

ON THE MOVEMENT OF SMALL PARTICLES SUSPENDED IN STATIONARY
LIQUIDS REQUIRED BY THE MOLECULAR-KINETIC THEORY OF HEAT

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It will be shown in this paper that, according to the molecular-kinetic theory of heat, bodies of microscopically visible size suspended in liquids must, as a result of thermal molecular motions, perform motions of such magnitude that these motions can easily be detected by a microscope. It is possible that the motions to be discussed here are identical with the so-called "Brownian molecular motion"; however, the data available to me on the latter are so imprecise that I could not form a definite opinion on this matter.

If it is really possible to observe the motion to be discussed here, along with the laws it is expected to obey, then classical thermodynamics can no longer be viewed as strictly valid even for microscopically distinguishable spaces, and an exact determination of the real size of atoms becomes possible. Conversely, if the prediction of this motion were to be proved wrong, this fact would provide a weighty argument against the molecular-kinetic conception of heat.

§1. *On the osmotic pressure attributable to suspended particles*

Let z gram-molecules of a nonelectrolyte be dissolved in the partial volume V^* of a liquid of total volume V . If the volume V^* is separated from the pure solvent by a wall that is permeable to the solvent but not to the dissolved substance, then this wall is subjected to the so-called osmotic pressure, which at sufficiently large values of V^*/z satisfies the equation

$$pV^* = RTz.$$

But if instead of the dissolved substance, the partial volume V^* of the liquid contains small suspended bodies that likewise cannot pass through the solvent-permeable wall, then according to the classical theory of thermodynamics we should not expect—at least if we neglect the force of gravity, which does not interest us here—that a force be exerted on the wall; because according to the customary conception, the "free energy" of the system does not seem to depend on the position of the wall and of the suspended bodies, but only on the total masses and properties of the suspended substance, the liquid, and the wall, as well as on the pressure and temperature. To be sure, the energy and entropy of the interfaces (capillary forces) should also be considered in the calculation of the free energy; but we can disregard them since the changes in the position of the wall and the suspended bodies considered here shall proceed without changes in the size and condition of the contact surfaces.

But from the standpoint of the molecular-kinetic theory of heat we are led to a different conception. According to this theory, a dissolved molecule differs from a suspended body in size *alone*, and it is difficult to see why suspended bodies should not produce the same osmotic pressure as an equal number of dissolved molecules. We will have to assume that the suspended bodies perform an irregular, even though very slow, motion in the liquid due to the liquid's molecular motion; if prevented by the wall from leaving the volume V^* , they will exert forces upon the wall exactly as dissolved molecules do. Thus, if n suspended bodies are present in the volume V^* , i.e., $n/V = \nu$ in the unit volume, and if the separation between neighboring bodies is sufficiently large, there will correspond to them an osmotic pressure p of magnitude

$$p = \frac{RT}{V^*} \frac{n}{N} = \frac{RT}{N} \cdot \nu,$$

where N denotes the number of true molecules per gram-molecule. It shall be shown in the next section that the molecular-kinetic theory of heat does indeed lead to this broader conception of osmotic pressure.

§2. *Osmotic pressure from the standpoint of the
molecular-kinetic theory of heat*¹

If $p_1 p_2 \dots p_\ell$ are state variables of a physical system that determine completely the system's instantaneous state (e.g., the coordinates and velocity components of all the atoms of the system), and if the complete system of the equations of change of these variables is given in the form

$$\frac{\partial p_\nu}{\partial t} = \varphi_\nu(p_1 \dots p_\ell) \quad (\nu = 1, 2, \dots, \ell),$$

where $\sum \frac{\partial \varphi_\nu}{\partial p_\nu} = 0$, then the entropy of the system is given by the expression

$$S = \frac{\bar{E}}{T} + 2\kappa \lg \int e^{-\frac{E}{2\kappa T}} dp_1 \dots dp_\ell.$$

Here T denotes the absolute temperature, \bar{E} the energy of the physical system, and E the energy as a function of the p_ν 's. The integral is to be extended over all combinations of values of p_ν consistent with the conditions of the problem. κ is connected with the constant N mentioned above by the relation $2\kappa N = R$. We therefore get for the free energy F

$$F = -\frac{R}{N} T \lg \int e^{-\frac{EN}{RT}} dp_1 \dots dp_\ell = -\frac{RT}{N} \lg B.$$

Let us now imagine a liquid enclosed in the volume V ; let the partial volume V^* of V contain n dissociated molecules or suspended bodies, which are retained in the volume V^* by a semipermeable wall; this will affect the integration limits of the integral B entering the expressions for S and F . Let the total volume of the dissolved molecules or suspended bodies

¹In this section it is assumed that the reader is familiar with the author's papers on the foundations of thermodynamics (cf. *Ann. d. Phys.* 9 (1902): 417 and 11 (1903): 120). Knowledge of the papers cited and of this section of the present paper is not essential for the understanding of the present paper's results.

be small compared with V^* . In accordance with the theory mentioned, this system shall be completely described by the state variables $p_1 \dots p_\ell$.

Even if the molecular picture were established down to the smallest detail, the calculation of the integral B would be so difficult as to make an exact calculation of F all but inconceivable. However, here we only have to know how F depends on the size of the volume V^* in which all the dissolved molecules or suspended bodies (hereafter briefly called "particles") are contained.

Let us denote by x_1, y_1, z_1 the rectangular coordinates of the center of gravity of the first particle, by x_2, y_2, z_2 those of the second, etc., and by x_n, y_n, z_n those of the last particle, and assign to the centers of gravity of the particles the infinitesimally small parallelepiped-shaped regions $dx_1 dy_1 dz_1, dx_2 dy_2 dz_2 \dots dx_n dy_n dz_n$, all of which shall lie in V^* . We now seek the value of the integral occurring in the expression for F , with the restriction that the centers of gravity of the particles shall lie in the regions just assigned to them. In any case, this integral can be put into the form

$$dB = dx_1 dy_1 \dots dz_n \cdot J,$$

where J is independent of $dx_1 dy_1$, etc., as well as of V^* , i.e., of the position of the semipermeable wall. But J is also independent of the particular choice of the *positions* of the center-of-gravity regions and of the value of V^* , as we will show immediately. For if a second system of infinitesimally small regions were assigned to the centers of gravity of the particles and denoted by $dx'_1 dy'_1 dz'_1, dx'_2 dy'_2 dz'_2 \dots dx'_n dy'_n dz'_n$, and if these regions differed from the originally assigned ones by their position alone, but not by their size, and if, likewise, all of them were contained in V^* , we would similarly have

$$dB' = dx'_1 dy'_1 \dots dz'_n \cdot J',$$

where

$$dx_1 dy_1 \dots dz_n = dx'_1 dy'_1 \dots dz'_n.$$

Hence,

$$\frac{dB}{dB'} = \frac{J}{J'}.$$

But from the molecular theory of heat, presented in the papers cited¹, it can easily be deduced that dB/B and dB'/B are equal to the probabilities that at an arbitrarily chosen moment the centers of gravity of the particles will be found in the regions $(dx_1 \dots dz_n)$ and $(dx'_1 \dots dz'_n)$, respectively. If the motions of the individual particles are (in sufficient approximation) independent of each other, and the liquid is homogeneous and no forces act upon the particles, then the probabilities corresponding to the two systems of regions must be the same if the size of the regions is the same, so that we have

$$\frac{dB}{B} = \frac{dB'}{B}.$$

But it follows from this equation and the one preceding it that

$$J = J'.$$

This proves that J does not depend on either V^* or $x_1, y_1 \dots z_n$. Integrating, we get

$$B = \int J dx_1 \dots dz_n = J V^{*n},$$

and from that

$$F = - \frac{RT}{N} \{ \lg J + n \lg V^* \}$$

and

$$p = - \frac{\partial F}{\partial V^*} = \frac{RT}{V^*} \frac{n}{N} = \frac{RT}{N} \nu.$$

This consideration demonstrates that the existence of osmotic pressure is a consequence of the molecular-kinetic theory of heat, and that, according to this theory, at great dilutions numerically equal quantities of dissolved molecules and suspended particles behave completely identically with regard to osmotic pressure.

¹A. Einstein, *Ann. d. Phys.* 11 (1903): 170.

§3. *Theory of diffusion of small suspended spheres*

Suppose that suspended particles are randomly distributed in a liquid. We wish to investigate their state of dynamic equilibrium under the assumption that a force K , which depends on the position but not on the time, acts on the individual particles. For the sake of simplicity, we will assume that the force is everywhere in the direction of the X -axis.

If the number of suspended particles per unit volume is ν , then in the case of thermodynamic equilibrium ν is such a function of x that the variation of the free energy vanishes for an arbitrary virtual displacement δx of the suspended substance. Thus

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

Let us assume that the liquid has a cross section 1 perpendicular to the X -axis, and that it is bounded by the planes $x = 0$ and $x = \ell$. We then have

$$\delta E = - \int_0^\ell K\nu\delta x dx$$

and

$$\delta S = \int_0^\ell R \frac{\nu}{N} \frac{\partial \delta x}{\partial x} dx = - \frac{R}{N} \int_0^\ell \frac{\partial \nu}{\partial x} \delta x dx.$$

Hence, the equilibrium condition sought is

$$(1) \quad -K\nu + \frac{RT}{N} \frac{\partial \nu}{\partial x} = 0$$

or

$$K\nu - \frac{\partial p}{\partial x} = 0.$$

The last equation states that the force K is balanced by the forces of osmotic pressure.

We use equation (1) to determine the coefficient of diffusion of the suspended substance. The state of dynamic equilibrium that we have just considered can be conceived as a superposition of two processes proceeding in opposite directions, namely,

1. a motion of the suspended substance under the influence of the force K which is exerted on each suspended particle,

2. a process of diffusion, which is to be conceived as the result of the random motions of the particles due to thermal molecular motion.

If the suspended particles are of spherical shape (where P is the radius of the sphere) and the coefficient of friction of the liquid is k , then the force K imparts to the individual particle the velocity¹

$$\frac{K}{6\pi k P} ,$$

and

$$\frac{\nu K}{6\pi k P}$$

particles pass through the unit cross section per unit time.

Further, if D denotes the coefficient of diffusion of the suspended substance and μ the mass of a particle, then

$$-D \frac{\partial(\mu\nu)}{\partial x} \text{ gram}$$

or

$$-D \frac{\partial\nu}{\partial x}$$

particles will pass through the unit cross section per unit time due to diffusion. Since there should be dynamic equilibrium, we must have

$$(2) \quad \frac{\nu K}{6\pi k P} - D \frac{\partial\nu}{\partial x} = 0.$$

From the two conditions (1) and (2) found for dynamic equilibrium we can calculate the coefficient of diffusion. We obtain

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi k P} .$$

¹Cf., e.g., G. Kirchhoff, "*Vorlesungen über Mechanik*" [Lectures on Mechanics], Lecture 26, §4.

Thus, apart from universal constants and the absolute temperature, the coefficient of diffusion of the suspended substance depends only on the coefficient of friction of the liquid and the size of the suspended particles.

§4. *On the random motion of particles suspended in a liquid
and their relation to diffusion*

We shall now turn to a closer examination of the random motions which, caused by thermal molecular motion, give rise to the diffusion investigated in the last section.

Obviously, we must assume that each individual particle performs a motion that is independent of the motions of all the other particles; similarly, the motions of one and the same particle in different time intervals will have to be conceived as mutually independent processes so long as we think of these time intervals as chosen not to be too small.

We now introduce into the consideration a time interval τ , which shall be very small compared with observable time intervals but still so large that the motions performed by a particle during two consecutive time intervals τ may be considered as mutually independent events.

Suppose, now, that a total of n particles is present in a liquid. In a time interval τ , the X -coordinates of the individual particles will increase by Δ , where Δ has a different (positive or negative) value for each particle. A certain frequency law will hold for Δ : the number dn of particles experiencing a displacement lying between Δ and $\Delta + d\Delta$ in the time interval τ will be expressed by an equation of the form

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

where

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

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

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

Now we investigate how the coefficient of diffusion depends on φ , restricting ourselves again to the case that the number ν of particles per unit volume depends only on x and t .

Let $\nu = f(x, t)$ be the number of particles per unit volume; we then calculate the distribution of the particles at time $t + \tau$ from their distribution at time t . From the definition of the function $\varphi(\Delta)$ we can easily obtain the number of particles found at time $t + \tau$ between two planes perpendicular to the X -axis with abscissas x and $x + dx$. We obtain

$$f(x, t + \tau) dx = dx \cdot \int_{\Delta=-\infty}^{\Delta=+\infty} f(x + \Delta) \varphi(\Delta) d\Delta.$$

But since τ is very small, we can put

$$f(x, t + \tau) = f(x, t) + \tau \frac{\partial f}{\partial t}.$$

Further, we expand $f(x + \Delta, t)$ in powers of Δ :

$$f(x + \Delta, t) = f(x, t) + \Delta \frac{\partial f(x, t)}{\partial x} + \frac{\Delta^2}{2!} \frac{\partial^2 f(x, t)}{\partial x^2} \dots \text{ad inf.}$$

We can perform this expansion under the integral since only very small values of Δ contribute anything to the latter. We obtain

$$f + \frac{\partial f}{\partial t} \cdot \tau = f \cdot \int_{-\infty}^{+\infty} \varphi(\Delta) d\Delta + \frac{\partial f}{\partial x} \int_{-\infty}^{+\infty} \Delta \varphi(\Delta) d\Delta + \frac{\partial^2 f}{\partial x^2} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2} \varphi(\Delta) d\Delta \dots$$

On the right-hand side, the second, fourth, etc., terms vanish since $\varphi(x) = \varphi(-x)$, while among the first, third, fifth, etc., terms, each subsequent term is very small compared with the one preceding it. From this equation we get, by taking into account that

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

putting

$$\frac{1}{\tau} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2} \varphi(\Delta) d\Delta = D,$$

and only considering the first and third term of the right-hand side:

$$(1) \quad \frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}.$$

This is the familiar differential equation for diffusion, and D can be recognized as the diffusion coefficient.

Another important consideration can be linked to this development. We assumed that all the individual particles are referred to the same coordinate system. However, this is not necessary since the motions of the individual particles are mutually independent. We will now refer the motion of each particle to a coordinate system whose origin coincides at time $t = 0$ with the position of the center of gravity of the particle in question, with the difference that $f(x, t)dx$ now denotes the number of particles whose X -coordinate has *increased* between the times $t = 0$ and $t = t$ by a quantity lying between x and $x + dx$. Thus, the function f varies according to equation (1) in this case as well. Further, it is obvious that for $x \geq 0$ and $t = 0$ we must have

$$f(x, t) = 0 \quad \text{and} \quad \int_{-\infty}^{+\infty} f(x, t) dx = n.$$

The problem, which coincides with the problem of diffusion from one point (neglecting the interaction between the diffusing particles), is now completely determined mathematically; its solution is

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

The frequency distribution of the changes of position occurring in the arbitrary time t is thus the same as the distribution of random errors, which was to be expected. What is of importance, however, is how the constant in the exponent is related to the coefficient of diffusion. With the help of this equation we now calculate the displacement λ_x in the direction of the X -axis that a particle experiences on the average, or, to be more precise, the

square root of the arithmetic mean of the squares of displacements in the direction of the X -axis; we get

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

The mean displacement is thus proportional to the square root of time. It can easily be shown that the square root of the mean of the squares of the *total displacements* of the particles has the value $\lambda_x\sqrt{3}$.

§5. *Formula for the mean displacement of suspended particles.*

A new method of determining the true size of atoms

In §3 we found the following value for the coefficient of diffusion D of a substance suspended in a liquid in the form of small spheres of radius P :

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

Further, we found in §4 that the mean value of the displacements of the particles in the direction of the X -axis in time t equals

$$\lambda_x = \sqrt{2Dt}.$$

Eliminating D , we get

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

This equation shows how λ_x must depend on T , k , and P .

We now wish to calculate the magnitude of λ_x for one second if N is taken to be $6 \cdot 10^{23}$ in accordance with the results of the kinetic theory of gases; water at 17°C ($k = 1.35 \cdot 10^{-2}$) shall be chosen as the liquid, and the diameter of the particles shall be 0.001 mm. We obtain

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

Thus, the mean displacement in 1 min. would be about 6 microns.

Conversely, the relation found can be used for the determination of N .
We obtain

$$N = \frac{t}{\lambda_x^2} \cdot \frac{RT}{3\pi kP}.$$

Let us hope that a researcher will soon succeed in solving the problem posed here, which is of such importance in the theory of heat!

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