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

(Communicated in the meeting of Jan. 25, 1919).

In these Proceedings L. S. ORNSTEIN and H. C. BURGER [1]) advance some objections to a theory of the Brownian movement developed by me [2]) I will briefly discuss some of them here.

I. The first rests entirely on a misunderstanding. It refers to a calculation of $x - x_0 = \Delta =$ the *measured* deviation of a suspended particle obtained in a certain *measured* time t. When determining the mean value of this quantity I omit a term with the product [3]) $\overline{\dot{x}_0 w(t)}$, because this mean will be zero. O. and B. think now that I mean that the equation:

$$\overline{\dot{x}_0\, w(t)} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

will be valid for every value of t. They justly object to this, and demonstrate that this would lead to absurd results. My meaning was, however, that this equation would only hold for times that are sufficiently great. It expresses precisely the same thing as O. and B. indicate in the graphical representation on p. 924 loc. cit., namely that $\overline{w(t)}^{u(0)}$ [4]) for t large again approaches zero. That the times in which

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[1]) L. S. ORNSTEIN and H. C BURGER. These Proceedings, Vol. XXI, 922.

[2]) J. D. VAN DER WAALS JR. These Proceedings, Vol. XX, p. 1254.

[3]) In this w represents the force that acts on the particle. Equation (1) somewhat resembles the equation:

$$\overline{u(t)\frac{du(t)}{dt}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

which has been repeatedly used by Miss SNETHLAGE and me in our considerations on the Brownian movement, and is among others derived by differentiating the equation $\overline{\{u(t)\}^2} =$ constant with respect to t. Equations 1 and 2, however, rest on very different considerations, and are used in a very different way, so that we should be very careful not to confuse them.

[4]) A line over a quantity denotes a mean. When no index is given, the mean has been taken over all the suspended particles. An index as here the $u(o)$ behind the line expresses that the mean has been taken over all the particles which had the definite velocity $u(o)$ at the moment $t = 0$.

the observed deviations are reached, are large enough to allow us to assume the equation for *those* values of t, is known. From this point of view my derivation is, therefore, not open to objection. [1])

II. A second objection of O. and B. refers to my assertion loc. cit. that most probably equation

$$\overline{Q \equiv w(t_1) \int_0^{t_1} w(\vartheta)(t_1 - \vartheta)\, d\vartheta} < 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

will be valid. I derive this from the consideration that $w(t)$ will satisfy the condition:

$$\overline{\int_0^{t_1} w(\vartheta)\, d\vartheta}^{\,w(t_1)} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now O. and B. are going to prove that this is erroneous. For this purpose they expand $w(t)$ into a series of FOURIER. Now it would be thought that the next step they had to take was to examine what influence the condition (3) would have on the mean value of the coefficients of this series. They do not speak, however, about equation (3), and do not subject the coefficients to any condition, and they *then* come to the conclusion that Q might just as well be positive as negative. Now it is not subject to any doubt that if $w(t)$ is not subjected to any condition, the sign of Q might be just as well $+$ as $-$. It does not require an expansion into series according to FOURIER io prove this. But the influence which condition (3) has on this sign, is left entirely unexplained by O. and B.

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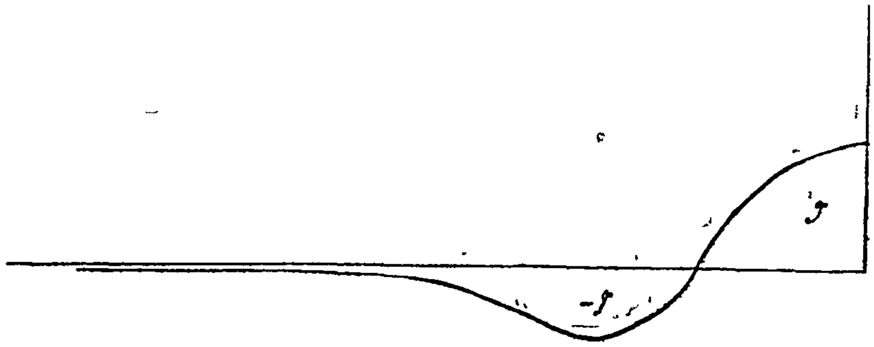
[1]) How greatly Messrs. O. and B. misunderstand my meaning appears in a remarkable way from this that on one side when they think they give my views, they repeatedly enunciate theories which are in contradiction with my meaning, but that on the other hand when they think they are in contradition with my theory drawing the graphical representation in question on page 429 of their paper, they in fact but represent in drawing a course of $\overline{w(t)}^{u(o)}$ entirely in agreement with what I have communicated about this quantity partly in collaboration with Miss SNETHLAGE.

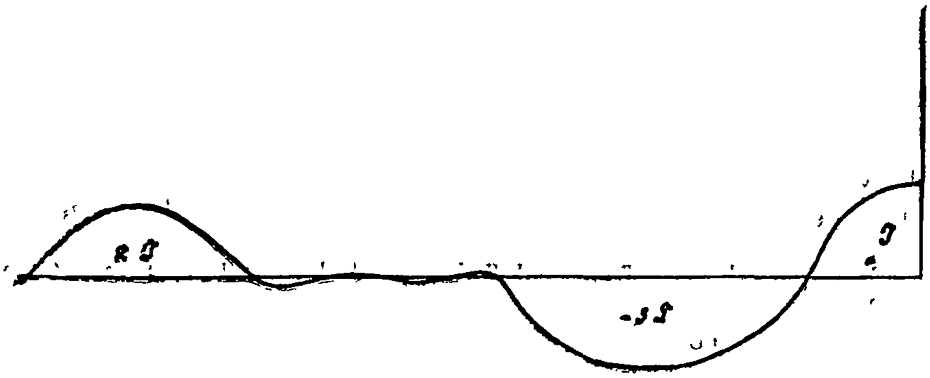
O. and B. admit that we were right in our contention that this curve begins with the value 0. That also for large value of t I assign the value 0 to $\overline{w(t)}^{u(o)}$ appears from the equation (1) discussed just now. That further for $u(o) > 0$ the value of $\overline{w(t)}^{u(o)}$ becomes negative for small value of t has already been expressed in the paper by Miss SNETHLAGE and me on the Brownian movement in the words: At the moment itself that the velocity $\mathfrak{w}$ exists the force is independent of $\mathfrak{w}$, so on an average zero, $K_0 = 0$. After some time however a force will act which exhausts

When we inquire into this influence it must be admitted that condition (3) alone does not lead to the negative sign in a mathematical strict way. I only claimed loc. cit. to make it "highly plausible" that the sign should be negative.

If the curve which represents $\overline{w(t)}$ as function of t, changes its sign only once, and therefore presents a shape of the type of fig. A,



A.



B

C.

the velocity. Finally loc cit. p. 1265 the equation occurs:

$$\int_0^t w(\vartheta)\, d\vartheta = -x_0$$

which as I indicate there, will be valid for not *too* small values of t, and which can hardly be reconciled with the supposition $\overline{\dot{x}_0 w(t)} = 0$ for every value of t.

the sign is certainly negative. But if, as is not excluded, $w(t)$ changes its sign more than once, (3) is not sufficient to lead rigorously to the negative sign. Possibly this may be shown by the aid of an analysis according to FOURIER, but it is simpler to derive this from fig. *B*, where a course of the curve has been drawn which does satisfy (3), and yet yields a positive value of Q. Nobody will, however, assume a course like that. If the curve presents more than one change of sign, it will probably be represented by a strongly damped oscillating line of the type of fig. *C*, in which the fact that it ends with a positive part at $w(t)$ and satisfies condition (3), renders the negative sign very probable for Q.

III. One of the principal objections of O. and B. refers to the fact that Miss SNETHLAGE and I repeatedly make use of the three equations which must be considered in connection with each other, viz.:

$$\frac{1}{m}\frac{d\mathfrak{K}_x}{dt} = \frac{d^2u(t)}{dt^2} = -p\,u(t) + q(t) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$p = \frac{1}{m}\frac{\overline{\mathfrak{K}^2(t)}}{\overline{u^2(t)}} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\overline{u(t)\,q(t)} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

O. and B. assert that it follows from this that $\overline{u^2}$ cannot be constant. When we now examine these equations, we see that (4) means only that we take $\frac{d^2u}{dt^2}$ for a definite particle, and add pu to it ($p =$ a positive constant that has been left undetermined for the present). As u is a function of t, this sum will also be so, and we can represent it by $q(t)$. Taken in this way this equation does not hold only for a definite moment $t = 0$, as ORNSTEIN asserts, but of course for any moment. It is an ordinary differential equation and it can be integrated without difficulty, though neither from the equation itself nor from the integral anything can be derived when it is not considered in connection with (5) and (6), which are derived as follows. We differentiate $\overline{u^2(t)} =$ constant twice with respect to t and get then:

$$\overline{u(t)\cdot\frac{d^2u(t)}{dt^2}} - \overline{\left(\frac{du(t)}{dt}\right)^2} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

As we can differentiate at any moment, also this equation holds, of course, for every value of t [1]).

If we now multiply (4) by $u(t)$ (*not* by $u(0)$ [1]), if we then average,

[1]) ORNSTEIN has repeatedly asserted that these equations do not hold for every value of t, that (4) is *no* differential equation, and that it may *not* be integrated. He has, however, never adduced any proof for these assertions. ORNSTEIN and

and if we combine the result with (7) it follows that (6) holds for every value of t, when the value of (5) is assigned to the constant p, which had been left undetermined at first.

Whereas (4) does not teach us anything, and must only be taken as a definition of q, (5) and (6) are a direct consequence of $\overline{u^2} =$ = constant. And if O. and B. should succeed in proving (as they pretend they do) that it follows from the complex (4) (5) and (6) that $\overline{u^2}$ cannot be constant, they would have done no less than proving that the mathematics used are in conflict with the principium contradictionis. When their proof is examined, we arrive at another conclusion. In the first place they substitute again another equation for ours, and write $\overline{q} = 0$ (for given u_0 and $\dot{u}_0$)[1], which must no doubt mean that $\overline{u_0 q(t)} = 0$ and $\overline{\dot{u}_0 q(t)} = 0$, instead of $\overline{u(t)q(t)} = 0$, as we derived. When averaging the square of u they accordingly erroneously omit the terms:

$$2u_0 \cos(\sqrt{p}\,.\,t) \times \frac{1}{p}\int_0^t q(\vartheta) \sin\{\sqrt{p}\,(t-\vartheta)\}\,d\vartheta \quad \text{and}$$

$$2\frac{\dot{u}_0}{\sqrt{p}} \sin(\sqrt{p}\,.\,t) \times \frac{1}{p}\int_0^t q(\vartheta) \sin\{\sqrt{p}\,(t-\vartheta)\}\,d\vartheta$$

They further expand $q(t)$ into a series of FOURIER and subject the coefficients of this series to the same suppositions as PLANCK introduced for radiation, though it is very much the question whether these suppositions hold here. For though it is true that the two curves in a certain sense are dependent on quantities determined by chance, yet there are correlations between the q's at different moments, which have influence on the mean values of the FOURIER-coefficients, which influence O. and B. have not examined.

I will not enter into other objections of Messrs. O. and B I think that they were already beforehand sufficiently refuted by what I wrote loc. cit. In particular this refers to the objection O. and B. advance loc. cit. p. 923 to the (apparent) occurrence of a term with t^2 in $\overline{\Delta^2}$, for which compare Remark II of my article loc. cit. p. 1265.

ZERNIKE *have*, however, rightly proved that the complex of the equations (4), (5), and (6) is *not* valid, when the means are extended over a group of particles which at the moment $t = 0$ have a definite velocity $\dot{u}(o)$ — and this is easy to see for $\overline{\dot{u}^2}$ is not constant for such a group — but this cannot be a reason why we should not be allowed to use the complex with means over *all* particles, in which case they *are* valid.

[1]) In consequence of a difference in notation they write $\overline{w} = 0$, p. 928 loc. cit.