Isotropic Rotational Brownian Motion

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The Brownian motion of the orientation of any rigid body (sphere, set of rectangular axes, etc.) is calculated for the case of individual random infinitesimal rotations whose probabilities are independent of the direction of the axis of rotation (isotropic case). The calculations are carried out by means of quaternions; the more important formulas are also given in terms of the rotation angle and axis direction. The unit solution, or distribution of orientations arising from a specified initial orientation, is found as a series converging rapidly for not-too-small times. It turns out to be expressible in terms of a theta function, and thus there is also available a series converging rapidly for small times. The use of the unit solution as a propagation function is discussed briefly, and is illustrated by verification of the iteration property of the unit solution.

INTRODUCTION

THE problem of isotropic rotational Brownian motion arose in connection with work of Purcell on spin relaxation in systems with more than two spins in the same molecule. The solution obtained here is used in work on spin relaxation by Purcell and Hubbard, to be published in the near future. It may find other applications to the effect of random three-dimensional rotations on functions of a number of coupled vectors.

The dynamics of rotational Brownian motion of a sphere around a given axis has been discussed briefly by Einstein in one of his early papers.[1] We have here to consider the possibility of rotations around axes arbitrarily oriented in three-dimensional space, and to find the more complicated formula that replaces the simple Gaussian unit solution found in the cases of translational motion and of rotation around a given axis. The complications arise from the noncommutativity of rotations and from the finite extent of the space of orientations.

We shall not devote space here to discussion of possible models for the elementary disturbances causing the rotational Brownian motion, or of possible physical causes.[2] The model used for the calculation is closely analogous to the random-walk model. We postulate that in the small time Δt there is a probability

$$\Delta t\cdot p(\epsilon)d\epsilon d\Omega_1 \tag{1}$$

for a rotation[3] through an angle between 2ϵ and $2(\epsilon+d\epsilon)$ around an axis with direction falling in the element of solid angle $d\Omega_1$. The integral of $p(\epsilon)d\epsilon d\Omega_1$ is taken to be finite, so that for small enough Δt the probability of a rotation is small, and that of more than one rotation in Δt can be neglected. Appreciable values of $p(\epsilon)$ occur only for ϵ so small that its powers beyond the second can be neglected.

As in the translational case, the probable effect of the random disturbances during a time in which many of them occur can be described in terms of a diffusion coefficient, which we here define by

$$D=\frac{1}{6}\int (2\epsilon)^2 p(\epsilon)d\epsilon d\Omega_1. \tag{2}$$

For sufficiently small time the angle of rotation remains small, and effects of noncommutativity and periodicity are negligible. The analogy to the translational case is then complete, and the probability for the resultant angle of rotation to fall between φ and $\varphi+d\varphi$ has the Gaussian form

$$F(\varphi)d\varphi=(4\pi Dt)^{-\frac{3}{2}}\exp(-\varphi^2/4Dt)\cdot 4\pi\varphi^2 d\varphi,\quad Dt\ll 1. \tag{3}$$

Section I is devoted to a statement of the geometrical descriptions of rotations that will be used. Section II contains a straightforward derivation of the diffusion equation from an integro-differential equation of the Boltzmann type. The unit solution is constructed in Sec. III; its use as a Green's function (propagation function) is described in Sec. IV, and is illustrated by showing that it generates the unit solution for $t+t_0$ from those for t and t_0. An appendix describes the isomorphism of quaternion rotation operators with the rotation operators for Pauli spin functions, which are more generally familiar to present-day theoretical physicists.

I. DESCRIPTIONS OF ROTATIONS

Perhaps the simplest geometrical representation of the possible rotations (orientations) of a rigid body is

[1] A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover Publications, New York, 1956), pp. 32–33. Original in Ann. Physik **19**, 371 (1906), pp. 379–380.

[2] Excellent discussions for translational cases are contained in the two review articles by S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943) and by M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945). [Both are reprinted in *Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, New York, 1954).] On the physical nature of the Brownian motion, the Einstein reprints (reference 1) are particularly useful.

[3] A physically more realistic postulate would involve changes of angular velocity rather than of orientation itself. We assume that the present simpler procedure gives correct results. This is known to be true in analogous translational cases, and the precise analogy of the result for short times, Eq. (3), with the translational case indicates that it is true for the present case provided the angle traversed during the relaxation time for loss of angular velocity is small.

that given by Wigner in his book on group theory.[4] Each rotation is represented by a point inside, or on the surface of, a sphere of unit radius. The distance from the origin to the point is φ/π, $\varphi \leq \pi$ being the angle of rotation from the standard or initial orientation. The direction of the vector from origin to representative point gives the direction of the axis of rotation, the sense of the vector being chosen by the right-hand-screw rule. Surface points at opposite ends of a diameter represent the same rotation (change of orientation), since rotations through π and $-\pi$ give the same result.

When we consider the Brownian motion of the orientation of the body, this question arises: What distribution of probability for the representative point corresponds to random orientation, which will be reached for $t \to \infty$, and which must give a stationary distribution? In other words, what is the statistical weight distribution in the "Wigner sphere"? The answer is[5]

$$\begin{aligned}(\text{weight in } d\varphi d\Omega) &\propto \tfrac{1}{4}(1-\cos\varphi)d\varphi d\Omega \\ &\propto \tfrac{1}{2}\sin^2(\varphi/2)d\varphi d\Omega.\end{aligned} \tag{4}$$

The statistical weight per unit volume in the sphere is thus proportional to $[\sin(\varphi/2)]^2/\varphi^2$. This result will be rederived in a very simple way as we proceed.

Of the various ways to calculate the resultant of a series of successive rotations, by far the most convenient for the present purpose is the use of quaternions. If the student of today encounters quaternions at all, it is almost certain to be in a discussion of their remarkable properties as an algebraic system, and without regard to their kinematical use. The writer knows of one published explanation[6] in which the nature of quaternions as rotation operators is made clear in a brief discussion taking full advantage of a previous knowledge of ordinary vector algebra. An even more rapid approach for physicists is now the isomorphism between quaternions and the Pauli matrices; the way in which this leads to the rotation operators is indicated in the Appendix.

The operation of turning through the angle $\varphi(\leq\pi)$ around the axis with direction cosines l, m, n, corresponds to the quaternion

$$c+ui+vj+wk=c+s(li+mj+nk), \tag{5}$$

with

$$s=\sin(\varphi/2), \quad c=\cos(\varphi/2)=(1-s^2)^{\frac{1}{2}}. \tag{6}$$

The resultant of two rotations is represented by the quaternion that is the product of those corresponding to the individual rotations; multiplication is associative and distributive, and

$$i^2=j^2=k^2=-1, \quad ij=-ji=k, \text{ etc.} \tag{7}$$

The left-hand factor represents the rotation performed last.

The standard or initial orientation can be taken to correspond to $1=1+0i+0j+0k$, and then the quaternion (5) represents both a rotation operation and the orientation it produces from the initial orientation. Each orientation can be represented by a point with rectangular coordinates u, v, w. This point is inside or on the surface of a unit sphere. The direction from the origin to the point gives the direction of the axis of the rotation that produces the given orientation; the distance from the origin is $s=\sin(\varphi/2)$. As for the Wigner sphere, surface points at opposite ends of a diameter of the "quaternion sphere" are identical in meaning.

From $d\varphi=2[\cos(\varphi/2)]^{-1}d\sin(\varphi/2)$, we see that the weight-distribution (4) in the Wigner sphere corresponds to the distribution

$$\begin{aligned}(\text{weight in } ds,\, d\Omega) &\propto [\cos(\varphi/2)]^{-1}s^2 ds d\Omega \\ &\propto c^{-1}s^2 ds d\Omega\end{aligned} \tag{8}$$

in the quaternion sphere. The proportionality factors are the same in Eqs. (4) and (8).

II. DERIVATION OF THE DIFFUSION EQUATION

We define the distribution function f so that

$$f(u,v,w;t)dudvdw = \text{probability that orientation is in } dudvdw \text{ at } u, v, w \text{ at time } t. \tag{9}$$

The infinitesimal rotation by angle 2ϵ around the axis with direction cosines l_1, m_1, n_1, is represented (to second order in ϵ) by the quaternion

$$1-\tfrac{1}{2}\epsilon^2+\epsilon(l_1i+m_1j+n_1k). \tag{10}$$

To get the new position of the representative point that was at u, v, w, we multiply the quaternion (5) by the quaternion (10); the result is a quaternion with the coefficients

$$\begin{aligned}c' &= c(1-\tfrac{1}{2}\epsilon^2)+\epsilon(-l_1u-m_1v-n_1w),\\ u' &= u(1-\tfrac{1}{2}\epsilon^2)+\epsilon(l_1c-n_1v+m_1w),\\ v' &= v(1-\tfrac{1}{2}\epsilon^2)+\epsilon(m_1c-l_1w+n_1u),\\ w' &= w(1-\tfrac{1}{2}\epsilon^2)+\epsilon(n_1c-m_1u+l_1v).\end{aligned} \tag{11}$$

The reciprocal of the quaternion (10) is (to order ϵ^2):

$$1-\tfrac{1}{2}\epsilon^2-\epsilon(l_1i+m_1j+n_1k). \tag{12}$$

Operating on the quaternion with coefficients (11), this gives back our original quaternion (5); (12) represents the operation inverse to that represented by (10). Their probabilities are equal.

[4] E. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Friedrich Vieweg und Sohn, Braunschweig, 1931), p. 99.

[5] Reference 4, pp. 162–163.

[6] G. Kowalewski, *Einführung in die Theorie der Kontinuierlichen Gruppen* (Chelsea Publishing Company, New York, 1950), pp. 21–24.

The change of f in the short time Δt is then

$$\{f(u,v,w;t+\Delta t)-f(u,v,w;t)\}dudvdw$$
$$=-\Delta t f(u,v,w;t)dudvdw\int p(\epsilon)d\epsilon d\Omega_1$$
$$+\Delta t\int p(\epsilon)d\epsilon d\Omega_1\cdot f(u',v',w';t)du'dv'dw'. \quad (13)$$

This is just analogous to Boltzmann's equation in kinetic theory. The first term on the right gives the probability that the representative point has been removed from $dudvdw$ in the time Δt; the second gives the probability that the point has been sent into $dudvdw$ by an operation inverse to one of those that might remove it.

Owing to the postulated properties of the fundamental probability distribution (1), we can readily obtain from Eq. (13), for $\Delta t\rightarrow 0$, a simple differential equation. We make the substitution.

$$du'dv'dw'=dudvdw\cdot\partial(u',v',w')/\partial(u,v,w). \quad (14)$$

Straightforward computation of the determinant from Eqs. (11) gives

$$\partial(u',v',w')/\partial(u,v,w)=c'/c. \quad (15)$$

By dividing Eq. (13) by $\Delta t\cdot dudvdw$ and letting $\Delta t\rightarrow 0$' we now obtain the equation

$$(\partial f/\partial t)=c^{-1}\int p(\epsilon)d\epsilon d\Omega_1\{c'f(u',v',w')-cf(u,v,w)\}. \quad (16)$$

A proof of the weight distribution (8) or (4) is contained essentially in Eq. (15), which relates the volume elements occupied by the same element of probability—or the same set of systems of an ensemble—before and after a given rotation. The truth of Eqs. (8), (4) is particularly evident from Eq. (16), which shows that the distribution that makes $cf(u,v,w)=\text{const}$ is stationary. By a procedure precisely analogous to the proof of Boltzmann's H theorem, one readily shows that the quantity

$$H=\int f\ln(cf)\cdot dudvdw \quad (17)$$

has negative or zero time-derivative, and is stationary only for $cf=\text{const}$, $f\propto c^{-1}$.

The reduction of Eq. (16) to a differential equation is accomplished by using Taylor's series to express the integrand to order ϵ^2 in terms of derivatives of f and the differences $c'-c$, $u'-u$, $v'-v$, $w'-w$ given by Eqs. (11). The resulting expressions are enormously simplified by replacing the direction cosines l_1, m_1, n_1 and their products by their average values

$$\langle l_1\rangle=\langle m_1\rangle=\langle n_1\rangle=\langle l_1m_1\rangle=\langle m_1n_1\rangle=\langle n_1l_1\rangle=0,$$
$$\langle l_1^2\rangle=\langle m_1\rangle^2=\langle n_1^2\rangle=\tfrac{1}{3}, \quad (18)$$

which must appear when we integrate over $d\Omega_1$. The final result is proportional to the diffusion coefficient D defined in Eq. (2); we obtain

$$(\partial f/\partial t)=\tfrac{1}{4}D[(1-u^2)(\partial^2f/\partial u^2)+(1-v^2)(\partial^2f/\partial v^2)$$
$$+(1-w^2)(\partial^2f/\partial w^2)-2uv(\partial^2f/\partial u\partial v)-2vw$$
$$\times(\partial^2f/\partial u\partial w)-2wu(\partial^2f/\partial w\partial u)-5u(\partial f/\partial u)$$
$$-5v(\partial f/\partial v)-5w(\partial f/\partial w)-3f]. \quad (19)$$

By using the identity

$$u(\partial/\partial u)+v(\partial/\partial v)+w(\partial/\partial w)=s(\partial/\partial s),$$

we can write Eq. (19) in the form

$$(\partial f/\partial t)=\tfrac{1}{4}D\{\nabla^2f-(\partial/\partial s)[s^2(\partial f/\partial s)]$$
$$-3s(\partial f/\partial s)-3f\}. \quad (20)$$

Here the Laplacian operator ∇^2 acts in the u, v, w space.

Instead of the distribution function f, which is the probability per unit volume with the volume element given by $dudvdw$, we can introduce a function g that gives the probability per unit weight, with the weight element given by $c^{-1}dudvdw$. We have

$$g=cf \quad (21)$$

and the diffusion equation for g is found to be

$$(\partial g/\partial t)=\tfrac{1}{4}D\{\nabla^2g-(\partial/\partial s)[s^2(\partial g/\partial s)]-s(\partial g/\partial s)\}. \quad (22)$$

This equation again makes obvious the fact that $cf=g=\text{const}$ is a stationary distribution.

If we denote by h a spherically symmetric solution of Eq. (22), then

$$(\partial h/\partial t)$$
$$=\tfrac{1}{4}D\{(s^{-2}-1)(\partial/\partial s)[s^2(\partial h/\partial s)]-s(\partial h/\partial s)\}. \quad (23)$$

As $(h/c)\cdot 4\pi s^2ds$ is an element of probability, normalization requires that

$$I=\int_0^1(h/c)\cdot 4\pi s^2ds=1. \quad (24)$$

Multiplying Eq. (23) by $(4\pi s^2/c)ds$ and integrating, we have

$$0=(dI/dt)$$
$$=\pi D\int_0^1\{c(\partial/\partial s)[s^2(\partial h/\partial s)]-s^3c^{-1}(\partial h/\partial s)\}. \quad (25)$$

The integrand is an exact derivative, and we obtain

$$\pi D[s^2c(\partial h/\partial s)]_0^1=0. \quad (26)$$

That is,

$$s^2(\partial h/\partial s)\rightarrow 0,\quad s\rightarrow 0$$
$$c(\partial h/\partial s)\rightarrow 0,\quad s\rightarrow 1 \quad (27)$$

are the boundary conditions that assure that there is no creation of probability at the origin and no flux of probability through the surface of the sphere. The first condition is automatically satisfied if h is nonsingular at $s=0$. If we change to the variable φ (or

φ/π, the radial coordinate in the Wigner sphere), we have, by Eqs. (6) and (27),

$$(\partial h/\partial\varphi)\rightarrow 0, \quad (\varphi/\pi)\rightarrow 1 \tag{28}$$

at the surface of the Wigner sphere. On the other hand, keeping the variable s but setting $h=cf$, we see that this boundary condition can also be written

$$c^2(\partial f/\partial s)-sf\rightarrow 0, \quad s\rightarrow 1. \tag{29}$$

Here the first term must be retained, because f is ordinarily singular on the surface of the quaternion sphere.

The boundary condition can be fixed for the general case, in which the distribution is not spherically symmetric, by using the general expression for the flux of probability. Equation (19) can be put in the form

$$(\partial f/\partial t)=-(\partial J_u/\partial u)-(\partial J_v/\partial v)-(\partial J_w/\partial w), \tag{30}$$

with

$$J_u=-(D/4)\{(1-u^2)(\partial f/\partial u) -u[v(\partial f/\partial v)+w(f/\partial w)+f]\}, \tag{31}$$

etc. This is the only expression linear in f and its derivatives that can be written to make the right-hand member of Eq. (19) a negative divergence. This expression for the flux of probability can be derived directly from kinematical considerations. The argument, which is rather more involved than that used above to derive Eq. (19), will not be presented here.

From Eq. (31) we have for the radial component of the flux:

$$J_s=(uJ_u+vJ_v+wJ_w)/s=-\tfrac{1}{4}D\{c^2(\partial f/\partial s)-sf\}. \tag{32}$$

Now, if a rotation sends the representative point out of the sphere at one end of a diameter, it sends the point into the sphere at the other end of that diameter. Accordingly, the general boundary condition is that the values of J_s at the two ends of any diameter are equal and opposite. For a spherically symmetric distribution this gives (29).

III. CONSTRUCTION OF THE UNIT SOLUTION

If, in Eq. (23), we introduce the independent variable φ by Eq. (6), we obtain

$$(\partial h/\partial t)=D\{(\partial^2 h/\partial\varphi^2)+\cot(\varphi/2)(\partial h/\partial\varphi)\}. \tag{33}$$

If h takes appreciable values only for φ so small that $\cot(\varphi/2)$ can be replaced by $2/\varphi$, Eq. (33) becomes the ordinary diffusion equation for a spherically-symmetric case.

We now eliminate the first-derivative term by a change of the dependent variable. With

$$h=[\sin(\varphi/2)]^{-1}y, \tag{34}$$

we have

$$(\partial y/\partial t)=D\{(\partial^2 y/\partial\varphi^2)+\tfrac{1}{4}y\}. \tag{35}$$

In terms of the variables y and φ, the boundary conditions (27) become

$$\begin{aligned} &y-2\sin(\varphi/2)(\partial y/\partial\varphi)\rightarrow 0, \quad \varphi\rightarrow 0,\\ &y\cos(\varphi/2)-2(\partial y/\partial\varphi)\rightarrow 0, \quad \varphi\rightarrow\pi. \end{aligned} \tag{36}$$

We wish to find the solution that takes the form

$$f=g=h=\delta(u)\delta(v)\delta(w), \quad t=0 \tag{37}$$

at the initial instant of time. In terms of the variable φ, the element of weight has the form given by Eq. (4). Our unit solution must be such that

$$y\rightarrow 0 \quad \text{for} \quad \varphi\neq 0, \quad t\rightarrow 0, \tag{38}$$

$$2\pi\int_0^\pi y\sin(\varphi/2)d\varphi=1, \quad t\geq 0. \tag{39}$$

The reason for the factor 2π rather than 4π in Eq. (39) can be seen by comparing Eqs. (4) and (8).

The required solution can be obtained as a linear combination of solutions having exponential time-dependences. We set

$$y=\textstyle\sum_n y_n(\varphi)\exp(-\gamma_n Dt). \tag{40}$$

Then, if we assume uniform convergence, which will be verified later, y will satisfy Eq. (35) provided that the $y_n(\varphi)$ satisfy

$$(d^2y_n/d\varphi^2)+(\gamma_n+\tfrac{1}{4})y_n=0. \tag{41}$$

Then the y_n are sinusoidal functions, and will individually satisfy the boundary conditions (36) if

$$y_n(0)=0, \quad y_n'(\pi)=0. \tag{42}$$

Equations (41), (42) are satisfied by

$$y_n=A_n\sin(n+\tfrac{1}{2})\varphi, \quad n=0,1,2,\cdots \tag{43}$$

$$\gamma_n=n(n+1). \tag{44}$$

The coefficients A_n will be found to be algebraic functions of n, so that the series (40) converges uniformly for all $t>0$. The convergence fails, of course, for $t=0$, as the function y takes on the singular behavior specified in Eqs. (37)–(39).

The coefficients in the expansion of a function $z(\varphi)$, for $0\leq\varphi\leq\pi$, in terms of the orthogonal functions $\sin(n+\frac{1}{2})\varphi$,

$$z(\varphi)=\sum_{n=0}^{\infty}B_n\sin(n+\tfrac{1}{2})\varphi \tag{45}$$

are given by

$$B_n=(2/\pi)\int_0^\pi z(\psi)\sin(n+\tfrac{1}{2})\varphi d\varphi. \tag{46}$$

Although the function defined by (38) and (39) for $t=0$ is highly singular, and the possibility of expanding it might be seriously doubted *a priori*, we proceed to evaluate the coefficients A_n, and the resulting function y will be found to be just what is required. By Eqs.

(38)–(40), (43), (45), and (46), we have

$$A_n=(2/\pi)\int_0^\pi y\sin(n+\tfrac{1}{2})\varphi d\varphi, \quad (47)$$

with the whole contribution coming from an infinitesimal neighborhood of the point $\varphi=0$. Here we can replace $\sin(n+\frac{1}{2})\varphi$ by $(2n+1)\sin(\varphi/2)$, and then by Eq. (39) we get

$$A_n=(2n+1)\pi^{-2}. \quad (48)$$

By Eqs. (34), (40), (43), (44), and (48), we now have

$$h=[\pi^2\sin(\varphi/2)]^{-1}\sum_{n=0}^{\infty}(2n+1)\sin(n+\tfrac{1}{2})\varphi \times\exp[-n(n+1)Dt]. \quad (49)$$

This is the unit solution expressed as a probability density in terms of an element of statistical weight; $(hdudvdw)/c$ is the probability that the representative point, which was at the origin for $t=0$, is in $dudvdw$. The probability that the resultant angle of rotation from the initial orientation is between φ and $\varphi+d\varphi$ is

$$F(\varphi)d\varphi=h(4\pi s^2/c)ds=h\cdot 2\pi\sin^2(\varphi/2)d\varphi$$
$$=(2/\pi)\sin(\varphi/2)\sum_{n=0}^{\infty}(2n+1)\sin(n+\tfrac{1}{2})\varphi \times\exp[-n(n+1)Dt]. \quad (50)$$

This can also be written

$$F(\varphi)d\varphi=\pi^{-1}\sum_{n=0}^{\infty}(2n+1)[\cos n\varphi-\cos(n+1)\varphi] \times\exp[-n(n+1)Dt]. \quad (51)$$

For $t\rightarrow\infty$ we get the equilibrium distribution

$$F(\varphi)d\varphi=\pi^{-1}(1-\cos\varphi)d\varphi,\quad t\rightarrow\infty, \quad (52)$$

which, of course, is just the distribution of statistical weight [Eq. (4)].

The expressions (49)–(51) are easy to evaluate when Dt is not too small, and, for $t>0$, clearly correspond to a function y that satisfies Eqs. (35) and (39). For purposes of evaluation when Dt is small, and to verify that the behavior as $t\rightarrow 0$ is in accordance with Eq. (38), a different sort of expansion is needed. This is provided by the fact that our solution can be written in terms of a ϑ function.

With the notation of Whittaker and Watson,[7] we have

$$h=-[\pi^2\sin(\varphi/2)]^{-1}e^{Dt/4}(\partial/\partial\varphi)\vartheta_2(\varphi/2,e^{-Dt}). \quad (53)$$

By the functional relations[8] between ϑ functions, we then obtain

$$h=-[\pi^3 Dt\sin^2(\varphi/2)]^{-\frac{1}{2}}e^{Dt/4}(\partial/\partial\varphi) \times\exp[-\varphi^2/(4Dt)]\vartheta_4[i\pi\varphi/(2Dt),\exp(-\pi^2/Dt)] \quad (54)$$

with the expansion

$$h=[4\pi^3D^3t^3\sin^2(\varphi/2)]^{-\frac{1}{2}}\exp[(Dt/4)-\varphi^2/(4Dt)] \times\{\varphi[1-2\exp(-\pi^2/Dt)\cosh(\pi\varphi/Dt)+\cdots] -4\pi[\exp(-\pi^2/Dt)\sinh(\pi\varphi/Dt) -2\exp(-4\pi^2/Dt)\sinh(2\pi\varphi/Dt)+\cdots]\}. \quad (55)$$

The corresponding expansion for the distribution function $F(\varphi)d\vartheta$ is obtained by multiplying by

$$2\pi\sin^2(\varphi/2)d\varphi.$$

For $Dt\ll 1$, only very small values of φ give appreciable values, and the expression reduces to that given in Eq. (3). This is obviously in accordance with the requirement (38).

IV. USE OF THE UNIT SOLUTION AS A GREEN'S FUNCTION

In order to keep the intuitive meaning of the expressions as clear as possible, it is advisable to work with the functions $g(u,v,w;t)$ that give the probability per unit statistical weight. The spherically-symmetric unit solution h is a special case of such a function.

The solution of the rotational diffusion problem in terms of a propagation function is

$$g(u',v',w';t_0+t)=\int G(u',v',w';t;u_0,v_0,w_0) \times g(u_0,v_0,w_0;t_0)c_0^{-1}du_0dv_0dw_0. \quad (56)$$

From the intuitive meanings of the g's and of our unit solution h, it is clear that the Green's function G should be just such a function h, but "centered" on the orientation u_0, v_0, w_0 rather than on 0, 0, 0.

Indeed,

$$G(u',v',w';t;u_0,v_0,w_0)=h(u,v,w;t)=h(\varphi,t), \quad (57)$$

where the rotation u, v, w, with rotation angle φ, is defined as the rotation that takes the orientation u_0, v_0, w_0 over into the orientation u', v', w'. Then

$$c'+u'i+v'j+w'k =(c+ui+vj+wk)(c_0+u_0i+v_0j+w_0k). \quad (58)$$

The quaternion $c+ui+vj+wk$ can be found explicitly by multiplying Eq. (58) from the right by $c_0-u_0i-v_0j-w_0k$. We require only the angle φ, which is thus found to be given by

$$c=c'c_0+u'u_0+v'v_0+w'w_0 \quad (59)$$

or

$$\cos(\varphi/2)=\cos(\varphi'/2)\cos(\varphi_0/2) +\sin(\varphi'/2)\sin(\varphi_0/2)\cos\Theta, \quad (60)$$

[7] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1927), p. 464.
[8] Reference 7, pp. 475–476.

where Θ is the angle between the axes of the rotations u', v', w' and u_0, v_0, w_0. This description of the composition of rotations in terms of a spherical triangle whose sides are the *half*-angles has a simple geometrical interpretation.[6]

The function $h(\varphi,t)$ used here is that given by Eqs. (49) and (55), but $\varphi=0$ is not at the center of the sphere over which the integration in Eq. (56) is taken. Thus, values of φ larger than π are involved. This is perfectly legitimate; the series still converge uniformly and satisfy the differential equation, and at the surface of the u_0, v_0, w_0 sphere the function $f=c_0^{-1}h(\varphi,t)$ satisfies the general boundary condition stated at the end of Sec. II; this last fact can be verified explicitly by a little trigonometric calculation, which we omit here. Note that $[\sin(\varphi/2)]^{-1}\sin(n+\frac{1}{2})\varphi$ is an even function of $\cos(\varphi/2)$, so that [from Eq. (49)]:

$$h(\varphi)=h(2\pi-\varphi). \tag{61}$$

In making any calculation with Eqs. (56) and (57), the value of φ has to be taken from Eq. (60). Sometimes the most convenient way to bring this relation in is to introduce as variables of integration the angles φ_0 and φ, and the azimuthal angle Φ between the plane containing the axes of the φ' and φ_0 rotations and a fixed plane (for given u', v', w') containing the axis of the φ' rotation. We have

$$\begin{aligned}
&c_0^{-1}du_0dv_0dw_0\\
&=c_0^{-1}s_0^2ds_0d\Omega_0\\
&=\sin^2(\varphi_0/2)d(\varphi_0/2)d(\cos\Theta)d\Phi\\
&=\sin^2(\varphi_0/2)\,|\partial\varphi/\partial(\cos\Theta)|^{-1}d(\varphi_0/2)d\varphi d\Phi\\
&=[\sin(\varphi'/2)]^{-1}\sin(\varphi/2)\,\sin(\varphi_0/2)\\
&\qquad\times d(\varphi_0/2)d(\varphi/2)d\Phi.
\end{aligned} \tag{62}$$

In the last step, use was made of Eq. (60). This change of variables makes the function G very simple to handle, but may bring in new difficulties in connection with the function $g(u_0,v_0,w_0)$ and the ranges of integration.

As an example that works out very simply, we take the case $g(u_0,v_0,w_0;t_0)=h(\varphi_0,t_0)$. Equation (56) then merely describes the further propagation of this unit solution, and it is obvious that the result must be just $h(\varphi', t_0+t)$. We substitute Eq. (62) in Eq. (56). The integrand does not involve Φ, and we get a factor 2π from $\int d\Phi$. The integration over $d\varphi$ will be performed next; the limits are $|\varphi'-\varphi_0|$ [$\Theta=0$ in Eq. (60)] and $\varphi'+\varphi_0(\Theta=\pi)$. Then we have

$$\begin{aligned}
g(u',v',w';t_0+t)&=[2\sin(\varphi'/2)]^{-1}\pi^{-3}\\
&\times\int_0^\pi\sum_{n_0}(2n_0+1)\sin[(n_0+\tfrac{1}{2})\varphi_0]\\
&\cdot\exp[-n_0(n_0+1)Dt_0]d\varphi_0\int_{|\varphi'-\varphi_0|}^{\varphi'+\varphi_0}\sum_n(2n+1)\\
&\times\sin[(n+\tfrac{1}{2})\varphi]\cdot\exp[-n(n+1)Dt]d\varphi.
\end{aligned} \tag{63}$$

A term of the last integral contains the factor

$$\begin{aligned}
&[2\cos(n+\tfrac{1}{2})\varphi]_{|\varphi'-\varphi_0|}^{\varphi'+\varphi_0}\\
&\qquad=4\sin[(n+\tfrac{1}{2})\varphi']\sin[(n+\tfrac{1}{2})\varphi_0].
\end{aligned} \tag{64}$$

The integration over $d\varphi_0$ now involves products of orthogonal functions, so that the only nonvanishing contributions are from $n_0=n$, and the result is

$$\begin{aligned}
&g(u',v',w';t_0+t)\\
&=[\pi^2\sin(\varphi'/2)]^{-1}\sum_n(2n+1)\sin(n+\tfrac{1}{2})\varphi\\
&\times\exp[-n(n+1)D(t_0+t)]=h(\varphi',t_0+t),
\end{aligned} \tag{65}$$

as expected.

APPENDIX. SPINNING ELECTRON AND QUATERNION ROTATION OPERATORS

The Pauli matrices satisfy

$$\sigma_x\sigma_y=i\sigma_z,\quad \text{etc.,} \tag{A1}$$

or

$$(-i\sigma_x)(-i\sigma_y)=(-i\sigma_z),\quad \text{etc.} \tag{A2}$$

Also

$$\sigma_x^2=\sigma_y^2=\sigma_z^2=1 \tag{A3}$$

or

$$(-i\sigma_x)^2=(-i\sigma_y)^2=(-i\sigma_z)^2=-1. \tag{A4}$$

Comparing with the quaternion relations, Eq. (7), we see the well-known isomorphism between the Pauli matrices and quaternions,

$$(-i\sigma_x)\leftrightarrow i,\quad (-i\sigma_y)\leftrightarrow j,\quad (-i\sigma_z)\leftrightarrow k. \tag{A5}$$

The Pauli matrices provide a matrix representation of the quaternion algebra.

In the quantum mechanics of a particle, an infinitesimal rotation by an angle $\delta\varphi$ around an axis in the direction given by the unit vector $\mathbf{n}$ is described by letting the operator

$$1-\delta\varphi\cdot(i/\hbar)(\mathbf{n}\cdot\mathbf{M}) \tag{A6}$$

act on the wave function ψ. Here $\mathbf{M}$ is the angular momentum operator. A part of $\mathbf{M}$ is the orbital angular momentum

$$\mathbf{L}=(\hbar/i)\mathbf{r}\times\nabla. \tag{A7}$$

Application of the part of the operator (A6) containing $\mathbf{L}$ to $\psi(\mathbf{r})$ accomplishes the change in the coordinates $\mathbf{r}$ required by the rotation; for a particle without spin this is the whole transformation. For spin $\frac{1}{2}$,

$$\mathbf{M}=\mathbf{L}+\mathbf{S},\quad \mathbf{S}=\tfrac{1}{2}\hbar\boldsymbol{\sigma}, \tag{A8}$$

$\mathbf{L}$ and $\mathbf{S}$ commute, and the infinitesimal operator (A6) can be regarded as the product of a factor obtained by replacing $\mathbf{M}$ by $\mathbf{L}$ and one with $\mathbf{M}$ replaced by $\mathbf{S}$. The factor with $\mathbf{S}$ accomplishes the change in the relative values of the two components of ψ as required by the rotation of the spin. Either factor by itself has all the algebraic (commutation) properties needed to give a representation of rotations.

The spin factor is, by Eqs. (A6) and (A8),

$$1+\tfrac{1}{2}\delta\varphi[l(-i\sigma_x)+m(-i\sigma_y)+n(-i\sigma_z)], \quad \text{(A9)}$$

where l, m, n are the components of the unit vector $\mathbf{n}$. The square of the quantity in square brackets is -1. As is well known, iteration of the operator (A9) by raising it to the power $\varphi/(\delta\varphi)$, with $\delta\varphi\rightarrow 0$, gives for rotation through the angle φ the operator

$$\cos(\varphi/2)+\sin(\varphi/2) \times[l(-i\sigma_x)+m(-i\sigma_y)+n(-i\sigma_z)]. \quad \text{(A10)}$$

With the isomorphism (A5), this gives the quaternion operator of Eq. (5).

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Theory of Inelastic Scattering of Cold Neutrons from Liquid Helium

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A measurement of the energy losses of monoenergetic neutrons scattered from liquid He II would permit a determination of the energy-*versus*-momentum relation for the elementary excitations (phonons and rotons) in the liquid. A major part of the scattering at a fixed angle arises from production or annihilation of a single excitation and appears as sharp lines in the energy spectrum. From the position of these lines the energy-*versus*-momentum relation of the excitations can be inferred. Other processes, such as production or annihilation of multiple excitations, contribute a continuous background, and occur at a negligible rate if the incident neutrons are slow ($\lambda\gtrsim 4$A) and the helium cold ($T<2°$K). The total cross-section data can be accounted for by production of single excitations; the theoretical cross section, computed from a wave function previously proposed to represent excitations, agrees with experiment over the entire energy range, within 30%. Line widths in the discrete spectrum are negligible at 1°K because of the long lifetime of phonons and rotons.

I. INTRODUCTION

THE possibility of a direct experimental determination of the energy-*versus*-momentum relation for phonons in a solid was pointed out by Placzek and Van Hove.[1] They proposed to study the energy distribution of very slow neutrons scattered inelastically and coherently from the solid; if the incident neutron beam is monochromatic and if the scattering process involves only the production or annihilation of a single phonon, energy and momentum conservation imply that the neutrons emerging at a given angle can have only certain discrete energies. The energy-momentum relation for the phonons can be inferred from the angular variation of this discrete spectrum. Other processes, such as multiple phonon production or annihilation, contribute a continuous background above which the discrete spectrum is still observable.

The purpose of the present paper is to suggest that the same technique be used to determine directly the energy-*versus*-momentum curve for the excitations in liquid helium, and to predict some details of the experiment. A direct measurement of this curve would be of considerable interest, since the shape of the curve has already been predicted in some detail by indirect methods. Landau[2] argued on theoretical grounds that the energy $E(k)$ of an excitation momentum $\hbar\mathbf{k}$ should rise linearly with slope $\hbar c$ for small k (c=speed of sound $=240$ m/sec), pass through a maximum, drop to a local minimum at some value k_0, and rise again when $k>k_0$. For small k, the excitations are called phonons and may be thought of as quantized sound waves; the excitations with $k\sim k_0$ are called rotons, and seem to be the quantum-mechanical analog of smoke rings.[3,4] At low temperatures, only the linear portion of the curve and the portion near the minimum are excited; if the curve is represented near the minimum by $E(k)=\Delta+\hbar^2(k-k_0)^2/2\mu$, the specific heat and second sound data can be fitted best with the values[5]

$$\Delta/\kappa=9.6°\text{K},\quad k_0=2.30\,A^{-1},\quad \mu=0.40\,m_{\text{He}},$$

and almost as well with the values[2]

$$\Delta/\kappa=9.6°\text{K},\quad k_0=1.95\,\text{A}^{-1},\quad \mu=0.77\,m_{\text{He}}.$$

A Landau-type curve has recently been obtained from first principles by the substitution of a trial function into a variational principle for the energy.[3,4] The resulting curve is an upper limit to the true spectrum, and gives $\Delta/\kappa=11.5°$K, $k_0=1.85$ A^{-1}, $\mu\sim 0.20$

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[1] G. Placzek and L. Van Hove, Phys. Rev. **93**, 1207 (1954). We have recently learned that some of the ideas in the present paper have been discussed by V. V. Tolmachev, Repts. Acad. Sci. U.S.S.R. **101**, No. 6 (1955).

[2] L. Landau, J. Phys. (U.S.S.R.) **5**, 71 (1941); **11**, 91 (1947).

[3] R. P. Feynman, Phys. Rev. **94**, 262 (1954).

[4] R. P. Feynman and M. Cohen, Phys. Rev. **102**, 1189 (1956).

[5] deKlerk, Hudson, and Pellam, Phys. Rev. **93**, 28 (1954).