On the Motion of Small Particles Suspended in Liquids at Rest Required by the Molecular-Kinetic Theory of Heat[*]

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[*]Originally published in *Annalen der Physik* 17 [1905]: 549-560

IN THIS PAPER it will be shown that, according to the molecular-kinetic theory of heat, bodies of a microscopically visible size suspended in liquids must, as a result of thermal molecular motions, perform motions of such magnitude that they can be easily observed with a microscope. It is possible that the motions to be discussed here are identical with so-called Brownian molecular motion; however, the data available to me on the latter are so imprecise that I could not form a judgment on the question. If the motion to be discussed here can actually be observed, together with the laws it is expected to obey, then classical thermodynamics can no longer be viewed as applying to regions that can be distinguished even with a microscope, and an exact determination of actual atomic sizes becomes possible. On the other hand, if the prediction of this motion were to be proved wrong, this fact would provide a far-reaching argument against the molecular-kinetic conception of heat.

1 On the Osmotic Pressure to be Ascribed to Suspended Particles

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

$$pV^* = RTz. \tag{1}$$

But if instead of the solute, the partial volume V^* of the liquid contains small suspended bodies that also 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–any pressure to be exerted on the wall; for according to the usual interpretation, 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 mass 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 when calculating the free energy; but we can disregard them here because changes in the position of the wall and suspended bodies will not cause changes in the size and state of the contact surfaces.

But a different interpretation arises from the standpoint of the molecular-kinetic theory of heat. According to this theory, a dissolved molecule differs from a suspended body only in size, and it is difficult to see why suspended bodies should not produce the same osmotic pressure as an equal number of dissolved molecules. We have to assume that the suspended bodies perform an irregular, albeit 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 pressure upon the wall just like molecules in solution. Thus, if n suspended bodies are present in the volume V^*, i.e., $n/V^* = \nu$ in a unit volume, and

if neighboring bodies are sufficiently far separated from each other, there will be a corresponding osmotic pressure p of magnitude

$$p = \frac{RT}{V^*}\frac{n}{N} = \frac{RT}{N} \cdot \nu, \tag{2}$$

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

2   Osmotic Pressure from the Standpoint of the Molecular-Kinetic Theory of Heat [1]

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

$$\frac{\partial p_\nu}{\partial t} = \varphi_\nu(p_1 \ldots p_l) \ \ (\nu = 1, 2, \ldots l), \tag{3}$$

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

$$S = \frac{\bar{E}}{T} + 2\kappa \ln \int e^{-\frac{E}{2\kappa T}} dp_1 \ldots dp_l. \tag{4}$$

Here T denotes the absolute temperature, $\bar{E}$ the energy of the system, and E the energy as a function of the p_ν. The integral extends over all possible values of p_ν consistent with the conditions of the problem. κ is connected with the constant N mentioned above by the relation $2\kappa N = R$. Hence we get for the free energy F

$$F = -\frac{R}{N}T \ln \int e^{-\frac{EN}{RT}} dp_1 \ldots dp_l = -\frac{RT}{N} \ln B. \tag{5}$$

Let us now imagine a liquid enclosed in volume V; let a part V^* of the volume V contain n solute molecules or suspended bodies, which are retained in the volume V^* by a semipermeable wall; the integration limits of the integral R occurring in the expressions for S and F will be affected accordingly. Let the total volume of the solute molecules or suspended bodies be small compared with V^*. In accordance with the theory mentioned, let this system be completely described by the variables $p_1 \ldots p_l$.

Even if the molecular picture were extended to include all details, the calculation of the integral B would he so difficult that an exact calculation of F is hardly conceivable. However, here we only need to know how F depends on the size of the volume V^* in which all the solute molecules or suspended bodies (hereafter called "particles" for brevity) are contained.

Let us call the rectangular coordinates of the center of gravity of the first particle x_1, y_1, z_1, those of the second x_2, y_2, z_2, etc., and those of the last particle x_n, y_n, z_n, and assign to the centers of gravity of the particles the infinitesimally small parallelepiped regions $dx_1 dy_1 dz_1, dx_2 dy_2 dz_2 \ldots dx_n dy_n dz_n$, all of which lie in V^*. We want to evaluate 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

$$dB = dx_1 dy_1 \ldots dz_n \cdot J, \tag{6}$$

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[1]In 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]: 170). Knowledge of these Papers and of this section of the present paper is not essential for an understanding of the results in the present paper.

where J is independent of $dx_1 dy_1$, etc., as well as of V^*, i.e., of the position of the semiperme-able 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 will be shown immediately. For if a second system of infinitesimally small regions were assigned to the centers of gravity of the particles and denoted by $dx_1' dy_1' dz_1', dx_2' dy_2' dz_2' \ldots dx_n' dy_n' dz_n'$, 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

$$dB' = dx_1' dy_1' \ldots dz_n' \cdot J', \tag{7}$$

where

$$dx_1 dy_1 \ldots dz_n = dx_1' dy_1' \ldots dz_n'. \tag{8}$$

Hence,

$$\frac{dB}{dB'} = \frac{J}{J'}. \tag{9}$$

But from the molecular theory of heat, as presented in the papers cited,[2] it is easily deduced that dB/B and dB'/B are respectively equal to the probabilities that at an arbitrarily chosen moment the centers of gravity of the particles will be found in the regions $(dx_1 \ldots dz_n)$ and $(dx_1' \ldots dz_n')$ respectively. If the motions of the individual particles are independent of one another (to a sufficient approximation) and if the liquid is homogeneous and no forces act on the particles, then for regions of the same size the probabilities of the two systems of regions will be equal, so that

$$\frac{dB}{B} = \frac{dB'}{B}. \tag{10}$$

But from this equation and the previous one it follows that

$$J = J'. \tag{11}$$

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

$$B = \int J dx_l \ldots dz_n = J V^{*n}, \tag{12}$$

and hence

$$F = -\frac{RT}{N} \{ \ln J + n \ln V^* \} \tag{13}$$

and

$$p = -\frac{\partial F}{\partial V^*} = \frac{RT}{V^*} \frac{n}{N} = \frac{RT}{N} \nu. \tag{14}$$

This analysis shows that the existence of osmotic pressure can be deduced from the molecular-kinetic theory of heat, and that, at high dilution, according to this theory, equal numbers of solute molecules and suspended particles behave identically as regards osmotic pressure.

3   Theory of Diffusion of Small Suspended Spheres

Suppose suspended particles are randomly distributed in a liquid. We will 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 shall assume that the force acts everywhere in the direction of the X-axis.

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[2]A. Einstein, *Ann. d. Phys.* 11 (1903): 170.

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

$$\delta F = \delta E - T\,\delta S = 0. \tag{15}$$

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

$$\delta E = -\int_0^l K\nu\,\delta x\,dx \tag{16}$$

and

$$\delta S = \int_0^l R\frac{\nu}{N}\frac{\partial \delta x}{\partial x}dx = -\frac{R}{N}\int_0^l \frac{\partial \nu}{\partial x}\delta x dx. \tag{17}$$

The required equilibrium condition is therefore

$$-K\nu + \frac{RT}{N}\frac{\partial \nu}{\partial x} = 0 \tag{18}$$

or

$$K\nu - \frac{\partial p}{\partial x} = 0. \tag{19}$$

The last equation asserts that the force K is equilibrated by the force of osmotic pressure.

We can use equation (18) to determine the diffusion coefficient of the suspended substance. We can look upon the dynamic equilibrium state considered here 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 that acts on each suspended particle.

2. A process of diffusion, which is to be regarded as the result of the disordered motions of the particles produced by thermal molecular motion.

If the suspended particles have spherical form (where P is the radius of the sphere) and the coefficient of viscosity of the liquid is k, then the force K imparts to an individual particle the velocity[3]

$$\frac{K}{6\pi kP}, \tag{20}$$

and

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

particles will pass through a unit area per unit time.

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

$$-D\frac{\partial(\mu\nu)}{\partial x} \text{ grams} \tag{21}$$

or

$$-D\frac{\partial \nu}{\partial x} \tag{22}$$

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[3]Cf., e.g., G. Kirchhoff, *Vorlesungen uber Mechanik*, 26. Vorl., 4 (*Lectures on Mechanics*, Lecture 26, sec. 4).

particles will pass across a unit area per unit time as the result of diffusion. Since dynamic equilibrium prevails, we must have

$$\frac{\nu K}{6\pi k P} - D\frac{\partial \nu}{\partial x} = 0. \tag{23}$$

From the two conditions (18) and (23) found for dynamic equilibrium, we can calculate the diffusion coefficient. We get

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi k P}. \tag{24}$$

Thus, except for universal constants and the absolute temperature, the diffusion coefficient of the suspended substance depends only on the viscosity of the liquid and on the size of the suspended particles.

4   On the Disordered Motion of Particles Suspended in a Liquid and its Relation to Diffusion

We shall now turn to a closer examination of the disordered motions that arise from thermal molecular motion and give rise to the diffusion investigated in the last section.

Obviously, we must assume that each individual particle executes a motion that is independent of the motions of all the other particles; the motions of the same particle in different time intervals must also be considered as mutually independent processes, so long as we think of these time intervals as chosen not to be too small.

We now introduce a time interval τ, which is very small compared with observable time intervals but still large enough that the notions performed by a particle during two consecutive time intervals τ can be considered as mutually independent events.

Suppose, now, that a total of n suspended 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 probability distribution law will hold for Δ: the number dn of particles experiencing a displacement that lies between Δ and $\Delta + d\Delta$ in the time interval τ will be expressed by an equation of the form

$$dn = n\varphi(\Delta)d\Delta, \tag{25}$$

where

$$\int_{-\infty}^{+\infty} \varphi(\Delta)d\Delta = 1, \tag{26}$$

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

$$\varphi(\Delta) = \varphi(-\Delta). \tag{27}$$

We will now investigate how the diffusion coefficient depends on φ, restricting ourselves again to the ease where the number ν of particles per unit volume only depends on x and t.

Let $\nu = f(x,t)$ be the number of particles per unit volume; we calculate the distribution of 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 $x + dx$. One obtains

$$f(x, t+\tau)dx = dx \cdot \int_{\Delta=-\infty}^{\Delta=+\infty} f(x+\Delta)\varphi(\Delta)d\Delta. \tag{28}$$

But since τ is very small, we can put

$$f(x, t + \tau) = f(x, t) + \tau \frac{\partial f}{\partial t}. \tag{29}$$

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

$$f(x + \Delta, t) = f(x, t) + \Delta \frac{\partial f(x, t)}{\partial x} + \frac{\Delta^2}{2!} \frac{\partial^2 f(x, t)}{\partial x^2} \dots \text{ad inf.} \tag{30}$$

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

$$f + \frac{\partial f}{\partial t} \cdot \tau = f \cdot \int_{-\infty}^{+\infty} \varphi(\Delta) d\Delta + \frac{\partial f}{\partial x} \int_{-\infty}^{+\infty} \Delta \varphi(\Delta) d\Delta + \frac{\partial^2 f}{\partial x^2} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2} \varphi(\Delta) d\Delta \dots \tag{31}$$

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

$$\int_{-\infty}^{+\infty} \varphi(\Delta) d\Delta = 1, \tag{32}$$

and putting

$$\frac{1}{\tau} \int_{-\infty}^{+\infty} \frac{\Delta^2}{2} \varphi(\Delta) d\Delta = D, \tag{33}$$

and taking into account only the first and third terms of the right-hand side, we get

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}. \tag{34}$$

This is the well-known differential equation for diffusion, and we recognize that D is the diffusion coefficient.

Another important point can be linked to this argument. We have assumed that the individual particles are all 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 with the position of the center of gravity of the particle in question at time $t = 0$, 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 that lies somewhere between x and $x + dx$. Thus, the function f varies according to equation (23) in this case as well. Further, it is obvious that for $x \neq 0$ and $t = 0$ we must have

$$f(x, t) = 0 \quad \text{and} \quad \int_{-\infty}^{+\infty} f(x, t) dx = n. \tag{35}$$

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

$$f(x, t) = \frac{n}{\sqrt{4\pi D}} \frac{e^{-\frac{x^2}{4Dt}}}{\sqrt{t}}. \tag{36}$$

The probability distribution of the resulting displacements during an arbitrary time t is thus the same as the distribution of random errors, which was to be expected. What is important, however, is how the constant in the exponent is related to the diffusion coefficient. With the help

of this equation we can 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 root-mean-square displacement in the X-direction; it is

$$\lambda_x = \sqrt{\overline{x^2}} = \sqrt{2Dt}. \tag{37}$$

The mean displacement is thus proportional to the square root of the time. It can easily be shown that the root-mean-square 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 Actual Size of Atoms

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

$$D = \frac{RT}{N} \frac{1}{6\pi kP}. \tag{38}$$

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

$$\lambda_x = \sqrt{2Dt}. \tag{39}$$

By eliminating D, we get:

$$\lambda_x = \sqrt{t} \cdot \sqrt{\frac{RT}{N} \frac{1}{3\pi kP}}. \tag{40}$$

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

We will now calculate how large λ_x is 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^oC ($k = 1.35 \cdot 10^{-2}$) is chosen as the liquid, and the diameter of the particles is 0.001 mm. We get

$$\lambda_x = 8 \cdot 10^{-5} \text{ cm } = 0.8 \text{ micron}. \tag{41}$$

Therefore, the mean displacement in one minute would be about 6 microns.

Conversely the relation can be used to determine N. We obtain

$$N = \frac{t}{\lambda_x^2} \cdot \frac{RT}{3\pi kP}. \tag{42}$$

Let us hope that a researcher will soon succeed in solving the problem presented here, which is so important for the theory of heat.