Rotational Brownian motion

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A survey of the present state of the theory of rotational Brownian motion is given. Chapters 1 and 2 expound the theory of rotational diffusion and the solution of the problem of rotational random walks. The probability distributions for the orientations of Brownian particles are written in terms of generalized spherical functions, which are matrix elements of irreducible representations of the rotation group. Methods are discussed for the experimental determination of the nature of Brownian rotation by the use of nuclear magnetic resonance, dielectric relaxation, and the Rayleigh scattering of light. Chapter 3 gives an exposition of generalized rotational diffusion, taking account of inertial effects in the Brownian motion. The influence of inertial effects on dielectric magnetic relaxation and on the scattering of light is discussed. The conclusion of the review gives a discussion of precession effects in Brownian motion.

CONTENTS

INTRODUCTION

The theory of Brownian motion, beginning with the papers of Einstein and of Smoluchowski,[1] is one of the important fields of modern physics. Recently there has been intensive study of rotational Brownian motion, owing to the important part it plays in the interpretation of such phenomena as nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR), of Rayleigh and Raman scattering, of the infrared absorption of light, of dielectric relaxation, and so on.

The purpose of the present review is to present the results of theoretical researches on rotational Brownian motion and to give a general idea of the most promising lines of development in this field. There have been no such papers in the Soviet literature since Frenkel's classic work,[2] and the existing reviews in foreign literature are by no means complete.

The present review consists of four chapters. The first chapter is devoted to the theory of rotational diffusion; historically this is the first theory of rotational Brownian motion, its sources going back to papers of Debye[3] and Perrin.[4] Following Favro,[5] we give a derivation of the equation of rotational diffusion. Its solution in the now generally accepted form, a series of generalized spherical functions, is given in accordance with[6-8]. The connection between the rotational-diffusion tensor and the friction tensor is established by Einstein's method (cf.[5]). The second chapter contains the solution of the problem of rotational random walk,[9,10] which has marked a new stage in the study of Brownian motion. In addition we discuss, on the basis of a criterion we have given (cf.[9,11]), the results of[12,13] on the determination of the character of the Brownian rotation of molecules. Steele's theory[14] of rotational Brownian motion with inclusion of inertial effects, and its applications to NMR and to dielectric relaxation, are considered in the third chapter. Here also, referring to papers by McClung and D. Kivelson[15] and by D. Kivelson, M. Kivelson, and Oppenheim,[16] we discuss precession effects and their role in EPR. The experimental

papers included in this review and directly connected with the fundamental theoretical problems of Brownian motion cannot, of course, claim completeness. In view of the basic purpose of the survey, the authors have not tried to give any profound idea of the level of experimental research in this field. The present state of such research is reflected in excellent monographs by Abragam,[17] Fabelinskiĭ,[18] and Shakhparonov[19] and in the reports of All-Union Conferences.[20-22]

1. ROTATIONAL DIFFUSION

a) <u>The diffusion equation.</u> We begin the study of rotational Brownian motion with the derivation of the equation of rotational diffusion for particles (molecules) with three rotational degrees of freedom. In specifying the orientation of the molecule one introduces a molecular, or movable, coordinate system (x, y, z) rigidly connected with the molecule. The orientation of the molecule, characterized by the rotation of the movable system (x, y, z) relative to the laboratory system (X, Y, Z), can be specified: 1) by the Euler angles φ, θ, ψ, 2) by the rotation matrix $g(\varphi, \theta, \psi)$, and 3) by the rotation vector Ω (its absolute value $|\Omega|$ is equal to the angle of rotation, and its direction is that of the axis of rotation). Besides these there are, of course, other ways of specifying orientations. For example, Furry[23] used quaternions for this purpose, and Favro[5] used Cayley-Klein parameters. The first three methods, however, have proved most suitable in the theory of Brownian motion,[6-8] since they permit direct use of the well-developed apparatus of the theory of representations of the rotation group. We further note that molecular rotations giving changes from one orientation to another are specified analogously.

A fundamental role in the theory of rotational Brownian motion is played by the distribution $p(\epsilon, \Delta t)d^3\epsilon$, which gives the probability of a rotation with vector ϵ in the range $(\epsilon, \epsilon + d\epsilon)$ during the time Δt. Brownian motion of the type of free rotational diffusion occurs for the following assumptions regarding $p(\epsilon, \Delta t)$: 1) $p(\epsilon, \Delta t)$ does not

depend on the orientation which the molecule had before the beginning of the rotation; 2) $p(\epsilon, \Delta t) = p(-\epsilon, \Delta t)$; 3) $\int p(\epsilon, \Delta t)\epsilon_i\epsilon_j d^3\epsilon$ is proportional to Δt; 4) there exists a small time interval Δt such that all moments of the distribution $p(\epsilon, \Delta t)$ higher than the second can be neglected. The first and second conditions are obviously satisfied if there are no external fields and the only torques acting on the molecule are random moments of forces caused by the interaction with surrounding molecules in a uniform medium.

With these assumptions about $p(\epsilon, \Delta t)$ we shall carry out the derivation of the equation of rotational diffusion, following Favro.[5] Let $P(\Omega, t)$ be the required probability that the orientation of the molecule at time t belongs to the invariant volume element $dv = \Gamma^{-1}d^3\Omega$, where Γ^{-1} = $4 \sin^2 (\Omega/2)/\Omega^2$.[24] It is more natural, however, to consider first the distribution $W(\Omega, t)d^3\Omega$, which gives the probability that the orientation of the molecule at time t belongs to the volume element $d^3\Omega$ ($d^3\Omega$ is not invariant under rotations). The connection between $P(\Omega, t)$ and $W(\Omega, t)$ is obvious:

$$P(\Omega, t) = \Gamma W(\Omega, t). \tag{1.1}$$

Starting from the law of multiplication of the probabilities of independent events, we find

$$W(\Omega, t + \Delta t) d^3\Omega = \int d^3\epsilon\, p(\epsilon, \Delta t)\, W(\Omega_0, t)\, d^3\Omega_0, \tag{1.2}$$

where the range of Ω_0 includes only those orientations which lead to the orientation Ω after the rotation ϵ. We shall take Eq. (1.2) in the molecular (movable) coordinate system (x, y, z). Changing from $W(\Omega, t)$ to $P(\Omega, t)$, we have from (1.2)

$$P(\Omega, t + \Delta t) d^3\Omega_0 = \int d^3\epsilon\, p(\epsilon, \Delta t)\, P(\Omega_0, t)\, d^3\Omega_0. \tag{1.3}$$

As a function over the group, the distribution of orientations at time t transforms on passage from Ω to Ω_0 according to the relation[25]

$$P(\Omega_0, t) d^3\Omega = \exp(i\epsilon M)\, P(\Omega, t) d^3\Omega, \tag{1.4}$$

where M_i (i = x, y, z) are infinitesimal operators which are the same as the quantum-mechanical angular-momentum operators. Thus it follows from (1.3) that

$$P(\Omega, t + \Delta t) = \int d^3\epsilon\, p(\epsilon, \Delta t) \exp(i\epsilon M)\, P(\Omega, t). \tag{1.5}$$

Expanding $\exp(i\epsilon \cdot M)$ in powers of ϵ_j and keeping terms up to and including the second powers, and also expanding $P(\Omega, t + \Delta t)$ on the left side of the equation in powers of Δt and using the expression linear in Δt, we get

$$\partial P(\Omega, t)/\partial t = -M_j D_{jk} M_k P(\Omega, t), \tag{1.6}$$

where

$$D_{jk} = \int d^3\epsilon\, \epsilon_j\epsilon_k p(\epsilon, \Delta t)/2\Delta t. \tag{1.7}$$

Equation (1.6) is the desired equation of rotational diffusion; the set of quantities D_{jk} is, by definition, the rotational diffusion tensor of the molecule. According to (1.7), the tensor D_{jk} is symmetric; like every symmetric second-rank tensor, it can be transformed to principal axes.

It is easily verified that the form of the equation of rotational diffusion for the orientation distribution P is independent of the way the orientation of the molecule is described. In particular, if the orientation is specified not by the vector Ω but by the Euler angles φ, θ, ψ, the equation for $P(\varphi, \theta, \psi)$ is still of the form (1.6). The explicit expressions for the infinitesimal operators M_i of

course depend on the particular parametrization of the orientations.

In some practically important cases the equation (1.6) can be given a simpler form. In the case when the rotational diffusion tensor is diagonal ($D_{jk} = D\delta_{jk}$) we have[6]

$$\partial P/\partial t = D\, \Delta P, \tag{1.8}$$

$$\Delta = \frac{\partial^2}{\partial\theta^2} + \mathrm{ctg}\,\theta\, \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\psi^2} - 2\cos\theta\, \frac{\partial^2}{\partial\psi\,\partial\varphi} + \frac{\partial^2}{\partial\varphi^2}\right). \tag{1.9}$$

With the appropriate change of form of the operator Δ Eq. (1.8) will also hold for particles with two rotational degrees of freedom, for example for diatomic molecules. We write the required expression for Δ, taking the spherical coordinates Θ and Φ as the parameters fixing the orientation of such a particle[26]

$$\Delta = \frac{\partial^2}{\partial\Theta^2} + \mathrm{ctg}\,\Theta\, \frac{\partial}{\partial\Theta} + \frac{1}{\sin^2\Theta}\, \frac{\partial^2}{\partial\Phi^2}. \tag{1.10}$$

In analogy with translational diffusion we can introduce a probability current density for rotational diffusion in the space of orientations Ω. To do so we consider a small area dA perpendicular to the direction of the Ω_1 axis and with the coordinates $(\Omega_1, \Omega_2, \Omega_3)$. We count how many molecules in the orientation space pass through dA in the time Δt in the positive direction of Ω_1. Consider a particular rotation ϵ. The molecules that have come through dA by executing the rotation ϵ differ from each other by the values of the "path" $\alpha\epsilon$ ($0 < \alpha < 1$) traversed from the beginning of the rotation to the area dA. Let us select the molecules with values of α in the range $(\alpha, \alpha + d\alpha)$. This part of the molecules passing through dA fills a parallelopiped with base dA and lateral vector-edge denoted by $\Delta\Omega$. For the projection of $\Delta\Omega$ along the axis Ω_1 (i.e., for the altitude of the parallelepiped) we have

$$\Delta\Omega_l = -id\alpha\, (\epsilon M)\, \Omega_l. \tag{1.11}$$

From this we find the invariant volume of the parallelepiped:

$$dv = \Gamma^{-1} d^3\Omega = \Gamma^{-1} dA\, d\alpha\, (-i\epsilon M)\, \Omega_l. \tag{1.12}$$

Let the volume dv correspond, before the rotation ϵ, to the volume dv' at the point Ω'. Obviously dv contains the number of molecules that was in dv', so that

$$P(\Omega', t) dv' = \exp(i\alpha\epsilon M)\, P(\Omega, t) dv. \tag{1.13}$$

The total number of molecules is of course to be taken equal to unity. The number of molecules that have executed the rotation and passed through dA in the time Δt is

$$p(\epsilon, \Delta t) d^3\epsilon \int_0^1 d\alpha\Gamma^{-1} dA\, (-i\epsilon M)\, \Omega_l \exp(i\alpha\epsilon M)\, P(\Omega, t). \tag{1.14}$$

The total number of molecules that have passed through dA in the time Δt is obtained by integrating over all ϵ. Dividing the result of the integration by $\Delta t dA$ and using only the terms linear in Δt, we get the desired expression for the probability current density:

$$J_l = \Gamma^{-1}(M_j\Omega_l) D_{jk} M_k P(\Omega, t) \equiv \hat{j}_l P(\Omega, t), \tag{1.15}$$

where

$$\hat{j}_l = \Gamma^{-1}(M_j\Omega_l) D_{jk} M_k. \tag{1.16}$$

The diffusion equation (1.6) can now be written in terms of J_1. In fact using (1.6) and (1.15), we find

$$\partial P/\partial t = -\Gamma \partial_l J_l, \tag{1.17}$$

where $\partial_l J_l$ is the divergence of the current density.

b) The Green's function of the equation of rotational

diffusion. The Green's function $G(\varphi, \theta, \psi; \varphi_0, \theta_0, \psi_0, t)$ $\equiv G(g, g_0, t)$ of the rotational diffusion equation (1.6) can be introduced in the usual way.[27] $G(g, g_0, t)dg$ is the probability that the orientation of the molecule at time t is in the element $dg = \sin\theta\, d\varphi\, d\theta\, d\psi$ if at time t = 0 the orientation was g_0. The solution $P(g, t)$ of the rotational diffusion equation (1.6) for a given initial distribution of orientations $P(g_0, 0^+)$ can be obtained from the Green's function as follows:

$$P(g, t) = \int P(g_0, 0^+)\, G(g, g_0, t)\, dg_0. \qquad (1.18)$$

The Green's function $G(g, g_0, t)$ was found by Favro.[5] In[6-8] $G(g, g_0, t)$ is obtained in terms of the generalized spherical functions $T^l_{mn}(g)$, which are matrix elements of irreducible representations of the rotation group. The use of these functions in practical calculations is a great advantage, because of the orthogonality relations for the $T^l_{mn}(g)$ over the rotation group. Following[6-8], we represent the desired Green's function as an expansion in the eigenfunctions of the operator $M_j D_{jk} M_k$, taking the axes of the molecular coordinate system along the principal axes of the tensor D_{jk}:

$$M_j D_{jk} M_k \Psi_\nu = D_\nu \Psi_\nu, \qquad (1.19)$$

$$G(g, g_0, t) = \sum_\nu C_\nu(t)\, \Psi_\nu. \qquad (1.20)$$

Substituting (1.20) in (1.6) and using (1.19), we get

$$\partial C_\nu/\partial t = -C_\nu D_\nu, \qquad C_\nu(t) = N_\nu e^{-D_\nu|t|}. \qquad (1.21)$$

The constant N_ν is determined from the initial condition

$$G(g, g_0, 0) = \delta(g - g_0), \qquad N_\nu = \Psi_\nu^*(g_0). \qquad (1.22)$$

Accordingly,

$$G(g, g_0, t) = \sum_\nu \Psi_\nu^*(g_0) \Psi_\nu(g) e^{-D_\nu|t|}. \qquad (1.23)$$

It is easily seen that with the replacement $D_{jk} \to \hbar^2 J_{jk}^{-1}/2$ the operator $M_j D_{jk} M_k$ becomes identical with the Hamiltonian for a top with the inertia tensor J_{jk}. Therefore the Ψ_ν in (1.23) are the orthonormal wave functions of the quantum-mechanical top, and the D_ν are obtained from the energy eigenvalues of the top by the indicated replacement. For $D_1 = D_2$, i.e., when the quantum-mechanical analog is a symmetric top, we have for D_ν and Ψ_ν the exact solution[28,29]

$$D_\nu = D^l_{mn} = D_1 l(l+1) + (D_3 - D_1)n^2, \qquad (1.24)$$

$$\Psi_\nu = \Psi^l_{mn} = [(2l+1)/8\pi^2]^{1/2} T^l_{mn}(g), \quad -l \leq m, n \leq l. \qquad (1.25)$$

Accordingly,

$$G(g, g_0, t) = \sum_{lmn} [(2l+1)\,8\pi^2]\, \overline{T}^l_{mn}(g_0) T^l_{mn}(g) \cdot \exp(-D^l_{mn}|t|). \qquad (1.26)$$

In the case when all three principal values of the rotational diffusion tensor are different, i.e., when the quantum-mechanical analog is an asymmetric top, we can obtain an approximate solution by a perturbation-theory method.[28,29] In applications one needs the expressions for Ψ_ν and D_ν with $l = 2$, $-2 \leq m$, $n \leq 2$.

We write them out:

$$D^2_{m-2} = 3(D + D_3), \quad \Psi^2_{m-2} = (5/16\pi^2)^{1/2}(T^2_{m2} - T^2_{m-2}),$$
$$D^2_{m-1} = 3(D + D_2), \quad \Psi^2_{m-1} = (5/16\pi^2)^{1/2}(T^2_{m1} - T^2_{m-1}),$$
$$D^2_{m0} = 3(D + D_1), \quad \Psi^2_{m0} = (5/16\pi^2)^{1/2}(T^2_{m1} + T^2_{m-1}),$$
$$D^2_{m1} = 6D + 2g_D, \quad \Psi^2_{m1} = (5/16\pi^2)^{1/2}[(c_+/4g_D)^{1/2}(T^2_{m2} + T^2_{m-2})$$
$$- (c_+/2g_D)^{1/2} T^2_{m0}],$$
$$D^2_{m2} = 6D - 2g_D, \quad \Psi^2_{m2} = (5/16\pi^2)^{1/2}[(c_-/4g_D)^{1/2}(T^2_{m2} + T^2_{m-2})$$
$$+ (c_-/2g_D)^{1/2} T^2_{m0}].$$

Here D_1, D_2, D_3 are the principal values of the tensor D_{jk}; $3D = \sum_j D_{jj}$; g_D is the anisotropy factor of the tensor D_{jk}: $g_D = (D_1^2 + D_2^2 + D_3^2 - D_1 D_2 - D_2 D_3 - D_3 D_1)^{1/2}$; $c_\pm = 2g_D \pm 3(D_3 - D_1)$. Solutions of the rotational diffusion equation in the form (1.18) with arbitrary initial conditions are as a rule not encountered in practical calculations. However, the Green's function is of fundamental importance; by means of it one can calculate correlation functions. For example, if we have a random function of time $F(g(t))$, whose random nature comes from the random dependence of the orientation of a molecule on the time t, its correlation function $K(t)$ can be calculated from the formula

$$K(t) = (8\pi^2)^{-1} \int \overline{F}(g_0)\, G(g, g_0, t)\, dg\, dg_0; \qquad (1.28)$$

here it is assumed that the initial orientations g_0 at t = 0 are equally probable; the bar denotes the complex conjugate.

c) The rotational diffusion tensor. The rotational diffusion tensor defined by (1.7) is connected with the tensor coefficient of the viscous forces acting on the rotating molecule. This connection can be established by the method of Einstein[1] in analogy with translational diffusion.[5]

Suppose the molecule is acted on by a weak external torque given by the potential $\varphi(\mathbf{\Omega})$:

$$\mathbf{N}(\mathbf{\Omega}) = i\mathbf{M}\varphi(\mathbf{\Omega}). \qquad (1.29)$$

A stationary distribution of orientations of the molecule is established in accordance with the Boltzmann law:

$$P^{(0)}(\mathbf{\Omega}) = c \exp(-\varphi/kT). \qquad (1.30)$$

Under stationary conditions the angular velocity $\boldsymbol{\omega}_\infty$ of the molecule as a function of its orientation can be determined from the stochastic equations of motion

$$\mathbf{I} \cdot \dot{\boldsymbol{\omega}} + \boldsymbol{\omega} \times (\mathbf{I} \cdot \boldsymbol{\omega}) = i M\varphi(\mathbf{\Omega}) - \boldsymbol{\xi} \cdot \boldsymbol{\omega}, \qquad (1.31)$$

where the dot denotes the inner product of a tensor and a vector,[30] ξ_{ij} is the viscous friction tensor, and I_{ij} is the moment of inertia tensor. Assuming that the angular velocity is sufficiently small, we neglect the second term on the left in Eq. (1.31). We also assume that φ changes weakly with change of $\mathbf{\Omega}$. The solution then has the form

$$\boldsymbol{\omega} = \exp(-\mathbf{I}^{-1}\boldsymbol{\xi} t)\, \boldsymbol{\omega}_0 + i\,[1 - \exp(-\mathbf{I}^{-1}\boldsymbol{\xi} t)]\, \boldsymbol{\xi}^{-1} M\varphi(\mathbf{\Omega}).$$

In the limit of large t ($\mathbf{I}^{-1}\boldsymbol{\xi} t \gg 1$) we get

$$\boldsymbol{\omega}_\infty = i\boldsymbol{\xi}^{-1} M\varphi.$$

For the rate of change of orientation $\dot{\mathbf{\Omega}}$ we then find

$$\dot{\mathbf{\Omega}} = -i\boldsymbol{\omega}_\infty M\Omega.$$

The current density $J_l^{(\varphi)}$ caused by the presence of the potential φ is given by

$$J_l^{(\varphi)} = W(\mathbf{\Omega})\,\dot{\Omega}_l = \Gamma^{-1} P(\mathbf{\Omega})\, (\xi_{ij}^{-1} M_j\varphi)\, (M_i \Omega_l).$$

Combining $J_l^{(\varphi)}$ and the diffusion current (1.15), we get the expression for the total current:

$$J_l = \Gamma^{-1} (M_i \Omega_l)(D_{ij} M_j P + P\xi_{ij}^{-1} M_j\varphi).$$

Under stationary conditions, when P has the form (1.30), we find

$$J_l^{(0)} = \Gamma^{-1} (M_i \Omega_l)(D_{ij} - kT\xi_{ij}^{-1})\, M_j P^{(0)}. \qquad (1.32)$$

Since the probability distribution for the orientation does

not depend on the time, we obtain from (1.17) and (1.32)

$$\partial J_i^{(0)}/\partial l = M_i (D_{ij} - kT\xi_{ij}^{-1}) M_j P^{(0)} = 0.$$

From this there follows the required relation between D_{ij} and ξ_{ij}:

$$D_{ij} = kT (\xi_{ij}^{-1} + \xi_{ji}^{-1})/2.$$

d) The friction coefficient and the intermolecular interaction. The calculation of the friction coefficient ξ_{ij} is an extremely complicated problem, still not completely solved. In Debye's theory of dielectric relaxation[3,31,32] the friction coefficient for spherical molecules was calculated on the basis of a hydrodynamical model. This means that the rotational motion of a molecule was treated like the rotation of a macroscopic sphere in a continuous viscous medium. The friction coefficient was then found to be isotropic and given by

$$\xi = \pi \eta d^3, \qquad (1.33)$$

where η is the viscosity of the liquid and d is the diameter of the molecule. If we measure the diffusion coefficient, and consequently the friction coefficient ξ, then from (1.33) we can determine the radius of a molecule. In the majority of liquids the molecular radii so found are much smaller than the true molecular radii. It is quite obvious that the source of this discrepancy cannot be ascribed to a solvation effect.

In a number of papers[33-35] the attempt was made to improve the relation (1.33) by taking into account the shape of the molecule. In particular, for ellipsoidal molecules the friction tensor ξ_{ij} was calculated from formulas of Edwards,[36] derived from a treatment of the rotation of a macroscopic ellipsoid in a continuous medium. However, these calculations did not lead to any successful explanation of the discrepancy between actual molecular radii and the values found from measured values of the friction coefficient.

Steele[14] has developed a theory for the calculation of the friction coefficient on a molecular-kinetic basis; it is, however, limited to the treatment of molecules of the spherical-top type, for which the principal values of the inertia tensor are equal ($I_1 = I_2 = I_3 = I$). For such molecules the stochastic equations for the Brownian rotation are

$$\mathbf{I} \cdot \dot{\boldsymbol{\omega}} + \boldsymbol{\xi} \cdot \boldsymbol{\omega} = N(t), \qquad (1.34)$$

where N(t) is the rapidly fluctuating part of the torque, and

$$\langle N(t) \rangle = 0, \quad \langle N(t) N(t') \rangle = F(N) \delta(t - t').$$

It is easy to show from (1.34) that the autocorrelation functions of the angular velocity components are of the form

$$\langle \omega_i(t) \omega_i(0) \rangle = (kT/I) \exp(-\xi_i t/I). \qquad (1.35)$$

From this follows the relation

$$kT/\xi_i = \int_0^\infty \langle \omega_i(0) \omega_i(0) \rangle \, dt.$$

By using the Hamiltonian equations to express the angular velocity components $\omega_i(t)$ in terms of the potential energy V of the rotating molecule, Steele[14] obtains an important formula for the principal values ξ_i of the viscous friction tensor:

$$\xi_i^2 = (2I/\pi) \langle \partial^2 V/\partial \xi_i^2 \rangle. \qquad (1.36)$$

It follows from (1.36) that there exists no simple relation

of the form (1.33) between the friction coefficient and the viscosity η of the liquid. The hydrodynamic model leads to a scalar friction coefficient for spherical molecules, while Eq. (1.36) indicates a tensor nature of the friction. The size of the various components ξ_i of the tensor depends strongly on the symmetry of the potential energy V. In particular, if V does not depend on some rotation component ϵ_i, then the corresponding component of the friction tensor is equal to zero. The case in which all or several components of the friction tensor are close to zero is of particular interest. We shall, however, leave the detailed discussion of this case for Sec. 3. We merely note that for small ξ_i inertial effects begin to play a large role in the rotational motion, and consequently for small time intervals ($\xi_i t \ll I$) the rotational diffusion equation in the form (1.6) is without meaning.

2. THE ROTATIONAL RANDOM-WALK PROBLEM

a) Formulation and solution of the problem. As is well known, the classical problem of translational random walk has been treated in the papers of Smoluchowski (cf.[1]). The general solution of the problem of translational random walk, given by Markov[37] in 1924, was the foundation of the branch of probability theory now called Markov processes. The solution of the problem of rotational random walk was not known, however. By using the apparatus of the theory of representations of the rotation group we have found this solution and indicated a criterion for the experimental determination of the nature of a rotational Brownian motion.

The problem of rotational random walk has two aspects: 1) the mathematical formulation and solution of the problem, and 2) determination of the status and significance of the problem in the theory of rotational Brownian motion. We begin with the formulation and solution of the problem.[9,10]

Suppose a molecule executes N successive random rotations, whose values are characterized by a distribution $p(g_1)$. The initial orientation of the molecule is regarded as given. It is required to determine P(g, N), the distribution of orientations of the molecule at the end of the N-th rotation. It is important to note that we shall look for the solution of the problem on the assumption that the distribution $p(g_1)$ for the values of the individual rotations does not depend on the orientation of the molecule.

It is easy to see that P(g, N) is connected with P(g, N − 1), in analogy with Eq. (1.3), by the obvious relation

$$P(g, N) \, dg = \int dg_1 p(g_1) P(k, N - 1) \, dk, \qquad (2.1)$$

where the integration goes over g_1. In (2.1) k includes only those orientations possessed by the molecule after N − 1 rotations which give the orientation g after the N-th rotation g_1.

The transformation of the functions (over the group) P(k, N − 1)dg upon the rotation g_1 is accomplished by means of the finite rotation operator $T(g_1)$:

$$P(g, N - 1) \, dg = T(g_1) P(k, N - 1) \, dk. \qquad (2.2)$$

Using the fact that $T^{-1}(g_1) = T(g_1^{-1})$, we get from (2.1) and (2.2)

$$P(g_1, N) \, dg = \int dg_1 p(g_1) T(g_1^{-1}) P(g, N-1) \, dg. \qquad (2.3)$$

We shall look for the solution of the system of integ-

ral equations (2.3) in the form of a series in the generalized spherical functions:

$$P(g, N) = \sum_{l, m, n} C^l_{mn}(N) T^l_{mn}(g). \qquad (2.4)$$

Substituting (2.4) in (2.3), we find recurrence relations for determining the coefficients C^l_{mn}:

$$C^l_{mn}(N) = \sum C^l_{sn}(N-1) \int p(g_1) T^l_{sm}(g_1^{-1}) dg_1, \qquad (2.5)$$

where we have used the transformation rule

$$T(g_1^{-1}) T^l_{mn}(g) = \sum_s T^l_{ms}(g_1^{-1}) T^l_{sn}(g). \qquad (2.6)$$

We introduce the notation

$$A_l = \int p(g_1) T^l(g_1^{-1}) dg_1. \qquad (2.7)$$

Then the relations (2.5) can be written in matrix form:

$$C^l(N) = A_l^T C^l(N-1), \qquad (2.8)$$

where the superscript T denotes transposition. From this we find

$$C^l(N) = (A_l^T)^N C^l(0). \qquad (2.9)$$

The matrix elements $C^l_{mn}(0)$ can be found from the expansion (2.4) for N = 0. In fact, since $P(g, 0) = \delta(g - g_0)$, we have

$$\delta(g - g_0) = \sum C^l_{mn}(0) T^l_{mn}(g). \qquad (2.10)$$

Multiplying this by $\overline{T^l_{mn}}$ and integrating over the entire group, on using the orthogonality relations

$$\int \overline{T^l_{ih}}(g) T^m_{jn}(g) dg = [8\pi^2/(2l+1)] \delta_{lm} \delta_{ij} \delta_{hn}, \qquad (2.11)$$

we get for C^l_{mn}:

$$C^l_{mn}(0) = (2l+1) \overline{T^l_{mn}}(g_0)/8\pi^2. \qquad (2.12)$$

Successive substitution of (2.12) in (2.9) and of (2.9) in (2.4) gives

$$P(g, N) = \sum_l [(2l+1)/8\pi^2] (A_l^T)^N_{mi} T^l_{in}(g_0) T^l_{mn}(g). \qquad (2.13)$$

Since

$$\overline{T^l_{in}}(g_0) = T^l_{ni}(g_0^{-1}),$$

owing to the unitarity of the irreducible representations we finally get for P(g, N):

$$P(g, N) = \sum_l [(2l+1)/8\pi^2] \mathrm{Sp}\, [T^l(g_0^{-1}) A_l^N T^l(g)]. \qquad (2.14)$$

The result (2.14) is the exact solution of the rotational random-walk problem.

Let us examine one important special case. Let the torques acting on the molecule be such that rotations through the same angle around different axes are equally probable. If g is the matrix for one such rotation, then the matrices for all the others are given by $g' = h^{-1}gh$, where h is an arbitrary element of the rotation group. It follows that for $g_0 = e$ the probability distribution (2.14) must satisfy the relation

$$P(g, N) = P(h^{-1}gh, N). \qquad (2.14')$$

This is possible only if the operators A_l and $T^l(h)$ commute:

$$A_l T^l(h) = T^l(h) A_l. \qquad (2.15)$$

By Shur's lemma an operator which commutes with all the matrices of an irreducible representation is a multiple of the unit operator, so that

$$A_l = \lambda_l E_l. \qquad (2.16)$$

Taking the trace on both sides of (2.16) and using the definition (2.7), we get a formula for calculating the coefficients λ_l:

$$\lambda_l = (2l+1)^{-1} \int \mathrm{Sp}\, e^{i\varepsilon M} p(\varepsilon) d^3\varepsilon, \qquad (2.17)$$

where

$$\mathrm{Sp}\, e^{i\varepsilon M} = \sin [(l + \tfrac{1}{2})\varepsilon] [\sin(\varepsilon/2)]^{-1}. \qquad (2.18)$$

Thus for this special case Eq. (2.14) takes the form

$$P(g, N) = \sum_l [(2l+1)/8\pi^2] \lambda_l^N \mathrm{Sp}\, [T^l(g_0^{-1}) T^l(g)], \qquad (2.19)$$

where the λ_l can be calculated from (2.17).

The probability distribution $p(\varepsilon)$ of the individual rotations is a characteristic of the random-walk process and is not calculated in the theory now being considered.

This distribution must either be postulated on the basis of physical considerations, or calculated, for example by the methods of statistical mechanics. In[9] we took a rectangular distribution for $p(\varepsilon)$. Egelstaff[38] takes for $p(\varepsilon)$ the expression

$$p(\varepsilon) = c \sin(\varepsilon/2) \exp(-\varepsilon \cdot \varepsilon_0), \qquad (2.20)$$

where ϵ_0 is the mean angle of rotation; for $\epsilon_0 \gg 2\exp(-\pi/\epsilon_0)$, c is of the form

$$c \approx 1/2[1 + (2/\epsilon_0)^2]. \qquad (2.21)$$

The solution of the rotational random-walk problem for particles with two orientational degrees of freedom (for example, for diatomic molecules) requires special consideration. The desired probability distribution for the orientations of diatomic molecules is most easily derived from (2.19) by the method of descent from three degrees of freedom to two. Without dwelling on the details of the derivation, we give the final result. Let Φ and Θ be the angles characterizing the orientation of a diatomic molecule. Then for the distribution $P(\Phi, \Theta; N)$ we have the formula[39]

$$P(\Phi, \Theta; N) = \sum_{l, n} Y^n_l(\Phi_0, \Theta_0) [(A_l)_{00}]^N \overline{Y^n_l}(\Phi, \Theta), \qquad (2.22)$$

where the Y^n_l are spherical functions and $(A_l)_{00}$ are integrals of the form

$$(A_l)_{00} = \int_0^\pi p(\Theta_1) P_l(\cos \Theta_1) d\Theta_1. \qquad (2.23)$$

In (2.23) $p(\Theta_1)$ is the probability of an individual rotation through the angle Θ_1, and $P_l(\cos \Theta_1)$ is a Legendre polynomial.

b) The rotational random-walk problem and rotational diffusion. The distribution P(g, t). For the calculation of correlation functions it is necessary to know the distribution of orientations of the molecules at time t, the original orientation g_0 being given. As in the theory of diffusion, this distribution will be denoted by P(g, t). If there have been exactly N rotations in the time t, P(g, t) is simply P(g, N). If, however, the number of rotations in the time t is a random quantity with the distribution $w_N(t)$, then

$$P(g, t) = \sum_{N=0}^{\infty} w_N(t) P(g, N). \qquad (2.24)$$

It is convenient to take for $w_N(t)$ the Poisson distribution

$$w_N(t) = (N!)^{-1} (t/\tau)^N e^{-t/\tau}, \qquad (2.25)$$

where τ is the average time between two successive rotations of a molecule. As is well known, the use of the

Poisson distribution assumes the following conditions: 1) the random-walk process must be uniform, i.e., the probability that N jumps occur in a time t is determined by the length of the interval t and does not depend on the time from which it is measured; 2) the number of rotations in a time t must not depend on the previous history of the process, i.e., there are no aftereffects in the random-walk process; 3) the probability that there are two rotations in an infinitely small time interval must be infinitely small (nonpathological nature of the process); 4) the probability that there is one rotation in an infinitely small time Δt is proportional to Δt.

Accordingly, we get from (2.24), (2.25), and (2.14) the required distribution:

$$P(g,\ t) = \sum [(2l+1)/8\pi^2]\, \text{Sp}\, \{T^l(g_0^{-1})\exp[-(t/\tau)(1-A_l)]\, T^l(g)\}. \quad (2.26)$$

It is natural to expect that for large t ($t \gg \tau$) the $P(g, t)$ given by this formula will agree with the Green's function of the equation of rotational diffusion. To verify this, in the definition (2.7) we change from the variable g_1 to the variable ϵ:

$$A_l = \int e^{i\epsilon M} p(\epsilon)\, d^3\epsilon. \quad (2.27)$$

We now expand $\exp(i\epsilon M)$ in (2.27) in powers of ϵ_i, keeping terms through the second degree:

$$A_l = 1 - \tau M_i D_{ij} M_j, \quad (2.28)$$

$$D_{ij} \equiv (2\tau)^{-1} \int \epsilon_i \epsilon_j p(\epsilon)\, d^3\epsilon. \quad (2.29)$$

The quantities D_{ij} obviously give the definition of the components of the rotational diffusion tensor. Equation (2.28) contains no term from the linear term in the expansion of $\exp(i\epsilon M)$, since we assume that $p(\epsilon) = p(-\epsilon)$.

Taking the principal axes of the tensor D_{ij} as the axes of the molecular reference system, we can bring (2.28) into the form

$$A_l = 1 - \tau [D^+ M^2 + (D_3 - D^+) M_3^2 + D^-(M_1^2 - M_2^2)], \quad (2.30)$$

where $D^\pm = (D_1 \pm D_2)/2$. Using the expression (2.30) for A_l in (2.26), which is legitimate for large t ($t \gg \tau$), we get the Green's function of the rotational diffusion equation. In particular, if $D_1 = D_2$, we get

$$P(g,\ t) = \sum [(2l+1)/8\pi^2]\, \overline{T^l_{mn}}(g_0)\, T^l_{mn}(g)\exp[-D^+ l(l+1) - (D_3 - D^+) m^2]\,t \quad (2.31)$$

For $D_1 = D_2 = D_3 = D$ Eq. (2.29) takes the simple form

$$P(g,\ t) = \sum [(2l+1)/8\pi^2]\, \overline{T^l_{mn}}(g_0)\, T^l_{mn}(g)\exp[-l(l+1)Dt]. \quad (2.32)$$

It is also easy to show that in the transition from rotational random walk to diffusion the integral equation (2.3) becomes the rotational diffusion equation (1.6).

The distribution $P(\Phi, \Theta; t)$ for diatomic molecules is constructed analogously. The final expression for $P(\Phi, \Theta; t)$ will be of the form

$$P(\Phi, \Theta;\ t) = \sum_{l,n} Y^n_l(\Phi_0, \Theta_0;\ t)\exp[-(t/\tau)(1-A_{l00})]\, Y^n_l(\Phi, \Theta). \quad (2.33)$$

For the transition from random walk to diffusion we expand the $P_l(\cos \Theta_1)$ in the definition of A_{l00} in powers of Θ_1. Because in the diffusion approximation $p(\Theta_1)$ is different from zero only for small Θ_1, we drop terms of higher degree than the second in Θ_1. We then get the result

$$P(\Phi, \Theta;\ t) = \sum_{l,n} Y^n_l(\Phi_0, \Theta_0)\, Y^n_l(\Phi, \Theta)\exp[-l(l+1)Dt], \quad (2.34)$$

where D is the diffusion coefficient for the diatomic molecule, given by

$$D = (4\tau)^{-1} \int_0^\pi p(\Theta_1)\, \Theta_1^2\, d\Theta_1. \quad (2.35)$$

The expression (2.34) is obviously the Green's function of the rotational diffusion equation for diatomic molecules.[26] We further note that

$$\overline{\Theta_1^2} = 4D\tau. \quad (2.36)$$

c) Determination of the nature of rotational Brownian motion from comparative study of NMR and dielectric relaxation. Two models of rotational Brownian motion have been studied: rotational diffusion and rotational random walk through finite angles. The question arises: Under what conditions is one model or the other realized? By answering this question we can essentially solve the second problem of the random-walk theory. It is generally supposed that both models can be realized in actuality. It was already assumed by Frenkel that the nature of the rotation of molecules in liquids depends on their size. The Brownian rotation of relatively large molecules is of the nature of rotational diffusion, i.e., rotations of the molecule through finite angles are made up of large numbers of small rotations. The Brownian rotation of relatively small molecules is of the nature of random walks through finite angles. Of course the final decision as to the realization of one model or the other in any concrete case must be determined by experiment.

As is well known, several physical phenomena in condensed media are determined by the nature of the rotational motion of the molecules. These effects include, in particular, dielectric relaxation, infrared absorption, Rayleigh and Raman scattering of light, the scattering of slow neutrons, NMR, and EPR. A method for determining the nature of the rotational Brownian motion on the basis of these effects was first proposed in[11]. The theoretical basis of the method is given in[9]. An experimental study of Brownian rotation by means of NMR and dielectric relaxation was soon carried out in[12]. With this same method, Pinnow, Candau, and Litovitz[13] have recently studied the Brownian rotation of molecules in a number of liquids, using Rayleigh scattering and dielectric relaxation.

Let us examine the theoretical arguments on which the method is based. The line shapes or the characteristic times for the effects in question are determined by the correlation functions of the spherical harmonics $Y^l_m(\theta, \varphi)$, as transformed from the molecular coordinate system (x, y, z) to the laboratory system (X, Y, Z) with the relation

$$Y^l_m(\theta,\ \varphi) = \sum_n T^l_{mn}(g)\, Y^l_n(\theta', \varphi'), \quad (2.37)$$

where g is the orientation of (x, y, z) relative to (X, Y, Z), which changes randomly with time, and $Y^l_n(\theta', \varphi')$ is a set of constant numbers in the system (x, y, z). Ordinarily the index l is equal to 1 or 2. For example, for infrared absorption and dielectric relaxation, associated with the correlation functions of a vector dipole moment, $l = 1$; for Rayleigh and Raman scattering of light, where the main part is played by correlation functions of the polarizability tensor of the molecule, $l = 2$.

The correlation functions K(t) of spherical harmonics are easily calculated from (1.28) both for rotational random walk with finite angle steps and for rotational

diffusion of the molecule. Using the distribution (2.26), we find that for the random-walk case

$$K(t) = (2l+1)^{-1} \exp[-(t/\tau)(1-\lambda_l)] \sum_m |Y_m^l(\theta', \varphi')|^2, \quad (2.38)$$

where τ is the time between two successive rotations. Thus the correlation time τ of the random function Y_m^l is given by the relation

$$\tau_l = \tau/(1-\lambda_l). \quad (2.39)$$

For rotational diffusion with $D_1 = D_2 = D_3 = D$, τ_l is given by

$$\tau_l = [l(l+1)D]^{-1}. \quad (2.40)$$

It follows that in the case of rotational diffusion the correlation between values of a tensor ($l = 2$) is lost three times as rapidly as that between values of a vector ($l = 1$), i.e., that

$$\tau_1/\tau_2 = 3. \quad (2.41)$$

If the molecule is subject to random rotations by finite angles, τ_1/τ_2 is in general less than three. For sharp turns through angles of the order of $2\pi/(2l+1)$ radians or more, the ratio is

$$\tau_1/\tau_2 = 1. \quad (2.42)$$

Thus, to determine the nature of the rotational Brownian motion of molecules (diffusion or sharp turns) it is necessary to work with two physical effects (if the molecules in question allow this). One effect must be determined by random changes of a vector ($l = 1$), the other by changes of a tensor ($l = 2$). The experimentally found value of τ_1/τ_2 must be close to 3 in the case of rotational diffusion and to 1 in the case of sharp turns. This is the essence of the method.

In the paper[12] to which we have referred studies were made of the Brownian rotation of nitrobenzene and camphor molecules in the solvents CS_2 and CCl_4. The value of τ_2 for the given molecules was determined from the experimental values of T_{1rot} by means of the theory of[8,40]. T_{1rot} was determined by measuring the relaxation time of the longitudinal magnetization of protons in a wide range of concentrations in the nonmagnetic CS_2 and weakly magnetic CCl_4 solvents, with subsequent extrapolation to zero concentration. With decreasing concentration of the given substance in the nonmagnetic solvent the intermolecular interactions between the given molecules decrease and the reaction rate T_1^{-1} is more and more determined by the intramolecular dipole interactions, perturbed by the Brownian rotational motion of the molecules. In the case of the solvent CCl_4 there is a small contribution to the total relaxation rate from intermolecular interactions between the molecules being studied and those of the solvent. Experiments and calculations show that in measurements by means of proton NMR this contribution can be neglected.

The correlation times of the constant dipole moments of nitrobenzene and camphor molecules dissolved in CS_2 and in CCl_4 were measured by the dielectric relaxation method in[41].

The values of τ_1 from[41] and τ_2 from[12] and of their ratio are shown in Table I.

Accordingly, we have as the experimental value of the ratio $\tau_1/\tau_2 = 3 \pm 0.5$. This obviously indicates that the rotational Brownian motion of nitrobenzene and camphor molecules in CS_2 and CCl_4 is of the rotational-diffusion type.

TABLE I

Substance studied	Solvent	$\tau_2 \times 10^{12}$, sec	$\frac{\tau_2 CS_2}{\tau_2 CCl_4} \cdot 10^{12}$, sec	$\frac{\tau_1 CS_2}{\tau_1 CCl_4}$	$\frac{\tau_1}{\tau_2}$
$C_{10}H_{16}O$	CS_2	2.12	7.5	0.7	3.5
	CCl_4	2.96	10.7		3.6
$C_6H_5NO_2$	CS_2	3.23	8.6	0.5	2.7
	CCl_4	6.04	15.2		2.5

d) Determination of the nature of rotational Brownian motion from comparative study of Rayleigh scattering of light and dielectric relaxation. Let us now turn to the results of the experimental determination of the nature of rotational Brownian motion as derived from the relaxation times of Rayleigh scattering and of dielectric relaxation.

The Rayleigh scattering of light in pure liquids is due to three causes: 1) density fluctuations at constant temperature; 2) temperature fluctuations at constant pressure; 3) fluctuations of the orientations of the molecules. In multicomponent liquids, in which we are not at the moment interested, local fluctuations of the concentrations of various components can play an important part. Since temperature fluctuations at constant pressure can be neglected,[42] in calculating the shapes and width of Rayleigh scattering lines in pure liquids one takes into account only density fluctuations at constant temperature and fluctuations of the orientations of the molecules. The most general theory of Rayleigh scattering is due to Rytov.[43] A detailed treatment of Rayleigh scattering by density fluctuations has also been given in[44]. We have given a calculation of the shape and width of a Rayleigh scattering line caused by fluctuations of molecular orientations in[6,7]. For the study of the nature of Brownian rotation we shall look at the theory of[6,7] in some detail.

The field E of the incident light wave induces in a molecule a dipole moment $\mu_i = \alpha_{ij}E_j$, which can be separated into parts independent of and dependent on the orientation of the molecule:

$$\mu_i^I = \alpha^I E_i, \quad \alpha^I = \frac{1}{3}\alpha_{ii}, \quad (2.43)$$

$$\mu_i^{II} = \alpha_{ij}^{II} E_j, \quad \alpha_{ij}^{II} = \alpha_{ij} - \alpha^I \delta_{ij}, \quad (2.44)$$

where α_{ij} is the polarizability tensor of the molecule, i, j = X, Y, Z. We are interested in the spectral composition of the light emitted by the components μ_i^{II}. The normalized spectral density of the radiation can be expressed as the Fourier component of the correlation function $K_{ii}(t)$ of the random function μ_i^{II}:

$$j_{ii}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(i\omega t) \frac{K_{ii}(t)}{K_{ii}(0)} dt, \quad K_{ii} = \langle \mu_i^{II}(0)\mu_i^{II}(t)\rangle. \quad (2.45)$$

Let us introduce the five independent components α_m of the tensor α_{ij} by the relations

$$\left. \begin{array}{l} \alpha_0 = (\sqrt{6}/2)\alpha_{ZZ}^{II}, \\ \alpha_{\pm 1} = \mp \alpha_{XZ}^{II} - i\alpha_{YZ}^{II}, \\ \alpha_{\pm 2} = (1/2)(\alpha_{XX}^{II} - \alpha_{YY}^{II}) \pm i\alpha_{XY}^{II}. \end{array} \right\} \quad (2.46)$$

When the coordinate system (X, Y, Z) is rotated into coincidence with the system (x, y, z) (by angles φ, θ, ψ) the components transform according to the law

$$\alpha_m = \sum_{n=-2}^{2} T_{mn}^2(\varphi, \theta, \psi)\alpha_n', \quad (2.47)$$

where the α_n' are defined in the movable system rigidly

connected with the molecule and are constants characterizing the molecules of the liquid.

If unpolarized light is incident along the X axis (one observes the light propagated in the direction of the Z axis), by using (2.46) and (2.47) we easily get

$$\mu_X^{II} = (1/2) \sum_n \alpha_n' [i E_Y (T_{-2n}^2 - T_{2n}^2) + E_Z (T_{-1n}^2 - T_{1n}^2)], \quad (2.48)$$

$$\mu_Y^{II} = (1/2) \sum_n \alpha_n' [-E_Y (T_{2n}^2 + T_{-2n}^2 + (2/\sqrt{6}) T_{0n}^2) + i E_Z (T_{-1n}^2 - T_{1n}^2)], \quad (2.49)$$

$$\mu_Z^{II} = (1/2) \sum_n \alpha_n' [i E_Y (T_{1n}^2 + T_{-1n}^2) + (4/\sqrt{6}) E_Z T_{0n}^2]. \quad (2.50)$$

Using the facts that $\langle E_Y^2 \rangle = \langle E_Z^2 \rangle$ and $\langle E_i E_j \rangle = 0$ for $i \neq j$, we can find from (2.48)–(2.50)

$$\langle | \mu_X^{II} |^2 \rangle = (1/5) \langle E_Y^2 \rangle \sum_n |\alpha_n'|^2 = (2/15) \langle E_Y^2 \rangle g_\alpha^2,$$

$$\langle | \mu_Y^{II} |^2 \rangle = \langle | \mu_Z^{II} |^2 \rangle = (7/30) \langle E_Y^2 \rangle \sum_n |\alpha_n'|^2 = (7/45) \langle E_Y^2 \rangle g_\alpha^2,$$

$$g_\alpha^2 = (1/2) [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 (\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)].$$

The correlation functions $K_{jj}(t)$ of the quantities $\mu_j^{II}(t)$ are calculated from Eqs. (1.27) and (1.28). The result is $(D_1 \neq D_2 \neq D_3 \neq D_1)$

$$K_{XX}(t) = \langle | \mu_X^{II} |^2 \rangle \sum |\Omega_n^\alpha|^2 \exp(-D_{m,n}^{(2)} |t| - i\omega_0 t),$$

$$j_{XX}^{II}(\Delta\omega) = \sum_n |\Omega_n^\alpha|^2 \rho(D_{m,n}^{(2)}) = j_{YY}^{II}(\Delta\omega),$$

$$|\Omega_{-2}^\alpha|^2 = \frac{3}{4} \frac{|\alpha_2 - \alpha_{-2}|^2}{g_\alpha^2} = 3 \frac{\alpha_{xy}^2}{g_\alpha^2}, \quad |\Omega_{-1}^\alpha|^2 = \frac{3}{4} \frac{|\alpha_1 - \alpha_{-1}|^2}{g_\alpha^2} = 3 \frac{\alpha_{xy}^2}{g_\alpha^2},$$

$$|\Omega_0^\alpha|^2 = \frac{3}{4} \frac{|\alpha_1 + \alpha_{-1}|^2}{g_\alpha^2} = 3 \frac{\alpha_{yz}^2}{g_\alpha^2}, \quad (2.51)$$

$$|\Omega_{1,2}^\alpha|^2 = \frac{3}{4 g_\alpha^2} \left| \sqrt{\frac{c_\pm}{4 g_D}} (\alpha_2 + \alpha_{-2}) \mp \sqrt{\frac{c_\mp}{2 g_D}} \alpha_0 \right|^2$$

$$= \frac{3}{4 g_\alpha^2} \left| \sqrt{\frac{c_\pm}{4 g_D}} (\alpha_{xx} - \alpha_{yy}) \mp \sqrt{\frac{c_\mp}{2 g_D}} \frac{\sqrt{6}}{2} \alpha_{yy} \right|^2,$$

$$\sum_n |\Omega_n^\alpha|^2 = 1,$$

$$\rho(D_{m,n}^{(2)}) = \frac{D_{m,n}^{(2)}}{\pi (D_{m,n}^{(2)2} + \Delta\omega^2)},$$

where $\Delta\omega$ is the frequency shift from the frequency ω_0 of the incident light.

As can be seen from (2.51), the shape of the Rayleigh line is the superposition of five Lorentz curves with widths $D_{m,n}^{(2)}$ and weights $|\Omega_n|^2$.

In the case with $D_1 = D_2$ the calculation of the spectral density must be done by using the Green's function (1.25).

The result is

$$|\Omega_2^s|^2 = |\Omega_{-2}^s|^2 = \frac{3}{2} \frac{|\alpha_2'|^2}{g_\alpha^2} = \frac{3}{2} \frac{\left[\alpha_{xy}^2 + \frac{1}{4}(\alpha_{xx} - \alpha_{yy})^2\right]}{g_\alpha^2},$$

$$|\Omega_1^s|^2 = |\Omega_{-1}^s|^2 = \frac{3}{2} \frac{|\alpha_1'|^2}{g_\alpha^2} = \frac{3}{2} \frac{\alpha_{xz}^2 + \alpha_{yz}^2}{g_\alpha^2}, \quad \Big\} \quad (2.52)$$

$$|\Omega_0^s|^2 = \frac{3}{2} \frac{|\alpha_0'|^2}{g_\alpha^2} = \frac{9}{4} \frac{\alpha_{zz}^2}{g_\alpha^2}, \quad \sum_n |\Omega_n^s|^2 = 1;$$

$$D_{m,2}^{(2)s} = D_{m,-2}^{(2)s} = 2D_1 + 4D_3, \quad D_{m,1}^{(2)s} = D_{m,-1}^{(2)s} = 5D_1 + D_3, \quad D_{m,0}^{(2)s} = 6D_1. \quad (2.53)$$

Accordingly, in the case $D_1 = D_2$ the shape of the Rayleigh line is the superposition of three Lorentz curves with the widths (2.53) and the weights (2.52).

In the special case with $D_1 = D_2 = D_3 = D$ we have $(D_{m,n}^{(2)} = 6D)$

$$j^{II}(\Delta\omega) = \rho(6D) = \tau_2/\pi [1 + (\tau_2 \Delta\omega)^2], \quad (2.54)$$

where $\tau_2 = 1/(6D)$.

It is easily verified that the Brownian rotation of the molecules is of the nature of isotropic random walks

through finite angles, then the spectral density of the Rayleigh line is still of the Lorentz form (2.54), but the time τ_2 must then be taken to mean the average time τ between two successive rotations.

Obviously all of these formulas are equally applicable to Raman scattering lines, if α_{ij} is replaced by $\partial_{ij}/\partial Q_v$ (Q_v are the vibrational normal coordinates of the molecule).

As we have already ascertained, the dielectric relaxation time τ_1 is equal to $3\tau_2$ in the case of rotational diffusion; in the case of sharp turns $\tau_1 = \tau_2$. From this there follows the possibility, mentioned in Sec. c) of this chapter, of determining the nature of the rotational Brownian motion by comparing the experimental dielectric relaxation time τ_1 with the time τ_2 given by the inverse halfwidth of the Rayleigh scattering line. It must be emphasized that the theoretical conclusion about the ratio of the times τ_1 and τ_2 is valid only if the changes with time of the dipole moment and of the polarizability tensor are determined by the same rotational motion. For example, molecules in which an internal rotation exists may not satisfy this requirement.

A convenient material for the study of Brownian rotation by this method is the liquid polyethylene glycols. As is well known, the molecules of these liquids are linear and the polarizability tensor is uniaxial. Experimental data on the Rayleigh scattering of light by three polyethylene glycols are reported in[13]. The dielectric relaxation times needed for calculating the ratio τ_1/τ_2 (or τ_2/τ_1) are given in[45,46]. The measured values of the ratio τ_2/τ_1 for n-octanol, 1,3 butanediol, and glycerine are respectively 0.3, 0.54, and 1.1. From this it follows that in n-octanol the Brownian rotation is of diffusive nature, and in glycerine it is sharp turns through angles of the order of 120°. In the case of 1,3 butanediol the Brownian rotation is of intermediate character between those of the other two substances. According to our formulas given in Sec. c) of this chapter, we can determine the angles of the elementary rotations from the measured values of τ_1 and τ_2. For n-octanol these angles are smaller than 20°, and for butanediol they are about 45°.

The authors of[13] make a bold assumption about the nature of the parameter τ, which we have introduced in solving the problem of rotational random walk. They suppose that the time τ, i.e., the time between two successive rotations of the molecule, is the same as the time of volume or structural relaxation $\tau_{V,P}$, as measured by the ultrasonic method at constant pressure.[46] This identification seems fairly well justified, since the time between two successive rotations is essentially the same as the correlation time of the free volume of the molecule, and this last can reasonably be identified with $\tau_{V,P}$.

The assumption that τ and $\tau_{V,P}$ are equal can be tested experimentally on the basis of the following considerations. The correlation time (2.39) of a tensor of rank l, calculated in the Egelstaff approximation (2.20) with use of the relation $\tau = \tau_{V,P}$, is of the form

$$1/\tau_l = l(l+1) D_r/[1 + l(l+1) D_r \tau_{V,P}], \quad (2.55)$$

where $D_r = \langle \epsilon^2 \rangle / 6\tau$. Writing Eq. (2.55) for $l = 1$ and $l = 2$ and eliminating D_r from the resulting equations, we find

$$\tau_2/\tau_1 = (2\tau_{V,P}/3\tau_1) + (1/3). \quad (2.56)$$

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TABLE II

Liquid	$\dfrac{\tau_2}{\tau_1}$ calculated	$\dfrac{\tau_2}{\tau_1}$ measured	$\dfrac{\tau_1}{\tau_{V,P}}$
n-octanol	0.35	0.3	40
1, 3-butanediol	0.48	0.54	4.3
Glycerine	0.78	1.1	1.5

Accordingly, we can either, as we already know, find the ratio τ_2/τ_1 directly from measurements of dielectric relaxation and Rayleigh scattering, or else calculate it from (2.56), after first measuring $\tau_{V,P}/\tau_1$. Agreement of the calculated and measured values of τ_2/τ_1 will give an indication as to the correctness of the assumption that τ and $\tau_{V,P}$ are equal.

Table II shows the measured values of $\tau_1/\tau_{V,P}$, and also the calculated and measured values of τ_2/τ_1 for polyethylene glycols. It is seen that the agreement between the calculated and measured values of τ_2/τ_1 is good for n-octanol and 1,3 butanediol, and is fairly satisfactory for glycerine. Accordingly, we can say that the experimental test on the whole indicates that the assumption $\tau = \tau_{V,P}$ is reasonable.

We point out one further interesting fact that follows from Eq. (2.56). We have so far used the ratio τ_1/τ_2 (or τ_2/τ_1) as a criterion for determining the nature of rotational Brownian motion, but according to (2.56) the ratio $\tau_1/\tau_{V,P}$ can also serve as such a criterion. Rotational diffusion is characterized by large values of $\tau_1/\tau_{V,P}$ ($\tau_1/\tau_{V,P} \gg 1$). For rotational random walk by angles of the order of 120° or more $\tau_1 = \tau_{V,P}$.

e) <u>Cooperative effects in Brownian motion.</u> In dealing with physical phenomena in liquids correlation effects in the Brownian rotation of different molecules have not been considered. If, however, there actually are such correlations, it may be impermissible to neglect them in some cases. There are great difficulties in constructing a theory of Rayleigh (and Raman) scattering with cooperative effects taken into account. Nevertheless one can use semiqualitative arguments to predict the main results of such a theory.

For simplicity let us consider molecules whose polarizability tensor can be represented by an ellipsoid of rotation. We take the axis of symmetry of the ellipsoid as the z axis of the moving coordinate system. If for the m-th molecule we denote the angle between the z and Z axes by θ_m, it is easily shown[13,38] that the spectral density $I(\omega)$ of the depolarized Rayleigh scattering line can be represented in the form

$$I(\omega) \sim \mathrm{Re} \int \left\langle \sum P_2(\cos\theta_m(t)) \, P_2(\cos\theta_n(0)) \right\rangle \exp(-i\omega t)\, dt, \quad (2.57)$$

where $P_2(\cos\theta)$ is the second-degree Legendre polynomial.

The exact calculation of the average in (2.57) cannot at present be done, since it requires a knowledge of the conditional probability density of the orientations of the interacting molecules of the ensemble. For this reason it is interesting to use a simple hypothetical model of cooperative Brownian rotation proposed by Egelstaff.[38]

Assume that some fixed pair of molecules rotates according to the scheme

$$\left.\begin{array}{l} \theta_1(t) = \theta_1(0), \\ \theta_2(t) = \theta_2(0), \end{array}\right\} \quad 2nt_1 \leqslant t \leqslant (2n+1)\,t_1, \quad n = 0, 1, 2, \ldots,$$

$$\left.\begin{array}{l} \theta_1(t) = \theta_2(0), \\ \theta_2(t) = \theta_1(0), \end{array}\right\} \quad (2n+1)\,t_1 < t \leqslant (2n+2)\,t_1, \quad n = 0, 1, 2, \ldots$$

This means that the chosen pair of molecules interchange their orientations after each time interval of duration t_1. In particular, during the time interval from 0 to t_1 the orientation of the first molecule is $\theta_1(0)$ and that of the second is $\theta_2(0)$; in the interval from t_1 to $2t_1$ that of the first is $\theta_2(0)$ and that of the second is $\theta_1(0)$. To generalize this scheme one can assume that after interchanging orientations with the second molecule the first molecule at time $2t_1$ interchanges orientations with a third molecule, and so on.

It is easy to see from (2.57) that this scheme, with the indicated generalization, leads to a spectral density of the form $I(\omega) \sim \delta(\omega)$. If in this case one were to use instead of (2.57) the simplified expression (2.45), one would find that the Rayleigh line has a width $\sim 1/t_1$. Thus inclusion of cooperative effects has led to a narrowing of the Rayleigh line. A similar conclusion could be reached about the Raman scattering lines.

It must be noted that this simple model of cooperative Brownian rotation is too simple and could not be actually realized in a pure form. Nevertheless we can expect that cooperative effects accompanied by exchange of orientations exist in certain systems and have a considerable influence on the shape and widths of observed Rayleigh and Raman scattering lines. For example, Egelstaff[38] has convincingly shown the presence of cooperative effects in a plastic modification of cyclohexane, by making comparisons between Rayleigh and Raman scattering of light and the incoherent scattering of slow neutrons. This research was essentially as follows.

The incoherent scattering of slow neutrons, caused by the rotational motion of molecules, is decidedly different from the scattering of light. The de Broglie wavelength of slow neutrons ($\lambda \approx 4$ Å) is comparable in order of magnitude with atomic dimensions. Owing to this the scattering of neutrons reflects the individual character of the Brownian rotational motion of the molecules. Mathematically this means that the differential scattering cross section $d^2\sigma/d\Omega\,d\omega$, which is the essential characteristic of neutron scattering, can be expressed in terms of correlation functions $\langle P_l(\cos\theta(t))\, P_l(\cos\theta(0))\rangle$ depending on the random rotations of individual molecules.[38,47]

Egelstaff calculates the correlation functions $\langle P_l(\cos\theta(t))\, P_l(\cos\theta(0))\rangle$ for various types of Brownian rotation of the individual molecule. In this way he finds the differential cross section both for rotational diffusion of the molecules and for rotational random walk by large angles (in the latter case he uses the solution of the rotational random walk problem given in Sec. (b) of this chapter). Comparison of the calculated differential cross sections with the experimental values gives the correlation times τ_2 corresponding to the different types of Brownian motion. It turns out that for any assumed mechanism of the individual molecular rotational motions the value of τ_2^{-1} is an order of magnitude larger than the width of the depolarization Rayleigh scattering line. This can be explained by assuming that in plastic cyclohexane the Brownian rotation of the molecules is of a cooperative nature, of the type of interchange of orientations. Namely, as we have seen, the presence of orientation exchange narrows the Rayleigh (or Raman) scattering line, but does not affect the scattering of slow neutrons. It can also be said that when there are cooper-

ative effects of the orientation-exchange type the "memory" (correlation time) of an individual rotating molecule will in general be shorter than that of a collective of rotating molecules. This last result can scarcely be regarded as obvious.

3. INERTIAL EFFECTS IN ROTATIONAL BROWNIAN MOTION

a) The generalized equation of rotational diffusion. As was already indicated in Sec. (a) of Chap. 2, for small time intervals ($\xi_i t \ll I$) the ordinary rotational diffusion equation (1.6) is without meaning. For small ξ_i such intervals can be quite large, so that the interpretation of physical phenomena in liquids on the basis of the rotational diffusion equation (1.6) can be incorrect. The reason that the theory of rotational diffusion developed in Chap. 1 is invalid for small t is that the fundamental equation (1.6) does not include the inertial characteristics of the molecules. In fact, for small time intervals the rotation of a molecule is practically determined by its inertia. The smaller the friction coefficient, the closer the rotation is to a free motion. Neglect of the inertial effects in the rotational motion of a molecule leads to the nonanalyticity of the correlation functions K(t) at t = 0. As we have seen in Sec. (d) of Chap. 2, the K(t) calculated on the basis of the distribution of orientations (1.26) have an exponential time dependence. From the physical point of view it is hard to explain the existence of a discontinuity of the derivative of a K(t) at t = 0.

A theory of rotational Brownian motion including inertial effects has been constructed by Steele.[14] For the desired probability distribution of the orientations Steele writes the equation of continuity

$$\partial P/\partial t = \nabla_\varepsilon J.$$ (3.1)

Under rather general assumptions the current density J can be written in the form[48,49]

$$J = R\nabla_\varepsilon P,$$ (3.2)

$$R_{ij}(t) = \int_0^t \langle \omega_i(0)\,\omega_j(t)\rangle\,dt;$$ (3.3)

here, as in the previous sections, ω_i are the components of the angular velocity along the moving axes. For R_{ij} we find from (1.35)

$$R_{ij}(t) = (kT/\xi_i)\,[1 - \exp(-\xi_i t/I)]\,\delta_{ij}.$$ (3.4)

From this we get the generalized rotational diffusion equation

$$\partial P/\partial t = \sum_i R_{ii}(t)\,\partial^2 P/\partial \varepsilon_i^2.$$ (3.5)

For $\xi_i t/I \gg 1$ Eq. (3.5) goes over into the ordinary rotational diffusion equation

$$\partial P/\partial t = \sum_i (kT/\xi_i)\,\partial^2 P/\partial \varepsilon_i^2,$$ (3.6)

where $kT/\xi_i = D$ give the components of the diffusion tensor. The solution of this equation in terms of Euler angles has already been treated in Sec. (b) of Chap. 1.

The solution of Eq. (3.5) for arbitrary t is derived on the assumption $\xi_x = \xi_y$ (the case of unequal ξ_i leads to difficulties and therefore will not be considered). Changing to Euler angles in (3.5) and using $\xi_x = \xi_y$, we have

$$\frac{\partial P}{\partial t} = R_{xx}(t)\left[\frac{\partial^2 P}{\partial \theta^2} + \mathrm{ctg}\,\theta\,\frac{\partial P}{\partial \theta} + \mathrm{cosec}^2\,\theta\,\frac{\partial^2 P}{\partial \varphi^2}\right.$$
$$\left. + \left(\mathrm{ctg}^2\,\theta + \frac{R_{zz}(t)}{R_{xx}(t)}\right)\frac{\partial^2 P}{\partial \psi^2} - 2\cos\theta\,\mathrm{cosec}\,\theta\,\frac{\partial^2 P}{\partial \varphi\,\partial \psi}\right].$$ (3.7)

We look for the solution of (3.7) as a series in generalized spherical functions:

$$P = \sum_{l,\,m,\,n} C_{mn}^l(t)\,T_{mn}^l(\varphi, 0, \psi).$$ (3.8)

On substituting (3.8) in (3.7) we find that the $C_{mn}^l(t)$ are of the form

$$C_{mn}^l(t) = a_{mn}^l D_{l,\,n}(t),$$ (3.9)

where the $D_{l,n}$ satisfy the equation

$$\partial \ln D_{l,\,n}(t)/\partial t = \Gamma_{l,\,n} R_{xx}(t) - n^2 R_{zz}(t);$$ (3.10)

here $\Gamma_{l,n} = n^2 - l(l+1)$. Solving (3.10), we easily find

$$D_{l,\,n} = \exp\left\{[n^2 - l(l+1)]\frac{IkT}{\xi_x^2}\left[\frac{\xi_x t}{I} - \exp\left(-\frac{\xi_x t}{I}\right) - 1\right]\right.$$
$$\left. - n^2\frac{IkT}{\xi_x^2}\left[\frac{\xi_z t}{I} + \exp\left(-\frac{\xi_z t}{I}\right) - 1\right]\right\}.$$ (3.11)

As was to be expected, for $\xi_i t/I \gg 1$, the $D_{l,n}(t)$ have exponential time dependence. For $\xi_i t/I \ll 1$, however, $D_{l,n}$ takes a Gaussian form:

$$\lim_{\xi_i t/I \to 0} D_{l,\,n}(t) = \exp\left[-\frac{1}{2}l(l+1)\frac{kT}{I}t^2\right].$$ (3.12)

The desired solution of the problem is obtained from (3.8), (3.9), and (3.11). The coefficients a_{mn}^l are determined from the given initial distribution. To obtain the Green's function of the equation (3.7) the initial condition must be taken as a δ function, as in Sec. (b) of Chap. 1.

Since we shall be discussing the influence of inertial effects on nuclear magnetic relaxation and dielectric relaxation, we give the correlation functions

$$K_{(l)}^{(m)} = \langle Y_l^m(\beta(t), \alpha(t))\,Y_l^m(\beta(0), \alpha(0))\rangle.$$ (3.13)

as calculated from (3.8). The angles β and α in (3.13) characterize the direction of some vector rigidly connected with the molecule relative to the laboratory coordinate system. For dielectric relaxation this vector is the dipole moment, and for NMR it is the vector drawn between a pair of spins in the molecule. Let the vector in question make the angle η with the z axis of the molecular (moving) coordinate system. According to the calculations of Steele[50] we have

$$K_{(1)}^{(0)}(t) = \cos^2\eta\exp(-2h_x) + \sin^2\eta\exp[-(h_x + h_z)],$$ (3.14)

$$K_{(2)}^{(m)}(t) = \left(1 - \frac{3}{2}\sin^2\eta\right)^2\exp(-6h_x) +$$
$$+ \frac{3}{4}\sin^2 2\eta\exp[-(5h_x + h_z)] + \frac{3}{4}\sin^4\eta\exp[-(2h_x + 4h_z)],$$ (3.15)

where

$$h_i = (IkT/\xi_i^2)\,[(\xi_i t/I) + \exp(-\xi_i t/I) - 1].$$ (3.16)

Since this theory holds for a molecule of the spherical-top type, the moving coordinate system can be chosen so that the vector under consideration is along the z axis, and we can set $\eta = 0$ in (3.14) and (3.15). For $\eta = 0$ and small ξ we get from (3.14) and (3.15) correlation functions of Gaussian form

$$K_{(1)}^{(0)} = \exp(-\tau^{*2}),$$ (3.17)

$$K_{(2)}^{(m)} = \exp(-3\tau^{*2}),$$ (3.18)

where $\tau^* = t(kT/I)^{1/2}$. Equations (3.17) and (3.18) are an important result of Steele's theory. A further investigation is required to find the limits of validity of these formulas. It turns out that (3.17) and (3.18) do not hold

for large ξ_j, as is evident from their derivation, and for small values of $\xi_j^* = \xi_j/(IkT)^{1/2}$, namely for $0 \le \xi_j^* \le \frac{1}{2}$. In fact, for sufficiently small ξ_j^* the rotation of the molecule will be "almost free", and it is completely free for $\xi_j^* = 0$. "Almost free" rotation is characterized by the fact that during the correlation time—the time in which there is a radical change of the correlation functions $K_{(1)}^{(0)}(t)$ and $K_{(2)}^{(m)}(t)$—the molecule can make one or more complete revolutions. For completely free rotation ($\xi_j^* = 0$) the correlation times become infinitely large. Under such conditions (i.e., for $\xi_j^* = 0$), as we know, Eq. (3.1) cannot be used for the probability distribution function of the orientations. The correlation functions calculated for the laws of free rotation[50] are of the form

$$K_{(1)}^{(0)}(t) = (2/3)(1-\tau^{*2})\exp(-\tau^{*2}/2) + (1/3), \tag{3.19}$$

$$K_{(2)}^{(m)}(t) = (2/5)(1-4\tau^{*2})\exp(-2\tau^{*2}) + $$
$$+ (2/5)(1-\tau^{*2})\exp(-\tau^{*2}/2) + (1/5). \tag{3.20}$$

The Gaussian approximation and the approximation of free rotation practically coincide for $t < (kT/I)^{1/2}$. Accordingly, the Gaussian correlation functions (3.17) and (3.18), derived from (3.14) and (3.15) by passage to the limit $\xi_j^* \to 0$, become completely invalid for sufficiently small ξ_j^* ($0 \le \xi_j^* \le \frac{1}{2}$). According to Steele's estimates, the region of values of ξ_j^* for which the Gaussian form is a good approximation is defined by the inequality $\frac{1}{2} \le \xi_j^* \le 2$. Thus as ξ_j^* varies from sufficiently large values ($\xi_j^* > 2$) to zero the shape of the correlation functions $K_{(1)}^{(0)}$ and $K_{(2)}^{(m)}$ changes continuously from exponential (for $\xi_j^* > 2$) to Gaussian ($\frac{1}{2} \le \xi_j^* \le 2$) and from Gaussian to the form (3.19), (3.20) for free rotation ($\xi_j^* = 0$).

It can easily be verified that the integral $\int_0^\infty K_{(2)}^{(m)}(t)\,dt$ takes a minimum value when $K_{(2)}^{(m)}(t)$ has the Gaussian form (i.e., when $\frac{1}{2} < \xi_j^* < 2$). As we shall see in the following section, this property plays an important part in the interpretation of experiments on NMR in liquids.

b) Inertial effects in NMR, dielectric relaxation, and the molecular scattering of light. In the fundamental paper by Bloembergen, Purcell, and Pound[51] and in many subsequent papers nuclear magnetic relaxation was interpreted on the basis of rotational and translational diffusion. The best agreement between measured and calculated nuclear magnetic relaxation times T_i was found for polar liquids, in particular for water. In the case of nonpolar liquids the theoretical values of T_1 deviate from the experimental values rather strongly. On the basis of Steele's theoretical work,[14,50] Moniz, Steele, and Dixon[52] have shown that in many cases these deviations can be overcome if in calculating T_1 one takes into account the inertial effects in the rotational Brownian motion of the molecules.

According to[51-53] the inverse nuclear magnetic relaxation time T_1^{-1} in a liquid is composed of two parts; one part, $(1/T_1)_{rot}$, is due to intramolecular dipole-dipole interactions of the spins, modulated by the rotational Brownian motion of the molecules, and the second part, $(1/T_1)_{trans}$, is due to the modulation of the intermolecular dipole interactions of spins by the translational Brownian motion, so that

$$1/T_1 = (1/T_1)_{rot} + (1/T_1)_{trans}. \tag{3.21}$$

Under conditions of strong narrowing $(1/T_1)_{trans}$ for $I = \frac{1}{2}$ (I is the nuclear spin) is given by[51-53]

$$(1/T_1)_{trans} = \pi\gamma^4\hbar^2\rho/4aD, \tag{3.22}$$

where γ is the gyromagnetic ratio, ρ is the density of nuclear spins, a is the radius of the molecule, and D is the translational diffusion coefficient. Assuming that for translational Brownian motion D and the viscosity η of the liquid are connected by the Stokes-Einstein relation

$$D = kT/6\pi a\eta, \tag{3.23}$$

we get from (3.22)

$$(1/T_1)_{trans} = 3\pi^2\gamma^4\hbar^2\rho\eta/2kT. \tag{3.24}$$

The formula for the intramolecular contribution to $1/T_2$ is[51-53]

$$(1/T_1)_{trans} = (3\gamma^4\hbar^2/20b^6)\,[J_{(2)}^{(1)}(\omega_n) + 4J_{(2)}^{(2)}(2\omega_n)], \tag{3.25}$$

where ω_n is the Larmor frequency, b is the distance between the pair of spins in the molecule, and $J_{(l)}^{(m)}(\omega_n)$ is the Fourier transform of the correlation function $K_{(l)}^{(m)}(t)$. Using the fact that $K_{(l)}^{(m)}(t)$ does not actually depend on m, for the strong narrowing case we can reduce (3.25) to the form

$$(1/T_1)_{rot} = (3\gamma^4\hbar^2/4b^6)\,J_{(2)}^{(m)}(0). \tag{3.26}$$

Calculations based on the assumption that the Brownian rotation of the molecule is of the simple diffusion type give for $J_{(2)}^{(m)}$

$$J_{(2)}^{(m)}(0) = \xi/3kT, \tag{3.27}$$

where ξ is the friction coefficient calculated by the hydrodynamic method ($\xi = 8\pi\eta a^3$).

Moniz, Steele, and Dixon[52] have pointed out that for most nonpolar liquids the nuclear relaxation times T_1 calculated from (3.21), (3.24), and (3.26) are much shorter than the observed times. This indicates that the assumed relaxation mechanism is "too effective." We can look for the source of the error in the theoretical calculations on the basis of the following considerations. The values of T_{1trans} calculated from (3.24) are rarely smaller than the observed values of T_1. On the other hand, the T_{1rot} calculated from (3.26) is almost always much shorter (by a factor 10 or more) than the measured T_1. It follows that the discrepancy between the theoretical and experimental values is due to an incorrect estimate of T_{1rot}. It is intuitively evident that the theoretical T_{1rot} must increase (and thus come closer to the experimental value) if one takes into account the inertial effects in the Brownian rotation. In fact, in the limiting case of free rotation with some fixed angular velocity the relaxation time is infinite. Therefore we can expect that inclusion of inertial effects in the rotational Brownian motion will in general lead to an increase of T_{1rot}. We now look at the quantitative relations.

The Fourier transform of an even correlation function $K_{(l)}^{(m)}(t)$ is of the form

$$J_{(l)}^{(m)}(\omega_n) = 2\int_0^\infty \cos(\omega_n t)\,K_{(l)}^{(m)}(t)\,dt. \tag{3.28}$$

We see that for the calculation of $(1/T_1)_{rot}$ we need the $J_{(l)}^{(m)}(\omega_n)$ with $l = 2$ and $m = 1, 2$. Under conditions of
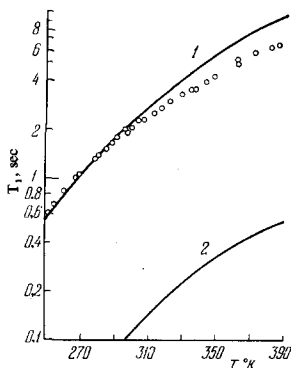
FIG. 1. Temperature dependence of the spin-lattice relaxation time of cis-decalene. The curves are the theoretical dependences found with (1) and without (2) inclusion of inertial effects.

rapid motion, when ω_n^{-1} is much larger than the characteristic time for decrease of $K_{(2)}^{(m)'}(t)$, $J_{(2)}^{(m)}$ is simply twice the "area" under the curve of $K_{(2)}^{(m)'}(t)$ for change of t from 0 to ∞: $J_{(2)}^{(m)} = 2S$, where

$$S = \int_0^\infty K_{(2)}^{(m)}(t)\, dt. \qquad (3.29)$$

As was shown in Sec. (a), the form of the time dependence of $K_{(2)}^{(m)}$ is determined by the nature of the Brownian rotation. The nature of the molecule's rotation in turn depends strongly on the friction coefficient ξ (we recall that we are discussing spherical-top molecules with a scalar friction coefficient). Thus S, and also $(1/T_1)_{rot}$, is a function of ξ. The calculations show that $S(\xi)$ takes its minimum value when ξ is in the region defined by the inequality $\frac{1}{4} < \xi/(IkT)^{1/2} < 2$, and that the minimum value of S is the value calculated in the Gaussian approximation (3.18). The time T_{1rot} corresponding to the Gaussian approximation is the largest:

$$(1/T_1)_{rot}^{Gauss} = (3\gamma^4\hbar^2/4b^6)\,(\pi I/3kT)^{1/2}. \qquad (3.30)$$

Equation (3.30) can also be applied to molecules of the asymmetric-top type, if we take I to mean an average moment of inertia defined by

$$\bar{I}^{-1} = (I_x^{-1} + I_y^{-1} + I_z^{-1})/3, \qquad (3.31)$$

where I_x, I_y, I_z are the principal moments of inertia.

For a number of nonpolar liquids Moniz, Steele, and Dixon have experimentally and theoretically studied the temperature dependence of T_1. The contribution to T_1 from the translational Brownian motion was calculated from (3.24). The agreement between measured and calculated values of T_1 as functions of the temperature is very good if the rotational contribution to T_1 is calculated with inertial effects included from (3.30), and is bad if one uses the formula (3.27) of Bloembergen, Purcell, and Pound to calculate T_{1rot}. As an example, Fig. 1 shows the experimental (circles) and theoretical temperature dependences of the spin-lattice relaxation time for cis-decalene.

Let us now discuss the role of inertial effects in dielectric relaxation. In the first theory of dielectric relaxation,[3,31] given by Debye on the basis of rotational diffusion, there are two essential difficulties. First, Debye assumes that the polarization of a dipole liquid in a constant field approaches the equilibrium value according to an exponential law. This assumption is actually equivalent to requiring that for a sharp change of the field the angular velocities of the molecules change instantaneously. The finite masses of the molecules make this requirement unrealistic. Second, Debye's formulas predict a constant nonvanishing absorption at high frequencies. It is well known, however, that the dielectric

relaxation absorption observed in the radio region is absent for visible light. Theories of dielectric relaxation[54-59] which take into account the influence of inertial effects are free from these shortcomings, although quantitatively they too lead to large disagreements with the experiments. We shall here discuss inertial effects in dielectric relaxation, following mainly a paper by Birnbaum and Cohen[60]. According to[60], the imaginary part of the complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$ is of the form

$$\epsilon''(\omega) = \frac{8\pi n}{3\hbar^2}\langle\mu(0)\mu(0)\rangle\,\mathrm{th}\left(\frac{\hbar\omega}{2kT}\right)\int_0^\infty \varphi(t)\cos\omega t\,dt, \qquad (3.32)$$

where n is the index of refraction and φ is the quantum-mechanical correlation function of the dipole moment, defined as

$$\varphi(t) = (1/2)\langle\mu(0)\mu(t)+\mu(t)\mu(0)\rangle/\langle\mu(0)\mu(0)\rangle. \qquad (3.33)$$

In (3.32) and (3.33) μ denotes the dipole moment operator. The real part of the complex dielectric constant can be found from the Kramers-Kronig relation

$$\epsilon'(\omega) - \epsilon_\infty = \pi^{-1}\mathcal{P}\int_{-\infty}^\infty \frac{\epsilon''(\omega)\,d\omega}{\omega'-\omega}. \qquad (3.34)$$

In the classical approximation ordinarily used for polar liquids, φ is of the form

$$\varphi(t) = \langle\mu(0)\mu(t)\rangle/\langle\mu(0)\mu(0)\rangle; \qquad (3.35)$$

where $\mu(t)$ is the classical dipole moment. Accordingly, in the classical approximation $\epsilon^*(\omega)$ satisfies the relation

$$[\epsilon^*(\omega) - \epsilon_\infty]/(\epsilon_0 - \epsilon_\infty) = L(-\dot\varphi) \equiv 1 - i\omega\int_0^\infty \varphi(t)\,e^{-i\omega t}dt. \qquad (3.36)$$

In (3.34), (3.36) ϵ_∞ and ϵ_0 are the dielectric constants in the respective limits of very large and very small frequencies.

We note that in (3.32) and (3.36) the reactive field has not been included. When it is taken into account (3.36) takes the form

$$(\epsilon^* - \epsilon_\infty)/(\epsilon_0 - \epsilon_\infty) = (2\epsilon_0 + \epsilon_\infty)\{\epsilon_0 - \epsilon_\infty + [3\epsilon_0/L(-\dot\varphi)]\}^{-1}. \qquad (3.37)$$

In our case $\hbar\omega \ll 2kT$, so that for $\epsilon_0 - \epsilon_\infty$ we have the approximation

$$\epsilon_0 - \epsilon_\infty = 4\pi\mu^2/3kT. \qquad (3.38)$$

We now proceed, following[60], to find $\varphi(t)$ for molecules of the spherical-top type with a scalar friction coefficient ξ. We first note that for sufficiently long time intervals t inertial effects do not affect $\varphi(t)$, which, according to the general theory (see Sec. (a)), must decrease exponentially with the time:

$$\varphi = \exp(-t/\tau_1), \qquad (3.39)$$

where $\tau_1 = \xi/2kT$. We can find the form of $\varphi(t)$ for small t by expanding it in a Taylor's series

$$\varphi(t) = \sum_{n=0}^\infty \frac{t^n}{n!}\varphi^{(n)}(0), \qquad (3.40)$$

where

$$\varphi^{(n)}(0) = \frac{d^n\varphi(0)}{dt^n} = \frac{\langle\mu(0)\mu^{(n)}(0)\rangle}{\langle\mu(0)\mu(0)\rangle}. \qquad (3.41)$$

For a system in thermal equilibrium $\langle A(t)B(t)\rangle$ is independent of t, and consequently $\langle A\dot B\rangle = -\langle\dot A B\rangle$. Applying this equation to (3.41), we get

$$\varphi^{(2n-1)}(0) = 0,$$

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$$\varphi^{(2n)}(0) = i^{2n} \langle |\mu^{(n)}(0)|^2 \rangle / \langle |\mu(0)|^2 \rangle. \qquad (3.42)$$

Dropping terms beyond the second power of t in (3.40) and using (3.41) and (3.42), we get

$$\varphi(t) = 1 + (1/2) t^2 \varphi^{(2)}(0) + \dots =$$
$$= 1 - (1/2) t^2 [\langle |\mu^{(1)}(0)|^2 \rangle / \langle |\mu(0)|^2 \rangle] + \dots \qquad (3.43)$$

According to Birnbaum and Cohen, for arbitrary t the correlation function $\varphi(t)$ is approximated by the function

$$\varphi(t) = \exp\{\delta - [\delta^2 + (t/\tau_1)^2]\}^{1/2}, \qquad (3.44)$$

where δ is a parameter chosen so that for small t Eq. (3.44) goes over into (3.43), i.e.,

$$(\tau_1^2 \delta)^{-1} = \langle |\mu^{(1)}(0)|^2 \rangle / \langle |\mu(0)|^2 \rangle. \qquad (3.45)$$

For large t (3.44) obviously agrees with (3.39). To see the physical meaning of the parameter δ, we compare $\varphi(t)$ for small times with the correlation function obtained by Steele. For $l = 1$ we have from (3.41)

$$\varphi(t) = 1 - (1/2) t^2 (2kT/I) + \dots \qquad (3.46)$$

On the other hand, we find from (3.44)

$$\varphi(t) = 1 - (1/2) t^2 (1/\tau_1^2 \delta) + \dots \qquad (3.47)$$

From (3.46) and (3.47) it follows that

$$\text{for} \qquad \delta = 2IkT/\xi^2.$$

The parameter δ can also be written in the form

$$\delta = \tau_J/\tau_1, \qquad (3.48)$$

where τ_J is the correlation time of the angular velocity (or of the angular momentum, since $J = I\omega$). In fact, for $\xi_i = \xi$ we have from (1.35)

$$\text{for} \qquad \tau_J = I/\xi.$$

Recalling that $\tau_1 = \xi/2kT$, we can verify that (3.47) and (3.48) are equivalent. For what follows we also note the relation

$$\tau_1 \tau_J = I/2kT.$$

This result was first derived by Hubbard.[61] Thus the form of the correlation function $\varphi(t)$ is determined by the correlation time τ_J of the angular momentum and the correlation time τ_1 of the orientation. For any finite τ_J, $\varphi(t)$ is an analytic function at $t = 0$.

The function $L(-\dot{\varphi})$, calculated by means of (3.37), is of the form

$$L(-\dot{\varphi}) = (1 + x^2)^{-1} [1 - x^2 \delta \psi(x, \delta) - ixe^\delta zK_1(z)],$$

Where $K_1(z)$ is the modified Bessel function of the second kind, or Macdonald function, and

$$x = \omega\tau, \quad z = \delta(1 + x^2)^{1/2}.$$

The function $\Psi(x, \delta)$ is defined as

$$\Psi(x, \delta) = \exp\delta \cdot \int_0^1 \exp\{-\delta[1 + x^2(1 - \eta^2)]^{1/2}\} d\eta.$$

From this we get the expression for the imaginary part of the dielectric constant:

$$\varepsilon'' \approx (\varepsilon_0 - \varepsilon_\infty) [\omega\tau_1/(1 + \omega^2\tau_1^2)] e^\delta \delta(1 + \omega^2\tau_1^2)^{1/2} K_1[\delta(1 + \omega^2\tau_1^2)^{1/2}]. \qquad (3.49)$$

This is the Debye function multiplied by $\exp\delta \cdot zK_1(z)$. For $\delta \ll 1$, $\exp\delta \approx 1$. Asymptotic forms of $K_1(z)$ for small and large z are

$$zK_1(z) \approx 1, \quad z \ll 1,$$
$$zK_1(z) \approx (\pi z/2)^{1/2} e^{-z}, \quad z \gg 1.$$

Accordingly, for small frequencies ($\omega\tau_1 \ll 1$) and $\delta \ll 1$ (i.e., when $z \ll 1$) $\varepsilon''(\omega)$ coincides with the Debye func-
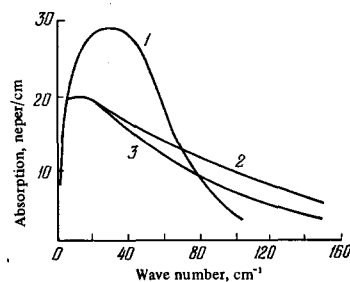
FIG. 2. Absorption coefficient of liquid methylchloroform at 20°C. 1—experiment; 2, 3-theory not including (2) and including (3) internal effects.

tion. In the high-frequency region ($\omega\tau_1 \gg 1$), however, the factor $zK_1(z)$ [Eq. (3.49)], which decreases practically exponentially with increasing z, plays the decisive role. Because of this the absorption coefficient $\alpha = \omega\varepsilon''/cn$ goes to zero for $\omega \to \infty$, in agreement with experiment.

A comparison of the calculated and measured values of $\alpha = \alpha(\omega)$ has been made for methylchloroform (Fig. 2). Values used in the calculation were $\varepsilon_0 = 7.11$, $\varepsilon_\infty = 2.06$, and $I = 345 \cdot 10^{-40}$ g-cm^2. The correlation time τ_1 was determined from the fall of the low-frequency wing of the function $\alpha(\omega)$ and was found to be $5.8 \cdot 10^{-12}$ sec. In the region up to 80 cm^{-1} the observed absorption is larger than the calculated. Beyond 80 cm^{-1}, however, the calculated absorption is larger than the measured. The cause of the numerical deviation may be that cooperative effects in the Brownian rotation of the dipoles were not taken into account in the calculations of $\varepsilon''(\omega)$.

Finally, let us dwell briefly on the role of inertial effects in the molecular scattering of light. These are discussed in more detail in the monograph[18].

Experimental and theoretical studies[18] show that for the most rigorous calculation of the spectral composition of depolarized light scattering (i.e., the wings of the Rayleigh line) in liquids one must take into account the influence of inertial effects in Brownian rotation. Such a calculation has been undertaken in papers by Starunov.[62,63] According to him, the part of the wing adjacent to the undisplaced line and extending 15 to 20 cm^{-1} out from it is due to Brownian rotation of the diffusion type. The rest of the wing is due to rotational oscillations of the molecules. The spectral density for both regions is found in[62,63].

c) Relaxation of angular momentum. Effects of free precession. In some cases, for example in calculations of the line width of EPR caused by spin-rotational interaction, the correlation time τ_J of the angular momentum of a molecule is of particular interest. For spherical-top molecules with a scalar friction coefficient τ_J is the same as the correlation time of the angular velocity [cf. Eq. (1.35)] and is given in the hydrodynamic approximation by

$$\tau_J = I/\pi\eta d^3, \qquad (3.50)$$

where d is the hydrodynamic "rotational diameter" of the molecule. We similarly find the correlation time of the momentum of the molecule by applying the Stokes-Einstein approximation to the translational motion:

$$\tau_p = m/6\pi r_a \eta, \qquad (3.51)$$

where r_a is the hydrodynamic (we do not say "translational") radius of the molecule. As was already indica-

ted in Sec. (d) of Chap. 1, the "rotational" radius $d/2$ is smaller than the true radius. On the other hand, the hydrodynamic radius found from (3.51) and the experimentally known τ_p and η is extremely close to the actual radius. Writing $d/2$ as κr_a ($0 < \kappa < 1$), for τ_J we get from (3.50)

$$\tau_J = I/8\pi\eta r_a^3 \kappa. \tag{3.52}$$

This expression for τ_J has been successfully used in a number of papers[64,65] to interpret the spin-rotational broadening of EPR lines, with the coefficient κ being chosen for each liquid to give the best agreement between theory and experiment. At the same time the shortcomings of (3.52) are obvious. First, there is no explanation of the nature of the formally introduced coefficient κ. Second, (3.52) is valid only for molecules of the spherical-top type.

McClung and D. Kivelson[15] and D. Kivelson, M. Kivelson, and Oppenheim[16] have developed a more general theory for calculating the correlation times τ_α of the components M_α of the angular momentum. According to their results,

$$\tau_\alpha^{-1} = (8\pi\eta r_a^3 \kappa_\alpha / I_\alpha) + 4\Delta_\alpha^2 (\tau_\beta^{-1} + \tau_\gamma^{-1})^{-1}; \tag{3.53}$$

here τ_α is the correlation time for the angular momentum component M_α (α = x, y, z), I_α are the principal values of the inertia tensor, and Δ_α is the precession frequency of the free rotation of the molecule:

$$\Delta_\alpha = (I_\beta - I_\gamma)^{1/2} (kT)^{1/2}/(I_\alpha I_\beta I_\gamma)^{1/2}. \tag{3.54}$$

For a spherical-top molecule Δ_α is obviously zero [in (3.53) and (3.54) the set of indices α, β, γ corresponds to the set x, y, z]. The quantity κ_α in (3.53) depends only weakly on the temperature and pressure and satisfies the approximate equation

$$4\kappa_\alpha r_a^3/3 \approx \langle N_\alpha^2 \rangle / \langle \dot{p}_x^2 \rangle,$$

with $0 \leq \kappa \leq 1$. Here, as in Sec. (d) of Chap. 1, N_α denotes a component of the torque. Thus the quantity κ_α is proportional to the ratio of the mean square of the corresponding torque component to the mean square of the force component [$\langle p_x^2 \rangle = \langle p_y^2 \rangle = \langle p_z^2 \rangle$ owing to the assumption that the liquid is isotropic], i.e., κ_α determines the weight of the anisotropic part of the potential energy of the molecule. The derivation of the formula (3.53) for τ_α (α = x, y, z) is rather complicated, and we shall not give it because of lack of space. We shall only point out the assumptions on which this theory is based. It is assumed that the correlation time of the force acting on the molecule from all the neighboring molecules is the same as that of the torque of this force. Furthermore the precession frequencies Δ_α are assumed to be small ($\Delta_\alpha \tau_\alpha \ll 1$). The first assumption is the most important, since it gives the expected relation between the characteristics of the rotational motion (τ_J, τ_1, τ_2, etc.) and the viscosity η of the liquid.

Equation (3.53) for the correlation time τ_α of the angular momentum component M_α contains two times. The first (predominant) term is due to the action of torques on the molecule in question, and the second to precession effects ($\Delta_\alpha \neq 0$). The relative contribution of the terms to τ_α^{-1} is governed by the coefficient κ_α. If the potential energy is strongly anisotropic κ_α is close to unity and the term in (3.53) containing Δ_α^2 can be neglected, so that τ_α is given by Eq. (3.52). For $\kappa_\alpha = 1$, τ is determined by the Stokes-Einstein approximation

(3.50). For smaller anisotropy of the potential energy κ_α is smaller and the contribution of free-precession effects to τ_α^{-1} is more important.

The EPR of free radicals ClO_2 was studied in the paper of McClung and Kivelson.[15] The width of the EPR line of ClO_2 is due to spin-rotation interaction and is consequently determined by the correlation time τ_α. Comparing the calculated and measured spin-lattice relaxation times T_1, the authors of[15] obtained values of κ (on the assumption that $\kappa_\alpha \equiv \kappa$ for all α) for ClO_2 molecules in various solvents. In carbon tetrachloride and n-pentane the values of κ are small, 0.0178 and 0.0237, respectively. In acetone, on the other hand, κ is rather large, 0.372. In a number of other solvents κ takes intermediate values; for example, in dichlormethane $\kappa = 0.178$. For acetyl acetonate complexes κ is large in all solvents; for example, in chloroform $\kappa = 0.818$.

Generally speaking, the experimentally observed dependence of the EPR line width on T/η for ClO_2 radicals in various solvents is nonlinear. The smaller κ, the larger the deviations from linearity. In the case of acetyl acetonate complexes of copper and vanadium, for which κ is large, the line width is proportional to T/η.[63,64] The theory given explains these facts. The approximation (3.52) for τ_J, which is valid for large κ, leads to a linear dependence of the width on T/η. For small κ, when precession effects are important, the formula (3.53) for τ_α predicts deviations from linearity. By choosing the value of κ ($0 \leq \kappa \leq 1$) one can achieve good agreement between theory and experiment for the dependence of T_1^{-1} (and consequently of the width) on T/η.[15]

4. CONCLUSION

We can state that the aspects of rotational Brownian motion in liquids that have at present been most studied are rotational diffusion, the rotational random-walk problem, and generalized diffusion with inertial effects taken into account.

The physical phenomena considered here are of course not all of the phenomena associated with Brownian rotation. The purpose set for this review did not, in particular, permit consideration of nuclear quadrupole relaxation and the Maxwell and Kerr effects, whose importance for the study of molecular motions in condensed media is well known.[18]

In future research rotational diffusion (including inertial effects) and the rotational random-walk problem will undoubtedly be further developed. There will also probably be much attention given to the study of cooperative effects.[1]

APPENDIX. REPRESENTATIONS OF THE ROTATION GROUP

The three-dimensional rotation group consists of all possible rotations of space around a fixed point (the origin of coordinates). As already noted in the main text, a rotation of space is specified by three parameters. For these we can use the components of the rotation vector ϵ, or else the Euler angles φ, θ, ψ. More often, however, rotations of space are specified by the rotation matrix g which transforms the "new" coordinates of some vector into the "old" coordinates. In terms of the Euler angles this matrix is

$$g = \begin{pmatrix} \cos\varphi\cos\psi - \cos\theta\sin\varphi\sin\psi & -\sin\varphi\cos\psi - \cos\theta\cos\varphi\sin\psi & \sin\psi\sin\theta \\ \sin\psi\cos\varphi + \cos\theta\cos\psi\sin\varphi & -\sin\varphi\sin\psi + \cos\theta\cos\varphi\cos\psi & -\cos\psi\sin\theta \\ \sin\varphi\sin\theta & \cos\varphi\sin\theta & \cos\theta \end{pmatrix}.$$

The operators T(g) of a representation of the rotation group form a matrix group homomorphic to the rotation group, and are completely determined by the infinitesimal operators M_i (i = x, y, z):

$$T(g) = \exp(i\varepsilon M).$$

The operators M_i correspond to infinitely small rotations around the coordinate axes, and thus are the same as the quantum-mechanical angular momentum operators.

The irreducible representation of the rotation group of dimension l is realized in the space whose basis vectors are the spherical functions Y_l^m. The explicit expressions for the matrix elements of this irreducible representation are of the form

$$T_m^k(\varphi, \theta, \psi) = e^{-im\varphi} P_{mn}^{(l)}(\cos\theta) e^{-in\psi};$$

here $P_{mn}^{(l)}(\cos\theta)$ are functions defined by

$$P_{mn}^{(l)}(\mu) = A(1-\mu)^{-\frac{n-m}{2}}(1+\mu)^{-\frac{n+m}{2}}\frac{d^{l-n}}{[d\mu^{l-n}]}[(1-\mu)^{l-m}(1+\mu)^{l+m}],$$

$$A \equiv \frac{(-1)^{l-m}i^{n-m}}{2^l(l-m)!}\left[\frac{(l-m)!(l+n)!}{(l+m)!(l-n)!}\right]^{1/2}.$$

Because the irreducible representations are unitary we have the equation

$$T_{mn}^l(g^{-1}) = \overline{T_{nm}^l(g)}.$$

The matrix elements $T_{mn}^l(g)$ have the property of orthogonality over the rotation group:

$$\int T_{mn}^l(g) T_{rq}^p(g) \, dg = [8\pi^2/(2l+1)]\delta_{lp}\delta_{mr}\delta_{nq}, \qquad (1)$$

where dg is the volume element in the rotation group. When the rotations are specified by the Euler angles dg is of the form

$$dg = \sin\theta \, d\varphi \, d\theta \, d\psi.$$

An important feature of the property (1) is that it enables us to expand an arbitrary square-integrable function f(g) over the rotation group in a series of generalized spherical functions $T_{mn}^l(\varphi, \theta, \psi)$:

$$f(g) = \sum_l c_{mn}^{(l)} T_{mn}^l(\varphi, \theta, \psi),$$

$$c_{mn}^{(l)} = \int \overline{T_{mn}^l(g)} f(g) \, dg.$$

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[1]While this review was being prepared for the press some new papers on rotational Brownian motion in crystals were published. [66,67] The results in these papers are unfortunately erroneous.

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Translated by W. H. Furry