Physics. — "*The Theory of the Brownian Motion and Statistical Mechanics*". By Prof. L. S. ORNSTEIN and Dr. F. ZERNIKE. (Communicated by Prof. H. A. LORENTZ).

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Prof. J. D. v. D. WAALS Jr. and Miss. Dr, A. SNETHLAGE have raised objections derived from statistical mechanics against the usual deductions from EINSTEIN's formula of the Brownian motion. These objections may be formulated as follows:

Firstly: It is not right to introduce a resistance on an emulsion particle, which is proportional to the velocity of that particle, as according to a well-known result of statistical mechanics velocities and forces are independent of each other, as is appearent from

$$\overline{vK} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Still more clearly this independence is visible, if one considers that the above equation is not only applicable to the average over a canonical ensemble, but even for any group of systems from that ensemble for which the particle considered has a definite velocity v, so that for such a group $\overline{K} = 0$.

Secondly: It is not right to apply to this force of resistance the formula of STOKES, as it supposes that the liquid around the particle has a motion dependent upon the velocity of the particle. This comes into conflict with statistical mechanics, for these teach, that

$$\overline{v\, v_1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where e.g. for v the velocity of the particle, for v_1 that of a molecule (both e.g. in the x-direction) in its neighbourhood may be taken. And so Miss SNETHLAGE has assumed for the calculation of the persistence of a particle in the Brownian motion, that the surrounding molecules have the usual Maxwellian distribution of velocity.

The authors mentioned have tried to give a theory of the Brownian motion which escapes these objections, by starting from (1). In what follows we want to show, that the equations (1) and (2) are much less far-reaching than it seems so that the objections to the usual theory may be considered to have fallen away, and on the other hand the reasoning given is proved not to be the right one.

In order to deduce the differential equation, which she wants to put in the place of the equation of LANGEVIN-EINSTEIN, Miss SNETHLAGE differentiates equation (1) according to t. This yields

$$\overline{v\frac{dK}{dt}} = -\overline{K\frac{dv}{dt}} = -\frac{\overline{K^2}}{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

From which she rightly concludes that $\frac{dK}{dt}$ is not independent of v. The nature of this dependence will be known, if for each value of v one knows the average $\overline{\frac{dK}{dt}}^{v} = F(v)$. Then there may be written for *one* system:

$$\frac{dK}{dt} = F(v) + w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

where w is an accidental quantity which on the average is zero $(\overline{w}^{v} = 0)$.

If we want to determine $F(v)$ it is apparently necessary to consider the group of systems with a definite value of v. We shall further on indicate an average in such a "v-group", the same as above by $\overline{}^{v}$, i. e. the average over the systems where in *one* definite moment v has a prescribed value, whilst the symbol — will indicate the average for the whole ensemble. As is proved by the following calculation equation (3) in not applicable, as (4) and (2), to every v-group in particular; and this Miss SNETHLAGE has left out of consideration.

Let K represent the force acting in the x-direction on the particle, v the velocity of this particle in that direction. Equation (1) is then found for the canonical ensemble, when K does not depend upon the velocities, and is exclusively a function of the coordinates $q_1 \ldots q_n$.

Let q_1 be the x coordinate of the particle, so that $\dot{q}_1 = v$. Then we have

$$\frac{dK}{dt} = \frac{\partial K}{\partial q_1} v + \frac{\partial K}{\partial q_2} \dot{q}_2 + \ldots \frac{\partial K}{\partial q_n} \dot{q}_n$$

and for the average at definite v

$$\overline{\frac{dK}{dt}}^{v} = \overline{\frac{\partial K}{\partial q_1}}^{v} v + \overline{\frac{\partial K}{\partial q_2}}^{v} \overline{\dot{q}_2}^{v} + \text{ etc.}$$

In order to reduce the last term we have made use of the well-known independence of the extension in velocity and configuration. These terms fall out because $\overline{\dot{q}_2}^{v} = 0$. The same independence has as its result that

$$\frac{\overline{\partial K^v}}{\partial q_1} = \frac{\overline{\partial K}}{\partial q_1}.$$

The last average is easily calculated from GIBBS' formulae.

$$\overline{\frac{\partial K}{\partial q_1}} = \frac{\int \frac{\partial K}{\partial q_1} e^{-\frac{\varepsilon}{\Theta}} dq_1 \ldots dq_n}{\int e^{-\frac{\varepsilon_q}{\Theta}} dq_1 \ldots dq_n}$$

Integrating by parts the denominater yields

$$\frac{1}{\Theta}\int K \frac{\partial \varepsilon}{\partial q_1} e^{-\frac{\varepsilon_q}{\Theta}} dq_1 \ldots dq_n$$

as the integrated part falls out ($\varepsilon = \infty$ at the limits).

Now

$$\frac{\partial \varepsilon}{\partial q_1} = - K \text{ and therefore } \overline{\frac{\partial K}{\partial q_1}} = - \frac{1}{\Theta} \overline{K^2}$$

Considering that $\Theta = M \overline{v^2}$, we obtain

$$\frac{\overline{dK^v}}{dt} = - \frac{v}{M \overline{v^2}} \overline{K^2} \quad \ldots \ldots \ldots \quad (5)$$

And so $F(v)$ has been found; equation (4) becomes

$$\frac{dK}{dt} = - \frac{\overline{K^2}}{M \overline{v^2}} v + w \quad \ldots \ldots \ldots \quad (5a)$$

i. e. the very form given to this equation without further proof by v. D. WAALS and Miss SNETHLAGE. (Miss SNETHLAGE equation 24, sees however the note of these Proc. **24**, 1278 where a calculation remotely analogous to ours is found, without however our conclusions being drawn from it.)

The fact that $\frac{\overline{dv^v}}{dt} = 0$ and $\frac{\overline{dK^v}}{dt} = - \frac{v}{M \overline{v^2}} \overline{K^2}$ or $\frac{\overline{d^2 v^v}}{dt^2} = - \frac{\overline{K^2}}{M^2 \overline{v^2}} v$

has great inportance for the theory of canonical ensembles. If at a given moment one chooses a group of systems in which the suspended particle has a definite velocity-component v, then the formulae found are applicable to this group. Now one ought to consider, that, if one follows these systems in the time, the velocity of the particles does not remain the same for all of them, but that different velocities are going to arise. Moreover our formulae indicate that, if we take the average velocity a very short time τ after the selection of the group, it has become smaller than v. By substitution of the above results in a series of TAYLOR we find namely:

$$\overline{v_t}^{v} = v\left(1 - \frac{\overline{K^2}}{2\,M^2\,\overline{v^2}}\tau^2 \ldots\right)$$

Now it is remarkable that, if we follow the systems back into the time, i. e. determine the average for a moment $-\tau$ for a group where at $t=0$ the velocity of the suspended particle is v, exactly the same formula can be applied. So that we get a reversible process and questions analogous to the problem of the tops of H curves solved by EHRENFEST arise. Our reasonings consequently also give in principle how the objections may be put aside, which ZERMELO has raised to the statistical mechanics of GIBBS (as well as to the molecular theories of BOLTZMANN concerning the H theorem [1]).

The result obtained may shortly be formulated in this way: the properties of a group of systems, chosen so that in all of them the suspension-particle has a velocity v — a v-group —, are dependent on the time elapsed since the selection.

We may also ask now after the change of $\overline{vK}^{v}$ with the time for the v-group selected at the moment $t=0$. From the preceding calculation results that

$$\frac{d}{dt}\overline{vK}^{v} = \overline{\frac{dv}{dt}K}^{v} + v\,\overline{\frac{dK}{dt}}^{v} = \frac{\overline{K^2}}{M}\left(1 - \frac{v^2}{\overline{v^2}}\right) \quad . \quad . \quad . \quad . \quad (6)$$

from which it follows that the relation

$$\overline{vK}^{v} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which is the right one for the moment in which the group was selected in the ensemble, is *not* right when this group is followed further.

It is true that the average for the last member of (6) for the ensemble is equal to zero, as is necessary with regard to the stationary character of the whole ensemble, which was already used in the deduction of (3).

Consequently we should be very careful in interchanging differentiation and determination of the average. So equation (5) will only be right for the first moment (just as (4)) and consequently also

[1] One ought to bear well in mind that the series-development given here is only right for a short time after the selection of the v-group from the ensemble. If one follows the group during a long time then the systems of which it consists will have spread themselves over the whole phase-extension with the density that belongs to a canonical ensemble.

For the importance of the EINSTEIN-LANGEVIN formula for this process compare the paper of one of us (ORNSTEIN), (preceding paper).

(5a), which accordingly *must not be looked upon as a differential equation*, Or: if we do consider (5a) right for later moments, we do not get in connection with it $\overline{w}^{v} = 0$, as it is made use of by Miss SNETHLAGE.

We are able to refute the second objection, viz. that statistical mechanics should not allow that the fluid moves with the particle in an analogous way. For this purpose we shall calculate the derivatives of

$$\overline{v v'}^{v} = 0$$

where v' is the x-velocity of an arbitrary molecule situated in the neighbourhood of the particle.

We have

$$\overline{\frac{d}{dt} v v'}^{v} = \overline{\frac{dv}{dt} v'}^{v} + v \overline{\frac{dv'}{dt}}^{v} = \frac{\overline{K}}{M} \overline{v'}^{v} + v \frac{\overline{K'}}{M'} = 0$$

as $\overline{v'}^{v}$ as well as $\overline{K'}$ are zero. Further

$$\frac{d^2}{dt^2} vv' = \frac{d^2v}{dt^2} v' + 2 \frac{dv}{dt}\frac{dv'}{dt} + v \frac{d^2v'}{dt^2} = \frac{1}{M}\frac{dK}{dt} v' + 2\frac{KK'}{MM'} + \frac{v}{M'}\frac{dK'}{dt}.$$

The average of the first term yields

$$\frac{1}{M}\overline{\left\{\frac{\partial K}{\partial q} v v' + \frac{\partial K}{\partial q'} v'^2 + \dots\right\}}^{v} = \frac{1}{M}\overline{\frac{\partial K}{\partial q'}}\,\overline{v'^2} = -\frac{\overline{KK'}}{M\Theta}\overline{v'^2} = -\frac{\overline{KK'}}{MM'}$$

and of the third term

$$\frac{v}{M'}\overline{\left\{\frac{\partial K'}{\partial q} v + \frac{\partial K'}{\partial q'} v' + \dots\right\}}^{v} = \frac{v^2}{M'}\overline{\frac{\partial K'}{\partial q}} = -\frac{v^2}{M'}\frac{\overline{KK'}}{\Theta} = -\frac{v^2}{\overline{v^2}}\frac{\overline{KK'}}{MM'}$$

so that

$$\frac{d^2}{dt^2}\overline{v v'}^{v} = \frac{\overline{KK'}}{MM'}\left(1 - \frac{v^2}{\overline{v^2}}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

For the change of v' with the time we have according to the preceding

$$\overline{\frac{dv'}{dt}} = 0$$

$$\overline{\frac{d^2v'}{dt^2}}^{v} = -\frac{\overline{KK'}}{MM'\,\overline{v^2}}\, v$$

Now K is the sum of the forces in the x-direction, which all other particles exercise on the first, K' the corresponding sum for the second particle.

If we develop the product of these sums, we shall obtain the average of the product of action and reaction that may be assumed to preponderate, so that we may expect that $\overline{KK'}$ is negative. The second derivative of $\overline{v'}^{v}$ consequently has the same sign as v, i.e. the movement of the surrounding matter with the particle, which does not exist at the moment of selection, arises after a short time. According to (8) there is on the average no question of a movement of the surrounding particles with the Brownian particle in an ensemble, as may be expected.

When we want to investigate statistically the qualities of a stationary system of molecules, we can make use of a statistically stationary ensemble and identify the qualities observed with the qualities of the most frequent system in this ensemble or with the corresponding averages.

The system that we consider at an investigation of the Brownian motion — a liquid with a particle suspended in it — is, it is true, not stationary, but all the same it changes only slowly: the moving particle changes its velocity only *slightly* by a *great number* of impacts. Consequently, in order to make use of ensembles for the study of the Brownian motion we must start from a "quasistationary" ensemble and deduce the qualities of the real Brownian motion from the properties of the most usual system in such an ensemble.

The calculations given show, that the groups chosen with definite v from a canonical ensemble do *not* form such quasi-stationary ensembles. However it seems probable to us that such a group, when we follow it a short time, will get to fulfill the requirements, though it will be difficult to show this by direct calculation. The v-group, which has become quasi-stationary at a later moment, would then correspond to the ensemble selected from the canonical ensemble, by selecting those systems in which the particle has already got the velocity v during a short time.

An indication with regard to the length of time required was found along another method by one of us in a former paper [1]).

The above quoted statistic-mechanical objections to the application of the law of STOKES thus probably have no justification for a real system, but only for the first moment of a v-group, i.e. at the very time when it cannot yet be made use of to represent the properties of a real system.

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[1]) L. S. ORNSTEIN. l. c. — This time must namely be of the order of the time during which there is a correlation between the irregular impulses, i. e. $\overline{F(\xi)F(\xi+\tau)}$ differs from zero.