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A PROBLEM IN BROWNIAN MOTION

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Abstract

Gerlach investigated the rotatorial Brownian motion of a small mirror suspended on a fine wire. It follows from the theorem of equipartition that the average square deviation of the mirror will depend on the temperature alone of the surrounding gas. Gerlach verified this for a large range of pressures (1 to 10^{-6} atm). The analogy which we found that exists between this problem and the well-known treatment of the shot effect by Schottky enables us to give a more detailed theory of this phenomenon. If the displacement, registered during a time, long compared with the characteristic period of the mirror, is developed into a Fourier series, we find the square of the amplitude of each Fourier component to be a function of the pressure and molecular weight of the surrounding gas as well as of its temperature, (formula 18). The sum of the squares, however, is a function of the temperature alone (proved in section 4). This explains why the curves registered by Gerlach at different pressures, though all giving the same mean square deviation, are quite different in appearance. To get the fluctuating torque on the mirror, the expression:

$$\overline{\delta_p^2}=\frac{16}{\pi}\cdot\frac{1}{n}\cdot\frac{1}{\bar{c}\Delta t\Delta o}$$

is obtained for the fluctuation in time of the pressure of a gas on the wall (section 5). In this n represents the number of molecules per cc, $\bar{c}$ is the mean velocity and Δo is the surface of the wall.

I. Introduction

INTERESTING experiments on Brownian motion around a position of equilibrium have been performed by Zeeman and Houdyk[1] in Amsterdam and by Gerlach[2] in Tübingen. The former registered the motion of the loose end of a suspended wire, the latter photographed by means of reflected light the rotational Brownian movement of a little mirror fixed on a very fine wire. The first experiment is theoretically more complicated, because one has to consider the many natural frequencies of the observed body. In the experiment of Gerlach on the other hand the observed system has only *one* characteristic frequency. We will restrict ourselves therefore in the following treatment to the latter case.

In both cases one can immediately predict by means of the equipartition theorem what the average square of the deflection will be. This will depend on the properties of the observed system and on *the temperature only* of the surrounding gas, *not* for instance on its pressure or molecular weight. The experiments however give *more* than merely the average square deviation; the registered curves show to some extend at least the time-dependence of

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[1] P. Zeeman and A. Houdyk, Proc. Acad. Amsterdam, **28,** 52 (1925).

[2] W. Gerlach, Naturwiss. **15,** 15 (1927).

the irregular Brownian motion. As Professor Gerlach kindly communicated to us, the general appearance of these curves is quite different at different pressures of the surrounding gas, though the average square deviation remains the same for any given temperature. The problem is therefore to give a more detailed theory of these curves.

It has occurred to us that this problem may be treated in a manner quite analogous to the method employed by Schottky,[3] to describe the well-known shot-effect. In the experiments of Hull and Williams,[4] the fluctuating voltage in the shot-circuit is coupled inductively with the amplification-circuit, which possesses only one characteristic frequency. In the experiments of Gerlach the fluctuating moment of momentum around the mirror-axis of the gas-molecules, is coupled, by means of collisions, with the "amplifying" mirror, which has also only one characteristic frequency.

The analogy is complete only when *the surrounding gas is much rarefied*, because only then are the moments of momentum given by the gas-molecules to the mirror in successive time-elements independent of each other.[5]

By applying the method of Schottky, we will show in Sections II and III that for this case the amplitudes of the Fourier components of the motion depend on the pressure and the molecular weight of the surrounding gas. This will explain the different forms of the observed curves under various circumstances.

II. THE FOURIER-ANALYSIS OF THE BROWNIAN MOTION

The equation of motion of the mirror is given by:

$$I\ddot{\phi}+f\dot{\phi}+D\phi=M(t)\,, \tag{1}$$

where: I is the moment of inertia around the mirror-axis; ϕ is the angle of deflection; f the friction-coefficient; D the directional force; and $M(t)$ the fluctuating torque, caused by the collisions of the gas molecules. When we introduce the frequency in 2π sec:

$$\omega=(D/I)^{1/2} \tag{2}$$

and the angular acceleration:

$$T(t)=M(t)/I \tag{3}$$

and put:

$$r=f/I \tag{4}$$

Eq. (1) becomes:

$$\ddot{\phi}+r\dot{\phi}+\omega^2\phi=T(t)\,. \tag{5}$$

For our further purposes it is essential to give now a more detailed discussion of the meaning of $M(t)$ or $T(t)$.

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[3] W. Schottky, Ann. der Phys. **57**, 541 (1918); **68**, 157 (1922). Comp. also: J. Tinbergen, Physica, **5**, 361 (1925).

[4] A. W. Hull and N. H. Williams, Phys. Rev. **25**, 147 (1925). Comp. also N. H. Williams and H. B. Vincent, Phys. Rev. **28**, 1250 (1926).

[5] For higher pressures, the problem becomes analogous to the problem of the shot effect for high current densities. Because of the space charge the numbers of electrons hitting the anode in successive time elements are then not more independent of each other, and the fluctuations decrease. Comp. N. H. Williams and H. B. Vincent, ref.[4] p. 1262 and N. H. Williams and W. S. Huxford, Phys. Rev. **33**, 773 (1929).

The actual microscopic $M^*(t)$ consists of a large number of sharp peaks, each corresponding to the impulse moment transferred to the mirror by the collision of one (or a few) molecules. We introduce now a "physically infinitely small" time-element Δt,[6] very small compared with the characteristic period $2\pi/\omega$ of the mirror but within which many collisions occur.[7] Our function $M(t)$ consists of the averages of all $M^*(t)$ values included in each time-element Δt. The actual value of $M(t_i)$ for the time-element Δt_i is of course unknown *a priori*, but we can tell some of its properties:

(*a*) $M(t_i)$ will have equal chance of being positive or negative, so that the average over all the time-elements is zero.

(*b*) In our case, when the surrounding gas is rarefied, the $M(t_i)$ in the time-element Δt_i will be independent of the value $M(t_j)$ in the time-element Δt_j.

(*c*) In Section V we will show that the mean of $M^2(t_i)$ over all the time-elements is given by:

$$\overline{M^2(t_i)} = 4m\bar{c}pI/\rho\Delta t \tag{6}$$

where: m is the mass of the gas molecules; $\bar{c}$ their mean velocity; p the pressure of the surrounding gas, and ρ the mass of the mirror per square cm.

Let τ be the time of observation, which must be long compared with the period of the mirror, so that:

$$\Delta t \ll 2\pi/\omega \ll \tau. \tag{7}$$

Develop $T(t)$ within the interval $(0,\tau)$ in a Fourier series:

$$T(t) = \sum_{k=0}^{\infty}(A_k \cos \omega_k t + B_k \sin \omega_k t) \tag{8}$$

where:

$$\omega_k = 2\pi k/\tau$$

$$\left.\begin{aligned} A_k &= \frac{2}{\tau}\int_0^\tau T(t) \cos \omega_k t \cdot dt \\ B_k &= \frac{2}{\tau}\int_0^\tau T(t) \sin \omega_k t \cdot dt \end{aligned}\right\} \tag{9}$$

We can now replace these integrals by the following sums:

$$\begin{aligned} A_k &= \frac{2}{\tau} \sum_1^z T(t_i) \cos \omega_k t_i \cdot \Delta t_i \\ B_k &= \frac{2}{\tau} \sum_1^z T(t_i) \sin \omega_k t_i \cdot \Delta t_i \end{aligned} \tag{10}$$

where Δt_i are the successive, equal time-elements, and $T(t_i)$, $\cos \omega_k t_i$, $\sin \omega_k t_i$ are evaluated at a time t_i included within the i^{th} element Δt_i. Z

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[6] We suppose them all equal.

[7] The introduction of such an "physically infinitely small" time element is characteristic in the kinetic theory of gases. Comp. e.g., P. and T. Ehrenfest, Enc. der Math. Wiss. Vol. IV, Art. 32, p. 39.

is the total number of time-elements. The motion of the mirror is then expressed by:

$$\phi(t)=\sum_k \phi_k(t)=\sum_k \frac{1}{(\omega^2-\omega_k{}^2)^2+r^2\omega_k{}^2}\left[\left\{A_k(\omega^2-\omega_k{}^2)-B_k r\omega_k\right\}\cos\omega_k t + \left\{A_k r\omega_k+B_k(\omega^2-\omega_k{}^2)\right\}\sin\omega_k t\right] \tag{11}$$

which is the solution of (5) under the conditions $\phi=\dot{\phi}=0$ for $t=0$. These conditions mean that we start our observations only when all external disturbances have been damped out, and the remaining motion is due only to collisions with the gas molecules, or in other words, we observe the Brownian motion around the position of equilibrium and not around an already existing vibration.

From this, we find for the time-average of $\phi_k{}^2$:

$$\overline{\phi_k{}^2}=\frac{1}{2}\,\frac{A_k{}^2+B_k{}^2}{(\omega^2-\omega_k{}^2)^2+r^2\omega_k{}^2}\,. \tag{12}$$

In the case of very low pressure it is now possible to predict from the three properties (*a*), (*b*) and (*c*) of $M(t)$ (or $T(t)$) the value of $A_k{}^2$ and $B_k{}^2$. From (10) we have

$$A_k{}^2=\frac{4}{\tau^2}\sum_{i=1}^{Z}\sum_{j=1}^{Z} T(t_i)T(t_j)\cos\omega_k t_i\cos\omega_k t_j\cdot\Delta t_i\Delta t_j\,. \tag{13}$$

Consider first in this double sum the terms with $i\neq j$. As a consequence of property (*b*), in the case of low pressure $T(t_i)$ and $T(t_j)$ are completely independent; hence these terms will have equal chances of being positive or negative and for large Z their sum will vanish. Consider next the terms with $i=j$, which are all positive. Due to our choice of Δt_i, for all frequencies ω_k of the order of magnitude of ω (and only those give according to (12) an appreciable $\overline{\phi_k{}^2}$,) $2\pi/\omega_k$ will be very large with respect to Δt_i, so that $\cos{}^2\omega_k t$ changes very little over many time-elements Δt_i. We may therefore replace $T^2(t_i)$ by its average value and obtain:

$$A_k{}^2=\frac{4}{\tau^2}\overline{T^2(t)}\sum_{i=1}^{Z}\cos^2\omega_k t_i(\Delta t_i)^2\,. \tag{14}$$

Finally, replacing the sum once more by an integral, we have:

$$A_k{}^2=2/\tau\ \overline{T^2(t)}\cdot\Delta t \tag{15}$$

Obviously the value of $B_k{}^2$ is the same.

III. DISCUSSION OF THE FINAL FORMULA

Formula (6), which will be developed in §5, together with equation (3) gives:

$$\overline{T^2(t)}=4m\bar{c}p/I\rho\Delta t\,. \tag{16}$$

In §6 we will prove, that for the case of low pressure, the friction-coefficient is given by:

$$f=2m\bar{c}p\rho I/kT\,. \tag{17}$$

Substituting (15), (16), (17) in (12), we get *the final formula:*

$$\overline{\phi_k{}^2}=\frac{\pi^{1/2}m^{1/2}(8kT)^{3/2}\cdot p}{\rho I\cdot\tau}\cdot\frac{1}{\pi kT(\omega^2-\omega_k{}^2)^2+32p^2\rho^2\omega_k{}^2} \tag{18}$$

in which the well-known relation is used that:

$$\bar{c}=(8kT/\pi m)^{1/2}.$$

From the analysis in Section II it is clear that this formula may be interpreted in the *two* following ways:

1. If we resolve into Fourier series *a great number of curves*, each observed over *a relatively short time* τ (which however must still fulfill the fundamental inequality (7)), the mean square of the amplitudes of the k^{th} components will be given by (18).

2. If we analyse *one curve*, observed over *a very long time* τ, then the square of the amplitudes of the k^{th} component will also be given by (18).

The formula (18) shows the noteworthy result, that $\overline{\phi_k^2}$ depends not only on the temperature, but also explicitly on *the pressure* and *the molecular weight* of the surrounding gas. As a test we must of course show, as we will do in §4, that *by summing over all values of* k, we obtain for the mean potential energy $\frac{1}{2}D\overline{\phi^2}$ the equipartition value $\frac{1}{2}kT$ which is *independent* of the pressure and the molecular weight of the surrounding gas.

The dependence on the pressure is rather complicated. For frequencies ω_k very near to ω, the $\overline{\phi_k^2}$ becomes inversely proportional to p, and for ω_k very large compared with ω, the $\overline{\phi_k^2}$ becomes almost directly proportional to p. These latter terms of course contribute very little to the total motion, the denominator being so large. When we plot therefore $\overline{\phi_k^2}$ against k, the resulting curve has a maximum in the neighborhood of ω, which rapidly becomes very sharp as the pressure decreases. The motion of the mirror than becomes more and more "monochromatic."

Appendix

IV. Proof of the Equipartition Theorem.

The average potential energy of the vibrating mirror is equal to:

$$\tfrac{1}{2}D\overline{\phi^2}=\tfrac{1}{2}D\sum_{k=0}^{\infty}\overline{\phi_k{}^2} \tag{19}$$

because the different Fourier components are independent of each other. Though we restricted ourselves to values of ω_k small with respect to $2\pi/\Delta t$, it is permissible to extend the summation to infinity, because the components with ω_k large compared to ω contribute very little to the sum.

Equation (15) shows, that A_k^2 and B_k^2 are independent of k; hence from (12) and (15):

$$\overline{\phi^2}=\sum_{k=0}^{\infty}\overline{\phi_k{}^2}=\frac{2}{\tau}\overline{T^2(t)}\cdot\Delta t\sum_{k=0}^{\infty}\frac{1}{(\omega^2-\omega_k{}^2)^2+r^2\omega_k{}^2}\,. \tag{20}$$

The last sum we now replace by an integral, substituting:

$$x_k=\omega_k/\omega=2\pi k/\tau\omega$$

which gives:

$$\sum_{k=0}^{\infty}\frac{1}{(\omega^2-\omega_k{}^2)r^2+{}^2\omega_k{}^2}\cong\frac{\tau\cdot}{2\pi\omega^3}\int_0^{\infty}\frac{dx}{(1-x^2)^2+(r^2/\omega^2)x^2}$$

with very good approximation. The value of the integral is $\pi\omega/2r$,[8] so that we obtain:

$$\overline{\phi^2}=\overline{T^2(t)}\cdot\Delta t/2\omega^2 r. \tag{21}$$

Introducing the relations (16) and (17), and substituting from (2) and (4) the values of ω^2 and r, we obtain immediately:

$$\tfrac{1}{2}D\overline{\phi^2}=\tfrac{1}{2}kT. \tag{22}$$

V. Proof of the Fluctuation Formula (6) or (16).

This relation follows from a consideration of *the fluctuations in time* of the pressure exerted upon a wall by a rarefied gas. Using Maxwell's distribution law one easily derives an expression for the probability that a molecule of a gas within a volume V at the temperature T gives to a portion Δo of the wall a momentum normal to the wall lying between G and $G+\Delta G$ during the time Δt. It is:[9]

$$W\Delta t\Delta o\Delta G=\frac{\pi}{2}\cdot\frac{1}{(2\pi mkT)^{3/2}}\cdot\frac{kT}{V}\cdot Ge^{-G^2/8mkT}\Delta t\Delta o\Delta G. \tag{23}$$

Let n_{ij} be the number of molecules, which in the time-element Δt_i give a momentum lying between G_j and $G_j+\Delta G_j$ to the portion Δo of the wall. Then the total momentum given to Δo during Δt_i becomes:

$$G(t_i)=\sum_{j=0}^{\infty}G_j n_{ij}.$$

Using the bar to denote the average over all time-elements, we find easily:

$$\overline{G^2(t_i)}-\overline{G(t_i)}^2=\overline{(\Sigma_j G_j n_{ij})^2}-(\overline{\Sigma_j G_j n_{ij}})^2=\Sigma_j G_j^2(\overline{n_{ij}^2}-(\bar{n}_{ij})^2) \tag{24}$$

because the cross-terms cancel, and the average over the time-elements Δt_i extends only over the n_{ij}. In general the fluctuation formula holds:

$$\overline{n_{ij}^2}-(\bar{n}_{ij})^2=\bar{n}_{ij} \tag{25}$$

and $\bar{n}_{ij}$ follows immediately from (23), after multiplying by the total number of molecules N. Substituting then (25) in (24), and replacing the sum by an integral, we obtain:

$$\overline{G^2(t_i)}-\overline{G(t_i)}^2=\frac{\pi}{2}\cdot\frac{p}{(2\pi mkT)^{3/2}}\Delta o\Delta t\cdot\int_0^\infty G^3\exp\left[-G^2/8mkT\right]dG=2m\bar{c}p\Delta o\Delta t \tag{26}$$

for:

$$p=NkT/V.$$

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[8] See W. Schottky, Ann. der Phys. **68,** 157 (1922).

[9] Integrating over G from 0 to ∞, we get for the probability that a molecule hits in the time Δt the surface element Δo:

$$w\Delta t\Delta o=\bar{c}\Delta t\Delta o/4V$$

corresponding to the well-known result for the mean number $\bar{n}$ striking 1 cm² of the wall per second:

$$\bar{n}=N\bar{c}/4V.$$

In the same way we find for the mean momentum given to the wall taken over all the molecules striking it:

$$\bar{G}=(2\pi mkT)^{1/2}$$

and for the mean square:

$$\overline{G^2}=8mkT$$

This, divided by Δt^2, expresses the fluctuation in time of the pressure on the portion Δo of the wall.[10] From this it follows obviously that for a disc of surface o inside the gas, the mean of the square of *the force* $K(t_i)$ taken over all the time-elements Δt_i is given by:

$$\overline{K^2(t_i)}=4m\bar{c}po/\Delta t \tag{27}$$

as for such a disc $\overline{K(t_i)}=0$, and the fluctuations on the right and left side are independent of each other.

For a case like the experiment of Gerlach we must consider the moment of momentum around the mirror axis instead of the momentum. The analogous formula for *the torque* is then:

$$\overline{M^2(t_i)}=\frac{4m\bar{c}p}{\Delta t}\iint x^2do=\frac{4m\bar{c}pI}{\rho\Delta t}$$

where x denotes the distance from the axis. This is equation (6).

VI. PROOF OF FORMULA (17) FOR THE FRICTION COEFFICIENT.[11]

Consider a portion Δo of the mirror, which moves, say to the right in the direction of the x-axis with the velocity u. The number of molecules per second, which strike this from the left, and which lie within a certain velocity-range $d\xi d\eta d\zeta$ is:

$$dN_1=\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{N}{V}(\xi-u)e^{-mc^2/2kT}\Delta o\, d\xi d\eta d\zeta \tag{28}$$

where we have used Maxwell's distribution law, because *in our case of very low pressure*, the mean free path is large with respect to the dimensions of the mirror, so that the motion of the mirror *does not disturb the velocity distribution* of the molecules. If x is the distance from Δo to the axis of the mirror, then the moment of momentum imparted per second by these molecules is:

$$dM_1=\left(\frac{m}{2\pi kT}\right)^{3/2}\cdot\frac{2Nm}{V}\cdot(\xi-u)^2\cdot x\cdot e^{-mc^2/2kT}\Delta o\, d\xi d\eta d\zeta. \tag{29}$$

Neglecting the term with u^2 and integrating over η and ζ from $-\infty$ to $+\infty$, and over ξ from 0 to $+\infty$, we get:

$$M_1=px\Delta o-m\bar{c}Nux\Delta oV^{-1}. \tag{30}$$

In the same way, we find for the moment of momentum given to Δo per second by molecules striking from the right:

$$M_2=-px\Delta o-m\bar{c}Nux\Delta oV^{-1} \tag{31}$$

so that the total moment of momentum given to Δo per second is:

$$M_1+M_2=-2m\bar{c}pux\Delta o/kT. \tag{32}$$

Now $u=x\dot{\phi}$, so that we find for the friction coefficient:

$$f=\frac{2m\bar{c}p}{kT}\iint x^2do=\frac{2m\bar{c}pI}{\rho kT}$$

which is formula (17).

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[10] This can be written in the form:

$$\frac{\overline{p}^2-(\overline{p})^2}{(\overline{p})^2}=\overline{\delta_p{}^2}=\frac{16}{\pi}\cdot\frac{1}{n}\cdot\frac{1}{\bar{c}\Delta t\Delta o}$$

when n is the number of molecules per cc. It has then the same form as the expression for the fluctuation in pressure of a gas inside a volume element Δv (see R. Furth, Die Schwankungserscheinungen in der Physik, Vieweg, Braunschweig, 1920, p. 58):

$$\overline{\delta_p{}^2}=\frac{C_p}{C_v}\cdot\frac{1}{n}\cdot\frac{1}{\Delta v}$$

but it cannot be derived from it.

[11] Comp. H. A. Lorentz, Les theories statistiques en thermodynamique, Leipzig, 1916, p. 53.