planck's formula for ρ in [8] and Eq. [8] into [7], Einstein obtained

$$\frac{\overline{\Delta^2}}{\tau} = \frac{1}{c} \left(h\nu\rho + \frac{c^3}{8\pi\nu^3} \rho^2 \right) dv \cdot f \quad [9]$$

Following backwards the above procedure, once the two terms appearing in [9] have been independently computed, Eq. [7] is a differential equation which allows one to compute the expression for ρ .

For what concerns the driving force, linked to the velocity of the molecule where the oscillator is sitting, which determines a net momentum transfer instead of momentum fluctuations like before, a unique expression is given containing both limiting cases. One may think in fact, at very low temperatures, no momentum transfer should occur inasmuch as the mean kinetic energy of the gas molecules tends to zero with the temperature, this fact already being present in the expression for P due to its relation with $\rho(\nu, T)$.

- 36) It appeared that by the procedure sketched here the zero-point energy must be set equal to $h\nu$ in order to arrive at Planck's radiation formula. Further investigations must show whether the discrepancy between this assumption and the assumption set as the basis of the investigation on hydrogen disappears in the case of a more rigorous calculation (Note of the authors).
- 37) M. Planck, *Wärmestrahlung*, 6. Aufl. p. 112 (Equation (168)) (Note of the Authors) - See note (35). Here ν is the frequency of the ordered motion at $T = 0$, which equals the proper frequency previously introduced by the authors as $\nu_0 = \frac{n_0}{T}$. In the expression for f_0^2 , σ is the constant
- $$\sigma = \frac{4\pi^2\nu_0 e^2}{3mc^3}$$
- characteristic for the damping of an oscillator through radiation (See note 17 in ref. (1)).
- 38) It is hardly worth stressing that this kind of procedure may be justified only by our ignorance of the effective resonator's law (Note of the Authors).

39) The formula has been corrected by multiplying the left hand side by ν .

40) A fundamental difference between Boyer's and Einstein and Stern's work is to be noted here. The former author assumes the existence of a fluctuating zero-point electromagnetic radiation, whose spectral density may be derived from the requirement of Lorentz invariance of the spectrum, superimposing on the thermal radiation; the treatment of the interaction between the resonator and the radiation is like in Einstein and Stern's work *except for the presence of a term linked to the stochastic field in the differential equation for $\rho(\omega, T)$*

$$\frac{1}{3} \frac{c^3 \pi^2}{kT \omega^2} \left(\rho^2(\omega, T) - \left(\frac{\hbar \omega^3}{2\pi^2 c^3} \right)^2 \right) = \rho(\omega, T) - \frac{1}{3} \omega \frac{d}{d\omega} \rho(\omega, T)$$

which determines the solution to be

$$\rho(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \left(\frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} + \frac{1}{2} \hbar \omega \right)$$

instead of that of Rayleigh and Jeans.

By further using the relation

$$E = \frac{\pi^2 c^3}{\omega^2} \rho(\omega, T) \quad [10]$$

(where E is the mean energy of a resonator in a fluctuating electromagnetic field) of classical electrodynamics, one obtains

$$E = \frac{\hbar \omega}{e^{\hbar \omega / kT} - 1} + \frac{1}{2} \hbar \omega$$

For Einstein and Stern it is the oscillator which has a zero-point energy and it is by introducing a term linked with this energy in the differential equation for $\rho(\omega, T)$ that it is possible to obtain the solution

$$\rho(\nu, T) = \frac{8\pi \nu^2}{c^3} \frac{\hbar \nu}{e^{\hbar \nu / kT} - 1}$$

At this stage, either one uses in the framework of Planck's second theory, the equation

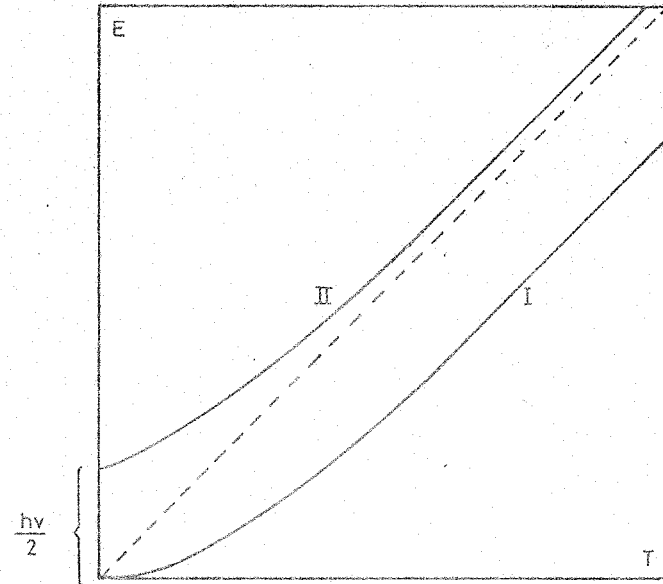
$$E = \left(\frac{c^3}{8\pi \nu^3} \rho + \frac{1}{2} \right) \hbar \nu$$

thus deriving for E expression [2], where the zero-point energy makes its appearance, or the classical Eq. [10], obtaining

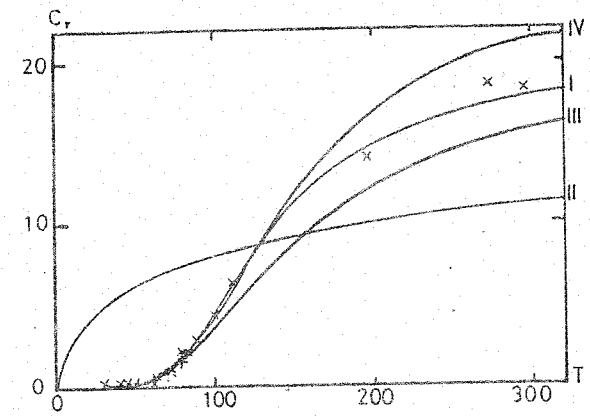
for E the expression

$$E = \frac{\hbar \nu}{e^{\hbar \nu / kT} - 1}$$

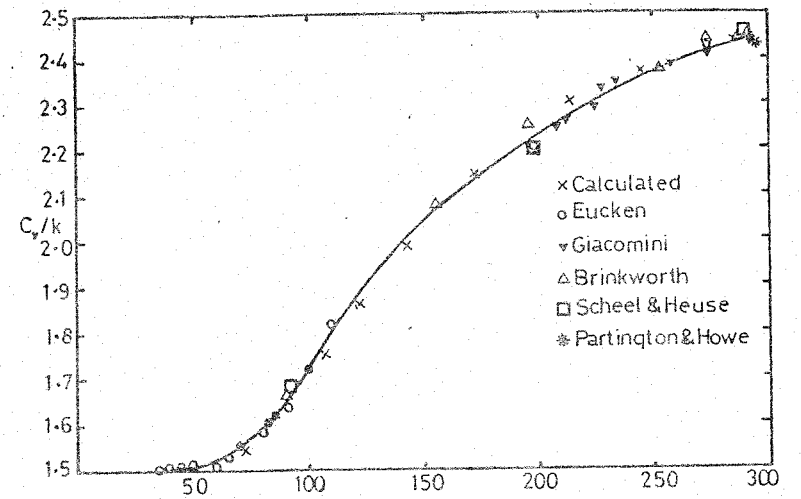
to which the zero-point term must be added.



Fig(i)



Fig(2)



Fig(3) (Cf. note 31)