



# IX. On the statistical theory of heat radiation

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47 sums wanted can be found by simple addition of the numbers in the 47 columns (omitting the third to the ninth columns,—whose sums are not wanted, and which may be written on a sheet by themselves; as these seven numbers have to be combined by addition and subtraction, it may be most convenient to arrange them in columns corresponding to the several observations, to effect their combinations in these columns, and to transfer the values of  $l_1$  and  $l_2$  thus found to the main sheets).

Worcester, Mass., U.S.A.,  
January 1, 1909.

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IX. *On the Statistical Theory of Heat Radiation.* By  
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*Montreal* \*

THE theory of the distribution of the energy in the spectrum of full radiation which we owe to Planck has recently been presented in a new and more general form by Sir J. Larmor †. In Planck's theory the energy is taken to be emitted by "resonators" contained in the body which are supposed to only gain and lose energy by certain finite increments the magnitude of which is proportional to the frequency of vibration. On this view it is not absolutely necessary to regard the radiation itself as made up of finite elements; but Einstein and others have shown that Planck's theory can be so interpreted. Larmor considers the radiation itself as made up of "elements of disturbance" which are regarded as definite entities possessing energy, but the energy in an element can vary continuously.

Larmor states that on his view "it would be the limiting differential ratio of energy element to extent of cell that is somehow predetermined, but now without any implication that energy is itself constituted on an atomic basis." I find that Larmor's theory seems to require the radiation to be made up of finite elements of the same magnitude as those contemplated by Planck and Einstein. This does not mean that energy itself has an atomic constitution, but it does appear to require some such sort of constitution for the radiation.

Larmor obtains the equation  $\epsilon\theta = \log\left(1 + \frac{N}{n}\right)$ , where  $\epsilon$  denotes the energy per element of disturbance of a particular wave-length,  $n$  the number of such elements, and  $N$  the

\* Communicated by the Author.

† Proc. Roy. Soc. A. vol. lxxxiii., 1909.

number of "cells" into which the æther is supposed divided for radiation of the wave-length under consideration.  $\theta$  is a function of the temperature, and is the same for all the different sets of cells.

To determine the relation between  $\theta$  and the temperature ( $t$ ) on the conventional absolute scale we have Boltzmann's expression for the entropy  $S = k \log W$ , where  $W$  denotes the number of ways in which the system can be arranged in its actual state. Hence

$$\frac{dS}{dn} = k \frac{d(\log W)}{dn} = k \log \left( 1 + \frac{N}{n} \right)$$

for the system consisting of the  $n$  elements distributed among  $N$  cells. If  $n$  is increased by unity, the increase of entropy is  $\epsilon/t$ , so that

$$\frac{\epsilon}{t} = k \log \left( 1 + \frac{N}{n} \right) = k\theta.$$

Hence

$$\theta = \frac{1}{kt}.$$

Larmor shows that  $N \propto 1/\lambda^3$  and  $\epsilon \propto 1/\lambda$ ; so that after multiplying by  $1/\lambda$  to allow for the variation of  $d\lambda$  we get, putting  $\epsilon = hc/\lambda$ ,

$$e_\lambda = C \lambda^{-5} \left( e^{\frac{hc}{\lambda kt}} - 1 \right)^{-1},$$

where  $e_\lambda$  denotes the energy density per unit range of wave-length and  $c$  the velocity of light. To get  $C$  we can make use of the value of  $e_\lambda$  for long wave-lengths calculated by H. A. Lorentz and Jeans, viz.,  $e_\lambda = 8\pi kt/\lambda^4$ . Hence

$$\frac{C}{\lambda^5} \frac{\lambda kt}{hc} = \frac{8\pi kt}{\lambda^4};$$

so that

$$C = 8\pi hc \text{ and } e_\lambda = \frac{8\pi hc}{\lambda^5} \left( e^{\frac{hc}{\lambda kt}} - 1 \right)^{-1}$$

which is Planck's formula.

In the formula  $n\epsilon = \frac{N\epsilon}{e^{\epsilon/kt} - 1}$  if we suppose  $\epsilon$  indefinitely diminished while  $\lambda$  is kept constant, we get  $n\epsilon = Nkt$ , so that the energy per cell is  $kt$  and is the same for all the sets of cells. This is merely equipartition of energy and corresponds with  $e_\lambda = 8\pi kt/\lambda^4$ . It seems therefore that  $\epsilon$  cannot be made

indefinitely small on Larmor's theory any more than on Planck's\*.

The total number of elements of energy per c.c. ( $\mathcal{N}$ ) is given by the equation

$$\mathcal{N} = \int_0^\infty \frac{8\pi hc\lambda}{hc\lambda^5} \left( e^{\frac{hc}{k\lambda t}} - 1 \right)^{-1} d\lambda.$$

Hence

$$\mathcal{N} = 16\pi \left( \frac{kt}{ch} \right)^3 \left( 1 + \frac{1}{2^3} + \frac{1}{3^3} + \dots \right).$$

The series in brackets is equal to  $1.20\dots = \alpha'$  say.

The total energy per c.c. is

$$E = \frac{48\pi ak^4 t^4}{c^3 h^3},$$

where  $\alpha = 1 + \frac{1}{2^4} + \frac{1}{3^4} + \dots = 1.0823$ .

Let  $\bar{\epsilon}$  denote the average energy per element so that

$$\bar{\epsilon} = \frac{E}{\mathcal{N}} = 3kt \frac{\alpha}{\alpha'}.$$

Now  $3kt/2$  is the average translational energy of a molecule of a gas, and

$$\frac{2\bar{\epsilon}}{3kt} = 2 \frac{\alpha}{\alpha'} = 1.80\dots$$

It appears, therefore, that the average energy per element of disturbance in the radiation is equal to 1.80 times the energy of a monatomic gas molecule. This result, it will be observed, is independent of the absolute values of the constants in Planck's formula.

The pressure ( $p$ ) of the radiation is equal to  $E/3$ , so that

$$p = \mathcal{N}kt \frac{\alpha}{\alpha'}.$$

For a gas we have  $p = \mathcal{N}kt$  if  $\mathcal{N}$  now denotes the number of molecules per c.c. Thus for a given pressure and temperature a gas contains 0.90 times as many molecules per c.c. as full radiation contains elements of energy. The elements of disturbance have on the average as much energy as if each possessed 5.4 degrees of freedom and equipartition held good. For a gas each molecule of which has six degrees of freedom

\* The value of  $\epsilon$  for any wave-length is of course given by  $\epsilon = hc/\lambda$ , using the value of  $h$  required by the observed values of  $e_\lambda$ .

we have  $p = \frac{E}{3}$ , where  $E$  denotes the total energy of the gas per c.c. Also for an adiabatic expansion of such a gas  $pv^{4/3} = \text{const.}$  These two equations also hold for full radiation, which suggests that the elements of disturbance ought to have energy corresponding to six degrees of freedom instead of only 5.4, but the energy is not distributed among the elements in the same way as among the gas molecules.

Consider the free expansion of full radiation from a volume  $v_1$  to a volume  $v_2$ . The chance that an element is in  $v_1$  when the volume is  $v_2$  is  $v_1/v_2$ . Thus the chance that all the  $\mathcal{N}_{v_1}$  elements are in  $v_1$  is  $\left(\frac{v_1}{v_2}\right)^{\mathcal{N}_{v_1}}$ ; hence the increase of entropy  $S_2 - S_1$  due to the free expansion is  $k\mathcal{N}_{v_1} \log \frac{v_2}{v_1}$ . If  $v_2 - v_1$  is very small, say  $dv$ , this becomes  $k\mathcal{N}dv = dS$ . Now

$$dS = \frac{dU + pdv}{t};$$

so that for an infinitesimal free expansion, if for the moment we regard  $t$  as unaffected, we have

$$dS = \frac{pdv}{t} = \frac{\mathcal{N}\bar{\epsilon}dv}{3t}.$$

Hence

$$k\mathcal{N}dv = \frac{\mathcal{N}\bar{\epsilon}}{3t}dv,$$

$$\text{or} \quad \bar{\epsilon} = 3kt \text{ instead of } \bar{\epsilon} = 3kt \frac{\alpha}{\alpha'}.$$

This makes  $\bar{\epsilon}$  equal to the energy of six degrees of freedom, but the supposed infinitesimal free expansion alters the temperature of the radiation by different infinitely small amounts for the energy of different wave-lengths. Consequently it is not clear that even after only an infinitesimal free expansion the radiation can be regarded as having a definite temperature differing infinitely little from  $t$ .

In the case of the gas we have in the same way for a free expansion

$$dS = k\mathcal{N}dv = \frac{pdv}{t} = \frac{1}{3} \frac{\mathcal{N}mu^2dv}{t},$$

where  $m$  is the mass of a molecule and  $u^2$  the average square of the velocity of the molecules. Hence  $\frac{3}{2}kt = \frac{1}{2}mu^2$ , which gives the value of  $k$  due to Planck. The known equation

$\lambda_m t = \frac{ch}{4.965k}$ , where  $\lambda_m$  is the wave-length for which  $e_\lambda$  has its maximum value, gives with the expression found for  $\mathcal{H}$

$$\mathcal{H} = \frac{16\pi\alpha^1}{(4.965\lambda_m)^3}.$$

Consequently the number of elements of disturbance per c.c. can be calculated from  $\lambda_m$  without knowing the density of the energy. Since  $\lambda_m t = 0.294$ , we get approximately

$$\mathcal{H} = 19.5 t^3.$$

Thus at  $2000^\circ$  on the absolute scale there are  $1.56 \times 10^{11}$  elements per c.c. in full radiation according to the theory considered here.

Montreal, April 13, 1910.

X. *The Amount of Thorium in Sedimentary Rocks.*—  
I. *Calcareous and Dolomitic Rocks.* By J. JOLY, F.R.S.\*

THE systematic determination of the amount of thorium in sedimentary rocks does not seem to have been hitherto attempted. Using a method already fully described by me (Phil. Mag., May and July 1909) I have recently measured the thorium content of calcareous and dolomitic rocks from various parts of the world and of various geological ages. The results are given below.

In all cases, the rock after being brought to a coarse powder was treated with 100 ccs. of HCl diluted to a bulk of 200 ccs. with distilled water. A test applied to 500 ccs. of the acid used showed no trace of thorium. After the first violent effervescence had ceased, the whole was heated for a couple of hours on the water-bath. The undissolved part was then filtered off, dried, and fused with about twice its weight of the usual fusion-mixture of the carbonates of sodium and potassium. The melt was then leached with water and acidified with sufficient acid rapidly stirred up with it. In most cases a clear or almost clear solution resulted, which could be added to the solution containing the soluble part of the rock. In a few cases, where the insoluble residue, obtained after treating the rock with HCl, was large, the

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