Physics. — *"On the theory of the Brownian motion."* By Prof. L. S. ORNSTEIN and Dr. H. C. BURGER. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of September 29, 1918).

Prof. VAN DER WAALS JR. has developed in these communications [1]) a new theory of the Brownian motion. We shall demonstrate in this paper, that he has made use of various wrong suppositions and theses in his reasoning.

1. VAN DER WAALS starts from the equation of motion of a Brownian particle in the formula:

$$\ddot{x} = w(t) \quad \ldots \quad \ldots \ldots \quad (1)$$

Here $w(t)$ is the force which the particle experiences from the molecules of the liquid. The force $w(t)$ is a magnitude depending upon chance.

In order to arrive at a theory of the Brownian motion V. D. WAALS introduced the supposition that $\dot{x}_0 w(t)$ — the product of the velocity at the time zero and the force at the time t — is zero "on an average over all particles [2]).

Now we can understand the average in two ways, viz.:

a. at a given initial velocity $\dot{x}_0$, thus $\overline{w(\vartheta)} = 0$.

b. at all possible initial velocities, in which case the distribution of velocity according to MAXWELL must be taken into consideration. VAN DER WAALS uses the average in the way last mentioned. We shall also examine to what the supposition leads if we apply the first way of determining the average and show that the determination according to (*a*) as well as V. D. WAALS uses it leads to impossible consequences.

In this purpose we take down the first integral of (1), which is

$$\dot{x} = \dot{x}_0 + \int_0^t w(\vartheta)\, d\vartheta \quad . \quad \ldots \ldots \quad (2)$$

If we determine the average according to (*a*) we obtain

[1]) These com. Vol. XX. 1918. p. 1254.

[2]) cf. p. 1258 of the paper quoted.

$$\overline{\dot{x}} = \dot{x}_0,$$

which in physics is an impossible result.

If we square (2) and determine the average according to (*a*), we obtain

$$\overline{\dot{x}^2} = \dot{x}_0^2 + \overline{\left\{ \int_0^t w(\vartheta)\, d\vartheta \right\}^2}$$

a result which, as is immediately obvious, is opposed to the theorem of equipartition, as the average of the second member is essentially positive, so that if e.g. $\dot{x}_0^2$ is more than the equipartition-value, this would also be the case with $\overline{\dot{x}^2}$. If we determine the average of the square of (2) in the supposition (*b*) we find

$$\overline{\dot{x}^2} = \overline{\dot{x}_0^2} + \overline{\left\{ \int_0^t w(\vartheta)\, d\vartheta \right\}^2}$$

And as now $\overline{\dot{x}_0^2}$ in this case has the equipartition-value, $\overline{\dot{x}^2}$ would be essentially more than this value, which contains a contradiction, as the average square of the velocity must be equal for all particles, at any moment.

VAN DER WAALS has made use of the second integral of (1) viz.

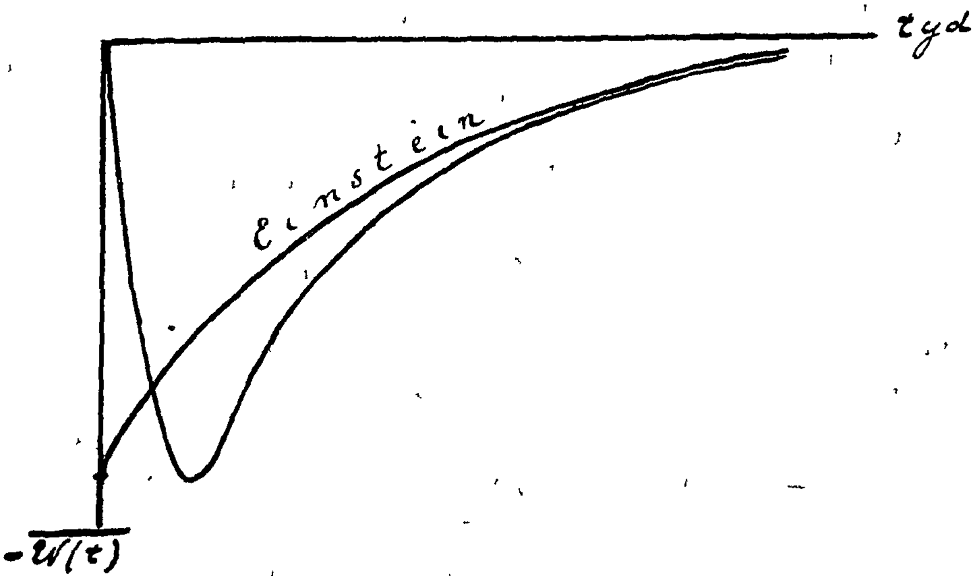
$$x = x_0 + \dot{x}_0 t + \int_0^t w(\vartheta)\,(t-\vartheta)\, d\vartheta$$

to arrive at his theory. In the same way as above we can demonstrate that this combined with his supposition $\overline{\dot{x}_0 w(t)} = 0$ leads to incorrect results, contrary to theory and observation. For if we make up $\overline{x-x_0} = \overline{\Delta^2}$, supposition (*a*) yields

$$\overline{\Delta^2} = \dot{x}_0^2 t^2 + \overline{\left\{ \int_0^t w(\vartheta)\,(t-\vartheta)\, d\vartheta \right\}^2}.$$

And as the average in the second member is positive the highest power of t which occurs in $\overline{\Delta^2}$ will as least be 2, consequently v. D. WAALS' supposition comes into conflict with the formula $\overline{\Delta^2} = bt$, which he applies himself (p. 1257 l.c.). If we determine the average according to (*b*) the only difference is that $\dot{x}_0^2$ must be replaced by the equipartition value of the velocity-square, so that also in determining the average according to VAN DER WAALS the formula used by him combined with his supposition $\overline{\dot{x}_0 w(t)} = 0$ leads to an incorrect result. Besides the negative conclusion that the theory of V. D. WAALS ought to be rejected some positive result can be deduced from our calculations.

The formula (1) is just as much a matter of course as it is right [1]) and consequently there must be a mistake in the supposition $\overline{\dot{x}_0 w(t)} = 0$, while there can be no difficulty for anyone in seeing that everything is all right when this magnitude can become negative for fixed values of t. We shall in this paragraph use the average according to (a). As $\dot{x}_0$ has been given once and for all, the above reasoning shows, that $\overline{w(t)}$ for certain values of t must possess the opposite sign of $\dot{x}_0$ [2]). Now VAN DER WAALS has rightly drawn attention to it, that according to statistical mechanics for $t = 0, \overline{w(t)} = 0$. Besides it is evident, that for t infinite the average value of $w(t)$ undergoes no influence from $\dot{x}_0$ and therefore must be zero. The course of $w(t)$ may consequently be imagined in a way as represented by the accompanying figure (where $\dot{x}_0$ has been supposed positive).



Of course the curve may be more complicated for example $\overline{w(t)}$ might oscillate round the axis. If now we calculate $\overline{w(t)}$ according to the EINSTEIN-LANGEVIN formula, we find, if we take into consideration that $\overline{F(t)}$ is equal to zero:

$$\overline{w(t)} = -\beta\overline{\dot{x}} + \overline{F(t)} = -\beta e^{-\beta t}\,\dot{x}_0$$

[1]) From the formula (1) we can deduce the relation $\overline{\Delta^2} = bt$ if we introduce suppositions, it is however impossible to find the value of b, without penetrating into the mechanism of the Brownian motion.

[2]) There are cases, when this is not so necessary according to what precedes, but if $\dot{x}_0$ is more than the equipartition value, it is certainly the case.

For $t = 0$ the line, which represents this course, deviates from the true curve. The important agreement existing between EINSTEIN's theory and the experiment now makes us presume, that the true $w(t) - t$ curve and the curve according to EINSTEIN only deviate from each other for short times after the departure of the particle with the velocity $\dot{x}_0$, that so the maximum in thé true curve lies close to $t = 0$, and that from this maximum onward it descends pretty well exponentially according to EINSTEIN's curve. It goes without saying that these are only assumptions, which a calculation of the true $\overline{w(t)}$ curve must prove from the molecular theory. We are however of opinion that it is worth while to point to this possible interpretation of EINSTEIN's master-stroke in the theory of the Brownian motion.

§ 2. VAN DER WAALS' theory further rests on the thesis that the magnitude

$$\overline{w(t)\int_0^t w(\vartheta)\,(t-\vartheta)\,d\vartheta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is essentially negative, if only t be not taken to small.

Perhaps it is not quite superfluous to demonstrate after what precedes, that this thesis is not right; expecially as an integral of the same kind used by one of us may be treated in the same way[1]).

When $w(t)$ is a function determined by chance, of which the character is not dependent upon the time, we can represent it for a long interval by a FOURIER-series, the coëfficients of the FOURIER-series determine the nature of the accidental character [2]). If so

$$w(t) = \Sigma_n \left(A_n \sin \frac{2\pi n t}{T} + B_n \cos \frac{2\pi n}{T} t\right),$$

when $\overline{w(t)} = 0$, we must have $B_0 = 0$.

The calculation of (3) becomes simple, when we apply that

[1]) Compare L. S. ORNSTEIN. On the Brownian motion. These Proc. XXV, 1917. p. 96.

[2]) When we have to do with a function of accidental character, even then the conduct of this function may very well depend upon the time. If we consider e.g. the length of the path in Brownian motion, we get for all times $\overline{\Delta} = 0$, but $\overline{\Delta^2} = bt$, for the velocity however we have $\overline{v} = 0$. $\overline{v^2}$ is constantly independent of the time. For the force something analogeous as for the velocity ought to be assumed. By going further into the mechanism of the motion, this can be rendered plausible.

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

or as the zero point of the time is arbitrary, it may be replaced by

$$\int_\zeta^{t+\zeta} w(\vartheta)\,(t+\xi+\vartheta)\,d\vartheta = \int_0^t dt \int_\zeta^{t+\xi} w(\vartheta)\,d\vartheta.$$

The average value in question may now be represented by

$$\overline{w(t)\int_0^t w(\vartheta)\,(t-\vartheta)\,d\vartheta} = \frac{1}{T}\int_0^T d\xi\, w(\xi+t)\int_0^t dt \int_\zeta^{t+\zeta} w(\vartheta)\,d\vartheta.$$

For the sake of simplification the time-unity may be chosen so that the time T is equal to 2π, thus we find

$$\int_\xi^{\xi+t} w(\vartheta)\,d\vartheta = \sum_n \left[-\frac{A_n}{n}\{\cos n(t+\xi) - \cos n\zeta\} + \frac{B_n}{n}\{\sin n(t+\xi) - \sin n\xi\}\right]$$

which once again integrated with respect to t from o to t yields

$$\sum_n \Big[-\frac{A_n}{n^2}\{\sin n(t+\xi) - \sin n\xi\} +$$

$$+\frac{A_n}{n}\,t\cos n\xi - \frac{B_n}{n^2}\{\cos n(t+\xi) - \cos n\xi\} - \frac{B_n}{n}\,t\sin n\xi\Big].$$

This expression must subsequently be multiplied by

$$w(t+\xi) = \sum_n\{A_n \sin n(t+\xi) + B_n \cos n(t+\xi)\}$$

and thus integrated with respect to ξ from zero to 2π. Then all terms of the product in which n has odd values fall out. At last the average value sought for is given by

$$\overline{w(t)\int_0^t w(\vartheta)\,(t-\vartheta)\,d\vartheta} = \frac{1}{2\pi}\sum\left(-\frac{C^2_n}{n} + \frac{C^2_n}{2n^2}\cos nt + \frac{C^2_n}{2n}\,t\sin nt\right)$$

where $C_n^2 = A_n^2 + B_n^2$. In the usual way this sum may be converted into an integral, in which the average value $\frac{C_n^2}{2\pi}$ is represented by $f(n)$[1]. In the average value described we find in this way

[1] By PLANCK, EINSTEIN, LAUE series of FOURIER have been applied in the discussion of questions of probability (e.g. average values).

$$\int_0^{\infty} \frac{f(n)}{2n^2} (nt \sin nt + \cos nt - 1)\, dn\ ^1).$$

The sign of this integral may for larger values of t be made quite arbitrarily by proper choice of $f(n)$. That it should be essentially negative is consequently not true [2]).

3. In the quoted paper by ORNSTEIN the first theory of the Brownian motion as developed by Dr. SNETHLAGE and J. D. v. D. WAALS was criticised on the basis of the fact that it comes into conflict with the theorem of equipartion.

There the thesis was made use of that

$$\overline{\left\{ \int_0^t w(\xi) \sin \varrho (t-\xi)\, d\xi \right\}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

is proportional to t. Here $w(\xi)$ is a function subjected to chance, so that the average value is zero [3]). In a note VAN DER WAALS says: "This change of sign (of $w(\theta)\, w(\theta+\sigma)$ was overlooked by ORNSTEIN. In consequence of this he arrived at the remarkable conclusion, that it is not allowed to accept that $\frac{d}{dt} \overline{u^2} = 0$. For from this it follows according to his calculation that $\overline{u^2}$ is not constant, but the sum of a lineary and periodical function of t!"

It is necessary to remark in contradiction to this, that the differential equation [4]) of v. D. WAALS—SNETHLAGE viz.

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[1]) For $t = \infty$ this expression becomes equal to $\frac{t}{4} f(0)$, is thus essentially positive (i.e. f is essentially positive)

For very great values of t we can require that the average is $\varphi(t)$, then we get

$$\frac{f(n)}{n} = \frac{2}{\pi} \int_0^{\infty} \frac{\varphi(\lambda)}{\lambda} \sin n\lambda\, d\lambda$$

for very small values of t the average value is also positive.

[2]) The proof that v. D WAALS gives of the disputed thesis by differentiating $\overline{\Delta^2}$ (p. 1331 of his paper) is not right. The formula $\overline{\Delta^2} = bt$ is deduced by a transition to a limit, and the process is such that in differentiating $\overline{\Delta^2}$ we do not get b as Δ cannot be differentiated.

[3]) Compare ORNSTEIN, these reports XXI, p. 96.

[4]) The equation, which is treated by both authors as a differential equation, does not apply, as they suppose, to arbitrary kinds, but only to the commencement of the movement, compare ORNSTEIN and ZERNIKE, These Proc. XXI, p. 109.

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$$\frac{d^2u}{dt^2} = -\varrho^2 u + w \qquad \overline{w} = 0 \text{ (given ad } \dot{u}_0 \text{ and } u_0\text{)}$$

eads to incorrect results. For we get according to their equation

$$\overline{u^2} = \left(u_0 \cos \varrho t + \frac{\dot{u}_0}{\varrho} \sin \varrho t\right)^2 + \frac{1}{\varrho^2} \overline{\left\{ \int_0^t w(\xi) \sin \varrho(t-\xi)\, d\xi \right\}^2}$$

and as we shall once again prove further on the last average value is proportional to t. From the suppositions of VAN DER WAALS and Miss SNETHLAGE the remarkable conclusion does really follow, that the velocity of a Brownian particle should increase infinitely.

The proof of the thesis that (5) is proportional to t, which is only slightly different from a deduction given by PLANCK already in another connection, runs as follows. The integral may be written in the form:

$$\overline{\int_0^t \int_0^t W(\xi)\, W(\eta) \sin \varrho (t-\xi) \sin \varrho(t-\eta)\, d\xi\, dy.}$$

or if we interchange integrating and determining the average:

$$\int_0^t \int_0^t \overline{W(\xi)\, W(\eta)} \sin \varrho(t-\xi) \sin \varrho(t-\eta)\, d\xi\, d\eta.$$

If now we introduce $\eta = \xi + \psi$, we get

$$\int_0^t d\xi \sin \varrho(t-)\xi \int_{-\xi}^{t-\xi} \overline{W(\xi)\, W(\xi+\psi)} \sin \varrho(t-\xi-\psi)\, d\psi$$

In this form we again introduce for W a FOURIER-series in which $\overline{W}_0 = 0$, whilst we must take $B = 0$.

We then find for the average value

$$\overline{W(\xi)\, W(\xi+\psi)} = \sum_n (A^2_n + B^2_n) \cos \frac{2\pi}{T} n\psi$$

So that the integral in question if for the sake of simplification we take $\frac{2\pi n}{T} = \varrho_n$ becomes

$$\int_0^t \sin \varrho\, (t-\xi) d\xi \int_{-\xi}^{t-\xi} \sum_n (A_n^2 + B_n^2) \sin \varrho\, (t-\xi-\psi) \cos \varrho_n \psi\, d\psi =$$

$$= \Sigma (A_n^2 + B_n^2) \int_0^t \sin \varrho(t-\xi) d\xi \int_{-\xi}^{t-\xi} \sin \varrho(t-\xi-\psi) \cos \varrho_n \psi\, d\psi.$$

While calculating these integrals we need only take into account terms, which get the highest power of $\varrho-\varrho_n$ in the denominator, as only these contribute in a way worth mentioning to the result. If we execute the quite elementary calculation we arrive at the result

$$\overline{\left\{\int_0^t W(\xi)\sin\varrho(t-\xi)d\xi\right\}^2} = \sum_n \frac{\sin^2\frac{\varrho-\varrho_n}{2}t}{(\varrho-\varrho_n)^2}(A_n^2+B_n^2)$$

When ϱt is great we can write for this

$$(A^2+B^2)\int_0^\infty \frac{\sin^2\frac{\varrho-\varrho_n}{2}t}{(\varrho-\varrho_n)^2}d\varrho_n = (A^2+B^2)\frac{t\pi}{4};$$

in which A and B are the coefficients of the terms of the series for which $\varrho_n=\varrho$, consequently $\frac{2\pi n}{T}=\varrho$, or rather the integer that lies closest to this.

As long as A^2+B^2 differs from zero the value of the average in question is proportional to the time. A^2+B^2 is *strictly* zero, this does not hold good, but there is not a single reason to suppose, that in the Brownian motion the term of which the frequency is determined by ϱ should just be missing in the FOURIER-series. But even should it be missing, we should on the basis of the suppositions of VAN DER WAALS and Dr. SNETHLAGE arrive at the improbable result, that the average value of the velocity of a Brownian particle never reaches the equipartiton value.

4. In VAN DER WAALS' paper it is urged that LANGEVIN's deduction of the formula $\overline{\Delta^2}$ would contain an inner inconsistency. This inconsistency is held not to appear in the theory that Mrs. Dr. DE HAAS-LORENTZ has worked out on the basis of EINSTEIN's formula. And as the starting point according to EINSTEIN and that of LANGEVIN are identical, it would be surprising if the one theory would be inwardly inconsistent and the other not, unless LANGEVIN should have made a blunder in calculation. This however is not the case, if we formulate the basis as was done in ORNSTEIN's paper, there exists no contradiction. As well EINSTEIN's theory as that of LANGEVIN rests on the following suppositions

$$\frac{du}{dt} = -wu + F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

$$\overline{F} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\beta)$$

$$\int_{-\infty}^{+\infty} \overline{F(\xi)\, F(\xi+\psi)}\, d\psi = \frac{kT}{m}\beta = \vartheta \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\gamma)$$

provided we start from particles which at the time $t = 0$, have the velocity u_0.

If we accept this set of equations, which kinetically have not been proved, which however contains the inconsistency developed in § 1, we *afterwards* do not arrive at any contradiction.

Van der Waals looked for it in the equation arising when (2) is multiplied by u and the average is determined, he wrote down [1])

$$\overline{u\frac{du}{dt}} = -\overline{wu^2}$$

which is really incorrect, but he forgot then that $\overline{Fu}$ is not zero, if we put ourselves on the standpoint of the suppositions $6(\alpha, \beta, \gamma)$; as Ornstein demonstrated on p. 1011 of his paper. If we introduce for $\overline{uF}$ the value found there the equation adopts the form

$$\overline{u\frac{du}{dt}} = \beta\left(u_0^2 - \frac{\vartheta}{2\beta}\right)e^{-2\beta t}$$

For times large with reference to $\frac{1}{\beta}$ this is zero, whilst if the average is determined over all particles it is always zero as $\overline{u_0^2} = \frac{\vartheta}{2\beta}$.

Now it is supposed in Langevin's proof that $\overline{xF} = 0$. It might be doubted perhaps whether this magnitude is equal to zero [2]). Yet this is the case. For we have

$$\frac{d^2x}{dt^2} = -\beta\frac{dx}{dt} + F$$

so

$$x = x_0 + \frac{u_0}{\beta}(1 - e^{-\beta t}) + \int_0^t e^{-\beta\xi}\, d\xi \int_0^\xi e^{\beta\eta} F(\eta)\, dy$$

so

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[1]) Langevin has not developed any reasonings that could give rise to the supposition that he puts $\overline{Fu} = 0$.

[2]) On the fact that $\overline{xF} = 0$ rests the very simple theory which Langevin gave of the Brownian motion.

$$\overline{F\dot{x}} = [x_0 + \frac{u_0}{\beta}(1-e^{-\beta t})]\overline{F} + \overline{F\int_0^{t} e^{-\beta\xi}d\xi\int_0^{\xi} e^{\beta\eta}F(\eta)dy}$$

The first term is zero according to 6β, for the second term we can write by partial integration

$$-\frac{1}{\beta}\overline{F(t)e^{-\beta t}\int_0^t e^{\beta\eta}F(\eta)\,dy} - \overline{F(t)\int_0^t F(\eta)\,dy}.$$

The two last integrals are equal, as $F(t)\,F(\eta)$ is different from zero only if η lies in the immediate neighbourhood of t. The value of both integrals, as proved in ORNSTEIN's paper, is $\frac{\vartheta}{2}$.

Thus it becomes clear that there is no question of inner contradiction, and that only the supposition about $W(t)$ — incorrect through the times of commencement — is an error in the theory of EINSTEIN and LANGEVIN. As we showed in § 1 of this paper the value which according to EINSTEIN's formula is obtained for the average force at a given velocity at the time zero $\overline{W(t)}$ only deviates for a very short time from the real value of this magnitude. The fact that EINSTEIN's formula leads to results which agree well with reality support the supposition that the relation

$$\overline{W(t)} = -\beta\dot{x}_0\, e^{-\beta t}$$

holds with a very good approximation already a very short time after the moment in which all emulsion-particles possess the velocity $\dot{x}_0$. The true kinetic theory of the Brownian motion will perhaps be able to give an account of this fact.

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