although the expression for the conductivity diverges at long wave lengths, arguments can be made for the introduction of a long wave length cutoff on the sums.

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Contribution to the Theory of Brownian Motion

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The statistical dynamical behavior of a large spherical particle in an n-dimensional harmonic crystal is studied. This Brownian sphere is formed by constraining the particles inside a large spherical region of the crystal to move as a single particle. Effective equations of motion for the Brownian sphere are derived. For the one-dimensional and three-dimensional crystals, these equations are identical with the Langevin equation for a free particle and a harmonic oscillator, respectively. For the Brownian sphere in a two-dimensional crystal, a generalized Langevin equation is derived which is a non-Markoffian linear integro-differential equation. These results for the Brownian sphere are compared with the results obtained by Hemmer and Rubin for a different crystal lattice model.

Introduction

The physical concepts and ideas which have evolved in the study of Brownian motion phenomena have pervaded many areas of physics, chemistry, astronomy, and mathematics.[2,3] In this paper, we continue a line of investigation[4-7] whose purpose is to gain some insight into the nature of the assumptions made in developing a theory of Brownian motion. These basic assumptions are best illustrated in the Langevin equation[2a]

$$M\ddot{X} + \beta\dot{X} - K(X) = A(t)$$

which has been used as a starting point for developing the theory. The Langevin equation is the equation of motion of a Brownian particle of mass M in an external force field $K(X)$. It is assumed in writing such an equation that the influence of the surrounding medium on the Brownian particle can be represented as the sum of two terms: $\beta\dot{X}$ a dynamical friction or viscous resistance proportional to particle velocity, and $A(t)$ a rapidly fluctuating random force whose intensity is related to the temperature of the medium. Starting from the Langevin equation, a complete description of the state of the Brownian particle is obtained in the form of a conditional probability distribution function (c.p.d.f.). The c.p.d.f. $W(\dot{X}_2, X_2, t_2 \mid \dot{X}_1, X_1, t_1)$ is the conditional probability that the velocity and position are $\dot{X}_2$ and X_2 at time t_2 when they were $\dot{X}_1$ and X_1 at the earlier time t_1.

In this paper, as in earlier work,[4-7] we consider a modification of a perfect harmonic n-dimensional crystal with nearest-neighbor central and noncentral forces. The effect of the modification is to introduce a Brownian particle into the crystal. These modified harmonic oscillator systems have the important feature that explicit exact expressions for the c.p.d.f. of the Brownian particle can be obtained directly from the equations of motion. The only assumption made is that the system is initially in thermal equilibrium. Once an explicit form of the c.p.d.f. has been obtained, the form of the associated Langevin equation (or generalized Langevin equation) can be inferred. Hemmer[5] and Rubin[4,6,7] modified the crystal by increasing the mass of one of the lattice particles to a very large value. In this paper we consider a different modification of the crystal in which the particles inside a large spherical region are assumed to be rigidly connected. This large spherical aggregate, which we will call a Brownian sphere, is treated as a single particle.

In the earlier work, it has been shown that for a very heavy particle in the one-dimensional crystal[5-7] the heavy particle behaves like a free Brownian particle. The Langevin equation, which is consistent with the c.p.d.f., has the form[2a]

$$M\ddot{X} + \beta_1\dot{X} = A(t)$$

where the friction constant β_1 is given in terms of lattice parameters. For the three-dimensional crystal,[7] again in the limit of a very heavy particle, the particle behaves like a Brownian oscillator. The Langevin equation which is consistent with the c.p.d.f. in this case has the form[2a]

$$M\ddot{X} + \beta_3\dot{X} + kX = A(t)$$

where β_3 and k are given in terms of lattice parameters. For the two-dimensional crystal, the results are less complete. It is shown[7] that the position and velocity of the heavy particle are non-Markoffian random variables[8] in contrast to the case of the one- and three-dimensional crystals where the position and velocity are shown to be Markoffian random variables. This is the extent of the results which have been obtained previously.

In studying the properties of the Brownian sphere, we shall need several results which have been estab-

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(2) (a) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943); (b) M. C. Wang and G. E. Uhlenbeck, *ibid.*, **17**, 323 (1945).

(3) J. L. Doob, "Stochastic Processes," John Wiley and Sons, Inc., New York, N. Y., 1953.

(4) R. J. Rubin, "Proceedings of the International Symposium on Transport Processes in Statistical Mechanics, Brussels, August, 1956," I. Prigogine, Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 155.

(5) P. C. Hemmer, Thesis, *Det Fysiske Seminar i Trondheim*, 2 (1959).

(6) R. J. Rubin, *J. Math. Phys.*, 1, 309 (1960).

(7) R. J. Rubin, *ibid.*, **2**, 373 (1961).

(8) A pair (or more) of random variables is said to be Markoffian if for $t_3 > t_2 > t_1$ the conditional probability distribution function $W(\dot{X}_3, X_3, t_3 \mid \dot{X}_2, X_2, t_2; \dot{X}_1, X_1, t_1)$ is independent of the values of $\dot{X}$ and X at time t_1, *i.e.*, if $W(\dot{X}_3, X_3, t_3 \mid \dot{X}_2, X_2, t_2; \dot{X}_1, X_1, t_1) = W(\dot{X}_3, X_3, t_3 \mid \dot{X}_2, X_2, t_2)$; otherwise the variables are said to be non-Markoffian.

lished[9] concerning the statistical dynamical description of one of the particles in a system of coupled oscillators. These results are:

(i) The c.p.d.f. $W(\dot{X}_2, X_2, t_2 \mid \dot{X}_1, X_1, t_1)$ is a gaussian function (bivariate normal) of $\dot{X}_2$ and X_2 independent of the dimensionality of the lattice. The c.p.d.f. is stationary in time, *i.e.*, all mean values depend only upon the time difference $t_2 - t_1$.

(ii) The conditional mean values $\langle \dot{X}_2 \rangle$, $\langle X_2 \rangle$, $\langle \dot{X}_2^2 \rangle$, $\langle X_2^2 \rangle$, and $\langle \dot{X}_2 X_2 \rangle$, which completely characterize the gaussian c.p.d.f., can all be expressed in terms of a single function which is a solution of the crystal lattice equations of motion corresponding to a special initial state.

(iii) In the special initial state ($t = 0$), all particles are at their equilibrium positions and all particles are at rest, except the particle whose statistical dynamical properties are of interest. This particle is given a unit velocity. The velocity of this particle at subsesequent times, $\dot{X}(t)$, is identically equal to $\langle \dot{X}_2 \rangle$, the velocity autocorrelation function, where $\langle \dot{X}_2 \rangle$ is a function of the time difference $t = t_2 - t_1$. All other mean values are expressible in terms of $\dot{X}(t)$, $X(t)$, and $\int_0^t X(t)\mathrm{d}t$.

(iv) The perfect lattice equations of motion

$$m \frac{\mathrm{d}^2}{\mathrm{d}t^2} U(\mathbf{R}) = K\{\Delta_1{}^2 + \ldots + \Delta_n{}^2\} U(\mathbf{R}) \quad (1)$$

where $U(\mathbf{R})$ is the displacement of lattice particle $\mathbf{R}$ from its equilibrium position in one of the lattice directions, and where $\Delta_i{}^2 U(\mathbf{R})$ denotes the second difference $U(\mathbf{R} + \mathbf{l}_i) - 2U(\mathbf{R}) + U(\mathbf{R} - \mathbf{l}_i)$ in the ith lattice direction, are a discrete form of the scalar wave equation for an elastic continuum

$$\rho \frac{\partial^2 u}{\partial t^2} = E\left\{\frac{\partial^2}{\partial x_1{}^2} + \ldots + \frac{\partial^2}{\partial x_n{}^2}\right\} u \quad (2)$$

Determination of Velocity Autocorrelation Function of the Brownian Sphere

We treat a modified n-dimensional simple cubic crystal with nearest-neighbor central and noncentral forces whose equations of motion are given in eq. 1. The modification is made by constraining all particles inside a large spherical surface inscribed in the crystal to move as a single particle, the Brownian sphere. The radius "a" of the sphere is assumed to be large compared to the lattice spacing. The total mass M_s of the sphere is associated with a density ρ_s which is in general different from the mean density of the lattice. The velocity autocorrelation function of the Brownian sphere can be determined by solving the equations of motion for the special initial condition described in (iii). In the limit in which the radius of the Brownian sphere is large compared to the lattice spacing, it turns out to be simpler, as well as adequate, to approximate the solution of the modified lattice equations of motion by the solution of the corresponding modified scalar wave equation for the analogous initial conditions: a large sphere of mass M_s and radius a embedded in an elastic continuum,[10] where the elastic continuum is at rest and unstrained and the sphere is given an initial unit velocity. The approximation of the behavior of a large Brownian sphere in a discrete system of particles by the behavior of the sphere in an elastic continuum can be expected to be accurate provided that the dominant frequency characteristics of the many-particle system fall in the low frequency range. This situation will certainly prevail when the radius of the sphere is large compared to the lattice spacing and the density of the sphere is comparable with the mean density of the crystal.

Since the initial conditions in (iii) have a spherical symmetry, the scalar wave equation will involve only one distance coordinate, r the radial distance measured from the equilibrium position of the rigid sphere. In n dimensions this equation has the form[11]

$$\rho \frac{\partial^2 u}{\partial t^2} = E\left\{\frac{\partial^2 u}{\partial r^2} + \frac{n-1}{r}\frac{\partial u}{\partial r}\right\} \quad (3)$$

where ρ is the density of the crystal medium and E is the elastic constant. The equation of motion of the rigid sphere is

$$M_s \frac{\mathrm{d}^2 X}{\mathrm{d}t^2} = S_n E \left.\frac{\partial u}{\partial r}\right|_{r=a} \quad (4)$$

where $E \left.\frac{\partial u}{\partial r}\right|_{r=a}$ is the force per unit area on the surface of the sphere and S_n is the surface area of the sphere. The displacement of the elastic continuum at the surface of the sphere $u(a,t)$ must always be equal to $X(t)$, the displacement of the center of the sphere. The initial conditions corresponding to those mentioned in (iii) are

$$u(r,0) = 0;\ \frac{\partial}{\partial t} u(r,t)|_{t=0} = 0;\ X(0) = 0; \text{ and } \dot{X}(0) = 1$$

The initial value problem for eq. 3 and 4 is readily solved using the method of Laplace transforms. If the Laplace transforms of $u(r,t)$ and $X(t)$ are denoted by

$$v(r,\sigma) = \int_0^\infty e^{-\sigma t} u(r,t)\mathrm{d}t \text{ and } \xi(\sigma) = \int_0^\infty e^{-\sigma t} X(t)\mathrm{d}t$$

then eq. 3 and 4 become

$$\frac{\mathrm{d}^2 v}{\mathrm{d}r^2} + \frac{n-1}{r}\frac{\mathrm{d}v}{\mathrm{d}r} - \frac{\sigma^2}{c^2} v = 0 \quad (5)$$

and

$$M_s[\sigma^2\xi(\sigma) - 1] = S_n E \frac{\mathrm{d}}{\mathrm{d}r} v(r,\sigma)|_{r=a} \quad (6)$$

with

$$\xi(\sigma) = v(a,\sigma) \quad (7)$$

(9) See ref. 7 for details. The generality of these results for arbitrary systems of coupled harmonic oscillators is demonstrated by M. Toda and Y. Kogure, *Progr. Theoret. Phys. Suppl.* (Kyoto), **No. 23**, 157 (1962); R. J. Rubin, *Phys. Rev.*, **131**, 964 (1963).

(10) M. Toda, *Progr. Theoret. Phys. Suppl.* (Kyoto), **No. 23**, 172 (1962). Toda has considered the behavior of the continuum model from a somewhat different point of view. He has examined the steady-state response of the sphere to a periodic external force in order to determine the conditions under which the sphere behaves like a simple oscillator.

(11) R. Courant and D. Hilbert, "Methods of Mathematical Physics, Vol. 2. Partial Differential Equations," Interscience Publishers, New York, N. Y., 1962.

where $c^2 = E/\rho$. In eq. 5 replace the variable $v(r,\sigma)$ by $v(r,\sigma) = r^{-(1/2)n+1}\phi(r,\sigma)$, and obtain

$$r^2\frac{d^2\phi}{dr^2} + r\frac{d\phi}{dr} - \left(\frac{\sigma^2}{c^2}r^2 + \left(\frac{1}{2}n - 1\right)^2\right)\phi = 0 \quad (8)$$

a form of Bessel's equation. The general solution of eq. 8 which remains bounded when $\sigma > 0$ and r approaches $+\infty$ is[12]

$$\phi(r,\sigma) = AK_{(1/2)n-1}(\sigma r/c)$$

or

$$v(r,\sigma) = Ar^{-(1/2)n+1}K_{(1/2)n-1}(\sigma r/c) \quad (9)$$

where $K_\mu(Z)$ is a modified Bessel function of the second kind. The constant A can be determined by substituting $v(a,r)$ from eq. 9 for $\xi(\sigma)$ in eq. 6. The result is

$$A = M_s\left\{M_s\sigma^2 a^{-(1/2)n+1}K_{(1/2)n-1}(\sigma a/c) - S_nE\frac{d}{dr}[r^{-(1/2)n+1}K_{(1/2)n-1}(\sigma r/c)]|_{r=a}\right\}^{-1} \quad (10)$$

Finally, the expression for the Laplace transform of the velocity of the sphere is, since $(d/dZ)Z^{-\nu}K_\nu(Z) = -Z^{-\nu}K_{\nu+1}(Z)$

$$\begin{aligned}\sigma\xi(\sigma) &= \sigma v(a,\sigma)\\ &= M_s\{M_s\sigma + s_nK_{(1/2)n}(\sigma a/c)/K_{(1/2)n-1}(\sigma a/c)\}^{-1}\end{aligned} \quad (11)$$

where $s_n = S_nE/c$.

Effective Equation of Motion for the Brownian Sphere

The complete dynamical description of this model involved the coupled equations of both the Brownian sphere and the surrounding lattice medium. Having determined eq. 11, an implicit approximate expression for the velocity (or velocity autocorrelation function) of the sphere, we now consider the question of inferring a single equation of motion for the Brownian sphere from it. If an equation can be found, then any influence of the medium, such as dynamic friction, effective restoring force, and possible non-Markoffian effects, should be implicitly contained in it. The effect of the medium on the Brownian sphere is lumped in the ratio

$$R_n = K_{(1/2)n}(\sigma a/c)/K_{(1/2)n-1}(\sigma a/c) \quad (12)$$

appearing in eq. 11. Upon examining the properties of this ratio, we find an obvious difference between odd- and even-dimensional systems. We first consider the simpler case which occurs when n is odd. Then the ratio of Bessel functions R_{2m+1} is a simple rational fraction in the variable σ. For example for $n = 1$, 3, and 5, one obtains[12]

$$R_1 = 1$$
$$R_3 = 1 + c/\sigma a$$

and

$$R_5 = (3c/\sigma a) + (1 + c/\sigma a)^{-1}$$

When the Laplace transform $\sigma\xi(\sigma)$ is a rational function in σ, it is a simple matter to construct a differential equation of motion by clearing the expression for $\sigma\xi(\sigma)$ of all fractions (or all negative powers of σ). In the remainder of this section we will describe the results in one and three dimensions, indicate the result in five dimensions, and then describe the results in two dimensions. The result in five dimensions sheds some light on the way in which the equation of motion becomes more complicated for this model in even-dimensional systems.

$n = 1$.—In case $n = 1$, eq. 12 becomes

$$\sigma\xi(\sigma) = M_s\{M_s\sigma + s_1\}^{-1} \quad (12_1)$$

or

$$M_s[\sigma^2\xi(\sigma) - 1] + s_1\sigma\xi(\sigma) = 0 \quad (13)$$

Equation 13 is the Laplace transform of the equation of motion

$$M_s\ddot{X} + s_1\dot{X} = 0 \quad (14)$$

with the initial conditions $\dot{X}(0) = 0$ and $X(0) \doteq 1$. This result has been obtained by the author,[13] by Toda,[10] and in a different context by others.[14] Thus the Brownian sphere (rod) in an infinite one-dimensional crystal behaves like a free particle moving in a medium where the resistance or dynamical friction is proportional to the velocity.[15] Similar behavior has been found in the single heavy particle model.[4-7]

$n = 3$.—In case $n = 3$, eq. 12 becomes

$$\sigma\xi(\sigma) = M_s\{M_s\sigma + s_3 + s_3c/\sigma a\}^{-1} \quad (12_3)$$

or

$$M_s[\sigma^2\xi(\sigma) - 1] + s_3\sigma\xi(\sigma) + s_3(c/a)\xi(\sigma) = 0$$

The associated equation of motion is that of a damped oscillator

$$M_s\ddot{X} + s_3\dot{X} + s_3(c/a)X = 0 \quad (15)$$

with the initial conditions $X(0) = 0$ and $\dot{X}(0) = 1$, a result equivalent to one obtained by Toda.[10] Similar behavior has been found in the earlier work[7] on the single heavy particle model. However, while the oscillations of the single heavy particle in a crystal are underdamped, the oscillations of the Brownian sphere in a crystal can be underdamped, critically damped, or overdamped depending upon the density of the sphere ρ_s compared to the density ρ of the crystal. The condition for critical damping can be obtained by determining the roots of the denominator $M_s\sigma + s_3 + s_3c/\sigma a = 0$ in eq. 12_3. They are

$$\sigma_\pm = -{}^1/_2(s_3/M_s)\left[1 \pm i\left({}^4/_3\frac{\rho_s}{\rho} - 1\right)^{1/2}\right]$$

where the density of the Brownian sphere is $\rho_s = M_s/(4\pi a^3/3)$. Thus when $\rho_s = {}^3/_4\rho$, the sphere is critically damped.

$n = 5$.—In case $n = 5$, eq. 12 becomes

$$\sigma\xi(\sigma) = M_s\{M_s\sigma + s_5(3c/\sigma a) + s_5(1 + c/\sigma a)^{-1}/\}^{-1} \quad (12_5)$$

(12) G. N. Watson, "A Treatise on the Theory of Bessel Functions," Cambridge University Press, Cambridge, 1962, p. 78.

(13) R. J. Rubin, *Bull. Am. Phys. Soc.*, [2] 1, No. 4, 221 (1956).

(14) A. E. H. Love, *Proc. London Math. Soc.*, 2 (2), 88 (1904); G. Beck and H. M. Nussenzveig, *Nuovo Cimento*, 16, 416 (1960).

(15) In a one-dimensional crystal, the single heavy particle model and the Brownian sphere model are identical.

or

$$M_s(a/c)[\sigma^3\xi(\sigma) - \sigma] + M_s[\sigma^2\xi(\sigma) - 1] + s_5(a/c)\sigma^2\xi(\sigma) + 3s_5\sigma\xi(\sigma) + 3s_5(c/a)\xi(\sigma) = 0 \quad (16)$$

The associated equation of motion of the Brownian sphere is

$$(M_s + s_5a/c)\ddot{X} + (a/c)M_s\dddot{X} + 3s_5\dot{X} + 3s_5(c/a)X = 0 \quad (17)$$

with initial conditions $X(0) = 0$, $\dot{X}(0) = 1$, and $\ddot{X}(0) = -s_5/M_s$. According to eq. 17, the effective mass of the Brownian sphere is $M_s + s_5a/c$ and, besides the familiar velocity-proportional damping $3s_5\dot{X}$ and linear restoring force $3s_5(c/a)X$, there is an additional effect of the medium represented by the term $(a/c)M_s\dddot{X}$.

$n = 2$.—We now consider the behavior in two dimensions when the ratio $R_2 = K_1(\sigma a/c)/K_0(\sigma a/c)$ involves arbitrarily high powers of σ. In this case the influence of the medium is represented by an infinite number of time derivatives. An alternative form for the infinite order differential equation of motion can be obtained by writing eq. 12 as

$$M_sK_0(\sigma a/c)[\sigma^2\xi(\sigma) - 1] + s_2K_1(\sigma a/c)\sigma\xi(\sigma) = 0 \quad (12_2)$$

Equation 12_2 is the Laplace transform of the integro-differential equation[16]

$$\int_{a/c}^{t} \frac{M_s\ddot{X}(t-\tau)}{(\tau^2 - a^2/c^2)^{1/2}}\,d\tau + s_2\int_{a/c}^{t} \frac{(\tau c/a)\dot{X}(t-\tau)}{(\tau^2 - a^2/c^2)^{1/2}}\,d\tau = 0 \quad (18)$$

with the initial conditions $X(0) = 0$ and $\dot{X}(0) = 1$. It is seen in eq. 18 that the state of the Brownian sphere at a given time depends explicitly upon all earlier values of $\dot{X}$ and $\ddot{X}$ as well as the initial values $X(0)$ and $\dot{X}(0)$. The structure of eq. 18 is consistent with that expected from a solution of the scalar wave equation in two dimensions[11] and is not inconsistent with that expected of a non-Markoffian equation of motion.

Conclusions Concerning the Form of the Langevin Equations for the Brownian Sphere

In deriving the equations of motion (14), (18), and (15) for the Brownian sphere in one-, two-, and three-dimensional crystals, we have dealt only with the special initial condition (iii) and ignored the additional effects of the thermal motion (excitation) of the surrounding lattice medium on the Brownian sphere. These effects can easily be included, but at the cost of a considerable complication in the solution of eq. 3 and 4 for the motion of the sphere. It can be shown that if account is taken in the initial conditions of the thermal agitation of the lattice then the equations of motion of the Brownian sphere in the one-, two-, and three-dimensional crystals are only altered by the addition of a time-dependent force $A_n(t)$. This additional force represents the delayed effect[13] of the lattice particles on the Brownian sphere. With the addition of $A_n(t)$, the equations of motion for the Brownian sphere in one and three dimensions are

$$M_s\ddot{X} + s_1\dot{X} = A_1(t) \quad (14')$$

and

$$M_s\ddot{X} + s_3\dot{X} + s_3(c/a)X = A_3(t) \quad (15')$$

These equations of motion are formally identical with the Langevin equations for a free particle and a harmonic oscillator, respectively. In the case of the two-dimensional lattice, we are led to a generalized Langevin equation

$$\int_{a/c}^{t} \frac{M_s\ddot{X}(t-\tau)}{(\tau^2 - a^2/c^2)^{1/2}}\,d\tau + s_2\int_{a/c}^{t} \frac{(\tau c/a)\dot{X}(t-\tau)}{(\tau^2 - a^2/c^2)^{1/2}}\,d\tau = A_2(t) \quad (18')$$

for the Brownian sphere.

In the three-dimensional crystal, the Brownian sphere may undergo underdamped, critically damped, or overdamped oscillations depending upon the density ratio ρ_s/ρ while in the earlier model the heavy particle exhibits underdamped oscillations only. In the two-dimensional crystal the Brownian sphere equation of motion is the generalized Langevin equation (18). In contrast to this result, our previous study of the heavy particle model in two dimensions did not lead to an explicit form for a Langevin equation, although it was shown that the heavy particle position and velocity are non-Markoffian random variables. In view of the nature of the results obtained for the Brownian sphere in even- and odd-dimensional crystal lattices in this paper, the non-Markoffian behavior found for the earlier heavy particle model[7] can be traced to the difference in the structure of solutions of the even- and odd-dimensional scalar wave equations,[11] *i.e.*, a property of the lattice medium.

(16) A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, "Tables of Integral Transforms," Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1954, p. 277.