Brownian Motion in the Theory of Irreversible Processes

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INTRODUCTION

IN the theory of Brownian motion, as it is usually presented, an assumption of randomness, expressible in any of several equivalent forms, is combined with the macroscopic law of viscous force to give a statistical description of the motion. A concise but comprehensive review of the theory so founded has been given by Wang and Uhlenbeck.[1] This procedure has the advantage that the part of the theory involving only the assumption of randomness can be developed in a very general form. The results can then be combined not only with macroscopic mechanical laws, to obtain a description of Brownian motion, but also with other macroscopic laws, those of electric networks, for example, to describe other phenomena of random fluctuation. The very generality of the method, however, leaves it somewhat detached from ordinary statistical mechanics. Although the resulting theory is both statistical and mechanical, the statistical and mechanical developments are nearly independent, instead of being related as in statistical mechanics.

The present paper is a sequel to one on the statistical theory of irreversible processes,[2] and its purpose is to treat some of the problems of Brownian motion from the point of view assumed there for the description of viscous forces. Its main feature is its use of the principles of statistical mechanics from the beginning, in an adaptation of the general method of Gibbs. In thus introducing statistical mechanics initially, it has some resemblance to an otherwise quite different method recently developed by Callen and Welton.[3]

The present method shares with most of the others a limitation on the types of Brownian motion for which solutions of the equations can be obtained. The only motions of which anything near a complete description can be given are those of bodies in uniform force fields in fluids and harmonic oscillators. This limitation necessarily involves a good deal of duplication of subject between this paper and that of Wang and Uhlenbeck.

Even these motions are treated only by means of an approximation. The approximation appears, however, to be well justified, and it is perhaps a point in favor of this method that it makes the approximation explicit, for a similar one seems to be implied in the initial assumptions of the method of random processes.

[1] M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. 17, 323 (1945).
[2] R. T. Cox, Revs. Modern Phys. 22, 238 (1950).
[3] H. B. Callen and T. A. Welton, Phys. Rev. 83, 34 (1951).

1. A GENERAL EQUATION AND ITS SOLUTION AT EQUILIBRIUM

Let the motion of a body be described in terms of a generalized coordinate q and the corresponding momentum p. This body is to be thought of as subject to forces exerted on it by a surrounding medium. The medium, or at least as much of it as directly affects the motion of the body, will be called the thermodynamic system, or merely the system, in the following discussion. Such a system has a very great number of quantized states, which may be labeled $1, 2, \cdots, i, \cdots$, each state having a different label, although many may have equal energies.

A displacement of the body will change the energies of at least some of the quantized states, so that E_i, the energy of a state i, is in general to be considered a function of the coordinate q. When the system is in state i, the force it exerts on the body is $-\partial E_i/\partial q$. For the sake of generality, let the body be supposed subject also to some other force—that of gravity, for example—derived from a Hamiltonian function H. The body may be of microscopic dimensions, but it is assumed still to be massive enough not to require quantum mechanics for the description of its motion. Hence, when the system is in state i, the motion of the body is described by the Hamiltonian equations,

$$dq/dt=\partial H/\partial p, \tag{1.1}$$

$$dp/dt=-\partial(H+E_i)/\partial q. \tag{1.2}$$

Let $P_i dqdp$ denote the probability that the system is in state i, the coordinate of the body in the element dq and its momentum in the element dp. P_i will be a function of q and p and, except in the case of equilibrium, it will be an explicit function of t also. The expression for the total derivative dP_i/dt is then

$$\frac{dP_i}{dt}=\frac{\partial P_i}{\partial t}+\frac{\partial P_i}{\partial q}\frac{dq}{dt}+\frac{\partial P_i}{\partial p}\frac{dp}{dt}.$$

Replacing dq/dt and dp/dt by their values in the Hamiltonian equations, we have

$$\frac{dP_i}{dt}=\frac{\partial P_i}{\partial t}+\frac{\partial P_i}{\partial q}\frac{\partial H}{\partial p}-\frac{\partial P_i}{\partial p}\frac{\partial(H+E_i)}{\partial q}. \tag{1.3}$$

In this equation dP_i/dt is the rate of change of P_i along the path in the phase space which the body follows when the system is in state i. If the system were to undergo no transitions, remaining always in the

state i, then dP_i/dt would be zero, according to Gibbs'[4] well-known demonstration of the conservation of density in phase. In the present discussion, however, transitions must be considered, and dP_i/dt will depend on the probability of their occurrence. It is through this probability that the element of randomness is introduced in the present method.

The thermodynamic system, which is the medium around the body, is itself surrounded by other matter, which does no work on the body but exchanges energy thermally with the system. This environment may be pictured as a heat bath having so great a thermal capacity that its equilibrium is not appreciably disturbed by its exchanges with the system. For a system immersed in such a heat bath, it has been shown[2] that the rate of change of P_i, owing to the probability of transitions, is given by

$$dP_i/dt=\sum_j[P_j\exp(E_j/kT)-P_i\exp(E_i/kT)]\mu_{ij}, \quad (1.4)$$

where T is the temperature of the environment, assumed uniform, and μ_{ij} is a positive quantity which depends on the probability of transition between the states i and j of the system. When the principle of microscopic reversibility is applicable,

$$\mu_{ji}=\mu_{ij}. \quad (1.5)$$

Onsager[5] has pointed out that this principle must be modified in the presence of magnetic or Coriolis fields. In the following discussion it will be assumed for convenience that no such fields are present. Magnetic or Coriolis forces, however, would not seem to change the conclusions which may be compared with the results of experiments, provided the motion is restricted to a single degree of freedom,[6] although they would require a change in the calculations leading to the conclusions.

Equating the expression for dP_i/dt in Eqs. (1.3) and (1.4), we have

$$\frac{\partial P_i}{\partial t}+\frac{\partial P_i}{\partial q}\frac{\partial H}{\partial p}-\frac{\partial P_i}{\partial p}\frac{\partial(H+E_i)}{\partial q}=$$
$$\sum_j[P_j\exp(E_j/kT)-P_i\exp(E_i/kT)]\mu_{ij}. \quad (1.6)$$

By this equation, if

$$P_i=C\exp[-(H+E_i)/kT] \quad (1.7)$$

for every value of i, then $\partial P_i/\partial t$ is zero and there is thermodynamic equilibrium among the body, the system, and the environment. The constant C is determined by the requirement that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\sum_i P_i dqdp=1. \quad (1.8)$$

Summing the members of Eq. (1.7) over all values of i gives

$$\sum_i P_i=C\exp(-H/kT)\sum_i\exp(-E_i/kT).$$

If $\sum_i P_i$ be denoted by P, then $Pdqdp$ is the probability that the coordinate and the momentum of the body are in the phase element $dqdp$. Also, if $\sum_i\exp(-E_i/kT)$ be denoted by $e^{-\Psi/kT}$, it is a result of statistical mechanics that Ψ can be identified with the Helmholtz free energy of the thermodynamic system. Thus

$$P=Ce^{-(\Psi+H)/kT}. \quad (1.9)$$

If p_i denote the probability that the system is in state i, the body being at some given point in the phase space, then

$$p_i=P_i/P=\exp[(\Psi-E_i)/kT]. \quad (1.10)$$

Let $\langle u\rangle$ denote the average, over an ensemble of identical systems and bodies, of any quantity u which is a function of q and p but not of the state of the system. In equilibrium $\langle u\rangle$ is also the time average for a single body and system. By Eq. (1.9)

$$\langle u\rangle=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}ue^{-(\Psi+H)/kT}dqdp\Big/\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}e^{-(\Psi+H)/kT}dqdp. \quad (1.11)$$

Integration by parts with respect to p gives the familiar results for the averages of the velocity and kinetic energy,

$$\langle\partial H/\partial p\rangle=0, \quad (1.12)$$

$$\tfrac{1}{2}\langle p(\partial H/\partial p)=\tfrac{1}{2}kT. \quad (1.13)$$

The force acting on the body, averaged over all states at a given value of q, is

$$-\sum_i[\partial(H+E_i)/\partial q]\exp[(\Psi-E_i)/kT],$$

and this is found equal to $-\partial(H+\Psi)/\partial q$. If $e^{-(\Psi+H)/kT}$ vanishes to a high enough order as q becomes infinite, then integration by parts with respect to q in Eq. (1.11) gives for the averages, over all states and the phase space, of the force and its virial

$$-\langle\partial(\Psi+H)/\partial q\rangle=0, \quad (1.14)$$

$$\tfrac{1}{2}\langle q[\partial(\Psi+H)/\partial q]\rangle=\tfrac{1}{2}kT. \quad (1.15)$$

In the special case of the harmonic oscillator, the average virial is also the average potential energy.

2. THE APPROACH TO EQUILIBRIUM: KRAMERS' EQUATION

Except at equilibrium, Eq. (1.6) cannot be solved. E_i and μ_{ij} are unknown functions of q and, even if they were known, the equations obtained with actual thermodynamic systems would be too complicated for solution.

[4] J. Willard Gibbs, *Collected Works* (Longmans, Green, and Company, New York, 1928), Vol. 2, Part 1, Chap. 1.
[5] L. Onsager, Phys. Rev. 37, 405 (1931); 38, 2265 (1931).
[6] This is inferred from some calculations of Mr. John S. Thomsen (to be published).

The solution for equilibrium, however, can be used as a guide to approximations which will be useful in describing the approach to equilibrium.

It will be convenient to suppose that the coordinate q has been so chosen that the Hamiltonian is given by

$$H=V(q)+\tfrac{1}{2}p^2/m, \tag{2.1}$$

V being the potential energy and m the mass or some other constant inertial quantity. Then Eqs. (1.3) and (1.4) become

$$\frac{dP_i}{dt}=\frac{\partial P_i}{\partial t}+\frac{\partial P_i}{\partial q}\frac{p}{m}-\frac{\partial P_i}{\partial p}\frac{\partial(V+E_i)}{\partial q}$$
$$=\sum_j[P_j\exp(E_j/kT)-P_i\exp(E_i/kT)]\mu_{ij}. \tag{2.2}$$

Summing over all values of i, replacing $\sum_i P_i$ by P, and making use of the fact that $\mu_{ji}=\mu_{ij}$, we find

$$\frac{\partial P}{\partial t}+\frac{\partial P}{\partial q}\frac{p}{m}-\frac{\partial P}{\partial p}\frac{\partial V}{\partial q}-\sum_i\frac{\partial P_i}{\partial p}\frac{\partial E_i}{\partial q}=0. \tag{2.3}$$

When

$$P_i=P\exp[(\Psi-E_i)/kT],$$

so that p_i has its equilibrium value, as given by Eq. (1.10), the two preceding equations become

$$\frac{dP_i}{dt}=\exp[(\Psi-E_i)/kT]\left[\frac{\partial P}{\partial t}+\frac{\partial P}{\partial q}\frac{p}{m}\right.$$
$$\left.+\frac{Pp}{mkT}\frac{\partial(\Psi-E_i)}{\partial q}-\frac{\partial P}{\partial p}\frac{\partial(V+E_i)}{\partial q}\right]=0 \tag{2.4}$$

and

$$\frac{\partial P}{\partial t}+\frac{\partial P}{\partial q}\frac{p}{m}-\frac{\partial P}{\partial p}\frac{\partial(\Psi+V)}{\partial q}=0. \tag{2.5}$$

In obtaining this last result, use is made of the equation for the average force at equilibrium exerted on the body by the system,

$$-\sum_i(\partial E_i/\partial q)\exp[(\Psi-E_i)/kT]=-\partial\Psi/\partial q.$$

Equations (2.4) and (2.5) may be combined to give

$$\frac{dP_i}{dt}=\exp[(\Psi-E_i)/kT]\frac{\partial(\Psi-E_i)}{\partial q}\left(\frac{Pp}{mkT}+\frac{\partial P}{\partial p}\right). \tag{2.6}$$

The members of this equation are exactly equal to one another only when the system and the body are in equilibrium and both members are equal to zero. When the body is not in equilibrium with the system but has a small average motion (as distinguished from its random motion at equilibrium), we assume provisionally that the equation holds approximately, or, in other words, that the two members, which are nearly equal to zero, are even more nearly equal to one another. The assumption will have to be justified later. As an approximation for this case, let

$$p_i=\exp[(\Psi-E_i)/kT](1+\xi_i),$$

where ξ_i is a small quantity, resulting from the disturbance of equilibrium, which will be assumed to be a function of q but not of p. Then, by Eq. (1.4),

$$dP_i/dt=Pe^{\Psi/kT}\sum_j(\xi_j-\xi_i)\mu_{ij},$$

and Eq. (2.6) becomes

$$\exp(-E_i/kT)\frac{\partial(\Psi-E_i)}{\partial q}\left(\frac{Pp}{mkT}+\frac{\partial P}{\partial p}\right)$$
$$=P\sum_j(\xi_j-\xi_i)\mu_{ij}. \tag{2.7}$$

In order to see how the quantities ξ_i are determined as functions of q, it is necessary to eliminate p from this equation. This can be done by integrating over all values of p and dividing by $\int_{-\infty}^{\infty}Pdp$. In the result,

$$\int_{-\infty}^{\infty}(\partial P/\partial p)dp=0,$$

since the probability of an infinite momentum is zero, and

$$\int_{-\infty}^{\infty}Ppdp\Big/\int_{-\infty}^{\infty}Pdp=\langle p\rangle_q, \tag{2.8}$$

where the subscript q denotes that the average is over all values of the momentum for a given value of the coordinate. Thus we obtain from Eq. (2.7) the result

$$\frac{1}{kT}\exp(-E_i/kT)\frac{\partial(\Psi-E_i)}{\partial q}\frac{\langle p\rangle_q}{m}=\sum_j(\xi_j-\xi_i)\mu_{ij}. \tag{2.9}$$

If we now introduce for each state of the system a function κ_i of q, defined by

$$\xi_i=\kappa_i\langle p\rangle_q/m,$$

so that

$$p_i=\exp[(\Psi-E_i)/kT](1+\kappa_i\langle p\rangle_q/m), \tag{2.10}$$

then, by Eq. (2.9),

$$\partial(\Psi-E_i)/\partial q=kT\exp(E_i/kT)\sum_j(\kappa_j-\kappa_i)\mu_{ij} \tag{2.11}$$

for every value of i. Also, by summing the members of Eq. (2.10) over all values of i and making use of the fact that $\sum_i p_i=1$ for any value of $\langle p\rangle_q$, we find

$$\sum_i\exp(-E_i/kT)\kappa_i=0. \tag{2.12}$$

These equations suffice exactly to determine the value of κ_i for every state of the system.

Multiplying the members of Eq. (2.9) by P, we obtain a right-hand member identical with that of Eq. (2.7). Equating the left-hand members, we find after removing common factors,

$$\frac{\partial P}{\partial p}=-\frac{(p-\langle p\rangle_q)P}{mkT}. \tag{2.13}$$

The solution of this equation may be written

$$P=F\exp[-(p-\langle p\rangle_q)^2/(2mkT)], \quad (2.14)$$

where F is an undetermined function of q and t but not a function of p. This is to be compared with the expression for P at equilibrium. When Eq. (2.1) gives the form of the Hamiltonian, Eq. (1.9) becomes

$$P=C\exp[-(\Psi+V)/kT]\exp[-p^2/(2mkT)].$$

Thus at equilibrium the distribution in momentum is Gaussian about the average value zero. Near equilibrium, the distribution, for a given value of the coordinate, is approximately Gaussian about $\langle p\rangle_q$, the average momentum at that position.

To find how P varies with time, we return to Eq. (2.3), replacing P_i by Pp_i and thus obtaining

$$\frac{\partial P}{\partial t}+\frac{\partial P}{\partial q}\frac{p}{m}-\frac{\partial P}{\partial p}\frac{\partial V}{\partial q}=\frac{\partial P}{\partial p}\sum_i p_i\frac{\partial E_i}{\partial q}. \quad (2.15)$$

To evaluate the expression on the right near equilibrium, we multiply together the corresponding members of Eqs. (2.10) and (2.11) and sum over all states. The result, when use is made of the relations $\sum_i p_i=1$ and $\mu_{ji}=\mu_{ij}$, is

$$\partial\Psi/\partial q-\sum_i p_i(\partial E_i/\partial q) = kTe^{\Psi/kT}(\langle p\rangle_q/m)\sum_i\sum_j\kappa_i(\kappa_j-\kappa_i)\mu_{ij}. \quad (2.16)$$

The value of the double summation on the right is unaltered if the labels of κ_i and κ_j are exchanged and those of μ_{ij} are left the same, since $\mu_{ji}=\mu_{ij}$. Hence,

$$\sum_i\sum_j\kappa_i(\kappa_j-\kappa_i)\mu_{ij}=\sum_i\sum_j\kappa_j(\kappa_i-\kappa_j)\mu_{ij}.$$

Either of these summations may be equated to half their sum, and thus

$$\sum_i\sum_j\kappa_i(\kappa_j-\kappa_i)\mu_{ij}=-\tfrac{1}{2}\sum_i\sum_j(\kappa_i-\kappa_j)^2\mu_{ij}.$$

Equation (2.16) may therefore be written

$$-\sum_i p_i(\partial E_i/\partial q)=-(\partial\Psi/\partial q)-\sigma\langle p\rangle_q/m, \quad (2.17)$$

where

$$\sigma=\tfrac{1}{2}kTe^{\Psi/kT}\sum_i\sum_j(\kappa_i-\kappa_j)^2\mu_{ij} \quad (2.18)$$

and is thus a positive quantity. The left-hand member of Eq. (2.17) is the force which the system exerts on the body, averaged over all states at a given value of q. The first term on the right is the conservative force and the second is the viscous force, which is proportional and opposed to the average velocity $\langle p\rangle_q/m$.

Substitution in Eq. (2.15) of the expression for the force given by Eq. (2.17) gives the result

$$\frac{\partial P}{\partial t}=\frac{\partial P}{\partial p}\left[\frac{\partial(V+\Psi)}{\partial q}+\frac{\sigma\langle p\rangle_q}{m}\right]-\frac{\partial P}{\partial q}\frac{p}{m}. \quad (2.19)$$

Differentiation of Eq. (2.13) with respect to p gives an expression for $\langle p\rangle_q(\partial P/\partial p)$ which can be substituted in Eq. (2.19) to eliminate $\langle p\rangle_q$. When this is done it is found that

$$\frac{\partial P}{\partial t}=\frac{\partial P}{\partial p}\frac{\partial(V+\Psi)}{\partial q}+\sigma\frac{\partial}{\partial p}\left(\frac{Pp}{m}+kT\frac{\partial P}{\partial p}\right)-\frac{p}{m}\frac{\partial P}{\partial q}. \quad (2.20)$$

This equation of Brownian motion was discovered by Kramers.[7]

The use of Eq. (2.6) under conditions other than those of equilibrium has still to be justified. At least it is necessary to justify as approximations the results obtained by the use of this equation. This can be done by substituting these results in the original equation (2.2). If an exact solution of this equation had been obtained, the result of the substitution would, of course, be an identity. The solution we have is not exact, and the result of the substitution will be to show what quantities have been ignored in the approximations employed.

The procedure, though simple, is somewhat tedious, and only the result will be given. The neglected quantities are found to be terms in the second and third powers of $\langle p\rangle_q$ and also terms in $\partial\langle p\rangle_q/\partial t$, $p\langle p\rangle_q$ and $p(\partial\langle p\rangle_q/\partial q)$. That the approximation is not valid for large values of $\langle p\rangle_q^2$ or $\partial\langle p\rangle_q/\partial t$ is easily understood. If the motion of the body is too rapid or too rapidly changing, the transitions of the system will not be fast enough in comparison to maintain even the approximate equilibrium which was assumed in the calculation. The limits within which the approximation is fair will thus be determined by the motion of the body and the structure of the system together, and they can generally be established only by experiment. Once the limits are established, the approximations are shown to be reasonable for any slower and more slowly changing motion.

That terms involving $p\langle p\rangle_q$ have also to be neglected in the solution indicates that the distribution in momentum for large values of p will not be Gaussian even though $\langle p\rangle_q$ is not large. This is not likely to be a source of serious error, however. For large values of p, the Gaussian probability is so small that an actual probability several times greater would still be unimportant.

3. AVERAGES IN THE APPROACH TO EQUILIBRIUM

Let u denote, as before, some function of q and p which does not depend on the state of the system and is not an explicit function of t. The average value of u over the ensemble will nevertheless generally change with time as P changes, and its rate of change will be given by

$$d\langle u\rangle/dt=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}u(\partial P/\partial t)dqdp. \quad (3.1)$$

When the expression for $\partial P/\partial t$ given by Eq. (2.19) is substituted here, integration by parts leads to the

[7] H. A. Kramers, Physica **7**, 284 (1940). A change of symbols makes Eq. (2.20) the same as Eq. (9) of his paper.

result

$$\frac{d\langle u\rangle}{dt}=\left\langle\frac{p}{m}\frac{\partial u}{\partial q}\right\rangle-\left\langle\left[\frac{\partial(\Psi+V)}{\partial q}+\frac{\sigma\langle p\rangle_q}{m}\right]\frac{\partial u}{\partial p}\right\rangle, \quad (3.2)$$

provided that P vanishes at the limits of integration to as high an order as may be required.

According to the equations defining σ, the coefficient of the viscous force, it may be a function of q. Actually, however, for the motion of a body through a fluid, it is independent of q and in some other cases it is approximately so for small motions. In these cases, σ may be taken outside the expression which is to be averaged, as of course $(1/m)$ may be also. Equation (3.2) then becomes

$$\frac{d\langle u\rangle}{dt}=\frac{1}{m}\left\langle p\frac{\partial u}{\partial q}\right\rangle-\left\langle\frac{\partial(\Psi+V)}{\partial q}\frac{\partial u}{\partial p}\right\rangle-\frac{\sigma}{m}\left\langle\langle p\rangle_q\frac{\partial u}{\partial p}\right\rangle. \quad (3.3)$$

In the last term on the right, it is to be understood that the momentum is first averaged at the point q, and the product of this average by $\partial u/\partial p$ is then averaged over all the phase space.

With q and p substituted in turn for u, this equation gives the expected results,

$$d\langle q\rangle/dt=\langle p\rangle/m \quad (3.4)$$

and

$$d\langle p\rangle/dt=-\langle\partial(\Psi+V)/\partial q\rangle-\sigma\langle p\rangle/m, \quad (3.5)$$

whence we obtain, by eliminating $\langle p\rangle$,

$$md^2\langle q\rangle/dt^2+\sigma d\langle q\rangle/dt+\langle\partial(\Psi+V)/\partial q\rangle=0. \quad (3.6)$$

Thus the average quantities follow the familiar equations for the motion of a body under a viscous force and a conservative force. This is a welcome result in that it shows that equations obtained by means of the approximations used in the preceding section are those which describe macroscopic observations, in which the average velocity is greater and changes more rapidly than in Brownian motion.[8] Thus the approximations are justified for Brownian motion.

Equations describing the deviations from the average motion also may be obtained from Eq. (3.2). Let $q-\langle q\rangle$ be denoted by Δq. The mean square deviation of q is given by

$$\langle(\Delta q)^2\rangle=\langle q^2-2q\langle q\rangle+\langle q\rangle^2\rangle=\langle q^2\rangle-\langle q\rangle^2.$$

Hence

$$d\langle(\Delta q)^2\rangle/dt=d\langle q^2\rangle/dt-2\langle q\rangle(d\langle q\rangle/dt)$$
$$=d\langle q^2\rangle/dt-2\langle p\rangle\langle q\rangle/m,$$

by Eq. (3.4).

Replacing u by q^2 in Eq. (3.2) gives

$$d\langle q^2\rangle/dt=2\langle pq\rangle/m. \quad (3.7)$$

Thus

$$d\langle(\Delta q)^2\rangle/dt=(2/m)(\langle pq\rangle-\langle p\rangle\langle q\rangle).$$

But

$$\langle pq\rangle-\langle p\rangle\langle q\rangle=\langle(p-\langle p\rangle)(q-\langle q\rangle)\rangle=\langle\Delta p\Delta q\rangle,$$

and hence

$$d\langle(\Delta q)^2\rangle/dt=(2/m)\langle\Delta p\Delta q\rangle. \quad (3.8)$$

Continuing in the same way, we find

$$d\langle\Delta p\Delta q\rangle/dt=\langle(\Delta p)^2\rangle/m+\langle\Delta Q\Delta q\rangle-\sigma\langle\Delta p\Delta q\rangle/m, \quad (3.9)$$

where Q has been written for $-\partial(\Psi+V)/\partial q$, the conservative force.

We find also that

$$d\langle(\Delta p)^2\rangle/dt=2\langle\Delta p\Delta Q\rangle-(2\sigma/m)(\langle\langle p\rangle_q^2\rangle-\langle p\rangle^2). \quad (3.10)$$

We may write

$$\langle\langle p\rangle_q^2\rangle-\langle p\rangle^2=(\langle p^2\rangle-\langle p\rangle^2)-(\langle p^2\rangle-\langle\langle p\rangle_q^2\rangle).$$

But

$$\langle p^2\rangle-\langle p\rangle^2=\langle(p-\langle p\rangle)^2\rangle=\langle(\Delta p)^2\rangle,$$

and

$$\langle p^2\rangle-\langle\langle p\rangle_q^2\rangle=\langle(p-\langle p\rangle_q)^2\rangle=mkT, \quad (3.11)$$

by Eq. (2.14). Thus Eq. (3.10) becomes

$$d\langle(\Delta p)^2\rangle/dt=2\langle\Delta p\Delta Q\rangle-(2\sigma/m)\langle(\Delta p)^2\rangle+2\sigma kT. \quad (3.12)$$

The procedure which has led from Eq. (3.8) to Eqs. (3.9) and (3.12) does not appear promising at first sight, since it introduces new unknowns faster than it provides equations to be solved for them. In two important cases, however, the force Q is such that the number of unknowns is reduced and a soluble set of equations is given.

4. A PARTICLE IN A FIELD-FREE FLUID OR A UNIFORM FIELD

The first of these cases is that in which there is either no conservative force, so that Q is zero, or at most a uniform force, so that ΔQ is zero. In this case $\langle\Delta Q\Delta q\rangle$ and $\langle\Delta p\Delta Q\rangle$ do not appear in Eqs. (3.8), (3.9), and (3.12), and the only unknowns left are $\langle(\Delta q)^2\rangle$, $\langle\Delta p\Delta q\rangle$, and $\langle(\Delta p)^2\rangle$. The solution of the equations thus simplified is

$$\langle(\Delta p)^2\rangle=mkT+Ae^{-2\sigma t/m}, \quad (4.1)$$

$$\langle\Delta p\Delta q\rangle=mkT/\sigma-(A/\sigma)e^{-2\sigma t/m}+Be^{-\sigma t/m}, \quad (4.2)$$

$$\langle(\Delta q)^2\rangle=(2kT/\sigma)t+(A/\sigma^2)e^{-2\sigma t/m}$$
$$-(2B/\sigma)e^{-\sigma t/m}+C, \quad (4.3)$$

where A, B, and C are constants determined by the initial conditions. It is evident from these equations that $\langle(\Delta p)^2\rangle$ approaches the equilibrium value mkT, in agreement with Eq. (1.13), and $\langle\Delta p\Delta q\rangle$ approaches the value mkT/σ, but $\langle(\Delta q)^2\rangle$ increases indefinitely, at a rate which approaches the constant value $2kT/\sigma$. This is the result of the well-known calculation of Einstein,[9]

[8] See the discussion of the "regression of fluctuations" in a paper by H. B. G. Casimir, "On Onsager's principle of microscopic reversibility," Revs. Modern Phys. **17**, 343 (1945).

[9] A. Einstein, *Investigations on the Theory of the Brownian Movement* (Methuen and Company, London, 1926), edited with notes by R. Fürth, translated by A. D. Cowper.

which was verified by the experiments of Perrin[10] and other observers.

It should be noticed that it makes no difference in these equations whether the force Q is zero or has some other constant value. In an ensemble of identical particles, diffusion from the center of mass is described by the same equations when the center of mass moves under a constant force as when it is at rest. For simplicity in discussion it is convenient to consider the force zero and the center of mass at rest. In this case, $\langle p\rangle=0$, and $\Delta p=p$ for any particle. The coordinate q may also be conveniently reckoned from the fixed center of mass, so that $\Delta q=q$ and $\Delta p\Delta q=pq$. The fact that $\langle pq\rangle$ does not become zero but instead attains the positive value mkT/σ indicates that the distribution of the ensemble in respect to momentum is not independent of the distribution in respect to position. On the contrary, a particle which has drifted from the center of mass in a given direction is somewhat more likely to have a momentum in the same direction than in the opposite one. In the kinetic theory of gases, a similar consideration, involving what is called the "persistence of velocity" appears in the treatment of transport phenomena.

The equations thus describe an ensemble of particles diffusing outward from a center at which they were initially clustered. They are strictly valid only for diffusion through an unlimited medium. If the particles are confined in a vessel, they will in time attain a condition of uniform density in which equal and opposite momenta are equally probable at every point, and therefore $\langle pq\rangle=0$. In such an ensemble, all points and all instants are equivalent. At any instant let a particle be chosen at random, and let Δq denote its displacement from its initial position during some time t. (This time must not be long enough to give the particle an appreciable chance of reaching the wall of the vessel.) In a great many observations, the expected value of $\langle(\Delta q)^2\rangle$ will be given by Eq. (4.3) after A, B, and C have been determined by the initial conditions, $\langle(\Delta p)^2\rangle=mkT$, $\langle\Delta p\Delta q\rangle=0$, and $\langle(\Delta q)^2\rangle=0$. The resulting expression is

$$\langle(\Delta q)^2\rangle=(2kT/\sigma)[t-(m/\sigma)(1-e^{-\sigma t/m})], \quad (4.4)$$

an equation discovered by Ornstein[11] and independently by Fürth.[12]

For a microscopic particle in a liquid medium, the interval of time denoted by m/σ is much smaller than the time t of even the briefest observation, and Ornstein's is practically equivalent to Einstein's equation

$$\langle(\Delta q)^2\rangle=(2kT/\sigma)t. \quad (4.5)$$

5. THE HARMONIC OSCILLATOR

The second case in which Eqs. (3.8), (3.9), and (3.12) are soluble is that of the harmonic oscillator, for which $Q=-cq$ and therefore $\Delta Q=-c\Delta q$, where c is a positive constant. The equations become

$$d\langle(\Delta q)^2\rangle/dt=(2/m)\langle\Delta p\Delta q\rangle, \quad (5.1)$$

$$d\langle\Delta p\Delta q\rangle/dt=-c\langle(\Delta q)^2\rangle-(\sigma/m)\langle\Delta p\Delta q\rangle+\langle(\Delta p)^2\rangle/m, \quad (5.2)$$

$$d\langle(\Delta p)^2\rangle/dt=-2c\langle\Delta p\Delta q\rangle-2(\sigma/m)\langle(\Delta p)^2\rangle+2\sigma kT, \quad (5.3)$$

and thus contain only three unknown variables.

The solutions of these equations for $\langle(\Delta q)^2\rangle$ and $\langle(\Delta p)^2\rangle$ may be written in the form

$$\tfrac{1}{2}c\langle(\Delta q)^2\rangle=(A+Be^{2i\omega t}+B^*e^{-2i\omega t})e^{-\beta t}+\tfrac{1}{2}kT, \quad (5.4)$$

$$\tfrac{1}{2}\langle(\Delta p)^2\rangle/m=(A+Ce^{2i\omega t}+C^*e^{-2i\omega t})e^{-\beta t}+\tfrac{1}{2}kT, \quad (5.5)$$

where

$$\omega^2=c/m-\tfrac{1}{4}(\sigma/m)^2 \quad (5.6)$$

and

$$\beta=\sigma/m, \quad (5.7)$$

so that $\omega/2\pi$ is the frequency of the free vibration of the oscillator and β is the decrement of the energy. The solution for $\langle\Delta p\Delta q\rangle$ is readily obtained from that for $\langle(\Delta q)^2\rangle$ by Eq. (5.1). The constants A and B are determined by the initial values of $\langle(\Delta q)^2\rangle$, $\langle(\Delta p)^2\rangle$, and $\langle\Delta p\Delta q\rangle$, and

$$C=B(\beta-2i\omega)/(\beta+2i\omega). \quad (5.8)$$

It may be remarked that the solutions are not affected by the initial averages of p and q themselves but only by those of the squares and products of their deviations.

It is evident from Eqs. (5.4) and (5.5) that, after the transient motion has ceased, the potential and kinetic energies have each the average value $\frac{1}{2}kT$, as given by Eqs. (1.13) and (1.15). The transient oscillatory terms are due to the imposition of initial conditions different from those of random motion. For example, let the oscillator, or rather each of an ensemble of identical oscillators, be clamped at its equilibrium position so firmly that $\langle(\Delta q)^2\rangle$ is practically zero. No clamp will altogether prevent their motion, so that $\langle(\Delta p)^2\rangle$ will have its equilibrium value mkT, but $\langle\Delta p\Delta q\rangle$ will be zero. At the initial instant let the clamps on all the oscillators be released. The oscillators will have various momenta, corresponding to the Boltzmann distribution in kinetic energy, and they will therefore begin to oscillate with the same period and the same or opposite phase but with different amplitudes. If there were no damping, these oscillations would continue indefinitely. If the decrement, though not zero, is very small, it can be shown that Eqs. (5.4) and (5.5), with the given initial conditions, become approximately

$$\tfrac{1}{2}c\langle(\Delta q)^2\rangle=\tfrac{1}{2}kT(1-e^{-\beta t}\cos^2\omega t), \quad (5.9)$$

$$\tfrac{1}{2}\langle(\Delta p)^2\rangle/m=\tfrac{1}{2}kT(1-e^{-\beta t}\sin^2\omega t). \quad (5.10)$$

Thus the average potential and kinetic energies pass through series of maxima with the value $\frac{1}{2}kT$, alter-

[10] J. Perrin, *Les Atomes* (Librairie Felix Alcan, Paris, 1920).
[11] L. S. Ornstein, Proc. Acad. Sci. Amsterdam **21**, 96 (1919).
[12] R. Fürth, Z. Physik **2**, 244 (1920).

nating with minima of diminishing depth, while their sum increases continuously toward the value kT.

The equations for the mean squares and product of the deviations of p and q given by Wang and Uhlenbeck in the paper referred to earlier can be obtained as solutions of Eqs. (5.1), (5.2), and (5.3) with $\langle(\Delta q)^2\rangle$, $\langle(\Delta p)^2\rangle$, and $\langle\Delta p\Delta q\rangle$ all initially zero.

6. THE FOURIER ANALYSIS OF BROWNIAN MOTION

Fourier analysis has been employed in the theory of random fluctuations, notably by Rice;[13] and Wang and Uhlenbeck, in the paper already referred to, have applied the method to Brownian motion. The discussion which follows is in part the same as that of these authors and in part different.

Let u now denote either the momentum p or the coordinate q of the body. In some interval of time with limits 0 and τ let the succession of its values be expressed as a Fourier series given by

$$u(t)=\bar{u}+\sum_{n=1}^{n=\infty}[a_n\exp(i\omega_n t)+a^*_n\exp(-i\omega_n t)], \quad (6.1)$$

where

$$\omega_n=2\pi n/\tau, \quad (6.2)$$

$$a_n=(1/\tau)\int_0^\tau u(t)\exp(-i\omega_n t)dt, \quad (6.3)$$

and $\bar{u}$ is the time average of u from 0 to τ, as distinguished from $\langle u\rangle$, the average over the ensemble at a given time.

The Brownian motion does not, of course, duplicate itself over an ensemble. The motion in the ensemble can be described only by an ensemble of functions $u(t)$, yielding an ensemble of values of a_n for each term of the Fourier series. These values, however, will differ mainly in phase rather than in amplitude, if the ensemble is not too far from equilibrium and the time is not too short. Hence the values of $a_n a_n{}^*$ for any one value of n, will not differ much from $\langle a_n a_n{}^*\rangle$, their average over the ensemble. To find $\langle a_n a_n{}^*\rangle$, we have

$$\langle aa^*\rangle=(1/\tau^2)\left\langle\int^\tau u(t)e^{-i\omega t}dt\int_0^\tau u(t)e^{i\omega t}dt\right\rangle.$$

The subscript n has been omitted for convenience, with the understanding that ω has one of the values allowed by Eq. (6.2).

Writing the product of the integrals as a double integral and using the symbols t' and t'' to distinguish t in the two integrations, we have

$$\langle aa^*\rangle=(1/\tau^2)\int_0^\tau\int_0^\tau\langle u(t')u(t'')\rangle e^{i\omega(t''-t')}dt'dt''. \quad (6.4)$$

[13] S. O. Rice, Bell System Tech. J. **23**, 282 (1944); **24**, 46 (1945).

Only the product $u(t')u(t'')$ needs to be averaged, since it is the only part of the integrand which varies over the ensemble.

It will be convenient to separate the part of the integration in which $t''>t'$ from that in which $t'>t''$. Thus we write

$$\langle aa^*\rangle=(1/\tau^2)\left[\int_{t'=0}^{t'=\tau}\int_{t''=t'}^{t''=\tau}\langle u(t')u(t'')\rangle e^{i\omega(t''-t')}dt''dt'+\int_{t''=0}^{t''=\tau}\int_{t'=t''}^{t'=\tau}\langle u(t')u(t'')\rangle e^{i\omega(t''-t')}dt'dt''\right].$$

Now let us change the variables, replacing t'' by $t'+t$ in the first integral and t' by $t''+t$ in the second. Thus t is positive in both intregals. So we obtain

$$\langle aa^*\rangle=(1/\tau^2)\left[\int_{t'=0}^{t'=\tau}\int_{t=0}^{t=\tau-t'}\langle u(t')u(t'+t)\rangle e^{i\omega t}dtdt'+\int_{t''=0}^{t''=\tau}\int_{t=0}^{t=\tau-t''}\langle u(t'')u(t''+t)\rangle e^{-i\omega t}dtdt''\right].$$

Let a change of notation be made in the second integral, t'' being replaced by t', with the result,

$$\langle aa^*\rangle=(1/\tau^2)\int_{t'=0}^{t'=\tau}\int_{t=0}^{t=\tau-t'}\langle u(t')u(t'+t)\rangle\times(e^{i\omega t}+e^{-i\omega t})dtdt'. \quad (6.5)$$

Let it now be assumed that the ensemble is initially in equilibrium. It will then be in equilibrium at all values of t' and t covered by the integration. At $t=0$, $\langle u(t')u(t'+t)\rangle$ is simply $\langle u^2(t')\rangle$ and, with the ensemble in equilibrium, $\langle u^2(t')\rangle=\langle u^2(0)\rangle$. On the other hand, in a long enough time t, the random action of the system on the body will obliterate all the influence of the motion at the earlier time, and there will thus be no correlation between $u(t')$ and $u(t'+t)$. Hence, for large values of t, $\langle u(t')u(t'+t)\rangle$ is equal to $\langle u(t')\rangle\langle u(t'+t)\rangle$ and, with the ensemble in equilibrium, to $\langle u(0)\rangle^2$.

With u denoting either p or q, $\langle u\rangle=0$ at equilibrium. Hence the integrand in Eq. (6.5) approaches zero with increasing t. The integral with respect to t is therefore practically independent of the upper limit if this limit is large enough, and for any large value of τ the upper limit may thus be taken as infinite. Also, with the ensemble at equilibrium, $\langle u(t')u(t'+t)\rangle$ is equal to $\langle u(0)u(t)\rangle$, because at equilibrium any instant may be taken as a new initial instant without changing the value of the average over the ensemble. Thus, for an ensemble at equilibrium and a large value of τ, Eq. (6.5) becomes approximately

$$\langle aa^*\rangle=(1/\tau^2)\int_{t=0}^{t=\infty}\int_{t'=0}^{t'=\tau}\langle u(0)u(t)\rangle(e^{i\omega t}+e^{-i\omega t})dt'dt.$$

Integrating with respect to t' and multiplying by τ, we have

$$\tau\langle aa^*\rangle=\int_0^\infty\langle u(0)u(t)\rangle(e^{i\omega t}+e^{-i\omega t})dt.$$

This expression, which is approximately valid for any large value of τ, is exact in the limit, when the Fourier series becomes the Fourier integral. Also the limit of τaa^* for a single body and thermodynamic system is the same as the limit of $\tau\langle aa^*\rangle$ for an ensemble, because the interval τ can be divided into an ensemble of intervals, each of which will approach infinity with τ. Thus we have, as an exact expression,

$$\lim_{\tau\to\infty}(\tau aa^*)=\int_0^\infty\langle u(0)u(t)\rangle(e^{i\omega t}+e^{-i\omega t})dt. \quad (6.6)$$

The simplest application of this equation is that in which u is the momentum (in one direction) of a particle in a field-free fluid. In this case, Eq. (3.5) becomes simply

$$d\langle p\rangle/dt=-\beta\langle p\rangle, \quad (6.7)$$

where $\beta=\sigma/m$. Hence, in an ensemble, the particles which have some particular momentum $p(0)$ at zero time will have the average momentum $p(0)e^{-\beta t}$ at any later time t. [The average momentum of these particles at an earlier time, $-t$, will not, however, have been $p(0)e^{\beta t}$, because reversibility is not statistical but only microscopic. The purpose of the change of variables by which t was restricted to positive values was just to make possible the use of such statistical equations as Eq. (6.7).] For these particles, then, the average value of $p(0)p(t)$ is $p^2(0)e^{-\beta t}$ and for all the particles of the ensemble

$$\langle p(0)p(t)\rangle=\langle p^2(0)\rangle e^{-\beta t}=mkTe^{-\beta t}. \quad (6.8)$$

With $\langle u(0)u(t)\rangle$ replaced by $mkTe^{-\beta t}$ in Eq. (6.6), the integration with respect to t gives

$$\lim_{\tau\to\infty}(\tau aa^*)=2mkT\beta/(\omega^2+\beta^2).$$

Now the part of the Fourier integral in the range of frequencies $d\nu$, contributes to the time average of the kinetic energy, $\overline{p^2}/(2m)$, an amount

$$(1/m)\ \lim_{\tau\to\infty}(\tau aa^*)d\nu.$$

If this contribution is denoted by $I_p d\nu$, I_p is the spectral intensity of the kinetic energy. Therefore we have, by the preceding equation,

$$I_p=2kT\beta/(\omega^2+\beta^2). \quad (6.9)$$

For another example, let the same method be applied to the coordinate of the harmonic oscillator, for which Eq. (3.6) has the familiar form

$$d^2\langle q\rangle/dt^2+\beta d\langle q\rangle/dt+(c/m)\langle q\rangle=0 \quad (6.10)$$

and the solution

$$\langle q\rangle=[b\exp(i\omega_1 t)+b^*\exp(-i\omega_1 t)]\exp(-\tfrac{1}{2}\beta t), \quad (6.11)$$

in which

$$\omega_1^2=c/m-(\tfrac{1}{2}\beta)^2 \quad (6.12)$$

and

$$b=\tfrac{1}{2}\langle q(0)\rangle-\tfrac{1}{2}(i/\omega_1)[\tfrac{1}{2}\beta\langle q(0)\rangle+\langle p(0)\rangle/m]. \quad (6.13)$$

Therefore, in an ensemble of oscillators, those which have at zero time particular values $q(0)$ and $p(0)$ of the coordinate and momentum will have at the later time t an average value of the coordinate given by Eq. (6.11) with

$$b=\tfrac{1}{2}q(0)-\tfrac{1}{2}(i/\omega_1)[\tfrac{1}{2}\beta q(0)+p(0)/m].$$

We find thus, for the whole ensemble,

$$\langle q(0)q(t)\rangle=\tfrac{1}{2}\exp(-\tfrac{1}{2}\beta t)\{\langle q^2(0)\rangle \times[\exp(i\omega_1 t)+\exp(-i\omega_1 t)]-(i/\omega_1)[\tfrac{1}{2}\beta\langle q^2(0)\rangle +\langle p(0)q(0)\rangle/m][\exp(i\omega_1 t)-\exp(-i\omega_1 t)]\};$$

but $\langle q^2(0)\rangle=kT/c$ and $\langle p(0)q(0)\rangle=0$, and hence

$$\langle q(0)q(t)\rangle=\tfrac{1}{2}ikT/(c\omega_1)\{(\tfrac{1}{2}\beta-i\omega_1) \times\exp[-(\tfrac{1}{2}\beta+i\omega_1)t]-(\tfrac{1}{2}\beta+i\omega_1)\exp[-(\tfrac{1}{2}\beta-i\omega_1)t]. \quad (6.14)$$

Substituting this expression in Eq. (6.6) and performing the integration, we find

$$\lim_{\tau\to\infty}(\tau aa^*)=\frac{2kT\beta}{c}\frac{\omega_0^2}{\omega^2\beta^2+(\omega^2-\omega_0^2)^2},$$

where

$$\omega_0^2=c/m. \quad (6.15)$$

The contribution to the average potential energy of the frequencies in the range $d\nu$ is $c\lim_{\tau\to\infty}(\tau aa^*)d\nu$. Denoting this contribution by $I_q d\nu$, we have for the spectral intensity of the potential energy of the oscillator

$$I_q=\frac{2kT\beta\omega_0^2}{\omega^2\beta^2+(\omega^2-\omega_0^2)^2}. \quad (6.16)$$

In the forced oscillation of the harmonic oscillator, the ratio of the kinetic to the potential energy is $(\omega/\omega_0)^2$. Hence the spectral intensity of the kinetic energy is given by

$$I_p=\frac{2kT\beta\omega^2}{\omega^2\beta^2+(\omega^2-\omega_0^2)^2}. \quad (6.17)$$

Equation (6.9) is the special case of this equation in which there is no restoring force and therefore $\omega_0=0$.

It is interesting to notice how little statistical mechanics is involved in the Fourier analysis of Brownian motion. The derivation of Eq. (6.5) depends only on the general properties of any Fourier series. Equation (6.6) follows for any ensemble in equilibrium, however the equilibrium is attained, provided $\langle u(0)u(t)\rangle$ approaches

zero rapidly enough with increasing t. The equation for $\langle p\rangle$ or $\langle q\rangle$ as a function of time, which is used to find an expression for $\langle u(0)u(t)\rangle$, is empirically known, independently of its statistical interpretation. It is only in the next step, when expressions for $\langle p^2(0)\rangle$, $\langle p(0)q(0)\rangle$, and $\langle q^2(0)\rangle$ are introduced, that any special considerations of statistical mechanics are involved, and the required expressions are immediate consequences of the Boltzmann distribution. This generality of the method makes possible its application to random fluctuations of quite different kinds.

7. BROWNIAN MOTION WITH SEVERAL DEGREES OF FREEDOM

The method described in the preceding sections is easily extended from a body with one degree of freedom to a dynamical system with any number of degrees of freedom. Let q^α denote a coordinate and p^α the corresponding momentum. The generalization of Eq. (1.6) is

$$\frac{\partial P^i}{\partial t}+\sum_\alpha\left[\frac{\partial P_i}{\partial q^\alpha}\frac{\partial H}{\partial p^\alpha}-\frac{\partial P_i}{\partial p^\alpha}\frac{\partial(H+E_i)}{\partial q^\alpha}\right]$$
$$=\sum_j[P_j\exp(E_j/kT)-P_i\exp(E_i/kT)]\mu_{ij}. \quad (7.1)$$

The distribution at equilibrium is described as before by Eqs. (1.7), (1.9), and (1.10) and, as before, it is found that $\langle\partial H/\partial p^\alpha\rangle=0$ and $\langle\partial(\Psi+H)/\partial q^\alpha\rangle=0$. Also

$$\tfrac{1}{2}\langle p^\alpha(\partial H/\partial p^\beta)\rangle=\tfrac{1}{2}kT\delta_{\alpha\beta} \quad (7.2)$$

and

$$\tfrac{1}{2}\langle q^\alpha[\partial(\Psi+H)/\partial q^\beta]\rangle=\tfrac{1}{2}kT\delta_{\alpha\beta}, \quad (7.3)$$

where $\delta_{\alpha\beta}$ is the Kronecker symbol.

When the Hamiltonian is given by

$$H=V+\tfrac{1}{2}\sum_\alpha(p^\alpha)^2/m^\alpha, \quad (7.4)$$

the same approximations as before in the approach to equilibrium give

$$P_i=P\exp[(\Psi-E_i)/kT](1+\sum_\alpha\kappa_i{}^\alpha\langle p^\alpha\rangle_q/m^\alpha), \quad (7.5)$$

$$P=F\exp[-\sum_\alpha(p^\alpha-\langle p^\alpha\rangle_q)^2/(2m^\alpha kT)], \quad (7.6)$$

$$\frac{\partial P}{\partial t}=\sum_\alpha\left\{\frac{\partial P}{\partial p^\alpha}\left[\frac{\partial(\Psi+V)}{\partial q^\alpha}+\sum_\beta\frac{\sigma^{\alpha\beta}\langle p^\beta\rangle_q}{m^\beta}\right]-\frac{\partial P}{\partial q^\alpha}\frac{p^\alpha}{m^\alpha}\right\}, \quad (7.7)$$

and a similar generalization of Kramers' equation, where

$$\partial(\Psi-E_i)/\partial q^\alpha=kT\exp(E_i/kT)\sum_j(\kappa_j{}^\alpha-\kappa_i{}^\alpha)\mu_{ij}, \quad (7.8)$$

$$\sigma^{\alpha\beta}=\sigma^{\beta\alpha}=\tfrac{1}{2}kTe^{\Psi/kT}\sum_i\sum_j(\kappa_i{}^\alpha-\kappa_j{}^\alpha)(\kappa_i{}^\beta-\kappa_j{}^\beta)\mu_{ij}, \quad (7.9)$$

F is a function of the coordinates and time but not of the momenta, and $\langle p^\alpha\rangle_q$ is the average value of p^α at a given point in the coordinate space.

Proceeding now to the equations for averages, we find

$$d\langle q^\alpha\rangle/dt=\langle p^\alpha\rangle/m^\alpha \quad (7.10)$$

and

$$d\langle p^\alpha\rangle/dt=\langle Q^\alpha\rangle-\sum_\beta\sigma^{\alpha\beta}\langle p^\beta\rangle/m^\beta, \quad (7.11)$$

where Q^α is the conservative force $-\partial\Psi/\partial q^\alpha$.

Because $\sigma^{\beta\alpha}=\sigma^{\alpha\beta}$, it is possible to define the Rayleigh dissipation function, given by

$$R=\tfrac{1}{2}\sum_\alpha\sum_\beta\sigma^{\alpha\beta}(\langle p^\alpha\rangle/m^\alpha)(\langle p^\beta\rangle/m^\beta) \quad (7.12)$$

and have the viscous force, which is the second term on the right in Eq. (7.11), equal to $-m^\alpha(\partial R/\partial\langle p^\alpha\rangle)$.

In the extension to several degrees of freedom, Eqs. (3.8), (3.9), and (3.12) are replaced by

$$d\langle\Delta q^\alpha\Delta q^\beta\rangle/dt=\langle\Delta p^\alpha\Delta q^\beta\rangle/m^\alpha+\langle\Delta p^\beta\Delta q^\alpha\rangle/m^\beta, \quad (7.13)$$

$$d\langle\Delta p^\alpha\Delta q^\beta\rangle/dt=\langle\Delta p^\alpha\Delta p^\beta\rangle/m^\beta+\langle\Delta Q^\alpha\Delta q^\beta\rangle-\sum_\nu\sigma^{\alpha\nu}\langle\Delta p^\nu\Delta q^\beta\rangle/m^\nu, \quad (7.14)$$

$$d\langle\Delta p^\alpha\Delta p^\beta\rangle/dt=\langle\Delta p^\alpha\Delta Q^\beta\rangle+\langle\Delta p^\beta\Delta Q^\alpha\rangle-\sum_\nu\sigma^{\alpha\nu}\langle\Delta p^\beta\Delta p^\nu\rangle/m^\nu-\sum_\nu\sigma^{\beta\nu}\langle\Delta p^\alpha\Delta p^\nu\rangle/m^\nu+2\sigma^{\alpha\beta}kT. \quad (7.15)$$

It has been understood that, with the coordinates chosen, the kinetic energy is expressed as $\frac{1}{2}\sum_\alpha(p^\alpha)^2/m$. Since it is possible to normalize two homogeneous quadratic forms simultaneously, a suitable choice of coordinates will normalize the dissipation function also, making $\sigma^{\alpha\beta}$ zero when α and β are different. When all the conservative forces are zero, or at least independent of the coordinates, the preceding equations, with the dissipation function as well as the kinetic energy normalized, become

$$d\langle\Delta q^\alpha\Delta q^\beta\rangle/dt=\langle\Delta p^\alpha\Delta q^\beta\rangle/m^\alpha+\langle\Delta p^\beta\Delta q^\alpha\rangle/m^\beta, \quad (7.16)$$

$$d\langle\Delta p^\alpha\Delta q^\beta\rangle/dt=\langle\Delta p^\alpha\Delta p^\beta\rangle/m^\beta-\sigma^{\alpha\alpha}\langle\Delta p^\alpha\Delta q^\beta\rangle/m^\alpha, \quad (7.17)$$

$$d\langle\Delta p^\alpha\Delta p^\beta\rangle/dt=-[(\sigma^{\alpha\alpha}/m^\alpha)+(\sigma^{\beta\beta}/m^\beta)]\langle\Delta p^\alpha\Delta p^\beta\rangle+2\sigma^{\alpha\beta}kT. \quad (7.18)$$

These in turn, if $\beta=\alpha$, take the same form as Eqs. (3.8), (3.9), and (3.12) with ΔQ equal to zero. The description of such a dynamical system is thus reducible to that of a number of bodies with one degree of freedom.

With a system of harmonic oscillators, it is possible to normalize either the dissipation function or the potential energy simultaneously with the kinetic energy, but not in general both of them. Normal modes of vibration do not in general exist for damped oscillations. There is always the possibility of an irreducible physical coupling. This coupling may be described as elastic, inertial, or viscous, according to the choice of coordinates, but the oscillations can not be uncoupled by the purely formal manipulation of symbols.

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