Theory of the Rotational Brownian Motion of a Free Rigid Body*

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The orientation of a rigid body is specified by the Cayley-Klein parameters. A system of such bodies subject to small random changes in orientation but not subject to any externally applied torque is then considered in some detail. A diffusion equation is derived with certain linear combinations of the Cayley-Klein parameters as independent variables. This equation is expressed in terms of quantum-mechanical angular momentum operators and a Green's function for the equation is obtained as an expansion in angular momentum eigenfunctions. This expansion can be used to calculate averages of various physical quantities in a nonequilibrium distribution of orientations. It may also be used to calculate the spectral density of fluctuating quantities in an equilibrium distribution. Illustrative examples of both of these applications are given.

INTRODUCTION

FURRY[1] has treated the problem of the rotational Brownian motion of a sphere. He represents the orientation of a rigid body by a quaternion. Then, using three components of the quaternion as independent variables, he derives a diffusion equation for the random rotational motion of spheres and finds a Green's function for the equation. The present paper is an attempt to generalize Furry's calculation to a body of arbitrary shape.

The description of rotations used here differs from Furry's in that the independent variables are derived from the Cayley-Klein parameters rather than the equivalent representation by quaternions and in that Furry's description uses laboratory coordinates while body coordinates are used here. This distinction between body and laboratory coordinates is trivial when the body is spherically symmetric but is quite important when this is not so. Therefore, Sec. I is devoted to a rather detailed discussion of the proper interpretation of the variables that are used in this paper.

Section II contains a derivation of the diffusion equation which applies to the random rotational motion of an asymmetrical rigid body. The method of derivation is essentially the same as Furry's and the resulting equation reduces to his when the body is a sphere. However, instead of being expressed explicitly as a differential equation in the variables as Furry's equation is, this equation is written in terms of certain rotation operators defined in Sec. I.

In Sec. III it is shown that it is possible to use a Green's function to solve the diffusion equation of Sec. II. It is also shown how one can exploit the similarity of the form of the diffusion equation to the form of the Schrödinger equation to expand the Green's function in quantum-mechanical rigid-rotator eigenfunctions.

Section IV treats the special case of a body with an axis of symmetry. It includes a derivation of expressions for quantum-mechanical angular-momentum eigenfunctions in terms of the present variables and an expansion of the Green's function in the derived eigenfunctions. This expansion is exact.

Section V treats the case of a completely asymmetric body but the expansion of the Green's function is only approximate. The first few eigenfunctions and their coefficients in the expansion are obtained and written in tabular form. In addition, it is shown how one may obtain higher order terms (but not the general term) in the expansion.

In Sec. VI the results of the previous sections are applied to the calculation of the expectation values of several simple functions of orientation in a nonequilibrium distribution of orientations. The use of the Green's function to calculate the spectrum of the fluctuations which occur in an equilibrium distribution is also illustrated by simple examples. It may be noted that the results in this section are all exact in spite of having been obtained from the approximate expansion of Sec. V. This is due to the fact that the neglected terms in that expansion make no contribution to any of the averages in this section.

Finally, in Sec. VII the parameters appearing in the diffusion equation in the form of a diffusion tensor are expressed in terms of the elements of the viscous drag tensor in a form commonly referred to as an "Einstein relation."

I. DESCRIPTIONS OF ROTATIONS

The orientation of a rigid body is completely determined by fixing one set of coordinates in the body and another set in the laboratory and specifying the rotation which transforms one set into the other. Consider the case in which the body coordinates are rotated away from the laboratory coordinates through an angle α about the axis specified by the unit vector $\hat{n}$. Such a rotation can be represented quite simply by

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[1] W. H. Furry, Phys. Rev. **107**, 7 (1957).

means of the Cayley-Klein parameters.[2] In this representation any vector $\mathbf{A}$ is replaced by a 2×2 matrix, $\boldsymbol{\sigma}\cdot\mathbf{A}$, where $\boldsymbol{\sigma}$ indicates the three Pauli spin matrices. The components of $\mathbf{A}$ in one coordinate system are then obtained from the components in the other by performing a unitary transformation on $\boldsymbol{\sigma}\cdot\mathbf{A}$. Thus,

$$(\boldsymbol{\sigma}\cdot\mathbf{A})_{\text{body}}=\mathbf{Q}(\boldsymbol{\sigma}\cdot\mathbf{A})_{\text{lab}}\mathbf{Q}^{\dagger}. \tag{1.0}$$

It is easily shown that $\mathbf{Q}$ may be written in terms of α and $\hat{n}$ as

$$\mathbf{Q}=\exp(i\alpha\hat{n}\cdot\boldsymbol{\sigma}/2), \tag{1.1}$$

or alternatively as

$$\mathbf{Q}=\Gamma+i\boldsymbol{\sigma}\cdot\boldsymbol{\Omega}, \tag{1.2}$$

where $\Gamma=\cos(\alpha/2)$ and $\boldsymbol{\Omega}=\hat{n}\sin(\alpha/2)$.

The four elements of the matrix $\mathbf{Q}$ are the Cayley-Klein parameters for the rotation $(\alpha\hat{n})$. Although these parameters themselves may be used as variables to describe the rotation (orientation) of the body, it is often more convenient to use the linear combinations Γ and $\boldsymbol{\Omega}$ defined above. This leads to two geometrical descriptions of the rotation. In the first description, the variables Ω_k are plotted as coordinates in a three-dimensional space with Γ defined merely as a function of $\boldsymbol{\Omega}$. In the second description, Γ and the Ω_k are treated symmetrically by plotting them as coordinates in a four-dimensional space with the subsidiary condition that $\Gamma^2+\boldsymbol{\Omega}^2=1$. In the first description, the region of interest is the interior and surface of the unit sphere centered at the origin. In the second description, this region is the surface of the unit four-sphere, also centered at the origin. In each case points at opposite ends of a diameter of the sphere are physically equivalent.[3] Therefore, any physically meaningful function of the orientation must assume the same value at both ends of a diameter.

The composition of two rotations is accomplished in the $\mathbf{Q}$ representation by multiplying the matrices involved. Thus, if one first performs the rotation $\mathbf{Q}_0$ and then performs $\mathbf{Q}_1$, the resultant rotation is given by $\mathbf{Q}=\mathbf{Q}_1\mathbf{Q}_0$. It is at this point that the important distinction between body and laboratory coordinates appears. The components of the vector $\hat{n}_1$ specifying the axis of the second rotation must be taken relative to the *rotated axes* as obtained with $\mathbf{Q}_0$ in order to possess a consistent description in terms of body coordinates. For a description in terms of laboratory coordinates, the components of $\hat{n}_1$ must be taken relative to the laboratory coordinates and $\mathbf{Q}^{\dagger}$ *exchanged for* $\mathbf{Q}$ *everywhere*. This last requirement is due to the fact that it is the inverse of (1.0) rather than (1.0) itself, which is the fundamental transformation in laboratory coordinates. Body coordinates are used throughout this paper since certain useful quantities associated with the shape of the body (inertia tensor, diffusion tensor, etc.) are constants when referred to these coordinates. Then, keeping in mind the fact that $\boldsymbol{\Omega}_1$ must be referred to the body axes, one obtains for the transformation $\mathbf{Q}=\mathbf{Q}_1\mathbf{Q}_0$,

$$\boldsymbol{\Omega}=\Gamma_0\boldsymbol{\Omega}_1+\Gamma_1\boldsymbol{\Omega}_0-\boldsymbol{\Omega}_1\times\boldsymbol{\Omega}_0, \tag{1.3}$$

and

$$\Gamma=\Gamma_1\Gamma_0-\boldsymbol{\Omega}_1\cdot\boldsymbol{\Omega}_0 \tag{1.4}$$

In addition to being regarded as a rule for the composition of rotations, (1.3) can be regarded as a change of independent variables from $\boldsymbol{\Omega}_0$ to $\boldsymbol{\Omega}$ in the three-dimensional $\boldsymbol{\Omega}$ space. The Jacobian associated with the change is

$$\left|\partial(\boldsymbol{\Omega})/\partial(\boldsymbol{\Omega}_0)\right|=\Gamma/\Gamma_0. \tag{1.5}$$

This leads to the important conclusion that the weight[4] associated with the volume $(d^3\Omega)$ is Γ^{-1}.

The matrices $\mathbf{Q}$ above suffice to describe any rotation or combination of rotations which a rigid body may undergo. However, it is often desirable to possess a rotation operator that operates directly in terms of the variables Ω_k. That is, it is desirable to possess an operator which, when applied to any function of $\boldsymbol{\Omega}$, produces the change of variables given by (1.3). The infinitesimal form of such an operator is given by the translation operator in $\boldsymbol{\Omega}$ space,[5]

$$T(\Delta\boldsymbol{\Omega})=1+(\Delta\Omega_j)\partial_j, \tag{1.6}$$

where ∂_j indicates differentiation with respect to Ω_j and $\Delta\Omega_j$ is obtained from (1.3) by putting $\Delta\boldsymbol{\Omega}=(\boldsymbol{\Omega}-\boldsymbol{\Omega}_0)$ and passing to the limit of small $\boldsymbol{\Omega}_1$. In this case $\boldsymbol{\Omega}_1$ is just half of the angle of rotation, say $\boldsymbol{\varepsilon}/2$, and the operator (1.6) is

$$T(\Delta\boldsymbol{\Omega})=1+\tfrac{1}{2}(\Gamma\epsilon_j\partial_j+\Omega_i\epsilon_j\epsilon_{ijk}\partial_k), \tag{1.7}$$

where ϵ_{ijk} is the usual completely antisymmetric unit tensor. This may be rewritten in the form,

$$T(\Delta\boldsymbol{\Omega})\equiv R(\boldsymbol{\varepsilon})=1-i\boldsymbol{\varepsilon}\cdot\mathbf{M}, \tag{1.8}$$

where a set of three operators $\mathbf{M}$ has been defined as

$$M_j=\tfrac{1}{2}i(\Gamma\partial_j+\Omega_i\epsilon_{ijk}\partial_k). \tag{1.9}$$

Equation (1.8) is the usual form given to rotation operators in quantum mechanics where $\mathbf{M}$ plays the role of the angular momentum operator. It may be iterated in the familiar fashion to obtain the operator for the finite rotation $(\alpha\hat{n})$,

$$R(\alpha\hat{n})=\exp(-i\alpha\hat{n}\cdot\mathbf{M}). \tag{1.10}$$

[2] See, for instance, H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1950), pp. 109–118.

[3] This double valuedness of the representation results from the fact that the transformation (1.0) is quadratic in $\mathbf{Q}$. Thus $\mathbf{Q}$ and $(-\mathbf{Q})$ are indistinguishable. In the three-dimensional description this affects only those points representing rotations through π away from the standard; in the four-dimensional description all representations are double-valued.

[4] The use of the word "weight" here may be clarified by thinking of ordinary spherical coordinates, (r,θ,ϕ), where the weight associated with $(dr,d\theta,d\phi)$ is $r^2\sin\theta$.

[5] The Einstein summation convention is henceforth to be applied to all indices repeated within a term.

The three operators M_j of course satisfy the usual angular momentum commutation relations,

$$[M_j,M_k]=i\epsilon_{jkl}M_l. \tag{1.11}$$

There exists, however, an additional set of three operators which satisfy these commutation relations.[6] These may be defined as

$$N_j=\tfrac{1}{2}i(-\Gamma\partial_j+\Omega_i\epsilon_{ijk}\partial_k), \tag{1.12}$$

so that

$$[N_j,N_k]=i\epsilon_{jkl}N_l. \tag{1.13}$$

Furthermore, it may be shown that $[N_j,M_k]=0$ and that $\mathbf{N}^2=\mathbf{M}^2$.

Both of these sets of "angular momentum" operators will be of considerable use in the later sections of this paper.

II. DIFFUSION EQUATION FOR ROTATIONAL MOTION

We now consider an ensemble of similar rigid bodies each of which undergoes a large number of small random rotations in any macroscopic interval of time. It is assumed that the probability of a body's undergoing the rotation $\boldsymbol{\varepsilon}$ in a time Δt is given in body coordinates by $p(\boldsymbol{\varepsilon},\Delta t)d^3\epsilon$ where[7]

(a) $p(\boldsymbol{\varepsilon},\Delta t)=p(-\boldsymbol{\varepsilon},\Delta t)$,
(b) $\int d^3\epsilon\, p(\boldsymbol{\varepsilon},\Delta t)\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}$ is proportional to Δt,
(c) it is possible to choose Δt so small that higher moments than (b) may be neglected.

Let $W(\boldsymbol{\Omega},t)d^3\Omega$ be the probability of finding the orientation of a randomly chosen member of the ensemble in the volume element $d^3\Omega$ at some time t after the establishment of the ensemble. This probability at some later time $t+\Delta t$ may be obtained from $W(\boldsymbol{\Omega},t)d^3\Omega$ by adding the contributions due to all possible elementary rotations $\boldsymbol{\varepsilon}$ which may take place in the time Δt This yields an integral equation for $W(\boldsymbol{\Omega},t)d^3\Omega$,

$$W(\boldsymbol{\Omega},t+\Delta t)d^3\Omega=\int d^3\epsilon\, p(\boldsymbol{\varepsilon},\Delta t)W(\boldsymbol{\Omega}_0,t)d^3\Omega_0. \tag{2.0}$$

$\boldsymbol{\Omega}_0$ here is just that orientation which, upon rotation through $\boldsymbol{\varepsilon}$, will yield $\boldsymbol{\Omega}$. Thus, by using a rotation operator of the form (1.10), one may write

$$W(\boldsymbol{\Omega}_0,t)d^3\Omega_0=\exp(i\boldsymbol{\varepsilon}\cdot\mathbf{M})W(\boldsymbol{\Omega},t)d^3\Omega. \tag{2.1}$$

Now, if one defines a weighted volume element $d\tau$ and a probability density per unit weight $P(\boldsymbol{\Omega},t)$ as

$$d\tau=\Gamma^{-1}d^3\Omega, \tag{2.2}$$

and

$$P(\boldsymbol{\Omega},t)=\Gamma W(\boldsymbol{\Omega},t), \tag{2.3}$$

Eq. (2.1) becomes with the aid of (1.5),

$$P(\boldsymbol{\Omega}_0,t)d\tau_0=d\tau\exp(i\boldsymbol{\varepsilon}\cdot\mathbf{M})P(\boldsymbol{\Omega},t). \tag{2.4}$$

The integral equation (2.1) may now be written in the form

$$P(\boldsymbol{\Omega},t+\Delta t)=\int d^3\epsilon\, p(\boldsymbol{\varepsilon},\Delta t)\exp(i\boldsymbol{\varepsilon}\cdot\mathbf{M})P(\boldsymbol{\Omega},t). \tag{2.5}$$

To first order in Δt this equation is

$$(\partial/\partial t)P(\boldsymbol{\Omega},t)=-M_jD_{jk}M_kP(\boldsymbol{\Omega},t), \tag{2.6}$$

where a diffusion tensor, D_{jk}, has been defined as

$$D_{jk}=\frac{1}{2}\int d^3\epsilon\,\epsilon_j\epsilon_k p(\boldsymbol{\varepsilon},\Delta t)/\Delta t. \tag{2.7}$$

Equation (2.6) will henceforth be referred to as the "diffusion equation" since it is the rotational analog of the ordinary translational diffusion equation. It may also be written in terms of a divergence of a current density in $\boldsymbol{\Omega}$ space,

$$(\partial/\partial t)P=-\Gamma\partial_i\mathfrak{j}_iP, \tag{2.8}$$

where the current density operator $\mathfrak{j}_l$ is defined as[8]

$$\mathfrak{j}_l=\tfrac{1}{2}\Gamma^{-1}i(\Gamma D_{lk}+\Omega_i\epsilon_{ijl}D_{jk})M_k. \tag{2.9}$$

If one considers $P(\boldsymbol{\Omega},t)$ to be a function defined in the three-dimensional $\boldsymbol{\Omega}$ space, in order to solve (2.6) it is necessary to apply boundary conditions on the surface $|\boldsymbol{\Omega}|=1$. It is clear physically that one such condition is that the *outward* normal component of the current density at one end of a diameter of the sphere must equal the *inward* normal component at the other end. This insures the conservation of total probability within the sphere. Another boundary condition is the obvious one that $P(\boldsymbol{\Omega},t)$ have the same value for points at opposite ends of a diameter of the sphere.

However, it is also possible to interpret $P(\boldsymbol{\Omega},t)$ as a function defined on the surface of a hypersphere in the four-dimensional $(\Gamma,\boldsymbol{\Omega})$ space. The "boundary" above is then just the surface between the two physically equivalent hemi-hyperspheres. Since this surface has no particular significance in four dimensions, we can make the space formally continuous across it. Thus, every point in the space is connected with other points on every side and there is no boundary upon which to apply conditions on P. However, this apparent loss of the boundary conditions is compensated for by the addition of the condition for physical meaningfulness on the four-sphere: P must be even under reflection through the center of the sphere. This last condition, which can be shown to be exactly equivalent to the

[6] The existence of another set of operators is a result of the possibility of describing the rotation $(\alpha\hat{n})$ as a *four-dimensional* rotation on the unit sphere in $(\Gamma,\boldsymbol{\Omega})$ space. In four dimensions there are six independent planes of rotation and hence six independent rotation operators.

[7] The absence of $\boldsymbol{\Omega}$ in the expression $p(\boldsymbol{\varepsilon},\Delta t)$ indicates that there is no externally applied torque tending to orient the body in any specific direction. Hence, the body described here is "free."

[8] A direct derivation of this expression for j_l is contained in an Appendix to this paper.

two boundary conditions above, will be used in this paper since it is more easily applied in practice.

III. USE OF A GREEN'S FUNCTION TO FIND $P(\Omega,t)$

Consider now another function $P'(\Omega,t'-t)$ satisfying the diffusion equation,

$$\partial P'/\partial(t'-t) = -M_j D_{jk} M_k P'. \tag{3.0}$$

After multiplying (2.6) by P' and (3.0) by P and subtracting one from the other one obtains,

$$(\partial/\partial t)(PP') = -\Gamma\partial_l(P'\mathfrak{j}_l P - P\mathfrak{j}_l P'). \tag{3.1}$$

This may be integrated over the three-sphere in Ω space with the weighted volume element $d\tau$ defined in (2.2) to obtain

$$(d/dt)\int P(\Omega,t)P'(\Omega,t'-t)d\tau = 0. \tag{3.2}$$

After integration over t from 0 to t' this becomes

$$\int P(\Omega,t')P'(\Omega,0^+)d\tau = \int P(\Omega,0^+)P'(\Omega,t')d\tau. \tag{3.3}$$

That particular function P' which satisfies the initial condition,[9] $P'(\Omega,0^+)=\delta(\Omega,\Omega')$ will be denoted by $G(\Omega,\Omega',t'-t)$ and referred to as the "Green's function" for the diffusion equation. From (3.3) it is apparent that $P(\Omega,t)$ may be found in terms of G and the initial value $P(\Omega,0^+)$ as,

$$P(\Omega',t') = \int P(\Omega,0^+)G(\Omega,\Omega',t')d\tau. \tag{3.4}$$

Furthermore, $G(\Omega,\Omega',t)$ may be obtained from $G(\Omega,0,t)$ by a simple change of origin in Ω space.[10] Thus the particular Green's function $G(\Omega,t)[\equiv G(\Omega,0,t)]$ suffices to solve the diffusion equation for any choice of initial conditions.

The calculation of $G(\Omega,t)$ is particularly simple if one possesses a complete set of eigenfunctions $\psi_n(\Omega)$ of the operator $M_j D_{jk} M_k$ for then one may write

$$\delta(\Omega,0) = \sum_n \psi_n^*(0)\psi_n(\Omega), \tag{3.5}$$

so that the Green's function becomes

$$G(\Omega,t) = \sum_n \psi_n^*(0)\psi_n(\Omega)e^{-E_n t}, \tag{3.6}$$

where E_n indicates the eigenvalue corresponding to ψ_n. Thus, the problem of finding the distribution $P(\Omega,t)$ has been reduced to one of finding the eigenvalues and eigenfunctions of $M_j D_{jk} M_k$. It will be noted that this operator is of the same form as the quantum-mechanical Hamiltonian, $M_j I_{jk}^{-1} M_k/2$ of a rigid rotator. Therefore, our problem is equivalent to the problem of finding the energy eigenvalues and eigenfunctions of a rotator. It is well known that this may be done exactly for a rotator with an axis of symmetry, but only approximately for a completely general rotator. The method used here will be to treat the axially symmetric case first and then obtain an approximation to the general case from it.

IV. DIFFUSION OF A BODY WITH AN AXIS OF SYMMETRY

In actual calculations it is convenient to use that set of body coordinates in which D_{jk} is diagonal so that the operator in the diffusion equation is $D_k M_k^2$. This may be rewritten as

$$D_k M_k^2 = D^+\mathbf{M}^2 + (D_3 - D^+)M_3^2 + D^-(M_1^2 - M_2^2), \tag{4.0}$$

where

$$D^\pm \equiv \tfrac{1}{2}(D_1 \pm D_2). \tag{4.1}$$

For a diffusion tensor with an axis of symmetry D^- may be put equal to zero. It is then apparent from (4.0) that the simultaneous eigenfunctions of $\mathbf{M}^2$ and M_3 are also eigenfunctions of $D_k M_k^2$. Since the operators $\mathbf{M}^2$ and M_3 do not form a complete set, their eigenfunctions are degenerate. It is usually convenient to remove this degeneracy by introducing one of the components of the operator $\mathbf{N}$ of (1.12) into the set. Therefore we shall obtain the eigenfunctions of the set $(\mathbf{M}^2, M_3, N_3)$. It will be observed that these operators form a complete commuting set, that they are Hermitian,[11] and that either $\mathbf{M}^2$ and M_3 or $\mathbf{M}^2(=\mathbf{N}^2)$ and N_3 can be considered to be, respectively, the square and third component of a quantum-mechanical angular momentum vector. The eigenvalues associated with the set are therefore[12]

$$\begin{aligned} &\mathbf{M}^2 \to j(j+1), \quad j=0,1,2,3, \text{ etc.}, \\ &M_3 \to m, \qquad m=-j, -j+1, \cdots, j, \\ &N_3 \to n, \qquad n=-j, -j+1, \cdots, j, \end{aligned} \tag{4.2}$$

and the eigenfunctions corresponding to the set of eigenvalues are complete and nondegenerate.

It is useful to define certain auxiliary operators to facilitate the calculation of the eigenfunctions of (4.2). The first of these and their associated eigenvalues are

$$\begin{aligned} &(M_3+N_3) \to \mu, \quad \mu = m+n, \\ &(M_3-N_3) \to \nu, \quad \nu = m-n. \end{aligned} \tag{4.3}$$

The other auxiliary operators are those which are usually referred to as "ladder" operators,

$$\begin{aligned} M^\pm &= M_1 \pm iM_2, \\ N^\pm &= N_1 \pm iN_2. \end{aligned} \tag{4.4}$$

[9] $\delta(\Omega,\Omega')$ here is the Dirac delta function so normalized that $\int\delta(\Omega,\Omega')d\tau = 1$.

[10] This change of origin may be interpreted as a change in the initial or "standard" orientation of the rotating body. Algebraically, the transformation os of the same form as (1.3) where the new coordinates of a point are Ω_1, and the new origin is located at Ω_0.

[11] This assumes that the scalar product (U,V) of two functions is defined as $\int U^*V d\tau$. The operators are not Hermitian if one uses the unweighted volume element $d^3\Omega$

[12] It may be observed that the half-integral values of j must be excluded since their eigenfunctions do not satisfy the requirements of evenness under inversion in four-space.

These operators, when applied to an eigenfunction $\psi_j^{m;n}$ of (4.2), produce the results

$$M^{\pm}\psi_j^{m;n}=[(j\mp m)(j\pm m+1)]^{\frac{1}{2}}\psi_j^{m\pm1;n},$$
$$N^{\pm}\psi_j^{m;n}=[(j\mp n)(j\pm n+1)]^{\frac{1}{2}}\psi_j^{m;n\pm1}. \quad (45)$$

We now introduce a new set of variables (ρ,Θ,Φ) defined as

$$\rho=(\Omega_1^2+\Omega_2^2)^{\frac{1}{2}},$$
$$\Theta=\tan^{-1}(\Omega_3/\Gamma), \quad (4.6)$$
$$\Phi=\tan^{-1}(\Omega_2/\Omega_1),$$

in terms of which we obtain,

$$\mathbf{M}^2=-\frac{1}{4}\left[(1-\rho^2)\partial_\rho^2+\left(\frac{1-3\rho^2}{\rho}\right)\partial_\rho+\left(\frac{1}{1-\rho^2}\right)\partial_\Theta^2+\frac{1}{\rho^2}\partial_\Phi^2\right], \quad (4.7)$$

$$M_3+N_3=-i\partial_\Phi,$$

$$M_3+N_3=i\partial_\Theta.$$

Now, putting $\psi_j^{m;n}=w_j^{\mu;\nu}$ we obtain from (4.7), (4.2), and (4.3),

$$w_j^{\mu;\nu}=g_j^{\mu;\nu}(\rho)e^{-i\nu\Theta}e^{i\mu\Phi}, \quad (4.8)$$

where

$$\left[(1-\rho^2)\partial_\rho^2+\left(\frac{1-3\rho^2}{\rho}\right)d_\rho-\left(\frac{\nu^2}{1-\rho^2}\right)-\frac{\mu^2}{\rho^2}+4j(j+1)\right]g_j^{\mu;\nu}=0. \quad (4.9)$$

This equation for $g_j^{\mu;\nu}$ may be put in a more easily recognized form by making the substitutions,

$$\xi=\rho^2, \quad \text{and} \quad g_j^{\mu;\nu}=(1-\xi)^{\frac{1}{2}|\nu|}\xi^{\frac{1}{2}|\mu|}f_j^{\mu;\nu}, \quad (4.10)$$

to obtain

$$\{(1-\xi)\xi\partial_\xi^2+[c-(a+b+1)\xi]\partial_\xi-ab\}f_j^{\mu;\nu}=0, \quad (4.11)$$

where

$$a=[(|\mu|+|\nu|)/2+j+1]; \quad b=[(|\mu|+|\nu|)/2-j]; \quad c=(|\mu|+1). \quad (4.12)$$

This is the hypergeometric equation satisfied by the hypergeometric function[13]

$$F(a;b;c;\xi)=\sum_{k=0}^{\infty}\frac{(a+k-1)!}{(a-1)!}\frac{(b+k-1)!}{(b-1)!}\frac{(c-1)!}{(c+k-1)!}\frac{\xi^k}{k!}. \quad (4.13)$$

[13] See, for instance, E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1927), pp. 281–296.

Thus the function $g_j^{\mu;\nu}$ may be written as

$$g_j^{\mu;\nu}=A_j^{\mu;\nu}(1-\rho^2)^{\frac{1}{2}|\nu|}\rho^{|\mu|}F([\tfrac{1}{2}(|\mu|+|\nu|)+j+1];[\tfrac{1}{2}(|\mu|+|\nu|)-j];(|\mu|+1);\rho^2). \quad (4.14)$$

The normalizing[14] constants $A_j^{\mu;\nu}$ may be determined by normalizing one function, say $g_j^{2j;0}$, and then using (4.5) to determine the ratios of the various constants by direct application of $M^{\pm}$ and $N^{\pm}$ to (4.14). The result of this calculation is

$$A_j^{\mu;\nu}=\left(\frac{-\mu}{|\mu|}\right)^{\mu}e^{i\nu\pi/2}\frac{(2j+1)^{\frac{1}{2}}}{\pi|\mu|!}\times\left(\frac{[j+\frac{1}{2}(|\mu|+|\nu|)]![j+\frac{1}{2}(|\mu|-|\nu|)]!}{[j-\frac{1}{2}(|\mu|+|\nu|)]![j-\frac{1}{2}(|\mu|-|\nu|)]!}\right). \quad (4.15)$$

It is now possible to write down the expansion of the Green's function $G(\boldsymbol{\Omega},t)$ for the special case $D_1=D_2$, In terms of the $w_j^{\mu;\nu}(=\psi_j^{m;n})$, from (3.6), (4.8), (4.13), (4.14), and (4.15) one obtains,

$$G(\boldsymbol{\Omega},t)\Big|_{D_1=D_2}=\pi^{-1}\sum_{j=0}^{\infty}(2j+1)^{\frac{1}{2}}\sum_{m=-j}^{j}(-1)^m w_j^{0;2m}\times\exp\{-[D^+j(j+1)+(D_3-D^+)m^2]t\}. \quad (4.16)$$

V. GENERAL CASE: COMPLETELY ANISOTROPIC DIFFUSION

The case in which the diffusion tensor possesses no axis of symmetry will now be considered. In this case one must diagonalize the complete operator (4.0). Because M_3 does not commute with this operator, the functions $\psi_j^{m;n}$ of the previous section are not eigenfunctions of it. In fact, a complete set of eigenfunctions of (4.0) is not available in any form. However, for many purposes one needs only those eigenfunctions with low values of j.[15] These may be obtained by diagonalizing (4.0) directly with the functions $\psi_j^{m;n}$ as the unperturbed basis functions. Since $\mathbf{M}^2$ will remain diagonal in this calculation the term involving it in (4.0) may be ignored. The remainder may be written as

$$R=(D_3-D^+)M_3^2+\tfrac{1}{2}D^-[(M^+)^2+(M^-)^2]. \quad (5.0)$$

In this form, the matrix elements of R are easily obtained by using (4.5). The result is

$$\langle m'n'|R|mn\rangle_j=[(D_3-D^+)m^2\delta_{mm'}+\tfrac{1}{2}D^-\partial A_j^m\delta_{m'm+2}+\tfrac{1}{2}D^-A_j\partial^-\delta_{m'm-2}]\delta_{n'n}, \quad (5.1)$$

where

$$A_j^m=[(j-m)(j+m+1)(j-m-1)(j+m+2)]^{\frac{1}{2}}. \quad (5.2)$$

Equation (5.1) shows that R never mixes even and odd values of m so that the secular equation may be

[14] The normalization assumed is $\int(w_j^{\mu;\nu})^*(w_j^{\mu;\nu})d\tau=1$ or $\int_0^1(g_j^{\mu;\nu})^*(g_j^{\mu;\nu})\rho d\rho=1/2\pi^2$.

[15] The reader will note that it is possible to maintain the index j on the eigenfunctions since $\mathbf{M}^2$ commutes with (4.0).

TABLE I. The terms appearing in G for $j=0,1,2$.[a]

$j=0$	$(\pi)^{-1}\Psi_0{}^{0;0}$
$j=1$	$(\pi)^{-1}(3)^{\frac{1}{2}}\Psi_1{}^{0;0}e^{-(D_1+D_2)t}$
	$(\pi)^{-1}(\frac{3}{2})^{\frac{1}{2}}(\Psi_1{}^{1;1}+\Psi_1{}^{1;-1})e^{-(D_3+D_1)t}$
	$(\pi)^{-1}(\frac{3}{2})^{\frac{1}{2}}(\Psi_1{}^{-1;1}-\Psi_1{}^{-1;-1})e^{-(D_3+D_2)t}$
$j=2$	$-(\pi)^{-1}(\frac{5}{2})^{\frac{1}{2}}(\Psi_2{}^{-2;2}-\Psi_2{}^{-2;-2})e^{-3(D+D_3)t}$
	$-(\pi)^{-1}(\frac{5}{2})^{\frac{1}{2}}(\Psi_2{}^{1;1}+\Psi_2{}^{1;-1})e^{-3(D+D_1)t}$
	$(\pi)^{-1}(\frac{5}{2})^{\frac{1}{2}}(\Psi_2{}^{-1;1}-\Psi_2{}^{-1;-1})e^{-3(D+D_2)t}$
	$\pm(4\pi\Delta)^{-1}(15)^{\frac{1}{2}}(D_1-D_2)\Psi_2{}^{2;0}e^{-(6D\pm2\Delta)t}$
	$(4\pi\Delta)^{-1}(5)^{\frac{1}{2}}\alpha^{\mp}\Psi_2{}^{0;0}e^{-(6D\pm2\Delta)t}$
	$(4\pi\Delta)^{-1}(\frac{5}{2})^{\frac{1}{2}}\alpha^{\pm}(\Psi_2{}^{2;2}+\Psi_2{}^{2;-2})e^{-(6D\pm2\Delta)t}$
	$\pm(4\pi\Delta)^{-1}(15/2)^{\frac{1}{2}}(D_1-D_2)(\Psi_2{}^{0;2}+\Psi_2{}^{0;-2})e^{-(6D\pm2\Delta)t}$

[a] The following notation has been adopted in this table:

$$D=\tfrac{1}{3}(D_1+D_2+D_3),$$
$$\Delta\equiv(D_1{}^2+D_2{}^2+D_3{}^2-D_1D_2-D_1D_3-D_2D_3)^{\frac{1}{2}},$$
$$\alpha^{\pm}\equiv 2\Delta\pm 3(D_3-D).$$

factored into an even and odd part by separating these values in the secular determinant. A further factorization may be effected by introducing a new set of basis functions defined as

$$\begin{aligned}\Psi_j{}^{m;n}&=2^{-\frac{1}{2}}(\psi_j{}^{m;n}+\psi_j{}^{-m;n}), \quad m>0,\\ \Psi_j{}^{m;n}&=2^{-\frac{1}{2}}(\psi_j{}^{-m;n}-\psi_j{}^{m;n}), \quad m<0,\\ \Psi_j{}^{0;n}&=\psi_j{}^{0;n}.\end{aligned} \tag{5.3}$$

It is then observed that there are no matrix elements connecting positive values of m with negative values of m. This combined with the even-odd factorization above produces a four-fold factorization of the secular equation. For even j, there are three factors of degree $j/2$ and one of degree $(j/2+1)$ while for odd j there are three factors of degree $(j+1)/2$ and one of degree $(j-1)/2$. This makes the solution of the secular equation relatively easy for low values of j. The eigenfunctions so obtained can then be substituted into (3.6) to obtain an approximate[16] expression for $G(\mathbf{\Omega},t)$.

Table I is a list of the terms appearing in G for the first three values of j while Table II exhibits the functions of Table I in terms of the variables (ρ,Θ,Φ). These were obtained by the method outlined above. In the next section they will be used to obtain the average values of various quantities associated with the orientation of a body.

VI. SOME APPLICATIONS OF THE THEORY

The Green's function of the previous section (represented by Table I) will now be used to obtain some physically meaningful results. The cases to be treated fall into two categories: the calculation of the average of some function of $\mathbf{\Omega}$ over a nonequilibrium distribution, and the calculation of the spectrum of the fluctuations of some function in an equilibrium distribution.

[16] The approximation here is the neglecting of higher values of j. The result is exact for the values of j which are treated.

As an example of a nonequilibrium distribution we shall take the Green's function itself. The most easily calculated averages are those of powers of the components of $\mathbf{\Omega}$. These quantities may be written in terms of (ρ,Θ,Φ) by means of the equations,

$$\begin{aligned}\Omega_1&=\rho\cos\Phi, &\Omega_2&=\rho\sin\Phi,\\ \Omega_3&=(1-\rho^2)^{\frac{1}{2}}\sin\Theta, &\Gamma&=(1-\rho^2)^{\frac{1}{2}}\cos\Theta,\end{aligned} \tag{6.0}$$

and then in terms of the $\Psi_j{}^{m;n}$ by using Table II. For instance, one may write as

$$\Omega_3{}^2=\tfrac{1}{4}\pi\left[\Psi_0{}^{0;0}+(\tfrac{1}{3})^{\frac{1}{2}}\Psi_1{}^{0;0}+(\tfrac{1}{6})^{\frac{1}{2}}(\Psi_1{}^{1;-1}+\Psi_1{}^{1;1}+\Psi_1{}^{-1;1}-\Psi_1{}^{-1;1})\right]. \tag{6.1}$$

The average of $\Omega_3{}^2$ may then be obtained by simple inspection of Table I since the $\Psi_j{}^{m;n}$ form an orthonormal set. The result is

$$\langle\Omega_3{}^2\rangle_t=\tfrac{1}{4}\left[1+e^{-3Dt}(e^{D3t}-e^{D2t}-e^{D1t})\right]. \tag{6.2}$$

The averages of $\Omega_1{}^2$ and $\Omega_2{}^2$ may be obtained from this result by permutation of the indices. Another class of nonvanishing[17] averages which will be useful in later calculations are the fourth order terms such as

$$\langle\Omega_1{}^2\Omega_2{}^2\rangle_t=\tfrac{1}{8}\left[\tfrac{1}{3}-\tfrac{1}{2}e^{-3Dt}(e^{D3t}-e^{-3D3t})+e^{-6Dt}(\Delta^{-1}(D_3-D)\sinh(2t\Delta)-\tfrac{1}{3}\cosh(2t\Delta))\right], \tag{6.3}$$

and

$$\langle\Omega_1{}^4\rangle_t=\tfrac{1}{8}\left[1+\tfrac{3}{2}e^{-3Dt}(e^{D_1t}-e^{D2t}-e^{D3t})+\tfrac{1}{2}e^{-3Dt}(e^{-3D1t}-e^{-3D2t}-e^{-3D3t})+e^{-6Dt}\cosh(2t\Delta)\right]. \tag{6.4}$$

It should be noted that the results above are exact in spite of the use of the approximate Green's function of Sec. V. This is due to the fact that the expansions of the functions averaged above contain no terms with j greater than 2. This is also true of all of the results which follow in this section.

Now consider the problem of finding the average values of the components in the laboratory system of

TABLE II. Expressions for the functions of Table I.

$j=0$	$\Psi_0{}^{0;0}=(\pi)^{-1}$
$j=1$	$\Psi_1{}^{1;\pm1}=(\pi)^{-1}(\frac{3}{2})^{\frac{1}{2}}[e^{\pm2i\Phi}\rho^2-e^{\pm2i\Theta}(1-\rho^2)]$
	$\Psi_1{}^{0;0}=(\pi)^{-1}(3)^{\frac{1}{2}}[1-2\rho^2]$
	$\Psi_1{}^{-1;\pm1}=(\pi)^{-1}(\pm1)(\frac{3}{2})^{\frac{1}{2}}[e^{\pm2i\Phi}\rho^2+e^{\pm2i\Theta}(1-\rho^2)]$
$j=2$	$\Psi_2{}^{0;0}=(\pi)^{-1}(5)^{\frac{1}{2}}[1-6\rho^2+6\rho^4]$
	$\Psi_2{}^{1;\pm1}=(\pi)^{-1}(\frac{5}{2})^{\frac{1}{2}}[e^{\pm2i\Phi}(3-4\rho^2)\rho^2-e^{\pm2i\Theta}(1-\rho^2)(1-4\rho^2)]$
	$\Psi_2{}^{-1;\pm1}=(\pi)^{-1}(\pm1)(\frac{5}{2})^{\frac{1}{2}}[e^{\pm2i\Phi}(3-4\rho^2)\rho^2+e^{\pm2i\Theta}(1-\rho^2)(1-4\rho^2)]$
	$\Psi_2{}^{2;\pm2}=(\pi)^{-1}(\frac{5}{2})^{\frac{1}{2}}[e^{\pm4i\Phi}\rho^4+e^{\pm4i\Theta}(1-\rho^2)^2]$
	$\Psi_2{}^{-2;\pm2}=(\pi)^{-1}(\pm1)(\frac{5}{2})^{\frac{1}{2}}[e^{\pm4i\Phi}\rho^4-e^{\pm4i\Theta}(1-\rho^2)^2]$
	$\Psi_2{}^{0;\pm2}=-(\pi)^{-1}(30)^{\frac{1}{2}}[e^{\pm2i(\Phi+\Theta)}(1-\rho^2)\rho^2]$
	$\Psi_2{}^{2;0}=-(\pi)^{-1}(15)^{\frac{1}{2}}[(1-\rho^2)\rho^2(e^{2i(\Phi-\Theta)}+e^{-2i(\Phi-\Theta)})]$

[17] Since $G(\mathbf{\Omega},t)$ is an even function of Ω_j, such averages as $\langle\Omega_1\rangle$, $\langle\Omega_1\Omega_2\rangle$, etc., vanish.

some vector $\mathbf{A}$ fixed in the body. Let the fixed body components be (A_1^0,A_2^0,A_3^0). Then, if (A_1,A_2,A_3) are the components in the laboratory system, our description of rotations is such that $\mathbf{A}$ is obtained from $\mathbf{A}^0$ by the unitary transformation

$$\boldsymbol{\sigma}\cdot\mathbf{A}=\mathbf{Q}^\dagger\boldsymbol{\sigma}\cdot\mathbf{A}^0\mathbf{Q}, \tag{6.5}$$

which yields $\mathbf{A}$ as a function of $\mathbf{A}^0$ and $\boldsymbol{\Omega}$,

$$\mathbf{A}(\boldsymbol{\Omega},\mathbf{A}^0)=(1-2\boldsymbol{\Omega}^2)\mathbf{A}^0+2(1-\boldsymbol{\Omega}^2)^{\frac{1}{2}}(\boldsymbol{\Omega}\times\mathbf{A}^0)+2(\boldsymbol{\Omega}\cdot\mathbf{A}^0)\boldsymbol{\Omega}. \tag{6.6}$$

Thus, the average value of $\mathbf{A}$ can be written as

$$\langle\mathbf{A}(\boldsymbol{\Omega},\mathbf{A}^0)\rangle_t=\langle 1-2\boldsymbol{\Omega}^2\rangle_t\mathbf{A}^0+2\langle\boldsymbol{\Omega}\boldsymbol{\Omega}\rangle_t\cdot\mathbf{A}^0. \tag{6.7}$$

By using (6.2) one can evaluate the averages in this expression explicitly to obtain

$$\langle A_j(\boldsymbol{\Omega},\mathbf{A}^0)\rangle_t=e^{-(3D-D_j)t}A_j^0. \tag{6.8}$$

The average of $\mathbf{A}$ for any other choice of initial orientation may be obtained from (6.8) by a transformation of the same type as (6.6).

Equation (6.8) describes how the vector $\mathbf{A}$ relaxes to the random state when the initial distribution is represented by a delta function. The interpretation that immediately suggests itself is the case in which $\mathbf{A}$ is an electric or magnetic dipole moment fixed rigidly in the rotating body but other interpretations are possible.

One can also calculate the averages of products of two components of $\mathbf{A}$. The calculations are essentially the same as the one above and are not given here. Typical results are

$$\langle A_1A_2\rangle_t=e^{-3(D+D3)t}A_1^0A_2^0, \tag{6.9}$$

and

$$\langle A_1^2\rangle_t=\{\tfrac{1}{3}\mathbf{A}^2+\Delta^{-1}e^{-6Dt}[(D_1-D)(A_1^0)^2+(D_3-D)(A_2^0)^2+(D_2-D)(A_3^0)^2]\sinh(2t\Delta)+e^{-6Dt}[(A_1^0)^2-\tfrac{1}{3}\mathbf{A}^2]\cosh(2t\Delta)\}. \tag{6.10}$$

So far we have thought of the function $G(\boldsymbol{\Omega},t)$ in terms of a nonequilibrium distribution relaxing to the equilibrium distribution. However, it also can be used to describe the fluctuations which occur in the equilibrium distribution. This is possible because the underlying random processes which cause each phenomenon are the same. The connection between the two phenomena is achieved mathematically by utilizing the Wiener-Khintchine theorem[18,19] and the ergodic hypothesis.

The Wiener-Khintchine theorem relates the correlation function $K(t)$ of a random variable $f(t)$,

$$K(t)=\lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}f(t')f(t'+t)dt', \tag{6.11}$$

to the Fourier transform $\bar{f}_T(\omega)$ of $f(t)$

$$f_T(\omega)=(2\pi)^{-\frac{1}{2}}\int_{-T}^{T}f(t)e^{i\omega t}dt. \tag{6.12}$$

The exact relationship is that $K(t)$ and the spectral density

$$g(\omega)=\lim_{T\to\infty}(2T)^{-1}|f_T(\omega)|^2 \tag{6.13}$$

are Fourier transforms of each other:

$$K(t)=\int_{-\infty}^{\infty}g(\omega)e^{-i\omega t}d\omega, \tag{6.14}$$

$$g(\omega)=(2\pi)^{-1}\int_{-\infty}^{\infty}K(t)e^{i\omega t}dt. \tag{6.14}$$

Thus, one can obtain the spectral density of a random variable from its correlation function. It will now be shown that the correlation function for a random variable associated with the orientation of a body can be obtained from $G(\boldsymbol{\Omega},t)$.

Suppose some function $f(t)$ derives its time dependence from a functional dependence on the orientation of a rotating body, i.e., $f(t)=F(\boldsymbol{\Omega}(t))$. The correlation function is then

$$K(t)=\lim_{T\to\infty}(2T)^{-1}\int_{-T}^{T}F(\boldsymbol{\Omega}(t'))F(\boldsymbol{\Omega}(t'+t))dt'. \tag{6.16}$$

By using the ergodic hypothesis, we may convert the time average in (6.16) to an average over the ensemble,

$$K(t)=\pi^{-2}\int\int F(\boldsymbol{\Omega}')F(\boldsymbol{\Omega})G(\boldsymbol{\Omega},\boldsymbol{\Omega}',|t|)d\tau d\tau'. \tag{6.17}$$

Here $d\tau'/\pi^2$ is the probability of finding the representative point at $\boldsymbol{\Omega}'$ and $t=0$, and $G(\boldsymbol{\Omega},\boldsymbol{\Omega}',|t|)d\tau$ is the probability of finding it at $\boldsymbol{\Omega}$ and $t=t$ if it was initially at $\boldsymbol{\Omega}'$.[20] This result together with (6.15) makes the desired connection between the diffusion process, represented by $G(\boldsymbol{\Omega},t)$, and the spectrum of a fluctuating variable, represented by $g(\omega)$.

As a specific example of the result above, consider $F(\boldsymbol{\Omega})$ to the the function $\mathbf{A}(\boldsymbol{\Omega},\mathbf{A}^0)$ given by (6.6). The correlation function may be written in terms of the components as

$$K_{jl}(t)=\pi^{-2}\int\int A_j(\boldsymbol{\Omega}',\mathbf{A}^0)A_l(\boldsymbol{\Omega},\mathbf{A}^0)\times G(\boldsymbol{\Omega},\boldsymbol{\Omega}',|t|)d\tau d\tau'. \tag{6.18}$$

This integral is most easily evaluated by transforming to coordinates centered at $\boldsymbol{\Omega}'$ so that the new variable

[18] N. Wiener, Acta Math. **55**, 117 (1930).
[19] A. Khintchine, Math. Ann. **109**, 604 (1934).

[20] The absolute value bars on t allow for the possibility of either $\boldsymbol{\Omega}$ or $\boldsymbol{\Omega}'$ being considered as the initial point.

of integration is

$$\boldsymbol{\Omega}''=\Gamma'\boldsymbol{\Omega}-\Gamma\boldsymbol{\Omega}'+\boldsymbol{\Omega}\times\boldsymbol{\Omega}', \tag{6.19}$$

and the function $\mathbf{A}(\boldsymbol{\Omega},\mathbf{A}^0)$ is

$$\mathbf{A}(\boldsymbol{\Omega},\mathbf{A}^0)=\mathbf{A}(\boldsymbol{\Omega}',\mathbf{A}(\boldsymbol{\Omega}'',\mathbf{A}^0)). \tag{6.20}$$

The correlation function is then

$$K_{jl}(t)=\pi^{-2}\int\int A_j(\boldsymbol{\Omega}',\mathbf{A}^0)A_l(\boldsymbol{\Omega}',\mathbf{A}(\boldsymbol{\Omega}'',\mathbf{A}^0)) \times G(\boldsymbol{\Omega}'',|t|)d\tau''d\tau'. \tag{6.21}$$

The integrations over $d\tau'$ and $d\tau''$ may now be done separately by first calculating

$$\langle A_j(\boldsymbol{\Omega}',\mathbf{A}^0)A_l(\boldsymbol{\Omega}',\mathbf{B}^0)\rangle_\infty =\pi^{-2}\int A_j(\boldsymbol{\Omega}',\mathbf{A}^0)A_l(\boldsymbol{\Omega}',\mathbf{B}^0)d\tau', \tag{6.22}$$

and then substituting the average

$$\langle\mathbf{A}(\boldsymbol{\Omega}'',\mathbf{A}^0)\rangle_{|t|}=\int\mathbf{A}(\boldsymbol{\Omega}'',\mathbf{A}^0)G(\boldsymbol{\Omega}'',|t|)d\tau'', \tag{6.23}$$

for the vector $\mathbf{B}^0$. The result is

$$K_{jl}(t)=\tfrac{1}{3}e^{-3D|t|}[(A_1{}^0)^2e^{D1|t|}+(A_2{}^0)^2e^{D2|t|} +(A_3{}^0)^2e^{D3|t|}]\delta_{jl}. \tag{6.24}$$

The spectral density of $\mathbf{A}$ in the laboratory system is then given by (6.15),

$$\lim_{T\to\infty}\frac{1}{2T}|\bar{A}_j(\omega)|^2=\frac{1}{3\pi}\left[\frac{(A_1{}^0)^2(D_2+D_3)}{(D_2+D_3)^2+\omega^2} +\frac{(A_2{}^0)^2(D_1+D_3)}{(D_1+D_3)^2+\omega^2} +\frac{(A_3{}^0)^2(D_1+D_2)}{(D_1+D_2)^2+\omega^2}\right]. \tag{6.25}$$

The final example which we shall consider is a problem that arises in the theory of nuclear magnetic relaxation.[21] The problem is to obtain the spectral density, or equivalently the correlation function for the dipole-dipole interaction of a system of spin-$\frac{1}{2}$ nuclei, say protons, which are rigidly bound together in the same molecule. This interaction is of the form

$$\sum_{j\neq k}\left[\frac{(\mathbf{I}_j\cdot\mathbf{I}_k)|\mathbf{r}_{jk}|^2-3\mathbf{I}_j\mathbf{I}_k:\mathbf{r}_{jk}\mathbf{r}_{jk}}{|\mathbf{r}_{jk}|^5}\right], \tag{6.26}$$

where $\mathbf{I}_j$ represents the jth spin and $\mathbf{r}_{jk}$ is the position vector of j relative to k. This depends on the orientation of the molecule through the dyadic $\mathbf{r}_{jk}\mathbf{r}_{jk}$. Its correlation function therefore involves terms of the form

$$K_{ijkl}=\lim_{T\to\infty}(2T)^{-1}\int_{-T}^{T}A_i(t')A_j(t')B_k(t'+t) \times B_l(t'+t)dt', \tag{6.27}$$

where $\mathbf{A}$ and $\mathbf{B}$ are vectors fixed in the molecule. This integral may be evaluated in the same fashion as K_{jl} to obtain

$$K_{ijkl}=\tfrac{1}{9}\mathbf{A}^2\mathbf{B}^2\delta_{ij}\delta_{kl} +\tfrac{1}{10}\gamma(t)e^{-6D|t|}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}-\tfrac{2}{3}\delta_{ij}\delta_{kl}), \tag{6.18}$$

where $\gamma(t)$ is defined as

$$\begin{aligned}\gamma(t)=\{&[(B_1{}^0)^2(A_1{}^0)^2+(B_2{}^0)^2(A_2{}^0)^2+(B_3{}^0)^2(A_3{}^0)^2\\ &-\tfrac{1}{3}\mathbf{B}^2\mathbf{A}^2]\cosh(2|t|\Delta)+[(D_1-D)\\ &\times((A_1{}^0)^2(B_1{}^0)^2+(A_2{}^0)^2(B_3{}^0)^2+(A_3{}^0)^2(B_2{}^0)^2)\\ &+(D_2-D)((A_2{}^0)^2(B_2{}^0)^2+(A_1{}^0)^2(B_3{}^0)^2\\ &+(A_3{}^0)^2(B_1{}^0)^2)+(D_3-D)((A_3{}^0)^2(B_3{}^0)^2\\ &+(A_1{}^0)^2(B_2{}^0)^2+(A_2{}^0)^2(B_1{}^0)^2)]\Delta^{-1}\sinh(2|t|\Delta)\\ &+2[A_1{}^0A_2{}^0B_1{}^0B_2{}^0e^{-3(D3-D)|t|}\\ &+A_1{}^0A_3{}^0B_1{}^0B_3{}^0e^{-3(D2-D)|t|}\\ &+A_2{}^0A_3{}^0B_2{}^0B_3{}^0e^{-3(D1-D)|t|}]\}.\end{aligned} \tag{6.29}$$

The complete correlation function for (6.26) will not be given here since it clearly depends on the specific structure of the molecule and in most cases many simplifications will result from using specific values of the vectors $\mathbf{r}_{jk}$.

VII. THE DIFFUSION TENSOR

In order to interpret the results of the previous section physically, it is necessary to have some means of calculating the diffusion tensor D_{jk} defined by (2.7). Perhaps the simplest way of doing this is to use the method used by Einstein[22] in his discussion of the translational Brownian motion. It is imagined that, in addition to the random motion represented by D_{jk}, there is an externally applied torque, derivable from a potential $\phi(\boldsymbol{\Omega})$, which causes the orientations of the members of the ensemble to change systematically. One then requires that the Boltzmann distribution

$$P^0(\boldsymbol{\Omega})=c\exp[-\phi/(kT)] \tag{7.0}$$

be stationary in time. This results in ones obtaining D_{jk} as a function of the temperature and the drag coefficients of the body.

The first step in the calculation is to obtain the current produced by the potential $\phi(\boldsymbol{\Omega})$. The torque on a typical body is

$$\mathbf{T}(\boldsymbol{\Omega})=i\mathbf{M}\phi(\boldsymbol{\Omega}), \tag{7.1}$$

[21] For a detailed discussion of this probelm and a calculation of correlation functions with Furry's Greens function, see P. S. Hubbard, Phys. Rev. **109**, 1153 (1958).

[22] A collection of translated reprints of A. Einstein's original papers on this subject has been published as *Investigations on the Theory of the Browian Movement*, edited by R. Furth, translated by A. D. Cowper (Dover Publications, New York, 1956).

so that its equation of motion in body coordinates is

$$\mathbf{I}\cdot(d/dt)\boldsymbol{\omega}+\boldsymbol{\omega}\times(\mathbf{I}\cdot\boldsymbol{\omega})=i\mathbf{M}\phi(\boldsymbol{\Omega})-\boldsymbol{\beta}\cdot\boldsymbol{\omega}, \quad (7.2)$$

where $\mathbf{I}$ is the inertia tensor and $\boldsymbol{\beta}$ the tensor representing the viscous drag on the body. Now we make several simplifying assumptions. First, we assume that $\boldsymbol{\omega}$ is so small that the nonlinear term $\boldsymbol{\omega}\times(\mathbf{I}\cdot\boldsymbol{\omega})$ may be neglected. Second, we assume that the variation of ϕ with $\boldsymbol{\Omega}$ is slow enough that the torque may be treated as a constant over a small interval so that the solution of (7.2) may be written as

$$\boldsymbol{\omega}-\exp(-\mathbf{I}^{-1}\cdot\boldsymbol{\beta}t)\cdot\boldsymbol{\omega}_0 =i[1-\exp(-\mathbf{I}^{-1}\cdot\boldsymbol{\beta}t)]\cdot\boldsymbol{\beta}^{-1}\cdot\mathbf{M}\phi(\boldsymbol{\Omega}). \quad (7.3)$$

Finally, it is assumed that effects which take place in time intervals less than a typical element of $\boldsymbol{\beta}^{-1}\cdot\mathbf{I}$ can be neglected. Then each element of the ensemble can be taken to be moving with the "terminal" angular velocity

$$\boldsymbol{\omega}_\infty=i\boldsymbol{\beta}^{-1}\cdot\mathbf{M}\phi. \quad (7.4)$$

The rate at which the quantity $\boldsymbol{\Omega}$ changes is then

$$(d/dt)\boldsymbol{\Omega}=-i\boldsymbol{\omega}_\infty\cdot\mathbf{M}\boldsymbol{\Omega}, \quad (7.5)$$

so that the current density due to ϕ is given by

$$J_{l\Phi}=W(\boldsymbol{\Omega})(d/dt)\Omega_l=\Gamma^{-1}P(\boldsymbol{\Omega})(\beta_{ij}^{-1}M_j\phi)(M_i\Omega_l). \quad (7.6)$$

The total current is this current plus the random current obtained with (2.9). This total current is

$$J_l=\Gamma^{-1}(M_i\Omega_l)(D_{ij}M_jP+P\beta_{ij}^{-1}M_j\phi), \quad (7.7)$$

which, for the special case of a Boltzmann distribution, is

$$J_l^0=\Gamma^{-1}(M_i\Omega_l)(D_{ij}-kT\beta_{ij}^{-1})M_jP^0. \quad (7.8)$$

The condition that P^0 be stationary is then

$$0=\partial_lJ_l^0=M_i(D_{ij}-kT\beta_{ij}^{-1})M_jP^0. \quad (7.9)$$

This yields the desired relationship between $\mathbf{D}$ and $\boldsymbol{\beta}$,

$$D_{ij}=\tfrac{1}{2}kT(\beta_{ij}^{-1}+\beta_{ji}^{-1}), \quad (7.10)$$

so that the problem of calculating the diffusion tensor is reduced to the problem of calculating the viscous drag tensor $\boldsymbol{\beta}$. It is this identification, (7.10), of the diffusion tensor which characterizes the random process as "Brownian" and distinguishes it from other processes which might cause the orientation of a body to vary randomly.

The most general calculation of the drag tensor $\boldsymbol{\beta}$ of which the author is aware is that due to Edwardes[23] for the ellipsoid represented by $x^2/a^2+y^2/b^2+z^2/c^2=1$. He obtains, as a typical element of the diagonalized tensor, the expression[24]

$$\beta_x=16\pi\eta(b^2+c^2)/3(b^2B+c^2C), \quad (7.11)$$

where

$$B=\int_0^\infty(b^2+\psi)^{-\frac{3}{2}}(a^2+\psi)^{-\frac{1}{2}}(c^2+\psi)^{-\frac{1}{2}}d\psi,$$
$$C=\int_0^\infty(c^2+\psi)^{-\frac{3}{2}}(a^2+\psi)^{-\frac{1}{2}}(b^2+\psi)^{-\frac{1}{2}}d\psi, \quad (7.12)$$

and η is the viscosity of the medium in which the body is immersed.

The validity of the approximations contained in (7.10) and (7.11) will not be discussed here since the analogous discussions for the translational case are readily available in the literature.[25] The only special precautions one must take in the rotational case is to insure oneself that the nonlinear term in (7.2) is indeed negligible and to be careful that the elementary rotations $\boldsymbol{\varepsilon}$ are not sufficiently large to introduce the effects of noncommutativity on the elementary level.

Note added in proof. It has been brought to the author's attention that some of the results contained in this paper have been published previously in a paper by Perrin.[26]

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APPENDIX

This Appendix contains a derivation of the expression for the current density operator j_l of (2.9). We consider an element of surface dA, normal to the direction of increasing Ω_l at the point $\boldsymbol{\Omega}$ in $\boldsymbol{\Omega}$ space, and fix our attention on small rotations of some fixed size $\boldsymbol{\varepsilon}$. All such rotations that cause the point in $\boldsymbol{\Omega}$ space to pass through the surface dA will contribute to the current through the surface. In general a fraction, α, of $\boldsymbol{\varepsilon}$ will be needed to reach the surface; the remainder, $(1-\alpha)\boldsymbol{\varepsilon}$, will cause the point to pass through the surface and beyond.

The probability transferred through the surface will be $P(\boldsymbol{\Omega}',t)d\tau'$ where $\boldsymbol{\Omega}'$ is the point of origin of the rotation. This may be written as

$$P(\boldsymbol{\Omega}',t)d\tau'=\exp(i\alpha\boldsymbol{\varepsilon}\cdot\mathbf{M})P(\boldsymbol{\Omega},t)d\tau.$$

The volume element $d\tau$ is now located at the point $\boldsymbol{\Omega}$. It is specified by a small parallelepiped seated on the

[23] D. Edwardes, Quart. J. Math. **26**, 70 (1892).

[24] The result given here actually differs from the one appearing in Edwardes paper by a factor of 6/5. This is a correction of an apparent misprint in the last equation of the derivation of β_x in that paper.

[25] The reader is especially referred to the collection of reprints published as *Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, New York, 1954).

[26] F. Perrin, J. phys. radium **5**, 497 (1934).

surface dA and oriented in the direction of the change in Ω under the rotation $\varepsilon d\alpha$,

$$\Delta\Omega=-id\alpha(\varepsilon\cdot\mathbf{M})\Omega.$$

This yields the expression for the volume element $d\tau$,

$$d\tau=\Gamma^{-1}dA\Delta\Omega_l=\Gamma^{-1}dAd\alpha(-i\varepsilon\cdot\mathbf{M}\Omega_l).$$

The probability passed through the surface due to all rotations of magnitude ε in the time Δt is then

$$p(\varepsilon,\Delta t)d^3\epsilon\int_0^1 d\alpha\,\Gamma^{-1}dA(-i\varepsilon\cdot\mathbf{M}\Omega_l)\times\exp(i\alpha\varepsilon\cdot\mathbf{M})P(\Omega,t).$$

This must be integrated over all possible values of ε to obtain the total probability passed through the surface. The result, to first order in Δt is

$$dA\Delta t\Gamma^{-1}(M_j\Omega_l)D_{jk}M_kP(\Omega,t).$$

This must be divided by dA and Δt to obtain the current density, J_l,

$$J_l=\Gamma^{-1}(M_j\Omega_l)D_{jk}M_kP(\Omega,t)\equiv\mathfrak{j}_lP(\Omega,t).$$

Thus

$$\mathfrak{j}_l=\Gamma^{-1}(M_j\Omega_l)D_{jk}M_k,$$

or

$$\mathfrak{j}_l=i\Gamma^{-1}\tfrac{1}{2}(\Gamma D_{lk}+\Omega_i\epsilon_{ijl}D_{jk})M_k.$$

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Surface-Dependent $1/f$ Noise in Germanium*

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The surface characteristics of $1/f$ noise have been investigated by using field effect techniques on 100 micron thick single crystal germanium filaments. The $1/f$ noise is independent of the surface potential when an accumulation layer is on the surface but increases rapidly as the surface conductivity gradually becomes inverted with respect to the bulk. No $1/f$ noise is observed due to charge transfer between the bulk and the slow surface states. An increase in the $1/f$ noise associated with the inversion layer occurs when the temperature of the germanium is decreased. The magnitude of the $1/f$ noise depends on the ambient, increasing as the slow state relaxation time decreases. An investigation of the relaxation processes associated with the charge transfer between the bulk and the slow surface states after the application of a dc electric field to the field effect electrode reveals a $1/f$ noise relaxation which is independent of the mode of the conductivity relaxation. The noise relaxes back to its original value with a logarithmic time dependence which is characteristic of a $1/\tau$ distribution in time constants and the conductance decays with a combination of exponential and logarithmic terms, depending on the surface conditions.

I. INTRODUCTION

SINGLE crystal semiconductor filaments generally exhibit a noise power spectrum which varies inversely with frequency over a wide range of frequencies.[1] The $1/f$ law has been observed at frequencies as low as 6×10^{-5} cps[2] and as high as 12 Mc/sec.[3] The absence of an appreciable temperature dependence[1,4] of $1/f$ noise has introduced difficulties into the formulation of a satisfactory physical explanation of the origin of this particular type of fluctuation.

While the exact physical origin of the $1/f$ noise is presently open to conjecture, there is considerable evidence that the surface of the semiconductor may be the source of at least part of this noise. $1/f$ noise seems to be dependent on the samples' ambient[5,6] as well as its surface to volume ratio.[7] The most promising experimental evidence for assigning the origin of $1/f$ noise to the surface is the $1/\tau$ distribution in relaxation times of the slow surface states,[8] which are located on the oxide layer of a semiconductor. A $1/\tau$ distribution in relaxation times will lead to a $1/f$ noise spectrum if individual noise spectra of the generation-recombination type are added.[9] It has been pointed out, however, that the experimentally observed $1/\tau$ distribution does not cover the range in times necessary to explain the complete $1/f$ noise spectrum.[10]

Even though it is well known that the surface has a

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[1] H. C. Montgomery, Bell System Tech. J. **31**, 950 (1952).
[2] T. E. Firle and H. Winston, J. Appl. Phys. **26**, 716 (1955).
[3] F. J. Hyde, Proc. Phys. Soc. (London) **B69**, 231 (1956).
[4] I. M. Templeton and D. K. C. MacDonald, Proc. Phys. Soc. (London) **B66**, 680 (1952).
[5] T. G. Maple, L. Bess, and H. A. Gebbie, J. Appl. Phys. **26**, 490 (1955).
[6] G. L. Pearson, H. C. Montgomery, and W. L. Feldman, J. Appl. Phys. **27**, 91 (1956).
[7] J. J. Brophy, J. Appl. Phys. **29**, 1377 (1958).
[8] A. L. McWhorter in *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, Pennsylvania, 1957), p. 207.
[9] J. Bernamont, Proc. Phys. Soc. (London) **49**, (extra part), 138 (1937).
[10] H. C. Montgomery (personal communication).