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[3] A detailed paper giving the full spectra of the light atoms with photographs will soon be published in the *Astrophysical Journal* in collaboration with Mr. I. S. Bowen.

[4] *Zeit. Physik*, **1**, 1920 (439).

[5] *Ibid.*, **2**, 1920 (470).

[6] This convention is more logical than that used in a former paper (cit.[2]) in naming the L_α line.

[7] *Astroph. J.*, **43**, 1916 (102).

THE AVERAGE OF AN ANALYTIC FUNCTIONAL AND THE BROWNIAN MOVEMENT

By Norbert Wiener

Department of Mathematics, Massachusetts Institute of Technology

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The simplest example of an average is the arithmetical mean. The arithmetical mean of a number of quantities is their sum, divided by their number. If a result is due to a number of causes whose contribution to the result is simply additive, then the result will remain unchanged if for each of these causes is substituted their mean.

Now, the causes contributing to an effect may be infinite in number and in this case the ordinary definition of the mean breaks down. In this case some sort of measure may be used to replace number, integration to replace summation, and the notion of mean reappears in a generalized form. For instance, the distance form one end of a rod to its center of gravity is the mean of its length with reference to its mass, and may be written in the form

$$\int l dm \div \int dm$$

where l stands for length and m for mass. It is to be noted that l is a function of m, and that the mean we are defining is the mean of a function. Furthermore, the quantity, here the mass, in terms of which the mean is taken, is a necessary part of its definition. We must assume, that is, a normal distribution of some quantity to begin with, in this case of mass.

The mean just discussed is not confined to functions of one variable; it admits of an obvious generalization to functions of several variables. Now, there is a very important generalization of the notion of a function of several variables: the function of a line. For example, the attraction of a charged wire on a unit charge in a given position depends on its shape. The length and area of a curve between two given ordinates depend on its shape. As a curve is essentially a function, these functions of lines may be regarded as functions of functions, and as such are known as functionals. Since a function is determined when its value is known for all arguments, a functional depends on an infinity of numerical determi-

nations, and may hence be regarded as in some wise a function of infinitely many variables.

To determine the average value of a functional, then seems a reasonable problem, provided that we have some convention as to what constitutes a normal distribution of the functions that form its arguments. Two essentially different discussions have been given of this matter: one, by Gâteaux, being a direct generalization of the ordinary mean in n-space;[1] the other, by the author of this paper,[2] involving considerations from the theory of probabilities. The author assumes that the functions $f(t)$ that form the arguments of his functionals have as their arguments the time, and that in any interval of the small length ϵ as many receive increments of value as decrements of equal size. He also assumes that the likelihood that a particle receive a given increment or decrement is independent of its entire antecedent history.

When a particle is acted on by the Brownian movement, it is in a motion due to the impacts of the molecules of the fluid in which it is suspended. While the retardation a particle receives when moving in a fluid is of course due to the action of the individual particles of the fluid, it seems natural to treat the Brownian movement, in a first approximation, as an effect due to two distinguishable causes: (1) a series of impacts received by a particle, dependent only on the time during which the particle is exposed to collisions; (2) a damping effect, dependent on the velocity of the particle. If we consider one component of the total impulse received by a particle under heading (1), we see that it may be considered as a function of the time, and that it will have the sort of distribution which will make our theory of the average of a functional applicable.

It will result directly from the previous paper of the author that if $f(t)$ is the total impulse received by a particle in a given direction when the unit of time is so chosen that the probability that $f(t)$ lie between a and b is

$$\frac{1}{\sqrt{\pi t}}\int_a^b e^{-\frac{x^2}{t}}\,dx$$

then the average value of

$$A + \int_a^b f(t)\,G(t)dt + \int_a^b\int_a^b f(s)\,f(t)\,H(s,t)\,ds\,dt \quad [H(s,t) = H(t,s)]$$

will be

$$A + \int_a^b\int_a^s t\,H(s,t)\,ds\,dt. \qquad (1)$$

We now proceed to a more precise and detailed treatment of the question.

2. Einstein[3] has given as the formula for the mean square displacement in a given direction of a spherical particle of radius r in a medium of viscosity η over a time t, under the action of the Brownian movement, the formula

$$\overline{d_t^2} = RTt \div 3\pi r\eta N$$

where R is the gas-constant, T the absolute temperature of the medium, and N the number of molecules per gram-molecule. In the deduction of this formula, Einstein makes two important assumptions. The first is that Stokes' law holds concerning forces of diffusion. Stokes' law states that a force F will carry particle of radius r through a fluid of viscosity η with velocity $F \div 6\pi r\eta$. Einstein's second assumption is that the displacement of a particle in some interval of time small in comparison with those which we can observe is independent, to all intents and purposes, of its entire antecedent history. It is the purpose of this paper to show that even without this assumption, under some very natural further hypotheses, the departure of $\overline{d_t^2}/t$ from constancy will be far too small to observe.

In this connection, it is well to take note of just what the Brownian movement is, and of the precise sense in which Stokes' law holds of particles undergoing a Brownian movement. In the study of the Brownian movement, our attention is first attracted by the enormous discrepancy between the apparent velocity of the particles and that which must animate them if, as seems probable, the mean kinetic energy of each particle is the same as that of a molecule of the gas. This discrepancy is of course due to the fact that the actual path of each particle is of the most extreme sinuosity, so that the observed velocity is almost in no relation to the true velocity. Now, Stokes' law is always applied with reference to movements at least as slow as the microscopically observable motions of a particle. It hence turns out that Stokes' law must be treated as a sort of average effect, or in the words of Perrin,[4] "When a force, constant in magnitude and direction, acts in a fluid on a granule agitated by the Brownian movement, the displacement of the granule, which is perfectly irregular at right angles to the force, takes in the direction of the force a component progressively increasing with the time and in the mean equal to $Ft \div 6\pi\zeta a$, F indicating the force, t the time, ζ the viscosity of the fluid, and a the radius of the granule."

It is a not unnatural interpretation of this statement to suppose that we may assume the validity of Stokes' law for the slower motions which are all that we see directly of the Brownian motion, so that we may regard the Brownian movement as made up (1) of a large number of very brief, independent impulses acting on each particle and (2) of a continual damping action on the resulting velocity in accordance with Stokes' law. It is to be noted that the processes which we treat as impulsive forces need not be the simple results of the collision of individual molecules with the particle, but may be highly complicated processes, involving intricate interactions between the particle and the surrounding molecules. It may readily be shown by a numerical computation that this is the case.

It follows from considerations discussed at the beginning of my paper on *The Average of an Analytic Functional* that after a time the probabil-

ity that the total momentum acquired by a particle from the impacts of molecules will lie between x_0 and x_1 is of the form

$$\frac{1}{\sqrt{\pi ct}}\int_a^b e^{-\frac{x^2}{ct}}dx$$

Superimposed on this momentum is that due to the viscosity acting in accordance with Stokes' law, namely $6\pi r\eta V$, where V is the velocity of the particle. We shall write Q for $6\pi r\eta \div M$, where M is the mass of a particle.

Let us write τ for ct. Let the total impulse received by a given particle in time t, neglecting the action of viscosity, be $f(\tau)$. Consider $m(t)$, the actual momentum of the particle, as a function of t. Then

$m(t+dt) = m(t) + f(ct+cdt) - f(ct) - Qm(ct+c\vartheta dt)dt \quad (o \leq \vartheta \leq 1)$.

We cannot treat this as a differential equation, as we have no reason to suppose that f has a derivative. We can make it into an integral equation, however, which will read

$$m(t) - m(o) = f(ct) - Q\int_o^t m(t)dt.$$

Clearly one solution of this integral equation is

$$m(t) = m(o)e^{-Qt} + f(ct) - Qe^{-Qt}\int_o^t f(ct)e^{Qt}dt,$$

and there is no difficulty in showing that an integral equation of this sort can have only one continuous solution.

Another integration gives for the distance traversed by the particle in time t

$$\begin{aligned} d_t &= \frac{1}{M}\left\{\left[-\frac{m(o)e^{-Qt}}{Q}\right]_o^t + \int_o^t f(ct)dt - \int_o^t Qe^{-Qt}\left[\int_o^t e^{Qt}f(ct)dt\right]dt\right\} \\ &= \frac{1}{M}\left\{\frac{m(o)}{Q}(1-e^{-Qt}) + e^{-Qt}\int_o^t e^{Qt}f(ct)dt\right\} \qquad (2) \\ &= \frac{1}{M}\left\{\frac{m(o)}{Q}(1-e^{-Qt}) + \frac{e^{-Qt}}{c}\int_o^\tau e^{\frac{Q\tau}{c}}f(\tau)d\tau\right\} \end{aligned}$$

Applying the methods of my previous paper, we get for the mean value of d_t^2, in accordance with (1);

$$\begin{aligned} \overline{d_t^2} &= \frac{1}{M^2}\left[\frac{m(o)}{Q}(1-e^{-Qt})\right]^2 + \frac{1}{M^2c^2}e^{-2Qt}\int_o^{ct}\int_o^{ct} A\{f(x)f(y)\}e^{\frac{Q(x+y)}{c}}dydx \\ &= \frac{1}{M^2}\left[\frac{m(o)}{Q}(1-e^{-Qt})\right]^2 + \frac{1}{M^2c^2}e^{-2Qt}\int_o^{ct}\left[\int_o^x ye^{\frac{Q(x+y)}{c}}dy\right]dx \\ &= \left[\frac{m(o)}{MQ}(1-e^{-Qt})\right]^2 + \frac{e^{-2Qt}}{M^2c^2}\int_o^{ct}\left[\frac{cx}{Q}e^{\frac{2Qx}{c}} - \frac{c^2}{Q^2}e^{\frac{2Qx}{c}} + \frac{c^2}{Q^2}e^{\frac{Qx}{c}}\right]dx \qquad (3) \\ &= \left[\frac{m(o)}{MQ}(1-e^{-Qt})\right]^2 + \frac{c}{4M^2Q^3}\left[2Qt - 3 + 4e^{-Qt} - e^{-2Qt}\right] \end{aligned}$$

Therefore

$$\left|\overline{d_t^2}/t - c/(2M^2Q^2)\right| \leq 1/t\left[m(o)(1-e^{-Qt})/(MQ)\right]^2 + c(3-e^{-Qt})(1-e^{-Qt})/(4M^2Q^3t)$$

$$\leq \left[m(o)/(MQ)\right]^2 + 3c/(4M^2Q^3)$$

This represents the absolute departure of $\overline{d_t^2}/t$ from constancy. Writing v for $m(o)/M$, the initial velocity of the particle, we get

$$\frac{|\overline{d_t^2}/t - c/(2M^2Q^2)|}{c/(2M^2Q^2)} \leq \frac{v^2/Q^2}{c/2M^2Q^2} + 3/2Q$$

This is a measure of the relative departure of $\overline{d_t^2}/t$ from constancy. v cannot exceed, on the average, the velocity given on the average to the particle on the basis of the equipartition of energy; actually it is much smaller. $c/(2M^2Q^2)$ can be found directly, as it is nearly the observed value of $\overline{d_t^2}/t$. Q can be readily computed from the constants of the particles. Taking as a typical case one of Perrin's experiments on gamboge, Q turns out to be of the order of magnitude of 10^8, $c/2M^2Q^2$ of the order of magnitude of 10^{-8}, and the kinetic energy velocity of the order of magnitude of 10^{-1}. Hence the proportionate error is of the order of magnitude of 10^{-8}.

A proportionate error thus small is quite beyond the reach of our methods of measurement, so that we are compelled to conclude that d_t^2/t, under the hypotheses we have here formulated, is sensibly constant. There are cases, however, which seem to give a slightly different value of $\overline{d_t^2}/t$ for small values of the time than for larger values. The explanation has been suggested[5] that over small periods the Einstein independence of an interval on previous intervals does not hold. The result of the present paper would be to suggest strongly, if not to demonstrate, that the source of the discrepancy, if, as appears, it is genuine, and not due to experimental error, is in the fact that Stokes' law itself is only a rough approximation, and that the resistance does not vary strictly as the velocity.

[1] *Paris, Bull. Soc. Math. France,* 1919, pp. 47–70.

[2] "The Average of an Analytic Functional," in the last number of these PROCEEDINGS.

[3] *Leipzig, Ann. Physik,* **17,** 1905 (549).

[4] *Ann. Chim. Phys.,* Sept., 1909; tr. by F. Soddy.

[5] Cf. Kleeman, *A Kinetic Theory of Gases and Liquids,* §§ 56, 60.