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ON THE THEORY OF THE BROWNIAN MOTION

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Abstract

With a method first indicated by Ornstein the mean values of *all* the powers of the velocity u and the displacement s of a free particle in Brownian motion are calculated. It is shown that $u-u_0\exp(-\beta t)$ and $s-u_0/\beta[1-\exp(-\beta t)]$ where u_0 is the initial velocity and β the friction coefficient divided by the mass of the particle, follow the normal Gaussian distribution law. For s this gives the exact frequency distribution corresponding to the exact formula for $\overline{s^2}$ of Ornstein and Fürth. Discussion is given of the connection with the Fokker-Planck partial differential equation. By the same method exact expressions are obtained for the square of the deviation of a harmonically bound particle in Brownian motion as a function of the time and the initial deviation. Here the periodic, aperiodic and overdamped cases have to be treated separately. In the last case, when β is much larger than the frequency and for values of $t\gg\beta^{-1}$, the formula takes the form of that previously given by Smoluchowski.

I. General Assumptions and Summary

In the theory of the Brownian motion the first concern has always been the calculation of the mean square value of the displacement of the particle, because this could be immediately observed. As is well known, this problem was first solved by Einstein[1] in the case of a *free* particle. He obtained the famous formula:

$$\overline{s^2} = 2Dt = \frac{2kT}{f}t \tag{1}$$

where f is the friction coefficient, T the absolute temperature and t the time. The influence of the surrounding medium is characterized by f as well as by T. For this Einstein used the formula of Stokes, because almost always the particle is immersed in a liquid or gas at ordinary pressure. In that case the mean free path of the molecules is small compared with the particle, and we may consider the surrounding medium as continuous and may use the results hydrodynamics gives for the friction coefficient for bodies of simple form (sphere, ellipsoid etc.). This will depend on the viscosity coefficient of the medium and therefore be *independent* of the pressure.

But of course, when the surrounding medium is a rarefied gas (mean free path of the molecules great in comparison with the particle), the friction

[1] A. Einstein, Ann. d. Physik **17**, 549 (1905). This and the further articles of Einstein have been collected in a book called: "Investigations on the theory of the Brownian Movement". Edited by R. Fürth, translated by A. D. Cowper. New York, Dutton. To this we shall always refer.

will change in character. Instead of a Stokes friction, we then get what we may call a Doppler friction and this can also be calculated for simple forms of the particle. It is based on the fact that a particle moving, say to the right, will be hit by more molecules from the right than from the left. This friction coefficient will be proportional to the pressure. To cover all cases, we will always leave the friction coefficient explicitly in the formulas.

The basis of formula (1), which since Einstein has been derived in various other ways,[2] has been almost always the equation of motion:

$$m\frac{du}{dt} = - fu + F(t) \tag{2}$$

where u is the velocity of the particle. Characteristically of this equation, the influence of the surrounding medium is split into two parts:
(1) a systematic part $-fu$, which causes the friction
(2) a fluctuating part $F(t)$. Concerning this we will naturally make the following assumptions:

A: The mean of $F(t)$, at given t, over an ensemble of particles (a large number of similar, but independent particles), which have started at $t=0$, with the same velocity u_0, is zero. We will denote this by:

$$\overline{F(t)}^{u_0} = 0. \tag{3}$$

B: There will be correlation between the values of $F(t)$ at different times t_1 and t_2 only when $|t_1-t_2|$ is very small. More explicitly we shall suppose that:

$$\overline{F(t_1)F(t_2)}^{u_0} = \phi_1(t_1 - t_2) \tag{4}$$

where $\phi_1(x)$ is a function with a very sharp maximum at $x=0$. More generally, when $t_1, t_2 \ldots . t_{n+1}$ are all lying very near each other, we assume:

$$\overline{F(t_1)F(t_2)\cdots F(t_{n+1})}^{u_0} = \phi_n(r, \theta_1, \theta_2 \cdots \theta_{n-1}) \tag{5}$$

where r is the distance perpendicular to the line $t_1=t_2= \ldots . =t_{n+1}$ in the $(n+1)$ dimensional $(t_1, t_2 \ldots . t_{n+1})$ space, and $\theta_1, \theta_2 \ldots . \theta_{n-1}$ are $(n-1)$ angles to determine the position of r in the subspace perpendicular to this line. The function ϕ_n has again a very sharp maximum for $r=0$. Further, when $t_1, t_2 \ldots . t_k$ are lying near each other, and also $t_{k+1}, t_{k+2} \ldots . t_l$ but far from the group $t_1, t_2 \ldots . t_k$ and so on, then:

$$\overline{F(t_1)\cdots F(t_k)F(t_{k+1})\cdots F(t_l)F(t_{l+1})\cdots F(t_m)\cdots}^{u_0}$$
$$= \overline{F(t_1)\cdots F(t_k)}^{u_0}\cdot\overline{F(t_{k+1})\cdots F(t_l)}^{u_0}\cdot\overline{F(t_{l+1})\cdots F(t_m)}^{u_0}\cdots \tag{6}$$

The justification, or eventually the criticism, of these assumptions must come from a more precise, kinetic, theory. We will not go into that.

[2] Compare G. L. de Haas-Lorentz: Die Brownsche Bewegung (Braunschweig, Vieweg, 1913).

§3. In the later development, especially when given outside forces like gravitation were also considered, so that (2) had to be replaced by:

$$m\frac{du}{dt} = - fu + F(t) + K(x) \tag{2a}$$

the attention was fixed more on the determination of the frequency distribution of quantities like the displacement or the velocity. Given the value ϕ_0 of the quantity ϕ at $t=0$, we wish to find the probability $F(\phi_0, \phi, t)d\phi$ that after the time t the value lies between ϕ and $\phi+d\phi$. It is clear, that when we know $F(\phi_0, \phi,t)$ *all* mean values are determined. For instance:

$$\overline{\phi^k}^{\phi_0} = \int \phi^k F(\phi_0, \phi, t)d\phi.$$

The frequency distribution is the most general thing the theory can predict. In the case of a free particle, the function $F(x_0, x, t)$, which will now depend only on $x-x_0=s$, was already determined by Einstein. He found:

$$F(x_0, x, t) = \left(\frac{1}{4\pi Dt}\right)^{1/2} e^{-(x-x_0)^2/4Dt} \tag{7}$$

of which (1) is an immediate consequence. He derived this, by finding for F a partial differential equation, which in this case is the *diffusion equation:*

$$\frac{\partial z}{\partial t} = D\frac{\partial^2 z}{\partial s^2} \tag{8}$$

and of which $F(x_0, x, t)$ is then the so-called fundamental solution. This is that solution of (8) which for $t=0$ becomes $\delta(x-x_0)$, when $\delta(x)$ means the function, defined by the properties:

$$\delta(x) = 0 \quad \text{for} \quad x \neq 0$$

$$\int_{-\infty}^{+\infty} \delta(x)dx = 1$$

This is clear from the definition of $F(x_0, x, t)$ because for $t=0$, there is certainty that $x=x_0$. Further there are boundary conditions, which express the behavior of the particle at the walls; in the case of a completely free particle they are simply $F=0$ for $x=\pm\infty$. The relation between the diffusion coefficient D and the friction coefficient f, Einstein then derived very simply, using the osmotic pressure idea.

This connection between the frequency distribution function and a partial differential equation of the parabolic type like (8), has later been generlized considerably by Smoluchowski, Fokker, Planck, Ornstein, Burger, Fürth and others.[3] The equation is generally called the Fokker-Planck equation. Especially for a particle under influence of outside forces, Smoluchowski showed that the generalization of (8) was:

$$\frac{\partial z}{\partial t} = -\frac{1}{f}\frac{\partial}{\partial x}(Kz) + D\frac{\partial^2 z}{\partial x^2} \tag{9}$$

For special forces (gravitation, elastic binding etc.) and by different boundary conditions, Smoluchowski, Fürth and others have determined the fundamental solution, and from this all sorts of mean values, which they have compared with experiments.

§4. With the results (1), (7), (8) and (9) of Einstein and Smoluchowski the problem seems completely solved. But there is one restriction, which was first stressed by Einstein. All these results hold only when t is large compared to m/f. The generalization of (1) for all times was given by Ornstein[4] and Fürth[5], independently of each other.
The result is:

$$\overline{s^2} = \frac{2mkT}{f^2}\left(\frac{f}{m}t - 1 + e^{-ft/m}\right) \tag{10}$$

For values of t large compared to m/f this becomes again Einstein's formula (1). For very short times on the other hand, we get:

$$\overline{s^2} = \frac{kT}{m}t^2 = \overline{u_0^2}t^2$$

as one would expect, because in the beginning the motion must be uniform.

The problem now arises to generalize the other results also. In part III we will do this for the frequency distribution $F(x_0, x, t)$. The result is rather complicated; for $t \gg m/f$ it goes over into (7), and (10) is an immediate consequence of it. The *method*, we used, was the momentum method. From the equation of motion (2), and using the assumptions (3) to (6), we could calculate the mean value of all the powers of

$$S = s - \frac{mu_0}{f}(1 - e^{-ft/m})$$

[3] M. v. Smoluchowski, Phys. Zeits. **17,** 557 (1916). A. Fokker, Dissertation Leiden, 1913, p. 000. M. Planck, Berl. Ber. p. 324, 1927. L. S. Ornstein, Versl. Acad. Amst. **26,** 1005 (1917). H. C. Burger, Versl. Acad. Amst; **25,** 1482 (1917); L. S. Ornstein and H. C. Burger, Versl. Acad. Amst. **27,** 1146 (1919); **28,** 183 (1919). R. Fürth, Ann. d. Physik **53,** 177 (1917). R. Fürth gives a survey in Riemann-Weber, Die Partiellen Differential-gleichungen der Mathematischen Physik (Edited by R. v. Mises and Ph. Frank, Braunschweig Vieweg 1928) Vol. II, p. 177. Comp. also the article of F. Zernike, Handbuch der Physik, Vol. III, p. 456 (Berlin, Springer, 1928).

[4] L. S. Ornstein, Versl. Acad. Amst. **26,** 1005 (1917) (=Proc. Acad. Amst. **21,** 96 (1919).

[5] R. Fürth, Zeits. f. Physik **2,** 244 (1920).

and prove that S follows the normal Gaussian distribution law. We did not succeed in generalizing the diffusion Eq. (8), and determining the distribution function by this method.

As a preparation we derive in part II the frequency distribution function $G(u_0, u, t)$ for the velocity of a free particle in Brownian motion, first with the momentum method, and then also with the Fokker-Planck equation.

This extension to short times becomes especially interesting in the case of outside periodic forces. In part IV we shall treat the problem of the Brownian motion of an elastically bound particle. By using the same method as before, we could get exact expressions for the mean square of the displacement as a function of the initial deviation and of the time. The periodic, aperiodic and overdamped cases have to be treated separately. The way in which the equipartition value is reached for $t \to \infty$ is different in the three cases. In the last case, for very strong damping and $t \gg m/f$ the formula goes over into the result of Smoluchowski, which is a consequence of the frequency distribution function following from (9).

II. The Frequency Distribution of the Velocity

§5. The problem is to determine the probability that a free particle in Brownian motion after the time t has a velocity which lies between u and $u+du$, when it started at $t=0$ with the velocity u_0.

The first method to solve the problem is by calculating all the mean values $\overline{u^k}$ for given u_0. As has first been shown by Ornstein[6] for $\bar{u}$ and $\overline{u^2}$, this is possible by integrating the equation of motion:

$$\frac{du}{dt} + \beta u = A(t)$$

when $\beta = f/m$ and $A = F/m$. Of course, the assumptions (3) to (6) hold for the fluctuating acceleration $A(\mathrm{t})$, as well as for the fluctuating force $F(\mathrm{t})$. Integrating we get:

$$u = u_0 e^{-\beta t} + e^{-\beta t} \int_0^t e^{\beta \xi} A(\xi) d\xi. \tag{11}$$

Taking the mean over an ensemble of particles, which have started at $t=0$ with the same velocity u_0, and using (3) we get:

$$\bar{u}^{u_0} = u_0 e^{-\beta t}. \tag{12}$$

The mean velocity goes down exponentially due to the friction. Squaring (11) and taking the mean, gives:

$$\overline{u^2}^{u_0} = u_0^2 e^{-2\beta t} + e^{-2\beta t} \int_0^t \int_0^t e^{\beta(\xi+\eta)} \overline{A(\xi) A(\eta)} d\xi d\eta.$$

[6] L. S. Ornstein, Proc. Acad. Amst. **21**, 96 (1919).

By taking $\xi+\eta=v$, $\xi-\eta=w$ as new variables and by using (4), we can write for the integral:

$$\frac{1}{2}e^{-2\beta t}\int_0^{2t} e^{\beta v}dv\int_{-\infty}^{+\infty}\phi_1(w)dw = \frac{\tau_1}{2\beta}(1 - e^{-2\beta t})$$

because $\phi_1(w)$ is such a rapidly decreasing function, that we may integrate from $-\infty$ to $+\infty$. The value of the constant

$$\tau_1 = \int_{-\infty}^{+\infty}\phi_1(w)dw$$

we find with the help of the theorem of the equipartition of energy. For $t\rightarrow\infty$, we must have:

$$\lim_{t\rightarrow\infty}\overline{u^2}^{u_0} = \frac{\tau_1}{2\beta} = \frac{kT}{m}$$

so that:

$$\tau_1 = \frac{2\beta kT}{m}\,. \tag{13}$$

Substituting, we get:

$$\overline{u^2}^{u_0} = \frac{kT}{m} + \left(u_0^2 - \frac{kT}{m}\right)e^{-2\beta t} \tag{14}$$

which shows, how the equipartition value is reached. So we can go on. Using the assumptions (3) to (6) for $A(t)$ and the fact that we must get the equipartition values for $t\rightarrow\infty$, we will prove in Note I, that for $u-u_0\exp(-\beta t)$ the normal Gaussian distribution law holds. For the velocity itself we get, therefore, the distribution law:

$$G(u_0, u, t) = \left(\frac{m}{2\pi kT(1 - e^{-2\beta t})}\right)^{1/2}\exp\left\{\frac{m}{2kT}\frac{(u-u_0e^{-\beta t})^2}{1-e^{-\beta t}}\right\} \tag{15}$$

which shows how the Maxwell distribution is reached, when at $t=0$ all the particles started with the same velocity u_0.

§6. The second method for deriving (15) is, as we have already said, by constructing the Fokker-Planck partial differential equation for the problem, of which $G(u_0\, u, t)$ is then the fundamental solution. We will first derive the equation in general and then later specialize to our case.[7] Consider the distribution function $F(\phi_0, \phi, t)$. When t increases by Δt, ϕ will increase by a $\Delta\phi$, which will be different for every particle. Let the probability for an increase between the limits $\Delta\phi$ and $\Delta\phi+d(\Delta\phi)$ be $\psi(\Delta\phi,\phi,t)d(\Delta\phi)$. Writing $\phi'=\phi+\Delta\phi$ we have then:

$$F(\phi_0, \phi', t + \Delta t) = \int F(\phi_0, \phi' - \Delta\phi, t)\psi(\Delta\phi, \phi' - \Delta\phi, t)d(\Delta\phi) \tag{16}$$

[7] Comp. F. Zernike, Handbuch der Physik, Vol. III, p. 457.

when we may suppose that the probability of an increase $\Delta\phi$ is *independent* of the fact that for $t=0$, $\phi=\phi_0$. We now develop the integrand after powers of $\Delta\phi$:

$$F(\phi_0, \phi' - \Delta\phi, t)\psi(\Delta\phi, \phi' - \Delta\phi, t) = F(\phi_0, \phi', t)\psi(\Delta\phi, \phi', t) - \Delta\phi(F'\psi + F\psi') + \frac{\Delta\phi^2}{2}(F''\psi + 2F'\psi' + F\psi'') + \cdots$$

The resulting integrals all have simple meanings, for instance:

$$\int \psi(\Delta\phi, \phi', t)d(\Delta\phi) = 1; \quad \int \Delta\phi\psi d(\Delta\phi) = \overline{\Delta\phi}; \quad \int \Delta\phi^2\psi'' d(\Delta\phi) = \frac{\partial^2}{\partial\phi'^2}\overline{\Delta\phi^2}$$

and so on. Developing the left hand side in powers of Δt, putting:

$$\lim_{\Delta t\to 0} \frac{\overline{\Delta\phi}}{\Delta t} = f_1(\phi', t); \quad \lim_{\Delta t\to 0} \frac{\overline{\Delta\phi^2}}{\Delta t} = f_2(\phi', t) \tag{17}$$

and supposing that:

$$\lim_{\Delta t\to 0} \frac{\overline{\Delta\phi^k}}{\Delta t} = 0 \quad \text{for} \quad k > 2 \tag{18}$$

we get, when we write again ϕ for ϕ':

$$\frac{\partial F}{\partial t} = \frac{1}{2}f_2\frac{\partial^2 F}{\partial\phi^2} + \left(\frac{\partial f_2}{\partial\phi} - f_1\right)\frac{\partial F}{\partial\phi} + \left(\frac{1}{2}\frac{\partial^2 f_2}{\partial\phi^2} - \frac{\partial f_1}{\partial\phi}\right)F. \tag{19}$$

We must of course in each special case determine the functions $f_1(\phi,t)$ and $f_2(\phi,t)$ and verify the supposition (18). We always can do that, when we know the equation of motion.

Let us return now to the velocity distribution. From the equation of motion we have:

$$u' - u = \Delta u = -\beta u\Delta t + \int_t^{t+\Delta t} A(\xi)d\xi$$

Using (3), we get therefore:

$$\overline{\Delta u} = -\beta u\Delta t = -\beta u'\Delta t$$

neglecting higher powers of Δt. From this:

$$\lim_{\Delta t\to 0} \frac{\overline{\Delta u}}{\Delta t} = f_1(u') = -\beta u'.$$

In the same way, we find using (4) as before:

$$\overline{\Delta u^2} = \tau_1\Delta t$$

so that:

$$f_2(u') = \tau_1 = \frac{2\beta kT}{m} = \text{const.}$$

All the higher powers of Δu become proportional to powers of Δt higher than the first, so that (18) is satisfied. We get therefore:[8]

$$\frac{\partial G}{\partial t} = \beta\frac{\partial}{\partial u}(uG) + \frac{\tau_1}{2}\frac{\partial^2 G}{\partial u^2}\cdot \tag{20}$$

The systematic way of finding the fundamental solution of this equation is by solving the equation:

$$\frac{\partial z}{\partial t} = \beta\frac{\partial}{\partial u}(uz) + \frac{\tau_1}{2}\frac{\partial^2 z}{\partial u^2}$$

when for $t=0$, $z=f(u)$. This is an ordinary boundary value problem, which can easily be solved by the method of particular solutions. By summing the infinite series which we get, one can write the solution:

$$z(u, t) = \int_{-\infty}^{+\infty} f(u_0)G(u_0 u t)du_0$$

and G is then clearly the fundamental solution. For the details, see Note II. The result is again formula (15). One can derive the same result much more briefly when one is so clever as to substitute in (20):

$$G = (\phi)^{1/2}\exp\{-(u-u_0\chi)\phi\}$$

where ϕ and χ are functions of t only.[9] This is suggested a little by the result one ought to expect. Substituting, one sees that (18) is fulfilled, when χ and ϕ are solutions of the ordinary differential equations:

$$\frac{d\chi}{dt} = -\beta\chi$$

$$\frac{1}{\beta}\frac{d\phi}{dt} = 2\phi - 4\phi^2.$$

These can be immediately integrated, and the integration constants can be determined from the fact that for $t=0$ we must get $\delta(u-u_0)$ and for $t=\infty$ the Maxwell distribution law.

III. The Frequency Distribution of the Displacement

§7. The problem is to determine the probability that a free particle in Brownian motion which, at $t=0$ starts from $x=x_0$ with the velocity u_0 after the time t lies between x and $x+dx$. It is clear that this probability will depend only on $s=x-x_0$, and on t.

[8] This equation has been derived already by Rayleigh (Phil. Mag. **32**, 424 (1891) = Scient. Papers III, p. 473) and he gives also the fundamental solution (15). Later it has again been treated by v. Smoluchowski (Krakauer Ber. 1913, p. 418). Because Rayleigh's proof is a little artificial, and the treatment of v. Smoluchowski is not easily accessible, we thought it not superfluous to give the proof again.

[9] Comp. Lord Rayleigh, reference 8.

We will use again the momentum method, and calculate all the mean values $\overline{s^k}^{u_0}$. This goes in an analogous way as with the velocity. By integrating (11) again we find:

$$x = x_0 + \frac{u_0}{\beta}(1 - e^{-\beta t}) + \int_0^t e^{-\beta\eta}d\eta \int_0^\eta e^{\beta\xi}A(\xi)d\xi \tag{21}$$

or integrating partially:

$$s = x - x_0 = \frac{u_0}{\beta}(1 - e^{-\beta t}) - \frac{1}{\beta}e^{-\beta t}\int_0^t e^{\beta\xi}A(\xi)d\xi + \frac{1}{\beta}\int_0^t A(\xi)d\xi.$$

Taking the mean, gives:

$$\bar{s}^{u_0} = \frac{u_0}{\beta}(1 - e^{-\beta t}) \tag{22}$$

which can be interpreted as the distance travelled in the time t with the mean velocity $\bar{u} = u_0 \exp(-\beta t)$. By squaring, averaging, and calculating the double integrals in the same way as before, we get:

$$\overline{s^2}^{u_0} = \frac{\tau_1}{\beta^2}t + \frac{u_0}{\beta^2}(1 - e^{-\beta t})^2 + \frac{\tau_1}{2\beta^3}(-3 + 4e^{-\beta t} - e^{-2\beta t}) \tag{23}$$

where the constant τ_1 is known from the corresponding calculation of $\overline{u^2}^{u_0}$. This result (23) was first derived by Ornstein; for very long times t it goes over in:

$$\overline{s^2}^{u_0} = \frac{\tau_1}{\beta^2}t = \frac{2kT}{m\beta}t$$

the result of Einstein. For very short times t on the other hand, we get:

$$\bar{s}^{u_0} = u_0 t$$

$$\overline{s^2}^{u_0} = u_0^2 t^2$$

The motion is then uniform with the velocity u_0. Taking a second average over u_0, remembering that $\overline{u^2_0} = kT/m$, we get:

$$\bar{\bar{s}} = 0$$

$$\overline{\overline{s^2}} = \frac{2kT}{m\beta^2}(\beta t - 1 + e^{-\beta t})$$

which is the result quoted above (formula 10). The calculation of the higher powers goes similarly. In the result we get constants $\tau_2, \tau_3 \cdots$ which have been determined in part II in the corresponding calculation of $\overline{u^k}^{u_0}$ from the equipartition law. We can show in this way that for:

$$S = s - \frac{u_0}{\beta}(1 - e^{-\beta t})$$

again the normal Gaussian distribution law holds. For the details of the proof, see Note III. We get therefore:

$$F(x_0, x, t) = \left(\frac{m\beta^2}{2\pi kT(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t})}\right)^{1/2} \exp\left[\frac{m\beta^2}{2kT}\,\frac{\{x - x_0 - u_0(1 - e^{-\beta t})/\beta\}^2}{2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}}\right] \quad (24)$$

For large t this becomes of course the distribution law (7), already derived by Einstein. For $t \rightarrow 0$ it becomes $\delta(x - x_0)$ as it should.

§8. When we want to derive (24) in the same way as $G(u_0, u, t)$ from a partial differential equation we run into the following difficulty. According to the general Eq. (19), we have to calculate $\overline{\Delta x}$ and $\overline{\Delta x^2}$. Now it follows from the equation of motion, when the prime denotes the value of the quantities at the time $t + \Delta t$, that:

$$u' - u = -\beta(x' - x) + \int_t^{t+\Delta t} A(\xi)d\xi$$

so that:

$$-\beta(\overline{x' - x}) = -\beta\overline{\Delta x} = \overline{u'} - \overline{u} = u_0 e^{-\beta t}(e^{\beta\Delta t} - 1)$$

or:

$$\overline{\Delta x} = u_0 e^{-\beta t}\Delta t. \quad (25)$$

When one now calculates in the same way $\overline{\Delta x^2}$, then one finds that $\overline{\Delta x^2}$ becomes proportional to Δt^2, so that the function f_2 in (19) would become zero, and the differential equation would become:

$$\frac{\partial F}{\partial t} = -u_0 e^{-\beta t}\frac{\partial F}{\partial t}$$

which does not become the diffusion equation for $t \gg \beta^{-1}$. On the other hand, when we suppose $t \gg \beta^{-1}$ and Δt so large that we may apply the formula of Einstein for $\overline{\Delta x^2}$, we have:

$$\begin{aligned} \overline{\Delta x} &= 0 \\ \overline{\Delta x^2} &= 2D\Delta t \end{aligned} \quad (26)$$

and this substituted in (19), gives immediately:

$$\frac{\partial F}{dt} = D\frac{\partial^2 F}{\partial x^2}\cdot$$

It seems impossible to derive from (19) the rigorous differential equation for $F(x_0,x,t)$, which for $t \gg \beta^{-1}$ would become the diffusion equation, and of which (24) would be the fundamental solution. The reason for this, it seems to us, is that in the derivation of (19) we suppose that the change Δx in the time Δt is independent of the fact that at the time $t = 0$ the particle is at $x = x_0$ and has the velocity u_0.

IV. The Brownian Motion of a Harmonically Bound Particle

§9. We will first derive, following Ornstein[10] the equation (9) first proposed by Smoluchowski from macroscopic considerations. We have to determine again $\overline{\Delta x}$ and $\overline{\Delta x^2}$. Now, when there are external forces the equation of motion is:

$$\frac{du}{dt} + \beta u = A(t) + \frac{1}{m}K(x).$$

Integrating as in §8, we get:

$$u' - u = -\beta(x' - x) + \int_t^{t+\Delta t} A(\xi)d\xi + \frac{1}{m}K\Delta t$$

from which follows, when we may neglect the influence of the initial velocity:

$$\beta\overline{\Delta x} = \frac{1}{m}K(x)\Delta t \qquad (27)$$

so that:

$$f_1(x) = \frac{1}{\beta m}K(x) = \frac{1}{f}K(x).$$

When again Δt is not too small, we may put:

$$\overline{\Delta x^2} = \frac{2kT}{m\beta}\Delta t = 2D\Delta t \qquad (28)$$

and substituting in the general equation (19), we get:

$$\frac{\partial F}{\partial t} = -\frac{1}{f}\frac{\partial}{\partial x}(KF) + D\frac{\partial^2 F}{\partial x^2}$$

which is (9).

Let us apply this to the case of a harmonically bound particle, for which:

$$\frac{1}{m}K(x) = -\omega^2 x$$

where ω is the frequency in 2π sec. We get then:

$$\frac{\partial F}{\partial t} = \frac{\omega^2}{\beta}\frac{\partial}{\partial x}(xF) + D\frac{\partial^2 F}{\partial x^2}\cdot$$

This is completely similar to the equation (20) for $G(u_0, u, t)$. We find therefore for the fundamental solution

$$F(x_0, x, t) = \left(\frac{\omega^2}{2\pi\beta D(1 - e^{-(2\omega^2/\beta)t})}\right) \exp\left\{-\frac{\omega^2}{2\beta D}\cdot\frac{(x - x_0 e^{-(\omega^2/\beta)t})}{1 - e^{-(2\omega^2/\beta)t}}\right\}$$

[10] L. S. Ornstein, Proc. Acad. Amst. **21,** 96 (1919).

which gives:

$$\bar{x}^{x_0} = x_0 e^{-(\omega^2/\beta)t}$$

$$\overline{x^2}^{x_0} = \frac{kT}{m\omega^2} + \left(x_0^2 - \frac{kT}{m\omega^2}\right)e^{-(2\omega^2/\beta)t}.$$

This shows how the equipartition value is reached. For ω^2 very small we get approximately:

$$\bar{x}^{x_0} = x_0$$

$$\overline{x^2}^{x_0} = x_0^2 + \frac{2kT}{m\beta}t$$

which are the results for a free particle. We may not expect though, that the equations are generally valid. According to the derivation, there are clearly *two* limitations:

a. Because we have used (27) and (28) which correspond to (26) in §8, we must expect (30) to hold only for times $t \gg \beta^{-1}$

b. Because we have in (28) used the result for a *free* particle, we must expect (30) to hold only when β is large, the motion therefore being strongly overdamped. This is also the reason why apparently there is no distinction be tween the periodic, aperiodic and overdamped cases in the result for $\overline{x^2}^{x_0}$.

§10. To get exact results, we have to use the same method as before. We have first to integrate the equation of motion, and then take the average. The periodic, aperiodic and overdamped case must now be treated separately. We will indicate the calculations only for the periodic case.

The equation of motion is:

$$\frac{d^2x}{dt^2} + \beta\frac{dx}{dt} + \omega^2 x = A(t)$$

when at $t=0$, $x=x_0$ and $u=dx/dt=u_0$ we get from this:

$$u = -\frac{2\omega^2 x_0 + \beta u_0}{2\omega_1}e^{-\beta t/2}\sin\omega_1 t + u_0 e^{-(\beta/2)t}\cos\omega_1 t$$
$$+ \frac{1}{\omega_1}\int_0^t A(\xi)e^{-\beta(t-\xi)/2}\left\{-\frac{\beta}{2}\sin\omega_1(t-\xi) + \omega_1\cos\omega_1(t-\xi)\right\}d\xi$$

$$x = \frac{\beta x_0 + 2u_0}{2\omega_1}e^{-(\beta/2)t}\sin\omega_1 t + x_0 e^{-(\beta/2)t}\cos\omega_1 t + \frac{1}{\omega_1}\int_0^t A(\xi)e^{-\beta(t-\xi)/2}\sin\omega_1(t-\xi)d\xi$$

where:

$$\omega_1^2 = \omega^2 - \frac{\beta^2}{4}\cdot$$

Supposing, in correspondence with (3):

$$\overline{A(\xi)}^{x_0 u_0} = 0$$

this gives immediately, for instance:

$$\bar{x}^{x_0u_0} = \frac{\beta x_0 + 2u_0}{2\omega_1} e^{-(\beta/2)t} \sin \omega_1 t + x_0 e^{-(\beta/2)t} \cos \omega_1 t. \tag{31}$$

The mean value here has to be understood as follows. We have a canonical ensemble of harmonic oscillators, from which at $t = 0$ we pick a sub-ensemble (A) of oscillators, which have a deviation and velocity x_0, u_0, resp. and which we follow in their motion. At the time t we take an average over the x of the different members of this sub-ensemble (A), and the result is then given by (31). If we would follow a *sub-ensemble* (B), of which the members at $t = 0$ had the deviation x_0 but arbitrary velocity, we would get at the time t a mean deviation, which will follow from (31) by taking the average over u_0. Since in a canonical ensemble of oscillators the deviation is not correlated with the velocity, we may put:

$$\bar{u}_0^{x_0} = 0$$
$$\overline{u^2}^{x_0} = \frac{kT}{m}. \tag{32}$$

Uisng this, we get:

$$\bar{\bar{x}}^{x_0} = x_0 e^{(-\beta/2)t}\left(\frac{\beta}{2\omega_1} \sin \omega_1 t + \cos \omega_1 t\right). \tag{33}$$

Let us now consider u^2 and x^2. Using again the assumption analogous to (4):

$$\overline{A(t_1)A(t_2)}^{x_0u_0} = \phi(t_1 - t_2)$$

where $\phi(x)$ is an even function with a sharp maximum at $x = 0$, and calculating the double integrals exactly as before, we get:

$$\overline{x^2}^{x_0u_0} = \left(\frac{\beta x_0 + 2u_0}{2\omega_1} e^{-(\beta/2)t} \sin \omega_1 t + x_0 e^{-(\beta/2)t} \cos \omega_1 t\right)^2 + \frac{\tau_1}{2\omega_1^2\beta}(1 - e^{-\beta t})$$
$$- \frac{\tau_2}{8\omega^2\omega_1^2}(\beta - \beta e^{-\beta t} \cos 2\omega_1 t + 2\omega_1 e^{-\beta t} \sin 2\omega_1 t)$$

where we have put:

$$\tau_1 = \int_{-\infty}^{+\infty} \phi(w) \cos \omega_1 w dw$$
$$\tau_2 = \int_{-\infty}^{+\infty} \phi(w) dw.$$

The condition, that for $t \to \infty$ we must get the equipartition value, gives us one relation between τ_1 and τ_2. One would expect that from:

$$\lim_{t \to \infty} \overline{u^2}^{x_0u_0} = \frac{kT}{m}$$

we would get a second relation, but the calculation of $\overline{u^2}^{x_0u_0}$ shows that this is the same as the first. The fact that $\phi(w)$ has such a sharp maximum suggests, that in the integral for τ_1 we may replace $\cos\omega_1 w$ by unity, which would make $\tau_1=\tau_2$. We can prove this more exactly by calculating $\overline{xu}^{x_0u_0}$[11] and determining the limit for $t\rightarrow\infty$, which must be zero, because for $t\rightarrow\infty$ sub ensemble (A) must again become a canonical ensemble. We get in this way:

$$\tau_1 = \tau_2 = \frac{2\beta kT}{m}\cdot$$

This solves the problem completely. Averaging again over u_0, using (32) we get:

$$\overline{\overline{x^2}}^{x_0} = \frac{kT}{m\omega^2} + \left(x_0^2 - \frac{kT}{m\omega^2}\right)e^{-\beta t}\left(\cos\omega_1 t + \frac{\beta}{2\omega_1}\sin\omega_1 t\right)^2 \tag{34}$$

which shows how the equipartition value is reached. So we can calculate all sorts of mean values. The further result is perhaps interesting, that:

$$\overline{\overline{xu}}^{x_0} = \frac{1}{\omega_1\omega^2}\left(\frac{kT}{m\omega^2} - x_0^2\right)e^{-\beta t}\sin\omega_1 t\left(\cos\omega_1 t + \frac{\beta}{2\omega_1}\sin\omega_1 t\right)$$

which shows how the correlation between x and u, beginning with being zero, oscillates and goes to zero again for $t\rightarrow\infty$. Of course, averaging over x_0, we get $\overline{\overline{\overline{xu}}}=0$ as it must be.

§11. In the aperiodic case we get:

$$\overline{\overline{x^2}}^{x_0} = x_0\left(1 + \frac{\beta t}{2}\right)e^{-(\beta/2)t} \tag{33a}$$

$$\overline{\overline{x^2}}^{x_0} = \frac{kT}{m\omega^2} + \left(x_0^2 - \frac{kT}{m\omega^2}\right)\left(1 + \frac{\beta t}{2}\right)^2 e^{-\beta t}. \tag{34a}$$

The equipartition value is now reached monotonously. The calculation goes similarly, except that instead of the integral τ_1, we have to introduce an integral:

$$\tau_1' = \int_{-\infty}^{+\infty} w^2\phi(w)dw.$$

The calculation of $\overline{xu}^{x_0u_0}$ proves then that this is zero, which could be expected.

In the overdamped case we get:

$$\overline{\overline{x}}^{x_0} = x_0 e^{-(\beta/2)t}\left(\cosh\omega' t + \frac{\beta}{2\omega'}\sinh\omega' t\right) \tag{33b}$$

$$\overline{\overline{x^2}}^{x_0} = \frac{kT}{m\omega^2} + \left(x_0^2 - \frac{kT}{m\omega^2}\right)e^{-\beta t}\left(\cosh\omega' t + \frac{\beta}{2\omega'}\sinh\omega' t\right)^2 \tag{34b}$$

[11] Here we use: $\int_{-\infty}^{+\infty}\phi(w)\sin\omega_1 w\, dw=0$, which follows from the fact that $\phi(w)$ is an even function.

where:

$$\omega'^2 = \frac{\beta^2}{4} - \omega^2 = -\omega_1^2.$$

The equipartition value is again reached monotonously. It is easy to show further, that when $\beta \gg 2\omega$ and $t \gg \beta^{-1}$ these last equations go over into the results (30) of v. Smoluchowski, as we would expect according to the remarks at the end of §9.

§12. The problem of the rotatorial Brownian motion of a small mirror suspended on a fine wire, has been treated recently by S. Goudsmit and one of us,[12] by a method analogous to the well-known treatment of the shot effect by Schottky.[13] If the displacement, registered during a time, long compared to the characteristic period of the mirror, is developed in a Fourier series, an expression was derived for the square of the amplitude of each Fourier component. It was found that this depended, besides on the temperature, on the pressure and molecular weight of the surrounding gas. This explains in principle, why the curves registered by Gerlach[14] at different pressures, though all giving the same mean square deviation, are quite different in appearance. The calculations were made under the condition that the surrounding gas is much rarified, and though they can easily be generalized, the exact comparison with the experimental data of Gerlach is very difficult.

The results (33) and (34) (when we replace m by the moment of inertia) are in this respect much better. They could be tested easily, and they hold for all pressures of the surrounding gas. They show that, though the mean square deviation depends only on the temperature, the correlation between successive values of the deviation depends in a more interesting way on the surrounding medium. Its influence is expressed by the friction coefficient β.

Notes

I. To prove that for $U = u - u_0 \exp(-\beta t)$ the normal Gaussian distribution law holds, we have to show that:

$$\begin{aligned} \overline{U^{2n+1}} &= 0 \\ \overline{U^{2n}} &= 1\cdot 3\cdot 5 \cdots (2n-1)(\overline{U^2}) \end{aligned} \tag{A}$$

We have from §5:

$$\bar{U} = 0$$

$$\overline{U^2} = \frac{\tau_1}{2\beta}(1 - e^{-2\beta t}).$$

From (11) we get further:

$$\overline{U^3} = e^{-3\beta t} \int_0^t \int_0^t \int_0^t e^{\beta(\xi_1+\xi_2+\xi_3)} \overline{A(\xi_1)A(\xi_2)A(\xi_3)} d\xi_1 d\xi_2 d\xi_3.$$

[12] G. E. Uhlenbeck and S. Goudsmit, Phys. Rev. **34**, 145 (1929).
[13] W. Schottky, Ann. d. Physik **57**, 541 (1918).
[14] W. Gerlach, Naturwiss. **15**, 15 (1927).

According to the assumptions made about $A(\xi)$ the integrand will be different from zero only in the neighborhood of the line $\xi_1=\xi_2=\xi_3$. Taking cylindrical coordinates with this line as z-axis, and using (5), we find:

$$\overline{U^3} = \frac{\tau_2}{\beta(3)^{1/2}}(1 - e^{-3\beta t})$$

where τ_2 denotes the constant:

$$\tau_2 = \int_0^\infty \int_0^{2\pi} \phi_2(r, \theta) r dr d\theta.$$

The value of τ_2 follows again from the equipartition law. For $t \to \infty$, $\overline{U^3}$ must go to zero, so that $\tau_2 = 0$.

Going to the fourth power we find:

$$\overline{U^4} = e^{-4\beta t} \int_0^t\int_0^t\int_0^t\int_0^t e^{\beta(\xi_1+\xi_2+\xi_3+\xi_4)} \overline{A(\xi_1)A(\xi_2)A(\xi_3)A(\xi_4)} d\xi_1 d\xi_2 d\xi_3 d\xi_4.$$

When ξ_1 and ξ_2 are lying near each other and also ξ_3 and ξ_4 (but far from ξ_1, ξ_2), we will have according to (6):

$$\overline{A(\xi_1)A(\xi_2)A(\xi_3)A(\xi_4)} = \overline{A(\xi_1)A(\xi_2)} \cdot \overline{A(\xi_3)A(\xi_4)}$$

so that this integration region will contribute:

$$e^{-4\beta t}\frac{\tau_1^2}{4\beta^2}(e^{2\beta t} - 1)^2.$$

We will get this 3 times because we can divide $A(\xi_1)\ A(\xi_2)\ A(\xi_3)\ A(\xi_4)$ into two pairs in 3 ways. There remains the region in the neighborhood of the line $\xi_1=\xi_2=\xi_3=\xi_4$. For this we get, introducing cylindrical coordinates and using (5):

$$\frac{\tau_3}{2\beta} e^{-4\beta t}(e^{4\beta t} - 1)$$

where:

$$\tau_3 = \int_0^\infty \iint \phi_3(r, \theta, \theta_2) dr dw$$

For $t \to \infty$ we get therefore:

$$\lim_{t\to\infty} \overline{U^4} = \frac{3\tau_1^2}{4\beta^2} + \frac{\tau_3}{2\beta}$$

but according to the Maxwell distribution law, we have:

$$\lim_{t\to\infty} \overline{U^4} = \lim_{t\to\infty} \overline{u^4} = 3(\lim_{t\to\infty} \overline{u^2})^2 = \frac{3\tau_1^2}{4\beta^2}$$

so that $\tau_3=0$ and we get:

$$\overline{U^4} = 3(\overline{U^2}).$$

To write down the general proof for (A) is tedious, because one has more and more integration regions to consider. However, since (A) holds for $t\to\infty$, one can convince oneself of the fact that only those regions where the ξ are lying in pairs near each other give a real contribution. All the other regions give contributions proportional to constants $\tau_k(k>1)$ which by the equipartition law prove to be zero. This gives A_1 immediately and since the number of ways in which we can divide $2n$ objects into n pairs is $1.3.5\cdots(2n-1)$ we get A_2 also.

II. When we substitute in (20):

$$x = \beta t$$

$$y = u\left(\frac{2\beta}{\tau_1}\right)^{1/2}$$

we get:

$$\frac{\partial z}{\partial x} = z + y\frac{\partial z}{\partial y} + \frac{\partial^2 z}{\partial y^2}$$

and we have to solve this when for $x=0$, $z=f(y)$ and for $y=\pm\infty$, $z=0$. By separating we find as a particular solution:

$$A_n e^{-nx} D_n(y) e^{-y^2/4}$$

where D_n denotes Weber's function of the nth order[15]
We have then to determine A_n:

$$f(y) = \sum_0^\infty A_n D_n(y) e^{-y^2/4}$$

which gives:

$$A_n = \frac{1}{n!(2\pi)^{1/2}}\int_{-\infty}^{+\infty} D_n(\eta) f(\eta) e^{-\eta^2/4} d\eta$$

and we get for the solution:

$$z(x, y) = \frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{+\infty} d\eta f(\eta) e^{(\eta^2-y^2)/4} \sum_0^\infty \frac{D_n(y)D_n(\eta)}{n!} e^{-nx} \qquad (B)$$

We have now to sum the infinite series. As Professor H. A. Kramers showed to us, this can be done in the following way. Put, suppressing the arguments y and η:

$$M(x) = \sum_0^\infty \frac{D_n D_n}{n!} e^{-nx}$$

[15] Comp. Whittaker-Watson, Modern Analysis, p. 347.

then:

$$-\frac{dM}{dx} = \sum_0^\infty \frac{D_{n+1}D_{n+1}}{n!}e^{-(n+1)x}.$$

Using the recurrence formula:

$$D_{n+1}(z) = zD_n(z) - nD_{n-1}(z)$$

we get:

$$-\frac{dM}{dx} = y\eta e^{-x}M - e^{-2x}\frac{dM}{dx} - \sum_0^\infty \frac{yD_{n+1}D_n + \eta D_nD_{n+1} - D_nD_n}{n!}e^{-(n+2)x}.$$

Calling the last sum N and using again the recurrence relation, we find:

$$N = (y^2 + \eta^2 - 1)e^{-2x}M - \sum_0^\infty \frac{yD_nD_{n+1} + \eta D_{n+1}D_n}{n!}e^{-(n+3)x}$$

Again using the recurrence relation, we find for the last sum

$$L = (2y\eta e^{-3x} - e^{-4x})M - e^{-2x}N.$$

Substituting back, we get for M the differential equation:

$$-(1 - e^{-2x})^2\frac{dM}{dx} = M\{y\eta e^{-x} - (y^2 + \eta^2 - 1)e^{-2x} + y\eta e^{-3x} - e^{-4x}\}$$

This we can immediately integrate, which gives:

$$M = \frac{C(y, \eta)}{(1-e^{-2x})^{1/2}}\exp\left\{-\frac{y^2 + \eta^2 - 2y\eta e^{-x}}{2(1-e^{-2x})}\right\}.$$

The integration constant $C(y,\eta)$ can be determined from the fact that:

$$\lim_{x\to\infty} M = D_0(y)D_0(\eta) = C(y, \eta)e^{-(y^2+\eta^2)/2}$$

which gives:

$$C(y, \eta) = e^{(y^2+\eta^2)/4}.$$

Substituting in the solution (B) gives finally:

$$z(x, y) = \frac{1}{(2\pi)^{1/2}}\int_{-\infty}^{+\infty} d\eta f(\eta)\frac{1}{(1 - e^{-2x})^{1/2}}\exp\left\{-\frac{(y - \eta e^{-x})^2}{2(1 - e^{-2x})}\right\}$$

which shows that the fundamental solution ($f(\eta)$ is then $\delta(y-y_0)$) is given by:

$$G(y_0, y, x) = \frac{1}{(2\pi(1 - e^{-2x}))^{1/2}}\exp\left\{-\frac{(y - y_0e^{-x})^2}{2(1 - e^{-2x})}\right\}.$$

Introducing again t and u, we get (15).

III. To prove that for $S = s - u_0/\beta(1 - e^{-\beta t})$ the Gaussian distribution law holds, we have to show again:

$$\overline{S^{2n+1}} = 0$$
$$\overline{S^{2n}} = 1\cdot 3\cdot 5 \cdots (2n-1)(\overline{S^2})^n \tag{C}$$

We have from §7:

$$\overline{S} = 0$$

$$\overline{S^2} = \frac{\tau_1}{2\beta^3}(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}).$$

The calculation of the 3-fold integrals in $\overline{S^3}$ is analogous to the calculation of $\overline{U^3}$ in Note I. We find that the result is proportional to τ_2, and from Note I we know that $\tau_2 = 0$, so that:

$$\overline{S^3} = 0.$$

In the 4-fold integrals occurring in $\overline{S^4}$ we have to consider only the regions where ξ_1, ξ_2, ξ_3, ξ_4 are lying in pairs near each other, because the other regions will give results proportional to τ_3 which is zero, as is proved in Note I. The calculation gives:

$$\overline{S^4} = 3(\overline{S^2})^2$$

as could be expected. The factor *3* comes again from the fact that we can divide ξ_1, ξ_2, ξ_3, ξ_4 into two pairs in three ways. In the same way as in Note I then, one convinces oneself further of the truth of the general relations (C).