THEORY OF ROTATIONAL BROWNIAN MOTION

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A theory of rotational Brownian motion for particles (molecules) of arbitrary shape is presented on the basis of a solution of the rotational random walk problem. In the limiting case when the mean angles of rotation of the molecule are small this theory is identical with the theory of rotational diffusion. Possibilities of an experimental determination of the nature of the rotational motion of molecules in a liquid are discussed.

ACCORDING to Frenkel[1] translational Brownian motion of a particle (molecule) in a liquid can be treated as an oscillation about a certain position of equilibrium which after remaining unchanged during a time τ is then displaced in a vanishingly short interval by a certain distance r_j. The problem of finding the total displacement $r = \Sigma r_j$ during a time t is thus reduced to the problem of a translational random walk.

As Chandrasekhar[2] and Torrey[3] have shown, one can always choose a sufficiently large interval of time t_0 so that for $t > t_0$ the total displacement r will be correctly described by the translational diffusion equation. The interval t_0 increases as the mean square displacement of the molecule $\overline{r_j^2}$ in a single step is increased, i.e., the smaller the dimensions of the molecule, the larger t_0. For large molecules one can with a high degree of approximation utilize the solution of the diffusion equation for arbitrary t. For small molecules for which the Brownian motion consists of a number of jumps by finite distances r_j[4] t_0 is sufficiently great so that the use of the diffusion equation for $t < t_0$ would lead to serious error. Therefore, the translational Brownian motion for small molecules should be investigated on the basis of the general solution of the random walk problem.

Analogous conclusions have been made long ago also for the case of rotational Brownian motion. Debye[5] and Frenkel'[6] have pointed out that the rotational motion of molecules of small dimensions has the nature of sharp turns and only the rotational motion of large molecules can be considered as rotational diffusion.

Nevertheless, until now no theory of the rotational random walk has been given. The analysis of magnetic and electrooptical phenomena in liquids both for the case of large and of small molecules has been carried out on the basis of rotational diffusion theory. The rotational diffusion tensor D_{ij} has usually been evaluated by the hydrodynamic method[7] in which the molecule is treated as a macroscopic body immersed in a viscous liquid. In particular, for a spherically symmetric molecule it was found that

$$D = kT/8\pi\eta a^3, \qquad (1)$$

a is the radius of the molecule and η is the viscosity of the liquid. However, it turned out that the experimental values of D exceed[8] those evaluated theoretically by means of formula (1) by a factor of 3—10.

The facts noted above indicate that it is insufficient to describe the rotational Brownian motion in terms of a single rotational diffusion constant D (or of the tensor D_{ij}) and that it is necessary to create a theory of rotational random walk. In this paper a theory of rotational Brownian motion is given based on the solution of the rotational random walk problem.

In Sec. 1 the solution of the rotational random walk problem is given for a particle of arbitrary shape. The probability of the particle having a specified orientation at time t taking into account the finite number of rotations during this time will be obtained in Sec. 2. In Sec. 3 a discussion is given of the possibility of the experimental determination of the nature of the rotational motion of molecules in liquids.

1. THE ROTATIONAL RANDOM WALK PROBLEM

We consider a particle (molecule) of arbitrary dimensions and shape which under the action of random rotational moments undergoes jerky rotational motion. We consider a coordinate system

ξ, η, ζ rigidly tied to the molecule. We shall characterize the orientation of the ξ, η, ζ system with respect to the laboratory coordinate system x, y, z by the Eulerian angles φ, θ, ψ or else directly by the rotation matrix $g(\varphi, \theta, \psi)$.

We assume that at the initial time the orientation g_0 of the molecule was fixed so that the probability distribution of the orientations has the form $P(g, 0) = \delta(g - g_0)$. In order to solve the rotational random walk problem it is necessary to find $P(g, N)$ —the probability density for the orientation g of the molecule after N rotations, with the probability of the individual rotation $p(g_1)$ being regarded as given.

It can be easily seen that $P(g, N)$ is related to $P(g, N-1)$ by the obvious relationship

$$P(g, N)\, dg = \int dg_1 p(g_1) P(k, N-1)\, dk, \qquad (2)$$

where the integration is performed over g_1. In (2) k is taken to denote only those orientations which the molecule had after $N-1$ rotations and which after the N-th rotation g_1 yield the orientation g.

Under the rotation g_1 the functions $P(k, N-1)dk$ transform in accordance with the infinite-dimensional reducible representation $T(g_1)$[9]:

$$P(g, N-1)\, dg = T(g_1) P(k, N-1)\, dk. \qquad (3)$$

On taking into account the fact that $T^{-1}(g_1) = T(g_1^{-1})$ we obtain from (2) and (3)

$$P(g, N)\, dg = \int dg_1 p(g_1) T(g_1^{-1}) P(g, N-1)\, dg. \qquad (4)$$

We shall seek the solution of the system of integral equations (4) in the form of a series in terms of generalized spherical harmonics:

$$P(g, N) = \sum_{l, m, n} C_{mn}^l(N) T_{mn}^l(g). \qquad (5)$$

On substituting (5) into (4) we obtain for the determination of the coefficients $C_{mn}^l(N)$ the recurrence relations

$$C_{mn}^l(N) = \sum C_{sn}^l(N-1) \int p(g_1) T_{sm}^l(g_1^{-1})\, dg_1, \qquad (6)$$

where we have taken into account the transformation rule

$$T(g_1^{-1}) T_{mn}^l(g) = \sum T_{ms}^l(g_1^{-1}) T_{sn}^l(g). \qquad (7)$$

We denote the expectation value of the transformation $T(g_1^{-1})$ for one rotational step by

$$A_l \equiv \int p(g_1) T^l(g_1^{-1})\, dg_1. \qquad (8)$$

Then relations (6) can be written in matrix form:

$$C^l(N) = A_l^T C^l(N-1), \qquad (9)$$

where the symbol T denotes the operation of transposition. From this we obtain

$$C^l(N) = (A_l^T)^N C^l(0). \qquad (10)$$

The matrix elements $C_{mn}^l(0)$ can be obtained from the expansion (5) for $N = 0$. Indeed, since $P(g, 0) = \delta(g - g_0)$, we have

$$\delta(g - g_0) = \sum C_{mn}^l(0) T_{mn}^l(g). \qquad (11)$$

By multiplying (11) by $\overline{T}_{mn}^l$ and by integrating over the whole group taking into account the orthogonality relations

$$\int \overline{T}_{ik}^l(g) T_{jn}^m(g)\, dg = \frac{8\pi^2}{2l+1}\, \delta_{lm}\delta_{ij}\delta_{kn}, \qquad (12)$$

we obtain for $C_{mn}^l(0)$

$$C_{mn}^l(0) = (2l+1)\, \overline{T}_{mn}^l(g_0)/8\pi^2. \qquad (13)$$

Successive substitution of (13) into (10), and of (10) into (5) yields

$$P(g, N) = \sum \frac{2l+1}{8\pi^2} (A_l^T)_{mi}^N T_{in}^l(g_0) T_{mn}^l(g). \qquad (14)$$

Since

$$\overline{T}_{in}^l(g_0) = T_{ni}^l(g_0^{-1}) \qquad (15)$$

in consequence of the unitarity of irreducible representations, we finally obtain for $P(g, N)$

$$P(g, N) = \sum \frac{2l+1}{8\pi^2} \mathrm{Sp}\, [T^l(g_0^{-1}) A_l^N T^l(g)]. \qquad (16)$$

This result completely solves the rotational random walk problem for a molecule.

In the case of a spherically symmetric molecule rotations through the same angle about different axes occur with the same probability. If g is the matrix for one such rotation, then the matrices of all other rotations are equal to[10] $g' = h^{-1}gh$ where h is an arbitrary element of the rotation group. From this it follows that the probability distribution (16) for $g_0 = e$ must satisfy the relation

$$P(g, N) = P(h^{-1}gh, N). \qquad (17)$$

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

$$A_l T^l(h) = T^l(h) A_l. \qquad (18)$$

On the basis of Schur's lemma, an operator which commutes with an irreducible representation must be a multiple of the identity operator[10] so that

$$A_l = \lambda_l E_l. \qquad (19)$$

By taking traces of both sides of (19) and by utilizing the definition (8) we obtain the formula for the evaluation of the coefficients λ_l:

$$\lambda_l = \frac{1}{2l+1} \int \mathrm{Sp}\, e^{i\varepsilon M} p\,(\varepsilon)\, d^3\varepsilon, \qquad (20)$$

where (cf. [10])

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

Thus, for a spherically symmetric molecule formula (16) assumes the simpler form:

$$P\,(g,\,N) = \sum_l \frac{2l+1}{8\pi^2}\, \lambda_l^N\, \mathrm{Sp}\,[T^l\,(g_0^{-1})\,T^l\,(g)], \qquad (21)$$

where λ_l is evaluated with the aid of (20).

2. THE PROBABILITY DISTRIBUTION W(g,t)

The fundamental problem in the theory of rotational Brownian motion is the determination of the probability density $W(g,t)$ for the orientations g of the molecule at time t under the condition that at the initial instant t = 0 the molecule had the orientation g_0. The distribution $W(g,t)$ can be easily found if we are given the probability $w_N(t)$ for N rotations to take place during the time t. Then we have

$$W\,(g,\,t) = \sum_{N=0}^{\infty} w_N\,(t)\, P\,(g,\,N). \qquad (22)$$

Usually $w_N(t)$ is taken to have the form of the Poisson distribution:

$$w_N\,(t) = (N!)^{-1}\,(t/\tau)^N\, e^{-t/\tau}, \qquad (23)$$

where τ is the average time between two successive rotations of the molecule. On substituting (16) and (23) into (22) we obtain after fairly straightforward calculations

$$W\,(g,\,t) = \sum \frac{2l+1}{8\pi^2}\, \mathrm{Sp}\,\left\{T^l\,(g_0^{-1})\exp\left[-\frac{t}{\tau}\,(1 - A_l)\right] T^l\,(g)\right\}, \qquad (24)$$

and this yields the desired result.

Rotational diffusion is a special case of rotational Brownian motion regarded as a rotational random walk process. Therefore, in expression (24) for $W(g,t)$ one can carry out the limiting transition to the Green's function for the equation of rotational diffusion. In order to show this we shall in the definition (8) go over to new variables of integration:

$$A_l = \int e^{i\varepsilon M} p\,(\varepsilon)\, d^3\varepsilon. \qquad (25)$$

Here M_j (j = 1, 2, 3) are the infinitesimal rotation operators, while the direction and the absolute magnitude of the vector ε specify the axis of rotation and the angle of rotation about this axis [9] with $(\varepsilon_x^2 + \varepsilon_y^2 + \varepsilon_z^2)^{1/2} \leq \pi$.

Further, we assume that the transition probability $p(\varepsilon)$ is such that only rotations through small angles have an appreciable probability. Then we expand $e^{i\varepsilon \cdot M}$ in (25) in series and retain terms up to quadratic terms in ε_j inclusive:

$$A_l = 1 - \tau M_i D_{ij} M_j, \qquad (26)$$

$$D_{ij} \equiv \frac{1}{2\tau} \int \varepsilon_i \varepsilon_j p\,(\varepsilon)\, d^3\varepsilon. \qquad (27)$$

The quantities D_{ij} define the components of the rotational diffusion tensor. The linear term in the expansion of $e^{i\varepsilon \cdot M}$ gives no contribution to (26) since in the absence of external fields $p(\varepsilon) = p(-\varepsilon)$.

The axes of the molecular system of coordinates ξ, η, ζ can always be chosen in such a way that the tensor D_{ij} will be diagonal, i.e., $D_{ij} = \delta_{ij} D_i$. In this case

$$A_l = 1 - \tau\{D^+ M^2 + (D_3 - D^+) M_3^2 + D^-\,(M_1^2 - M_2^2)\}, \qquad (28)$$

where $D^\pm = \frac{1}{2}\,(D_1 \pm D_2)$.

For large time intervals ($t \gg \tau$) $W(g,t)$ in (24) varies slowly with time. Therefore A_l in (24) can be replaced for $t \gg \tau$ by the approximate expression (28). In particular, if the molecule has the shape of a symmetric top ($D^- = 0$), then we have

$$W\,(g,\,t) = \sum \frac{2l+1}{8\pi^2}\, \overline{T}_{mn}^l\,(g_0)\, T_{mn}^l\,(g) \exp\,[-D^+ l\,(l+1) \\ -(D_3 - D^+)\, m^2]\, t. \qquad (29)$$

For a spherical molecule ($D_1 = D_2 = D_3 = D$) (29) simplifies to the form

$$W\,(g,\,t) = \sum \frac{2l+1}{8\pi^2}\, \overline{T}_{mn}^l\,(g_0)\, T_{mn}^l\,(g) \exp\,[-l\,(l+1)Dt]. \qquad (30)$$

Expressions (29) and (30) are identical with the Green's functions for the equation of rotational diffusion obtained previously [11,12].

3. THE POSSIBILITY OF EXPERIMENTAL DETERMINATION OF THE NATURE OF ROTATIONAL BROWNIAN MOTION

The nature of rotational motion of molecules in liquids can be determined from the widths of vibrational lines. As Valiev [13] has shown, the ratio q of the width of the Raman scattering line to the width of the infrared absorption line is equal to unity if the rotational motion has the character of sharp jerks, and $1 < q \leq 3$ in the case of rotational diffusion (q = 3 when the contribution of the translational motion to the line width is negligibly small).

Valiev obtained the ratio q = 1 on the basis of qualitative considerations. He assumed that in the case of sharp jerky rotations the correlation times

for the random components of a constant dipole moment of the molecule (in infrared absorption) and of the components of the polarizability tensor (in Raman scattering) are identical in the laboratory system of coordinates and are equal to the average time between two successive rotations. As we shall see below, this assumption is given a rigorous justification in our theory. Moreover, an average minimum angle of rotation of the molecule ϵ_{min} will obtained beyond which the ratio q = 1 will hold.

We assume that in the molecular system of coordinates there exists a set of constant quantities Φ_n ($-k \le n \le k$) which transform in transition to the laboratory system in accordance with the relation

$$F_m(g) = \sum_n T^k_{mn}(g)\,\Phi_n. \tag{31}$$

In the case of Raman scattering (k = 2) the quantities Φ_n are the components of the polarizability tensor; in infrared absorption (k = 1) Φ_n are the components of the constant dipole moment along the axes of the molecular system of coordinates.

The components $F_m(g)$ in the laboratory system are random functions due to the random orientation g of the molecule. The correlation functions corresponding to them are calculated, as is well known, in accordance with the formula

$$K(t) = \frac{1}{8\pi^2} \int F_m(g)\,\overline{F}_m(g_0)\,W(g_0, 0; g, t)\,dg_0\,dg, \tag{32}$$

where $W(g_0, 0; g, t)$ is the distribution function (24). On utilizing (31) we obtain

$$K(t) = (2k+1)^{-1}\exp\left[-\frac{t}{\tau}(1-\lambda_k)\right]\sum|\Phi_n|^2. \tag{33}$$

As t increases from 0 to $\tau_r^{(k)}$ where

$$\tau_r^{(k)} = \tau/(1-\lambda_k), \tag{34}$$

the correlation function (33) is reduced by a factor e. Therefore, it is natural to call the quantity $\tau_r^{(k)}$ the correlation time for the random function $F_m(g)$ ($-k \le m \le k$).

The correlation time $\tau_r^{(k)}$ depends on the weight k of the irreducible representation $T^k_{mn}(g)$ in (31). The specific form of this dependence will be determined by the type of motion (diffusion or sharp rotations) taking place.

The last conclusion forms a basis for the possibility of experimental determination of the nature of the rotational motion of the molecules. Indeed, if the rotational motion of a spherically symmetric molecule has the nature of diffusion, then it follows from (26) that

$$\lambda_k = 1 - [D\tau/(2k+1)]\,\mathrm{Sp}\,\mathbf{M}^2 = 1 - k(k+1)D\tau, \tag{35}$$

where D is the rotational diffusion constant (1). For the correlation time we obtain from (34) and (35)

$$\tau_{rd}^{(k)} = [k(k+1)D]^{-1}. \tag{36}$$

Thus, in the case of rotational diffusion the correlation between the values of the tensor (k = 2) is lost more rapidly by a factor 3 than the correlation between the values of the vector (k = 1). This leads[13] to 1 < q ≤ 3.

But if the spherical molecule executes sharp rotations through angles which differ little from the average angle of rotation ϵ_0, then we can take for the probability of an individual rotation ϵ

$$p(\epsilon) = \frac{w(\epsilon)}{4\pi\epsilon^2}\;;\quad \int_0^\pi w(\epsilon)\,d\epsilon = 1,$$

$$w(\epsilon) = \begin{cases} 0, & 0 \le \epsilon < \epsilon_0 - \sigma/2 \\ \sigma^{-1}, & \epsilon_0 - \sigma/2 \le \epsilon \le \epsilon_0 + \sigma/2, \\ 0, & \epsilon_0 + \sigma/2 < \epsilon \le \pi \end{cases} \tag{37}$$

where σ is the width of the rectangular distribution $w(\epsilon)$.

On substituting (37) into (20) we obtain

$$\lambda_k = \frac{4}{(2k+1)\sigma}\left\{\sum_{n=1}^{k}\frac{1}{n}\cos n\epsilon_0 \sin\frac{n\sigma}{2} + \frac{\sigma}{4}\right\}. \tag{38}$$

For small σ we have $\sin(n\sigma/2) \approx n\sigma/2$ so that λ_k assumes the form

$$\lambda_k = \frac{2}{2k+1}\left\{\sum_{n=1}^{k}\cos n\epsilon_0 + \frac{1}{2}\right\} = \frac{\sin(k+\frac{1}{2})\epsilon_0}{(2k+1)\sin(\epsilon_0/2)}. \tag{39}$$

It can be easily verified that the last formula could also be obtained by assuming $w(\epsilon) = \delta(\epsilon - \epsilon_0)$.

Figure a shows graphs of λ_k as functions of the mean angle of rotation of the molecule ϵ_0 calculated in accordance with (39). Figure b shows the function $\lambda_2(\epsilon_0)$ for different values of σ (for clarity σ_2 and σ_3 are taken sufficiently large) calculated in accordance with (38). In actual fact the width σ, apparently, is not great ($\sigma \ll 1$), and, therefore, to a good degree of approximation one can always utilize (39) in place of (38).

As ϵ_0 increases from 0 to $\epsilon_0^{(k)} = 2\pi/(2k+1)$ the curves of $\lambda_k(\epsilon_0)$ fall off from 1 to 0; as ϵ_0 increases further they oscillate about the horizontal axis remaining small in comparison with 1. On setting in (34) $\lambda_k = 0$ for $\epsilon_0 \gtrsim \epsilon_0^{(k)}$ we obtain $\tau_{rw}^{(k)} = \tau$. This means that if the mean angle of rotation of the molecule $\epsilon_0 \gtrsim \epsilon_0^{(k)}$ then the correlation between the values of $F_m(g)$ practically disappears in the course of a single rotation. We shall call $\epsilon_0^{(k)}$ the correlation angle of the random quantity
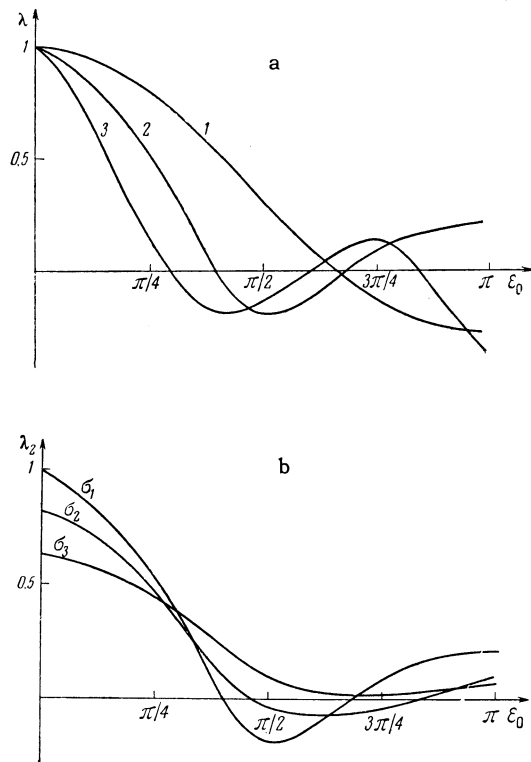
a-curves of $\lambda_k(\epsilon_0)$ for $k = 1,2,3$ and $\sigma = 0$; b-curves of $\lambda_2(\epsilon_0)$ for $\sigma_1 = 0$, $\sigma_2 = \pi/2$ and $\sigma_3 = 3\pi/4$.

$F_m(g)$. The correlation angle for $F_m(g)$ has a magnitude which is the larger the smaller the weight of the irreducible representation which determines the angular dependence of $F_m(g)$.

In the case when there exist two random quantities of the type (31) $F_m(-k \le m \le k)$ and F'_n $(-k' \le n \le k')$ the relations

$$\tau_{rw}^{(k)} = \tau, \quad \tau_{rw}^{(k')} = \tau \quad (k \ne k') \tag{40}$$

will be satisfied simultaneously if the mean angle of rotation of the molecule $\epsilon_0 \gtrsim \epsilon_0^{\min(k',k)}$ where $\epsilon_0^{\min(k',k)}$ is the greatest of the correlation angles for F_m and F'_n.

In particular, for $k = 1$ and $k' = 2$ $\epsilon_0^{\min(k',k)}$ = 120°. From this it follows that the ratio of the width of the Raman scattering line to the width of the infrared absorption line $q = 1$ if the mean angles of rotation $\epsilon_0 \gtrsim 120°$. The angle $\epsilon_{\min} = 120°$ is the minimum angle for which it is still possible to distinguish between sharp rotations and rotational diffusion from the widths of the vibrational lines.

The nature of rotational motion of molecules in a liquid can also be determined by the method of comparing the characteristic times for dielectric ($k = 1$) and nuclear magnetic ($k' = 2$) relaxations. The general conclusions obtained above remain in force also for this case.

CONCLUSIONS

1. The solution of the rotational random walk problem for a molecule of arbitrary shape is given by formula (16).

2. The probability $W(g,t)$ for the orientation g of a molecule at time t is determined by two parameters: $p(g_1)$ (the probability of an individual rotation) and τ (the mean time interval between two successive rotations).

3. In the limiting case when the mean angle of rotation of the molecule is small and $t \gg \tau$ the distribution $W(g,t)$ is identical with the Green's function for the equation of rotational diffusion.

4. The theory developed here confirms the possibility of experimental determination of the nature of rotational motion of molecules in a liquid. In particular, if the mean angle of rotation of the molecule is greater than $\epsilon_{\min}$ = 120° then the ratio of the width of the Raman scattering line to the width of the infrared absorption line must be equal to unity.

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