Planck's Law and the Light-Quantum Hypothesis

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The phase space of a light-quantum in a given volume is divided up in 'cells' of size h^3. The number of possible distributions of the light-quanta of a macroscopically defined radiation among the cells gives the entropy and with that all the thermodynamic properties of the radiation.

Planck's formula for the distribution of energy in the radiation of a blackbody forms the starting point for the quantum theory which has been developed in the last 20 years and has been very fruitful in all parts of physics. Since its publication in 1901 many methods for the derivation of this law has been proposed. It is recognized that the fundamental assumptions of the quantum theory are incompatible with the laws of classical electrodynamics. All derivations till now use the relation

$$\varrho_\nu \, d\nu = \frac{8\pi\nu^2 d\nu}{c^3} E,$$

that is, the relation between the density of radiation and the average energy of an oscillator, and they make assumptions about the number of degrees of freedom of the ether, which enters the above equation (the first factor on the right hand side). This factor could, however, be derived only from the classical theory. This is an unsatisfactory feature in all derivations, and it is not surprising that efforts are made again and again to give a derivation free from this logical flaw.

Einstein has given a remarkably elegant derivation. He has recognized the logical flaw in all previous derivations and has tried to deduce the formula independently of classical theory. Starting from very simple assumptions about the energy exchange between molecules and the radiation field, he finds the relation

$$\varrho_\nu = \frac{\alpha_{mn}}{e^{\frac{\varepsilon_m - \varepsilon_n}{kT}} - 1}.$$

In order to make this formula agree with that of Planck he has to use Wien's displacement law and Bohr's correspondence principle. Wien's law is based on classical theory and the correspondence principle assumes that the quantum theory agrees with the classical theory in certain limiting cases.

In all cases it appears to me that the derivations are not sufficiently justified from a logical point of view. On the other hand, the light-quantum hypothesis combined with statistical mechanics (as adapted by Planck to comform to the requirements of quantum theory) appears sufficient for the deduction of the law independent of classical theory. In the following I shall sketch the method briefly.

Let the radiation be enclosed in a volume V and its total energy be E. Suppose there are different types of quanta each having number N_s and energy $h\nu_s$ (s = o to $s = \infty$). The total energy is then

$$E = \sum_s^r N_s h \nu_s = V \int \varrho_\nu d\nu. \tag{1}$$

The solution of the problem then requires the determination of of N_s which in turn determine ρ_ν. If we can give the probability for each distribution characterized by arbitrary values of N_s, then the solution is determined by the condition that this probability is a maximum subject to the subsidiary condition (1). We now want to find this probability.

The quantum has a momentum of magnitude $\frac{h\nu_s}{c}$ in the direction of its motion. The instantaneous state of the quantum is characterised by its coordinates x, y, z and the corresponding momenta p_x, p_y, p_z. These six quantities can be considered to be the coordinates of a point in a six dimensional space, where we have the relation

$$p_x^2 + p_y^2 + p_z^2 = \frac{h^2 \nu^2}{c^2},$$

by virtue of which the point is forced to lie on the surface of a cylinder determined by the frequency of the quantum. The phase space belonging to the frequency interval $d\nu_s$ is.

$$\int dx\, dy\, dz\, dp_x\, dp_y\, dp_z = V \cdot 4\pi \left(\frac{h\nu}{c}\right)^2 \frac{h\, d\nu}{c} = 4\pi \frac{h^3 \nu^2}{c^3} V d\nu.$$

If we divide the total phase space volume in cells of size h^3, then $4\pi V \frac{\nu^2}{c^3} d\nu$ cells will belong to the frequency interval $d\nu$. Nothing definite can be said about the method of this division. In any case, the total number of cells must be regarded as the number of possible arrangements of a quantum in the given volume. It seems, however, appropriate to multiply this number once again by 2 in order to take into account the fact of polarization, so that we obtain $8\pi V \frac{\nu^2 d\nu}{c^3}$ as the number of cells belonging to $d\nu$.

Now it is easy to calculate the thermodynamic probability (macroscopically defined) of a state. Let N^s be the number of quanta belonging to the frequency range $d\nu^s$. In how many ways can these be distributed among the cells belonging to $d\nu^s$? Let p_o^s be the number of empty cells, p_1^s those which contain one quantum, p_2^s those which contain two quanta and so on. The number of possible distributions is then,

$$\frac{A^s!}{p_0^s!\,p_1^s!\ldots}, \quad \text{where} \quad A^s = \frac{8\pi\nu^2}{c^3}\,d\nu^s,$$

and

$$N^s = 0\,.\,p_0^s + 1\,.\,p_1^s + 2\,p_2^s \ldots$$

is the number of quanta belong to the range $d\nu^s$.

The probability of the state defined by all p_r^s is clearly

$$\prod_s \frac{A^s!}{p_0^s!\,p_1^s!\ldots}.$$

Taking into account that we can consider p_r^s to be large numbers, we have

$$\lg W = \sum_s A^s \lg A^s - \sum_s \sum_r p_r^s \lg p_r^s,$$

where

$$A^s = \sum_r p_r^s.$$

This expression must be a maximum with the constraints

$$E = \sum_s N^s h\nu^s; \quad N^s = \sum_r r p_r^s.$$

Carrying out the variation, we obtain the conditions

$$\sum_s \sum_r \delta p_r^s (1 + \lg p_r^s) = 0, \qquad \sum_s \delta N^s h\nu^s = 0$$

$$\sum_r \delta p_r^s = 0 \qquad \delta N^s = \sum_r r\,\delta p_r^s.$$

From this it follows that

$$\sum_s \sum_r \delta p_r^s (1 + \lg p_r^s + \lambda^s) + \frac{1}{\beta} \sum_s h\nu^s \sum_r r\,\delta p_r^s = 0.$$

Next it follows from this that

$$p_r^s = B^s e^{-\frac{rh\nu^s}{\beta}}.$$

But since

$$A^s = \sum_r B^s e^{-\frac{r h \nu^s}{\beta}} = B^s \left(1 - e^{-\frac{h\nu^s}{\beta}}\right)^{-1},$$

therefore

$$B_s = A^s \left(1 - e^{-\frac{h\nu^s}{\beta}}\right).$$

We further have

$$N^s = \sum_r r p_r^s = \sum_r r A^s \left(1 - e^{-\frac{h\nu^s}{\beta}}\right) e^{-\frac{r h\nu^s}{\beta}}$$

$$= \frac{A^s e^{-\frac{h\nu^s}{\beta}}}{1 - e^{-\frac{h\nu^s}{\beta}}}.$$

Taking into account the value of A^s found above, we get

$$E = \sum_s \frac{8\pi h {\nu^s}^3 d\nu^s}{c^3} V \frac{e^{-\frac{h\nu^s}{\beta}}}{1 - e^{-\frac{h\nu^s}{\beta}}}.$$

Using the results found so far, one further finds

$$S = k\left[\frac{E}{\beta} - \sum_s A^s \lg\left(1 - e^{\frac{h\nu^s}{\beta}}\right)\right],$$

Whence, using the relation $\frac{\partial S}{\partial E} = \frac{1}{T}$, if follows that $\beta = kT$. Substituting this in the equation for E, we get

$$E = \sum_s \frac{8\pi h {\nu^s}^3}{c^3} V \frac{1}{e^{\frac{h\nu^s}{kT}} - 1} d\nu^s,$$

which is the same as Planck's formula.

(Translated by A. Einstein)

Translator's remarks :

In my opinion Bose's derivation signifies an important advance. The method used here gives the quantum theory of an ideal gas as I will work out elsewhere.

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