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1. INVESTIGATIONS ON THE THEORY OF THE BROWNIAN MOVEMENT¶

1.1. ON THE MOVEMENT OF SMALL PARTICLES SUSPENDED IN A STATIONARY LIQUID DEMANDED BY THE MOLECULAR-KINETIC THEORY OF HEAT¶

In this paper it will be shown that according to the molecular-kinetic theory of heat, bodies of microscopically-visible size suspended in a liquid will perform movements of such magnitude that they can be easily observed in a microscope, on account of the molecular motions of heat. It is possible that the movements to be discussed here are identical with the so-called "Brownian molecular motion"; however, the information available to me regarding the latter is so lacking in precision, that I can form no judgment in the matter (1).

If the movement discussed here can actually be observed (together with the laws relating to it that one would expect to find), then classical thermodynamics can no longer be looked upon as applicable with precision to bodies even of dimensions distinguishable in a microscope: an exact determination of actual atomic dimensions is then possible. On the other hand, had the prediction of this movement proved to be incorrect, a weighty argument would be provided against the molecular-kinetic conception of heat.

1.1.1. § ON THE OSMOTIC PRESSURE TO BE ASCRIBED TO THE SUSPENDED PARTICLES¶

Let z gram-molecules of a non-electrolyte be dissolved in a volume V forming part of a quantity of liquid of total volume V . If the volume V is separated from the pure solvent by a partition permeable for the solvent but impermeable for the solute, a so-called "osmotic pressure," p , is exerted on this partition, which satisfies the equation

$$pV^* = RTz$$

when V^*/z is sufficiently great.

On the other hand, if small suspended particles are present in the fractional volume V^* in place of the dissolved substance, which particles are also unable to pass through the partition permeable to the solvent: according to the classical theory of thermodynamics—at least when the force of gravity (which does not interest us here) is ignored—we would not expect to find any force acting on the partition.

But a different conception is reached from the standpoint of the molecular-kinetic theory of heat. According to this theory a dissolved molecule is differentiated from a suspended body solely by its dimensions, and it is not apparent why a number of suspended particles should not produce the same osmotic pressure as the same number of molecules. We must assume that the suspended particles perform an irregular movement—even if a very slow one—in the liquid, on account of the molecular movement of the liquid; if they are prevented from leaving the volume V by the partition, they will exert a pressure on the partition just like molecules in solution. Then, if there are n suspended particles present in the volume V , and therefore $n/V^* = v$ in a unit of volume, and if neighboring particles are sufficiently far separated, there will be a corresponding osmotic pressure p of magnitude given by

$$p = \frac{RT}{V^* N} n = \frac{RT}{N} v$$

where N signifies the actual number of molecules contained in a gram-molecule.

1.1.2. § OSMOTIC PRESSURE FROM THE STANDPOINT OF THE MOLECULAR-KINETIC THEORY OF HEAT ¶

If p_1, p_2, \dots, p_l are the variables of state of a physical system which completely define the instantaneous condition of the system, and if the complete system of the equations of change of these variables of state is given in the form

$$\frac{\partial p_v}{\partial t} = \phi_v(p_1 \dots p_l) \quad (v = 1, 2, \dots, l)$$

whence

$$\sum \frac{\partial \phi_v}{\partial p_v} = 0$$

then the entropy of the system is given by the expression

$$S = \frac{\bar{E}}{T} + 2x \lg \int e^{-\frac{E}{2xT}} dp_1 \dots dp_l$$

where T is the absolute temperature, \bar{E} the energy of the system, E the energy as a function of p_v . The integral is extended over all possible values of p consistent with the conditions of the problem. x is connected with the constant N referred to before by the relation $2xN = R$. We obtain hence for the free energy F ,

$$F = -\frac{RT}{N} \lg \int e^{-\frac{EN}{RT}} dp_1 \dots dp_l = -\frac{RT}{N} \lg B$$

Now let us consider a quantity of liquid enclosed in a volume V ; let there be n solute molecules (or suspended particles respectively) in the portion V of this volume V which are retained in the volume V by a semi-permeable partition; the integration limits of the integral B obtained in the expressions for S and F will be affected accordingly. The combined volume of the solute molecules (or suspended particles) is taken as small compared with V^* .

We will call x_1, y_1, z_1 the rectangular coordinates of the centre of gravity of the first particle, x_2, y_2, z_2 those of the second, etc., x_n, y_n, z_n those of the last particle, and allocate for the centres of gravity of the particles the indefinitely small domains of parallelopiped form $dx_1, dy_1, dz_1; dx_2, dy_2, dz_2, \dots, dx_n, dy_n, dz_n$, lying wholly within V^* .

1.1.3. § THEORY OF THE DIFFUSION OF SMALL SPHERES IN SUSPENSION ¶

Suppose there be suspended particles irregularly dispersed in a liquid. We will consider their state of dynamic equilibrium, on the assumption that a force K acts on the single particles, which force depends on the position, but not on the time. It will be assumed for the sake of simplicity that the force is exerted everywhere in the direction of the x axis.

Let v be the number of suspended particles per unit volume; then in the condition of dynamic equilibrium v is such a function of x that the variation of the free energy vanishes for an arbitrary virtual displacement δx of the suspended substance. We have, therefore,

$$\delta F = \delta E - T\delta S = 0$$

It will be assumed that the liquid has unit area of cross-section perpendicular to the x axis and is bounded by the planes $x = 0$ and $x = l$. We have, then,

$$\delta E = - \int_0^l K v \delta x dx$$

and

$$\delta S = \int_0^l R \frac{v}{N} \frac{\delta x}{\delta x} dx = -\frac{R}{N} \int_0^l \frac{\partial v}{\partial x} \delta x dx$$

The required condition of equilibrium is therefore

$$-Kv + \frac{RT}{N} \frac{\partial v}{\partial x} = 0$$

or

$$Kv - \frac{\partial p}{\partial x} = 0$$

The last equation states that equilibrium with the force K is brought about by osmotic pressure forces.

If the suspended particles have spherical form (radius of the sphere = P), and if the liquid has a coefficient of viscosity k, then the force K imparts to the single particles a velocity

$$\frac{K}{6\pi kP}$$

and there will pass a unit area per unit of time

$$\frac{vK}{6\pi kP}$$

particles.

We can calculate the coefficient of diffusion from the two conditions found for the dynamic equilibrium. We get

$$D = \frac{RT}{N} \frac{1}{6\pi kP}$$

The coefficient of diffusion of the suspended substance therefore depends (except for universal constants and the absolute temperature) only on the coefficient of viscosity of the liquid and on the size of the suspended particles.

1.1.4. § ON THE IRREGULAR MOVEMENT OF PARTICLES SUSPENDED IN A LIQUID AND THE RELATION OF THIS TO DIFFUSION¶

We will turn now to a closer consideration of the irregular movements which arise from thermal molecular movement, and give rise to the diffusion investigated in the last paragraph.

For the value of Δ a certain probability-law will hold; the number dn of the particles which experience in the time-interval τ a displacement which lies between Δ and Δ + dΔ, will be expressed by an equation of the form

$$dn = n\varphi(\Delta)d\Delta$$

where

$$\int_{-\infty}^{+\infty} \phi(\Delta)d\Delta = 1$$

and ϕ only differs from zero for very small values of Δ and fulfils the condition

$$\varphi(\Delta) = \varphi(-\Delta)$$

The probable distribution of the resulting displacements in a given time t is therefore the same as that of fortuitous error, which was to be expected. But it is significant how the constants in the exponential term are related to the coefficient of diffusion. The solution is:

$$f(x,t) = \frac{n}{\sqrt{4\pi D}} \frac{e^{-\frac{x^2}{4Dt}}}{\sqrt{t}}$$

We will now calculate the displacement λx in the direction of the X-axis which a particle experiences on an average, or—more accurately expressed—the square root of the arithmetic mean of the squares of displacements in the direction of the X-axis; it is:

$$\lambda_x = \sqrt{x^2} = \sqrt{2Dt}$$

1.1.5. § FORMULA FOR THE MEAN DISPLACEMENT OF SUSPENDED PARTICLES. A NEW METHOD OF DETERMINING THE REAL SIZE OF THE ATOM[J](#)

By eliminating D we obtain

$$\lambda_x = \sqrt{t} \sqrt{\frac{RT}{N} \frac{1}{3\pi kP}}$$

This equation shows how λx depends on T, k, and P.

We will calculate how great λx is for one second, if N is taken equal to 6·10²³ in accordance with the kinetic theory of gases, water at 17° C. is chosen as the liquid (k = 1.35·10⁻²), and the diameter of the particles .001 mm. We get

$$\lambda_x = 8 \cdot 10^{-5} \text{ cm} = 0.8\mu$$

The mean displacement in one minute would be, therefore, about 6μ.

On the other hand, the relation found can be used for the determination of N. We obtain

$$N = \frac{1}{\lambda_x^2} \frac{RT}{3\pi kP}$$

It is to be hoped that some enquirer may succeed shortly in solving the problem suggested here, which is so important in connection with the theory of Heat.

Berne, May, 1905. (Received, 11 May, 1905.)