

dynamical probability". This is proportional to the mathematical probability, but not quite equal to it. The mathematical probability is a fraction, while the thermodynamical probability is a whole number. Planck has developed methods for calculating the thermodynamical probability of different systems—*e.g.*, a perfect gas and black body radiation. As is well known, this idea led, in the hands of its author, to the development of the Quantum theory, which is now responsible for progress along all lines in physical science.

There are, however, a few points which are not yet clear. Some of these refer to the fundamental assumptions of the theory, others refer to the mode of application of the fundamental ideas. The exact nature of these obscure points can only be made clear by reference to the actual working, which we now proceed to do.

§ 1. *Theory of Perfect Gases*¹

Let us take a large number N of molecules enclosed within a volume V in the gas-kinetic sense. To calculate the probability of the system, the volume is divided into a number of cells denoted by 1, 2, 3, ... n , containing $N_1, N_2, N_3 \dots N_n$ molecules respectively. The thermodynamical probability is defined as the total number of complexions (*i.e.*, the total number of ways in which this distribution can be effected). It is easy to see that

$$W_n = \frac{N!}{N_1! N_2! \dots N_n!} \dots (2)$$

The mathematical probability

$$W_{mn} = \frac{W_n}{\sum W_n} = W_n \cdot n^{-N} \dots (2.1)$$

The summation $\sum W_n$ is taken over all positive values of N_1, N_2 , etc. consistent with the condition

$$N_1 + N_2 + \dots + N_n = N.$$

Let $\frac{N_1}{N} = w_1, \frac{N_2}{N} = w_2 \dots$

Then with the help of Stirling's formula, it can be easily shown that

$$\log W_n = -N \sum_{r=1}^{r=n} w_r \log w_r \dots (3)$$

The actual or equilibrium value of $\log W_n$ is obtained by making it maximum subject to the prescribed conditions. Let ϵ_r = average energy per molecule in the cell r . Then the total energy

$$E = N_1 \epsilon_1 + N_2 \epsilon_2 + \dots + N_n \epsilon_n = N \sum w_r \epsilon_r = \text{const.} \dots (4)$$

and $\sum w_r = 1. \dots (5)$

From equations (3), (4), (5), we can deduce that in case of equilibrium

$$w_r = a \rho^{-\beta \epsilon_r} \dots (6)$$

From the relation $\frac{\partial S}{\partial E} = \frac{1}{T}$ it can be shown that

$$\beta = \frac{1}{kT} \dots (7)$$

From equations (5) and (6)

$$a = \frac{1}{\sum e^{-\frac{\epsilon_r}{kT}}} \dots (8)$$

and it can easily be shown that the free energy

$$F = kNT \log a; \dots (9)$$

a , however, remains indeterminate, and it cannot be calculated without the introduction of some further hypothesis.

By an application of Liouville's law, Planck shows that for a system obeying the canonical laws of Hamilton the motion is completely defined if the positional (q) and the momenta (p) coordinates corresponding to each individual degree of freedom of each particle are given. In this case he shows that the phase integral

$$H = \dots \iiint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f \dots (10)$$

(the integral being taken for all the degrees of freedom for a particle), remains unchanged by subsequent events. H is known as the extension of the elementary region of the phase space. According to classical theory, H may have any infinitely small value up to zero, but according to the quantum theory H has always got a finite, though small, invariant value.

The summation $\sum e^{-\frac{\epsilon_r}{kT}}$ can now be effected.

$$\sum e^{-\frac{\epsilon_r}{kT}} = \frac{\sum e^{-\frac{\epsilon_r}{kT}} \int \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f}{H} \dots (11)$$

For monatomic gases, H must refer to the representative particle in the cell r , having the coordinates x_r, y_r, z_r , and velocity components u_r, v_r, w_r .

Taking $\epsilon_r = \frac{1}{2} m(u_r^2 + v_r^2 + w_r^2) + \epsilon_0, \dots (12)$

where ϵ_0 denotes the unalterable internal energy of an atom at rest, and

$$dp_1 dp_2 dp_3 = m^3 du_r dv_r dw_r.$$

We obtain

$$\sum e^{-\frac{\epsilon_r}{kT}} = \frac{V}{H} e^{-\frac{\epsilon_0}{kT}} (2\pi mkT)^{\frac{3}{2}} \dots (13)$$

With this value of $\sum e^{-\frac{\epsilon_r}{kT}}$, neglecting ϵ_0 ,

$$S = kN \left\{ \frac{V}{H} (2\pi mkT)^{\frac{3}{2}} \right\} + \frac{3}{2} kN \dots (14)$$

¹ The subject matter of this section is merely an abstract of §113-§134 of Planck's 'Warmestrahlung,' 5th edition.

Comparing the two expressions,

$$W = \frac{\{\gamma\}}{h^{3N} N!} \dots (20)$$

§ 3

Ehrenfest and Trkal have not traced any connexion between $\{\gamma\}$ and W . But from equations (18), (19), and (20), it is possible not only to connect W and $\{\gamma\}$ for any general system, but also to lay down a general theorem for the calculation of the probability of any system. This we now proceed to do.

According to Planck, the probability W is a whole number. But whenever in physics we wish to determine the absolute value of any quantity, we must as well lay down a "unit" for it. Now let us see what is meant by "Unit Probability."

The idea of "Unit Probability" is intimately connected with the zero of entropy; for $S = k \log W$, and when $W = 1$, $S = 0$. According to the second law of thermodynamics, this takes place when a condensed system is reduced to absolute zero; for a reversible engine acting between this system and another system at a finite temperature T will be able to convert all the heat energy abstracted into mechanical work.

We can suppose this to take place in another way. Suppose we have a gas at a finite temperature. The particles are moving in a chaotic way and at a distance from each other. Suppose all of them suddenly begin to move with identical velocity in the same direction, with the proviso, however, that the total kinetic energy remains the same. Then if this system, on coming into contact with another body and suffering inelastic collision, transfers the whole of its energy to that body, we can say that the heat motion has been completely converted into mechanical work. Thus the idea of absolute zero, and zero of entropy, presupposes a system of particles absolutely devoid of all motion. But this is not sufficient. If the particles which are devoid of all motion remain at a distance from each other, then, owing to mutual attraction and there being no motion, they will begin to move towards each other, and kinetic energy will again be developed and can again be converted into mechanical work. For an attracting system, motion, and with it the energy available from the system, will entirely stop when the particles are packed together in the closest manner possible.

We assume that such a system possesses unit probability. Let the value of γ -space for such a system be denoted by $\{\gamma\}$.

We may remark here that these considerations apply only if we regard the atoms as the final constituents of matter. This, however, is not the case, and therefore, even when the state pictured above has been reached, the electrons of one atom will react mechanically on the other atoms and

electrons; and motion will never be entirely absent. Thus we cannot conceive of an absolute zero of temperature unless we picture to ourselves a state in which the protons and electrons have combined in some unknown way and annihilated all matter. We can therefore talk of absolute zero in a world where there is no matter. But according to the generalized theory of relativity, there can be neither space time, nor any physical quantity in a world which is entirely devoid of matter. Hence we come to a conclusion which has been previously reached by Nernst, viz., in the phenomenal world it is impossible to reach the absolute zero of temperature.

We shall now proceed to calculate the thermodynamical probability of a system in the terms of $\{\gamma\}$, as unity. The probability of the state of a system is proportional to the phase space $\{\gamma\}$ described by the system. Therefore the thermodynamical probability at a finite temperature

$$W = \frac{\{\gamma\}}{\{\gamma\}_0} \dots (21)$$

We have now to find out the value of $\{\gamma\}_0$.

Let us suppose that in the system there are N particles, each particle having f degrees of freedom. We shall follow Ehrenfest's considerations in calculating $\{\gamma\}_0$. According to the definition, for a single particle

$$\{\mu\} = \dots \iint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f = h^f \dots (16)$$

Let us suppose that each particle is a Planck-resonator and confine our attention to one degree of freedom only. According to the quantum theory its phase-point (q, p) must lie at $p=0$, $q=0$, or on one of the ellipses $h, 2h, \dots$, the area between two consecutive ellipses being given by

$$\iint dq dp = h^2$$

Ehrenfest attaches a "weight" h to each one of these ellipses, and in particular also to the point $(p=0, q=0)$. Now, in our case, *i.e.*, for a system at absolute zero, none of the degrees of freedom of any particle is excited: or the phase of every particle for each degree of freedom is at $(p=0, q=0)$.

Hence, for a single particle,

$$\{\mu\} = \dots \iint \dots dq_1 dp_1 dq_2 dp_2 \dots dq_f dp_f = h^f$$

For the whole system

$$\prod_N \{\mu\} = h^{fN} \dots (22)$$

Again the N particles can be arranged amongst themselves in $N!$ ways. Combining this with (22), we obtain

$$\{\gamma\}_0 = h^{fN} N! \dots (23)$$

⁴ Vide Ehrenfest and Trkal, Proc. Amst. Soc. xxiii. p. 179 (1920).

To sum up, the thermodynamic probability in Planck's sense is given by

$$W = \frac{\{\gamma\}}{h^{5N} \cdot N!} \dots (20.1)$$

This will cover all cases.

On the basis of this law we shall now calculate the entropy of a system consisting of diatomic molecules.

§ 4. Entropy of a Gas consisting of Diatomic Molecules.

In this case we shall ignore the rotation of molecules about the axis of symmetry and also all internal motions of atoms in the molecule. Therefore, each molecule has only five degrees of freedom, three of these being translational and two rotational.

$$\begin{aligned} \text{Thus } \{\gamma\}_0 &= h^{5N} N! \\ &= h^{5N} N, \end{aligned} \dots (24)$$

where N denotes the total number of molecules considered.

Now, for a single molecule,

$$\begin{aligned} \{\mu\} &= \int \dots dx dy dz d\theta d\psi dp_1 dp_2 dp_3 dp_4 dp_5 \\ &= V \cdot 4\pi \cdot \int \dots dp_1 \dots dp_5 \end{aligned} \dots (25)$$

Therefore γ -space for the total system is given by

$$\begin{aligned} \{\gamma\} &= \prod_{\mu} \{\mu\} \\ &= V^N \cdot (4\pi)^N \cdot \int \dots dp_{1r} dp_{2r} \dots dp_{5r} \dots \end{aligned} \dots (26)$$

the integrals being taken for all molecules, dp_{1r} , dp_{2r} , etc. denote the momenta of the different molecules.

The total kinetic energy of the molecules being given, the integration is to be taken over all possible values of the momenta which are consistent with it. If E be the kinetic energy given, we have

$$\sum \frac{p_{1r}^2}{2m} + \frac{p_{2r}^2}{2m} + \frac{p_{3r}^2}{2m} + \frac{p_{4r}^2}{2a} + \frac{p_{5r}^2}{2b} = E, \dots (27)$$

where m is the molecular mass and a and b represent the

moments of inertia. The molecules being all similar, these quantities (m , a , and b) have the same values for all the molecules. The total number of terms in the left-hand side of equation (27) is $5N$.

Hence

$$\begin{aligned} \{\gamma\} &= V^N \cdot (4\pi)^N \cdot \int \dots dp_{1r} dp_{2r} \dots dp_{5r} \dots \\ &= V^N \cdot (4\pi)^N \cdot \sqrt{\pi^{5N}} \cdot \frac{\sqrt{E^{5N-1}}}{\left(\frac{5N}{2}\right)} \cdot \{(2m)^{3/2} \cdot (2a)^{1/2} \cdot (2b)^{1/2}\}^N \end{aligned} \dots (28)$$

since N is very large, we may put $5N$ for $5N-1$.

$$\begin{aligned} \{\gamma\} &= V^N \cdot (4\pi)^N \cdot \frac{\sqrt{2\pi E^{5N}}}{\left(\frac{5N}{2}\right)} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N \\ &= \frac{V^N \cdot (4\pi)^N \cdot \sqrt{2\pi E^{5N}} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N}{\left(\frac{5N}{2}\right)!} \end{aligned} \dots (28.1)$$

Hence

$$\begin{aligned} W &= \frac{\{\gamma\}}{\{\gamma\}_0} = \frac{\{\gamma\}}{h^{5N} \cdot N!} \dots (29) \\ &= \frac{V^N \cdot (4\pi)^N \cdot \sqrt{2\pi E^{5N}} \cdot (m^{3/2} \cdot a^{1/2} \cdot b^{1/2})^N}{h^{5N} \cdot N! \cdot \left(\frac{5N}{2}\right)!} \end{aligned} \dots (29.1)$$

Using Stirling's formula and putting $E = \frac{5}{2} NkT$, we obtain

$$W = \left\{ \frac{e^{7/2} \cdot 4\pi V \cdot (2\pi kT)^{5/2} \cdot m^{3/2} \cdot a^{1/2} \cdot b^{1/2}}{N \cdot h^5} \right\}^N \dots (29.2)$$

$$S = k \log W$$

$$= Nk \log \left\{ \frac{e^{7/2} \cdot 4\pi V \cdot m^{3/2} \cdot a^{1/2} \cdot b^{1/2} \cdot (2\pi kT)^{5/2}}{N \cdot h^5} \right\} \dots (30)$$

It may be emphasized here that the theorems $E = \frac{3}{2} NkT$ for monatomic gases and $E = \frac{5}{2} NkT$ for diatomic gases have not been assumed here, but followed directly from the theory. The calculations have not been reproduced here.

32. ON ENTROPY OF RADIATION II*

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In a previous paper, it has been shown that the thermodynamical probability of a system is given by the law,

$$W = \{\gamma\} / \{\gamma\}_0 \dots (1)$$

Where $\{\gamma\}$ = phase-space described by the system at temperature T_0 , $\{\gamma\}_0$ = phase-space described at absolute

zero. It was shown that the absolute value of entropy of perfect gases could be deduced from this theorem.

The same formula can be applied for deducing the entropy of radiation. Since the time when Bartoli deduced the existence of radiation pressure from thermodynamical reasoning, it has been customary to look upon radiation as

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