Physics. — "*On the Theory of the Brownian-Movement*". By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS.)

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Pretty numerous are the methods by which it has been tried to calculate the mean path to be expected of a "Brownian" particle suspended in a liquid or gas. Most of the methods of calculation start from the supposition that such a particle will experience a friction in its movement. This means that it is assumed that from the force acting on such a particle, a term may be separated opposite to and proportional to its velocity, and that the remaining part of the force will be independent of the velocity Both forces are a consequence of the collisions of the surrounding molecules of the substance in which the particle is suspended. The methods of calculation based on this supposition arrive at a result which EINSTEIN was the first to communicate, namely that:

$$\overline{\Delta^2} = \frac{RT}{N}\frac{1}{3\pi\zeta a}t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

In this $R =$ the absolute gas constant
$N =$ the number of molecules per gramme-molecule
$\zeta =$ the coefficient of viscosity of the medium
$a =$ the radius of the particle
$t =$ the time
$\Delta =$ the deviation in the time t in a definite direction, e.g. in the direction of the X-axis. I shall call Δ briefly the deviation in what follows. I shall further speak of the force, when I mean the X-component of the force. The dash over Δ^2 denotes that the mean value has been taken for *all* the suspended particles (a great number).

In the derivation of this formula it has been assumed that the force of friction may be represented by the formula given for it by STOKES:

$$\mathfrak{K} = 6\,\pi\,\zeta\,a\,\dot{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let us examine the way in which e.g. LANGEVIN arrives at the formula for Δ^2. He starts from:

$$m\,\ddot{x} = -\,6\,\pi\,\zeta\,a\,\dot{x} + X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which X will be the irregular force that does not depend on the velocity. By multiplication by x we get:

$$\frac{m}{2}\frac{d^2x^2}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = -3\pi\zeta a\frac{dx^2}{dt} + Xx.$$

We then take the mean values, in which Xx falls out; we also put $\frac{dx^2}{dt} = z$ and $m\left(\frac{dx}{dt}\right)^2 = \frac{RT}{N}$, which yields the differential equation:

$$\frac{m}{2}\frac{dz}{dt} + 3\pi\zeta a z = \frac{RT}{N},$$

through the integration of which LANGEVIN arrives at equation (1). Now it is clear that this contains an inconsistency. When equation (3) is multiplied by $\dot{x}$, and this is then averaged over all the particles, we get:

$$\overline{m\dot{x}\ddot{x}} = -6\pi\zeta a\overline{\dot{x}^2}.$$

The lefthand member is $\frac{m}{2}\frac{d\overline{\dot{x}^2}}{dt}$, which quantity is therefore smaller than zero. Hence $\overline{\dot{x}^2}$ cannot remain constant, but it must exponentially descend to zero. This means that the Brownian movement would not always continue, but that the particles would soon be reduced to rest in consequence of the viscosity. Yet LANGEVIN puts $m\overline{\dot{x}^2} = \frac{RT}{N}$. And it is only owing to this inconsistency that he finds the value of (1*a*) for Δ^2.

Not every derivation of (1*a*) which rests on the supposition of a friction against the thermal movement [1]) of the Brownian particles is open to the above-mentioned objection to the same extent. By the method of EINSTEIN and HOPF, which, originally developed for another problem, was adapted for the calculation of $\overline{\Delta^2}$ by Mrs. DE HAAS-

[1]) I shall understand by *thermal* or *true* velocity of a particle the velocity that a particle has at a definite moment, for which therefore holds $m\dot{x}^2 = \frac{RT}{N}$. I shall put over against it the *measurable* velocity. This will be defined by $\frac{\Delta}{t}$, in which Δ is the deviation reached in a measurable time t. t will be of the order of magnitude of 1 sec. Of course the mean value of the measurable velocity will be independent of the moment at which the measurement begins. It will, however, be dependent on the length of the interval t, as the mean value of Δ increases only proportional to $\sqrt{t}$. Compare further Remark IV at the end of this paper.

Lorentz in her Thesis for the Doctorate, equation (3) is first integrated over a small time τ, so small that the velocity *changes not much* during τ. We then get:

$$m(\dot{x}_2 - \dot{x}_1) = -6\pi\zeta a(x_2 - x_1) + \int_0^\tau X\,dt.$$

And now it is not assumed that the equation $\overline{X\dot{x}} = 0$ holds for any moment, but that $\dot{x}_1 \int_0^\tau X dt$ is zero on an average. As $\dot{x}$ does not differ much from $\dot{x}_1$ during τ, the difference between the two suppositions is not great. But whereas $\overline{X\dot{x}} = 0$ excludes the performance of work by the force X — at least of a work the *mean value* of which differs from 0 — this is not the case with the supposition $\dot{x}_1 \int_0^\tau X dt = 0$. Here the possibility exists that X on an average performs positive work of such an amount that it compensates the loss of kinetic energy by the viscosity.

Yet it seems to me that when has once it been seen that the splitting up of the force into a "force of viscosity" and "irregular forces" is untenable, also the splitting up of the force into two terms, as it has been applied by Mrs. de Haas, becomes problematical. At bottom also this splitting up is after all based on the idea of a friction against the thermal movement of the particles.

Miss Snethlage and I [1]) have therefore thought we had to take another course to arrive at an equation for Δ^2. We started for this purpose from the postulate that:

$$\overline{\mathfrak{K}\dot{x}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

When this equation is differentiated with respect to t, it yields:

$$\overline{\frac{d\mathfrak{K}}{dt}\dot{x}} + \frac{1}{m}\overline{\mathfrak{K}^2} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (B)$$

This is satisfied in the simplest way by putting:

$$\frac{d\mathfrak{K}}{dt} = -p^2\dot{x} + q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (C)\ ^{2})$$

in which q will be a function of t that repeatedly changes its sign

[1]) These Proc. Vol. XVIII, p. 1322.

[2]) See for the justification of this equation the exposition in Remark I at the end of this paper.

and the value of which is *statistically independent* of $\dot{x}$. By the aid of kinetic considerations we derived from this formula a formula for $\overline{\Delta^2}$ which had the form:

$$\overline{\Delta^2} = \frac{C}{a^2} t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

C represents a constant the value of which we can leave undetermined for the present. When we compare this value with EINSTEIN's value (equation (1a)), we see that they may both be represented by:

$$\overline{\Delta^2} = b\,t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

with b = constant, i.e. that the mean deviation is proportional to $\sqrt{t}$. This is nothing but the well-known result of the calculus of probability for the sum of a great number of terms when the mathematical expectation for that sum is zero. I shall assume in the future that Δ^2 will certainly be represented by an equation of the form (1)[1]. Then it only remains the question to calculate b. The difference between (1a) and (1b) is that this quantity is in inverse ratio to a according to (1a), and to a^2 according to (1b). The experiments carried out by Miss SNETHLAGE[2], have demonstrated that equation (1b) can certainly not be accurate, which is the more remarkable, because also other kinetic derivations of Δ^2 had yielded equations of this form[3].

Thus we were confronted by the difficulty that experiment pronounced in favour of equation (1a), whereas the derivation of (1b), though doubt as to its validity is not excluded, seemed nevertheless much less assailable to me than the introduction of a force of viscosity against the thermal movement, which was the foundation on which (1a) was based. I have had an opportunity to discuss the derivation of the two formulae with several physicists as LORENTZ, EINSTEIN, EHRENFEST, ORNSTEIN, and ZERNIKE, and it is partly owing to their remarks that I think that I am now able to give a method of calculation of $\overline{\Delta^2}$, which without starting from the supposition of a friction against the thermal velocity, leads to the accurate result, (1a), at least as far as the dependence of a is concerned.

For this I shall start from the simple formula:

$$\ddot{x} = w(t)$$

[1] A further proof of this supposition is found in Remark II at the end of this paper.

[2] A. SNETHLAGE. Moleculair-kinetische verschijnselen in gassen, inzonderheid de Brownsche Beweging. Academisch Proefschrift. Amsterdam 1917. B. Experimenteel gedeelte.

[3] VON SMOLUCHOWSKI. Ann. d. Phys. 21 p. 769. Ann. 1906.
A. SNETHLAGE l. c. Hoofdstuk II.

which, integrated, yields:

$$x = x_0 + \dot{x}_0 t + \int_0^t w(\theta) . (t-\theta)\, d\theta. \quad . \quad . \quad . \quad . \quad (4)\ ^{1)}$$

The path travelled over in the time t is $x - x_0 = \Delta$. When this equation is multiplied by $w(t)$, and when the mean values for all the particles are taken, then $\overline{\dot{x}_0 w(t)}$ becomes $= 0$, hence:

$$\overline{\Delta \ w(t)} = \overline{w(t) \int_0^t w(\theta) . (t-\theta)\, d\theta} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The lefthand side is negative, it is a constant which I shall represent by Q, i.e. it is independent of the value of t, provided this is not taken too small. The proof of this I shall give in remark III at the end of this paper. When we divide this equation by t, it appears that also

$$\overline{\frac{\Delta}{t} . w(t)} < 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

in virtue of this we may put:

$$w(t) = -r^2 \frac{\Delta}{t} + s \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)\ ^{2)}$$

in which

$$\overline{s\Delta} = 0 \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

When this equation is multiplied by Δ, and averaged, we get:

$$\overline{\Delta . w(t)} = -r^2 \frac{\overline{\Delta^2}}{t} = -Q \quad \text{or} \quad r^2 = \frac{Q}{b} \quad . \quad . \quad . \quad . \quad (8)$$

Equation (6) may be expressed in words as follows: The force that acts on a particle at a given moment, may be split up into a *force of viscosity against the measurable movement* and a term that is independent of the *measurable* velocity. The splitting up of the force into a force of viscosity and an irregular force is, therefore, permitted *provided we assume that the measurable velocity, not the thermal velocity, is damped by such a force.* If we could compute r^2 by a kinetic way, we might arrive at a complete derivation of EINSTEIN's formula for $\overline{\Delta^2}$. The calculation of r^2 will, however, be no doubt attended with great difficulties. It seems, however, not very hazardous to me, to assume the value $6\pi\zeta a$ from STOKES's formula for it; possibly the value corrected by CUNNINGHAM. This

1) Compare Remark II at the end of this paper.
2) Compare Remark I at the end of this paper.

seems arbitrary at first sight, but it seems to me that it will not be thought so arbitrary, when it is fully realized what the friction given by STOKES's formula, really is.

Let us imagine a particle suspended in a gas which is made to fall under the influence of gravitation, in order to determine its radius in the usual way. Here too there is a measurable movement (here the motion of falling), and a thermal movement. Now we get a correct formula for the measurable motion by assuming that a force of viscosity $-6\pi\zeta a\dot{z}$ opposes *this* movement. And as we demonstrated that also in the Brownian movement a force: a constant $\times$ the measurable velocity, opposes the measurable movement, it is very natural to assign the value $-6\pi\zeta a$ to this constant. This becomes still more plausible when we think of equation (C)

$$\frac{d\mathfrak{K}}{dt} = -p^2\dot{x} + q\,.$$

It contains that if there is a velocity $\dot{x}$, this will try to bring about a force in opposite sense; hence to cause the product force $\times$ velocity to become negative. It is counteracted in this by the fact that the force tries to develop a velocity in its own sense; hence to make the product in question positive. If $\dot{x}$ is the thermal velocity, the two tendencies counterbalance each other: the product remains zero on an average. The thermal velocity varies its sign repeatedly. If, however, there is a velocity in the same sense for a longer time, $\frac{d\mathfrak{K}}{dt}$ continues to keep the same sign all this time, and a force opposite to that velocity will be developed. And this will take place independent whether this velocity of longer duration is owing to gravity, or whether it represents a measurable velocity of the Brownian movement.

When we assign this value to r^2, (7) yields:

$$\overline{\Delta^2} = Q\,\frac{1}{6\pi\zeta a}\,t$$

Q is defined by equation (5). It would, however, not be possible to derive its value from it without introducing further, perhaps pretty uncertain, hypotheses. Fortunately, however, it is possible to find a value for $\overline{\Delta^2}$ in another way, namely by multiplying (6) by Δ, bearing in mind that $\frac{d\Delta}{dt} = \dot{x}$ and $\frac{1}{m}\dot{w}(t) = \frac{d^2\Delta}{dt^2}$. We then find:

$$\Delta\frac{d^2\Delta}{dt^2} = \tfrac{1}{2}\,\frac{d^2\Delta^2}{dt^2} - \left(\frac{d\Delta}{dt}\right)^2 = -\frac{1}{m}\,.\,6\,\pi\,\zeta\,a\,\frac{\Delta^2}{t} + s\,.\,\Delta \quad . \quad . \quad (9)$$

When on account of $\overline{\Delta^2} = bt$, we put $\frac{d^2\overline{\Delta^2}}{dt^2} = 0$, and further $\overline{\left(\frac{d\Delta}{dt}\right)^2} = \overline{x^2} = \frac{RT}{mN}$, we find when again we take the mean value for all particles:

$$\overline{\Delta^2} = \frac{RT}{N} \frac{1}{6\pi\zeta a} t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1c)$$

This result has half the value of that of equation (1*a*). The good result that Miss SNETHLAGE found when calculating N from her observations, shows that (1*a*) is to be preferred to (1*c*). Though accordingly it does not lead to the accurate result, I hope that the above derivation will contribute to give us a clearer insight in the theory of the Brownian movement.

When we do not want to start from the supposition $\overline{\Delta^2} = bt$, equation (9) can also be solved, when first mean values have been taken in a way that strongly reminds of LANGEVIN's. When we put $\overline{\Delta^2} = \xi$ and $\overline{\left(\frac{d\Delta}{dt}\right)^2} = \frac{RT}{mN}$ we find for ξ the differential relation [1]):

$$\frac{1}{2} \frac{d^2\xi}{dt^2} + r^2 \frac{\xi}{t} = \frac{RT}{Nm} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

When we first take this equation without the second member, and when we substitute $\xi = \eta\sqrt{t}$, we get:

$$\frac{d^2\eta}{dt^2} + \frac{1}{t}\frac{d\eta}{dt} + \left(\frac{2r^2}{t} - \frac{1}{4t^2}\right)\eta = 0\,.$$

When we put besides $t = \frac{\tau^2}{8r^2}$, we find:

$$\frac{d^2\eta}{d\tau^2} + \frac{1}{\tau}\frac{d\eta}{d\tau} + \left(1 - \frac{1}{\tau^2}\right)\eta = 0\,.$$

This is Bessel's differential equation for $n = 1$, the solution of which runs in the current notation:

$$\eta = A\, I_1(\tau) + B\, Y_1(\tau)\,.$$

Hence:

$$\overline{\Delta^2} = \sqrt{t}\,[A\, I_1(2\,r\sqrt{2t}) + B\, Y_1(2\,r\sqrt{2t})]$$

would be the solution of the equation without the second member.

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1) The solution of this equation following here I owe to a kind communication from Prof. W. KAPTEYN of Utrecht to whom I gladly express my gratitude here.

For the equation with the second member we must add to it the term:

$$\overline{\Delta^2} = \frac{RT}{N} \frac{1}{6\pi\zeta a} t.$$

When we again write $\frac{6\pi\zeta a}{m}$ for r^2, it appears that for t of the order 1 sec. the argument of I_1 and Y_1 becomes of the order 10^4. For such large arguments the terms with the Bessel's functions may be neglected, so that equation (1*c*) is left.

Remark 1. The equation (*C*) on p. 1256 $\frac{d\mathfrak{K}}{dt} = -p^2 \dot{x} + q$ has been derived by Miss SNETHLAGE and me from equation (*A*):

$$\overline{\mathfrak{K}\dot{x}} = 0$$

and used for the calculation of $\overline{\Delta^2}$. ORNSTEIN and ZERNIKE have advanced objections to this equation and the use we have made of it. Erroneously as it seems to me. But the fact that they make objections to it shows that the validity of this and simular equations requires further elucidation. In itself equation (*C*) is of course not inaccurate, but nothing can be derived from it. It only gets its meaning from the significance that is assigned to p^2 and q.

When we multiply (*C*) by $m\dot{x}$, we get[1]):

$$m\dot{x}\frac{d\mathfrak{K}}{dt} = -mp^2\dot{x}^2 + mq\dot{x}.$$

When we then average over all the particles, and when equation (*B*) is taken into account, we find:

$$-\overline{\mathfrak{K}^2} = -mp^2\overline{\dot{x}^2} + \overline{mq\dot{x}}.$$

Up to now we have left p^2 and q entirely undetermined. When we now, however, choose

$$p^2 = \frac{\overline{\mathfrak{K}^2}}{m\overline{\dot{x}^2}} \quad \text{. . . . . (D)}$$

it appears that:

$$\overline{q\dot{x}} = 0 \quad \text{. . . . . (E)}$$

p^2 = constant for a swarm of suspended particles that are in a stationary state. Hence the equation (*C*) simply means this that for a definite particle I separate the $\frac{d\mathfrak{K}}{dt}$ into two terms. I choose as

[1]) I owe this derivation to an oral communication by Mr. ZERNIKE.

first term $-p^2\dot{x}$ with $\overline{p^2} = \frac{\overline{\mathfrak{K}^2}}{m\dot{x}^2}$. I call the function of t that is left, q; it has the property that $\overline{q\dot{x}} = 0$, provided I average over all the particles. When I write $\frac{d\mathfrak{K}}{dt} = m\frac{d^2\dot{x}}{dt^2}$, (C) becomes a differential equation, which can be integrated. And afterwards mean values can be taken over the different particles. What objections ORNSTEIN and ZERNIKE have to this way of procedure, is not clear. It is entirely incomprehensible why they assert that (C) would not be a differential equation. Their statement that (C) would not hold at any moment, is clearer. But it is not valid. (A), (B), (C), (D), and (E) hold of course at any moment, because the different moments are equivalent for a stationary movement. Strictly speaking ORNSTEIN and ZERNIKE do not mean that these equations would not always be valid, but they assert this about other equations which are obtained when all the averages are not taken over all the particles, but over a v-group. They understand by this a group comprising all the particles that possessed the same velocity $\dot{x}_0$ at the moment t_0. When we now average over this group, equation (B) does not even hold at the moment t_0, whereas (A) and (E) do hold at the moment t_0, but not at another moment[1]). When we write the equations with such group means:

$$\overline{\mathfrak{K}\dot{x}}^{v} = 0 \qquad (A\ bis)\ etc.$$

ORNSTEIN and ZERNIKE are undoubtedly right in their assertion that $(A\ bis) \ldots . (E\ bis)$ are not always valid. But it is equally certain that they are wrong when they assert that the validity of these equations has been assumed by Miss SNETHLAGE or me, or has been used in our reductions. We have always concerned ourselves with averages over all the particles, never with such averages of a v-group.

When, therefore, accessory misunderstandings are left out of account, it seems to me that ORNSTEIN and ZERNIKE's objection might be defined like this: that they think that we ought to have made use of averages over a v-group, and that we wrongly failed to do

1) The authors calculate this more at length. Qualitatively this is, however, easy to see. For such a group $\overline{\dot{x}^2}$ is not constant. At t_0 we have, namely, $\overline{\dot{x}^2} = \dot{x}^2_0$ and after not too short a time $\overline{\dot{x}^2} = \frac{RT}{Nm}$.

so. In connection with this I remind of the fact that equation (C) with the value $p^2 = \frac{\overline{\mathfrak{K}^2}}{mx^2}$ is valid for each particle separately, and is not dependent on any mean value. It may be integrated without reservation, after which, if it is thought desirable, equation (E) can be taken into account. When $\overline{\Delta^2}$ is to be calculated, the general mean is always taken. How and why an average over a v-group could be introduced for the calculation of this quantity, is not clear to me; nor has it been demonstrated by ORNSTEIN and ZERNIKE [1]).

Accordingly it seems to me that ORNSTEIN and ZERNIKE have not succeeded in pointing out an error in our derivation. Nevertheless I do not doubt but it must exist. I think I have pointed out the error above in equation (6). Formely we had always thought that Δ was the sum of a number of terms that were statistically independent of each other. Equation (6) shows that the increments setting in after a moment t are dependent on the deviation already reached at that moment. And it is obvious that we shall not find the accurate amount for the mean value of the deviations, when we leave this correlation out of account.

It might now be imagined that this remark entailed that also the result $\overline{\Delta^2} = bt$ should be considered as doubtful. The thesis of the calculus of probability cited for it is namely only valid when the different terms of the sum are independent of each other, which is not the case here. It has been demonstrated on p. 1260 and 1261 that yet there is no reason to doubt the validity of this formula, and that it can even be derived from equation (6).

Above I have derived equation (C) from (B). I have done so because such a derivation is also valid for other analogous cases, e.g. for equation (6) on p. 1258. When we only wish to derive equation (C), we can do so also in another way, as has been done by Miss SNETHLAGE and me [2]). This derivation even brings us farther than the above given one. It justifies us in the statement that the

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[1]) The formulae derived by the writers for averages over a v-group might possibly be of value for another question, namely this: how do the particles that at first have the same velocity, spread over the different velocities?

[2]) Messrs. ORNSTEIN and ZERNIKE state l.c. that we give formula (C) without a proof, after which they furnish a proof, which, however, does not depart from ours except in this detail that we average *immediately* over all the particles, and they in stages first over the particles of a v-group, and then over the different v-groups. The result is, of course, identical.

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quantity q is statistically quite independent of $\dot{x}$. This statement involves $\overline{q\dot{x}} = 0$, but it comprises more. From it follows e.g. $\overline{q^2}^{\dot{x}} =$ independent of the value of $\dot{x}$ for which the $\dot{x}$-group[1]) has been taken, which cannot be derived from the simple fact that $\overline{q\dot{x}} = 0$.

The derivation given here justifies at the same time the derivation of the above given equations (6) and (7) from (5a). These equations give, however, occasion to the following remarks. In the first place the constancy of r^2 is to be demonstrated. It follows directly from (8). We might also have started from (5), viz. $\Delta \, . \, w(t) < 0$ without dividing by t first.

Then we might have put:

$$w(t) = - r'^2 \, \Delta + s' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6a)$$

Multiplication by Δ and subsequent averaging would have yielded:

$$\overline{\Delta \, . \, w(t)} = - r'^2 \, \overline{\Delta^2} = - Q$$

so that r'^2 had not become constant. For this reason I have preferred to divide (5) first by t, and to put:

$$w(t) = - r^2 \frac{\Delta}{t} + s$$

with $r^2 =$ constant. Besides the idea of "measurable velocity" can now be applied to $\frac{\Delta}{t}$, which may lead to the application of STOKES's formula.

Another remark in connection with formula (6) is the following. When we consider the deviations Δ, Δ', Δ'' etc., obtained in the times t, t', t'', etc., which have been chosen so that they all finish at the moment t_2, hence begin at different moments t_1, t'_1, t''_1 etc., the quantities $w(t_2)$ are of course the same: the accelerations of the particles at the moment t_2. They are, however, divided into two terms in different ways. When we put again $r^2 = \frac{Q}{b}$ we may write:

$$w(t_2) = - r^2 \frac{\Delta}{t} + s \ \text{ with } \overline{s \, \Delta} = 0$$

but also:

$$w(t_2) = - r^2 \frac{\Delta'}{t} + s' \ \text{ with } \overline{s' \, \Delta'} = 0$$

or

$$w(t_2) = - r^2 \frac{\Delta''}{t} + s'' \ \text{ with } \overline{s'' \, \Delta''} = 0 \text{ etc.}$$

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[1]) By a $\dot{x}$-group we simply mean the group of the particles for which $\dot{x}$ has a definite value. Accordingly it is something different from a "v-group of ORNSTEIN and ZERNIKE", which contains the particles which *at the moment t_0 had a definite value v*, but which have very different velocities at the moment at which we consider the group.

The same particles which form together a group with the same Δ, will not all have the same Δ'. This circumstance does not detract from the validity of (6) and (7), nor from the use made of it.

Remark II. At a cursory view equation (4):

$$\Delta = \dot{x}_0 t + \int_0^t w(\theta)(t-\theta)\, d\theta$$

looks rather strange. It seems to be quite in contradiction with $\Delta^2 = bt$. For when we take the square and when we average, a term $\dot{x}_0^2 t^2$ appears which is by no means small compared with the other terms. When we, however, choose the group particles that have a definite velocity $\dot{x}_0$ at the moment $t = 0$, we may write for this group that:

$$\overline{\int_0^t w(\theta)\, d\theta} = -\dot{x}_0$$

For at the moment t they will be distributed over all the velocity groups, and they will have a mean velocity zero. At least this will be so when t is not taken *too* small. When t is of the order of 1 sec., this is amply sufficient. Hence the terms:

$$\left\{ \dot{x}_0^2 + \left(\int_0^t w(\theta)\, d\theta \right)^2 + 2 \,.\, \dot{x}_0 \,.\, \int_0^t w(\theta)\, d\theta \right\} t^2$$

will neutralize each other in the expression for $\overline{\Delta^2}$. A direct discussion of the way in which the remaining terms depend on t will be very difficult. But in this way it is at least seen that the striking appearance of terms with t^2 is only apparent. The form of (4) is, accordingly, more or less misleading, which, however, is no objection to the use made of it above. That (4) is really compatible with $\overline{\Delta^2} = bt$, follows from the reduction via equations (5) to (10).

Remark III. We have assumed on p. 1258 that:

$$\overline{w \Delta} < 0$$

This can be demonstrated in different ways. In the first place we might start from the relation $\overline{\Delta^2} = bt$, proved on p. 1257 which after a double differentiation, yields:

$$\overline{\mathfrak{K}\, \Delta} = -m \overline{\left(\frac{d\Delta}{dt}\right)^2}$$

When we again put $\mathfrak{K} = - 6\pi\zeta a \frac{\Delta}{t} + s$ with $\overline{s\Delta} = 0$, we find at once:

$$6\pi\zeta a \frac{\overline{\Delta^2}}{t} = -m\left(\frac{d\Delta}{dt}\right)^2 \overline{=} \frac{RT}{N}$$

We can, however, also follow the course indicated in the text p. 1258, and show, or make it at least highly plausible, that:

$$w(t_2)\int_{t_1}^{t_2} w(\theta)(t-\theta)\,d\theta < 0 \quad . \; . \; . \; . \; . \; . \; . \quad (5a)$$

For this purpose we remember that the movement is reversible. I shall suppose the reversed movement (in which of course *all* the velocities, both those of the particles and those of the molecules of the medium must be reversed) to take place between the times t_3 and t_4. Of course then $t_4 - t_3 = t_2 - t_1$. We have further $w(t_4) = w(t_1)$ and $w(t_3) = w(t_2)$, for the forces that in the direct movement occur at the beginning of the interval, in the reversed movement occur at the end and vice versa. Finally the path $\Delta' = - \Delta$ is travelled over in the reversed movement. For the reversed movement the expression analogous to (5a) becomes:

$$\overline{w(t_4)\,.\,\Delta'} = \overline{w(t_4)\int_{t_3}^{t_4} w(\theta)\,.\,(t_4-\theta)\,d\theta} < 0 \quad . \; . \quad . \quad (5b)$$

This becomes for the direct movement:

$$\overline{-w(t_1)\,\Delta} = \overline{w(t_1)\int_{t_1}^{t_2} w(\theta)(\theta-t_1)\,d\theta} < 0\,, \quad . \; . \; . \quad (5c)$$

for what for the reversed movement is expressed by $t_4 - \theta$, for the direct movement becomes $\theta - t_1$.

If therefore we have proved the validity of (5c), we have proved (5b) for the reversed movement. On account of the equivalence of the direct and the reversed movement, we may also consider (5a) proved for the direct movement. This appeal to the reversed movement is not necessary. The validity of (5a) might have been demonstrated in the same way as has been done with (5c). The representation and the mode of expression seemed somewhat simpler when I started from (5c).

Superficially considered the sign of this expression would be expected exactly the contrary. When we namely choose a group of particles which all have the same $w(t_1)$ on t_1, and when we take the $w(\theta)$ for these particles at a later moment, and then the mean of $w(\theta)$ over the group, which quantity I shall represent by $\overline{w(\theta)}^{w(t_1)}$ we shall find that the particles have assumed all kinds of values of w, so that $\overline{w(\theta)}^{w(t_1)} = 0$. At least this will be so when $(\theta - t_1)$ is not very small; only for very small values of $(\theta - t_1)$ there exists correlation between the values of $w(\theta)$ and $w(t_1)$, and then the product $w(\theta)\, w(t_1)$ will be positive on an average.

This would, indeed, be accurate, and would lead to the opposite sign for (5c), when $\overline{w(\theta)}^{w(t_1)}$ approached to zero aperiodically. This is, however, not the case. In order to see this we observe that in virtue of the mutual independence of distribution in configuration and in velocity we may write in a notation that is easy to understand:

$$\overline{\dot{x}_{t_1}}^{w(t_1)} = 0$$

When we take:

$$\int_{t_1}^{t} w(\theta)\, d\theta = \dot{x} - \dot{x}_{t_1}$$

and when we again average for the $w(t_1)$ group, in which it may be assumed that with sufficiently long $t - t_1$ the initial $w(t_1)$ has no longer any influence on the final velocity, so that $\overline{\dot{x}(t)}^{w(t_1)} = 0$, we find:

$$\overline{\int_{t_1}^{t} w(\theta)\, d\theta}^{w(t_1)} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

When $w(t_1)$ is thought positive, $\overline{w(\theta)}^{w(t_1)}$ will also be < 0 for very small values of θ. The fact that the integral is zero means therefore that the positive interval is succeeded by a negative interval, before the value of $\overline{w(\theta)}^{w(t_1)}$ falls to zero[1]). When under the integral sign

[1]) This may also be expressed by stating that $\overline{w(\theta)\, w(\theta+\delta)}$ is positive for very small values of δ; for somewhat larger values it is negative, descending to zero for large values. This change of sign of the product has been overlooked by ORNSTEIN (Zittingsverslag Dec. 1917, p. 1008, § 2). In consequence of this he arrives at the remarkable conclusion that the assumption $\frac{d}{dt}\overline{u^2} = 0$ is not justified. For according to his computation it follows from this that $\overline{u^2}$ is not constant, but the sum of a linear and a periodic function of t!

we multiply by $\theta - t_1$, this factor becomes greater for the negative interval than for the positive, so that:

$$\int_{t_1}^{t} w(\theta)\,(\theta - t_1)\,d\theta < 0 \qquad \text{when} \qquad w(t_1) > 0.$$

In the same way appears of course:

$$\int_{t_1}^{t} w(\theta)\,(\theta - t_1)\,d\theta > 0 \qquad \text{when} \qquad w(t_1) < 0.$$

It is true that the course of $\overline{w(\theta)}^{w(t_1)}$ can be more intricate than I have assumed here. Instead of one there may take place more reversals of sign. Not improbably $\overline{w(\theta)}^{w(t_1)}$ is represented by a damped periodic function, or at least it has a course closely resembling it. But in any case equation (11) must hold for not *too* small values of t, and in this the values of $\overline{w(\theta)}^{w(t_1)}$ which agree in sign with $w(t_1)$, will undoubtedly have smaller abscissa than those that differ in sign from it, which warrants the validity of (5*c*).

Remark IV. I pointed out on p. 1260 that the obtained result for $\overline{\Delta^2}$ probably amounts only to half or about half the true value. It is natural to try to bring a correction in this by the assumption of another value for the measurable velocity. We defined the quantity $\frac{\Delta}{t}$ as "measurable velocity". But it is the question whether this is really the quantity that is to be multiplied by $6\pi\zeta a$ in order to find STOKES's force of friction. We might, of course, define $\frac{\Delta}{t}$ as the time-average of the measurable velocity of a particle that travels over a path Δ in the time t. And when a force of viscosity opposes this displacement, it is the question whether this force may be taken proportional to the time average. It is to be expected that the measurable movement is not uniform. When we divide the interval t into sub-intervals, it is to be expected that the displacements obtained in the first of these sub-intervals will have less influence on the force of viscosity that prevails at the end of the interval t than the displacements obtained in the later sub-intervals. And this force of friction at the end of the interval was the quantity that we had in view when executing our computation.

When we further bear in mind that $\Delta_m = \sqrt{bt}$ and $v_m = \sqrt{\frac{b}{t}}$, when Δ_m represents the mean displacement and v_m the mean value of the time average of the measurable velocity, we see that v_m decreases with increase of t. It is therefore natural to suppose that a measurable velocity can be introduced that decreases with the time, thus being smaller in the later sub-intervals than in the first. If in virtue of this the force of friction at the end of t should also be put smaller than we did, namely at half the value[1]), we should find for $\overline{\Delta^2}$ exactly the value of EINSTEIN's formula.

A simple calculation, however, teaches that the desired correction is not to be obtained on the ground of these considerations. For this we point out that the chance that a particle gets a deviation Δ in a time t, is represented by:

$$C e^{-\frac{\Delta^2}{m^2}} d\Delta \text{ in which } m^2 = \tfrac{2}{3}\,\overline{\Delta^2}.$$

When we now choose the group of particles that all have the same Δ, and when we divide t into two sub-intervals t_1 and t_2, the different particles of the Δ-group will travel over different paths Δ_1 in the time t_1, and over different paths Δ_2 in the time t_2, in which of course $\Delta_1 + \Delta_2 = \Delta = \text{constant}$ for the group.

When for this group we now examine the middle value of Δ_1, a simple calculation teaches:

$$\overline{\Delta_1}^{\Delta} = \Delta \frac{t_1}{t}$$

so that also:

$$\overline{\Delta_2}^{\Delta} = \Delta \frac{t_2}{t}$$

In this it has been assumed that the values of Δ_1 and Δ_2 are statistically independent of each other, when not a Δ-group, but the collection of all the particles is considered. It is known that this may be assumed as long as t_1 and t_2 are not too small, i.e. t_1 and t_2 must be sufficiently large to allow us to neglect the influence of the initial velocity and of the initial force.

It appears from this that we may divide the velocity of the particles during the interval t into two terms. a *uniform* velocity $\frac{\Delta}{t}$ and an irregular term, which, independent of the value of Δ for

1) We should exactly obtain this factor $^1/_2$ when we did not derive v_m by dividing Δ_m by t, but by differentiating Δ_m with respect to t.

the considered particle is equally probably positive as negative. Hence it is very probable that we may also divide the force of friction into a term $-6\pi\zeta a\frac{\Delta}{t}$, and an irregular term k. As $\overline{k.\Delta}=0$, we may insert k in s, so that we may write:

$$w(t)=-6\pi\zeta a\frac{\Delta}{t}+s \qquad \text{with } \overline{s\Delta}=0$$

as we did on p. 1258.

Remark V. In conclusion I want still to make a remark in connection with a derivation given by ORNSTEIN [1]) of the formula $\overline{\mathfrak{K}x}=0$. In this he starts from equation (3), which he writes:

$$\frac{du}{dt}=-\beta u+F \quad . \quad . \qquad . \quad . \quad . \quad . \quad (3a)$$

and he proves that when F is a function of t, which is prescribed without taking u into account, and which further fulfils certain conditions [2]), the solution of the differential equation (3a) yields such a value for u that $\overline{Fu}=\overline{\beta u^2}$, so that $\overline{u\frac{du}{dt}}=0$.

This result is in perfect agreement with the thesis pronounced by Miss SNETHLAGE and me that $\overline{\mathfrak{K}u}=0$, and in conflict with the thesis from which EINSTEIN and HOPF, LANGEVIN and others start, viz. that $\overline{Fu}=0$.

Remarkable is the conclusion drawn by ORNSTEIN out of this. It runs, namely, that there is no objection to accepting equation (3a) with $\overline{Fu}=0$. It is astonishing that ORNSTEIN has not noticed this contradiction. In reality he nowhere introduces the supposition $\overline{Fu}=0$ into his calculation. He simply integrates equation (3a), and then demonstrates that $\overline{Fu}$ is *not* zero, but equal to $\overline{\beta u^2}$.

It follows from $\overline{Fu}=\overline{\beta u^2}$ that we may represent F by:

$$F=\beta u+F' \text{ in which } \overline{F'u}=0,$$

so that $\mathfrak{K}=-\beta u+F=-\beta u+\beta u+F'=F'$ with $\overline{F'u}=0$.

In so far this derivation teaches nothing new. Yet it is interesting

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1) L. S ORNSTEIN, Zittingsverslag Dec. 1917, p. 1011

2) F is a continuous function, which, however, repeatedly changes its sign, and which has another value for every particle. $\overline{F^2}$ taken over all the particles, and also the mean squares of the first and higher time derivatives of F are constant in the time. Also the mean value of F^2 for a single particle taken over a sufficiently long time is constant in the time and constant for the different particles.

because it is very well adapted to help us to form a true conception about the forces that appear in the Brownian movement. Let us consider a sphere of finite dimensions immersed in a viscous liquid, and fastened to a cord. By means of this cord the sphere can be moved in the x direction both in positive and in negative sense. Let us now assume that a force $F(t)$ is applied, the value of which is fixed without our taking the velocities acquired by the sphere into account. We may e.g. imagine that the value of F for different moments is determined by some lottery or other, and that F further satisfies the conditions mentioned on the preceding page.

The equation of motion of the sphere will then be:

$$m\frac{du}{dt} = -\beta u + F.$$

ORNSTEIN integrates this equation and shows that $\overline{Fu} = \beta\overline{u^2}$.

Though the value of F has been fixed independently of u, yet F and u are statistically not independent of each other. And this is owing to this that the velocity u is not independent of the force F, which has given rise to it.

When we now again return to the Brownian movement, the force F will no longer be exerted by pulling a cord, but by collisions of molecules. But for the rest everything remains the same. We may, indeed, assume a friction, also counteracting the momentary velocity. And there may be reason to do so, just as was the case for the larger sphere attached to a cord. But then the motive force F does not satisfy the condition $\overline{Fu} = 0$, as is generally assumed, but we may put:

$$F = +\beta u + F' \quad \text{with} \quad \overline{F'u} = 0,$$

so that the force of friction $-\beta u$ may not be introduced, without the introduction of another force $+\beta u$ that again neutralizes it. The only remaining force F' is then independent of u.