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The Quasicrystal Model of Rotational Brownian Motion

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The quasicrystal model of the rotational Brownian motion in a liquid has been studied. The probability distribution of orientations of a Brownian particle is given in the form of a series of generalized spherical functions.

KEY WORDS: Rotational Brownian motion; liquid; probability distribution of orientations; model of Frenkel.

Three principal models of rotational Brownian motion are studied theoretically. They are (i) rotational diffusion, (ii) rotational displacements by rotations at random angles, (iii) rotational diffusion taking account of inertial effects. The theory of rotational diffusion has been developed by Perrin,(1) Furry,(2) Favro,(3) Valiev and Eskin,(4) and Valiev.(5) Beginning with the work by Debye(6) on dielectric relaxation and by Bloembergen *et al.*(7) on nuclear magnetic resonance, this theory has been used with variable success for the interpretation of different physical phenomena in liquids.

The problem of rotational displacements is worked out in Ref. 8, and various works(9–13) have dealt with applications of this problem. Valiev(14) has suggested a method of experimentally defining Brownian motion, i.e., the experimental determination of the rotation angle for a single rotational jump. This method was employed(13,15) for the study of Brownian rotation in liquids.

The theory of rotational diffusion including inertial effects was developed

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by Steele.(16) According to Steele, the Brownian rotation of molecules, when the intervals of observation are small, appears to be inertial rotation, transforming into rotational diffusion as the intervals increase in size. Steele's interpretation of Brownian rotation was employed in a number of works on dielectric and magnetic relaxation and infrared absorbtion. It is important to emphasize, however, that the Steele theory does not correspond to the conventional idea of the Brownian motion of particles in condensed media, introduced for the first time by Frenkel.(17) According to Frenkel, the motion of molecules in a liquid (both translational and rotational) consists of oscillations in transient equilibrium positions and jumps from one kind of equilibrium position into another. This description corresponds to the quasicrystal model of the liquid. In the Steele theory inertial rotation is suggested in place of rotational oscillation.

The present work introduces a new version of the theory of the rotational Brownian motion of molecules in liquids. The theory is based on Frenkel's ideas and includes all the basic elements of the quasicrystal model of the liquid. While the further elaboration of the theory of the rotational Brownian motion of molecules in condensed media is an urgent problem, various papers do not even mention it for instance, (see Fabelinsky's work(18)). The author believes that the quasicrystal model of the liquid must become the basis for theoretical reasoning in this area.

Rahman *et al.*(19) treated translational Brownian motion in the quasicrystal model. It is noteworthy that the calculations of effective differential cross sections for slow neutron scattering in water and liquid lead made on the basis of the quasicrystal model are in good agreement with the experiment.

For the consideration of the quasicrystal model of rotational Brownian motion the same principles apply as those used for the study of the quasicrystal model of translational Brownian motion. The mathematical notation suggested by the author elsewhere(8,9) will also be used in the present work.

It is known(16) that when dynamic effects are present the Brownian motion of particles (molecules) cannot be described by the diffusion equation. In this case the distribution of coordinates (orientations in particular) of the Brownian particle can be found from either the Einstein–Fokker–Planck equation or the generalized Mori–, Oppenheim–Ross(20) equation. We use the latter equation, the rotational analog of which has the following appearance:

$$\partial W/\partial t = \nabla_\epsilon \cdot \mathbf{D} \cdot \nabla_\epsilon W \tag{1}$$

where W is the probability distribution for orientations at time t; ϵ is the projection aggregation of the ϵ_i vectors determining the orientation; $\mathbf{D}$ is the tensor whose components are related to correlation functions of the angular velocity $\langle\omega_i(0)\omega_j(t)\rangle$ by the relationship

$$D_{ij}(t) = \int_0^t \langle\omega_i(0)\,\omega_j(t)\rangle\,dt \tag{2}$$

We select the moving frame of reference attached to the molecule in such a way that the tensor $D_{ij}(t)$ becomes diagonal; Eq. (1) simplies:

$$\partial W/\partial t = \sum_{i=1}^{3} D_{ii}(t)\,\partial^2 W/\partial\epsilon_i^{\,2} \tag{3}$$

When deriving W from (3) it is convenient to transform from the variables ϵ_i to the Euler angles φ, θ, ψ. The resultant expression looks simpler when $D_{xx} = D_{yy}$ (this takes place when the friction coefficient tensor represents an ellipsoid of rotation(16):

$$\begin{aligned}\frac{\partial W}{\partial t} = D_{xx}(t)\left\{\frac{\partial^2 W}{\partial\theta^2} + (\cot\theta)\frac{\partial W}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 W}{\partial\varphi^2}\right.\\ \left. + \left[\cot^2\theta + \frac{D_{zz}(t)}{D_{xx}(t)}\right]\frac{\partial^2 W}{\partial\psi^2} - 2(\cot\theta)\frac{\partial^2 W}{\partial\varphi\,\partial\psi}\right\}\end{aligned} \tag{4}$$

The solution of (4) is found as the decomposition of generalized spherical functions(21):

$$W(g(t), g(0)) = \sum_{lmn} C^l_{mn}(t)\,T^l_{mn}(\varphi, \theta, \psi) \tag{5}$$

where g is the aggregation of the three Euler angles. Substituting (5) into (4), we find(8,9)

$$W(g(t), g(0)) = \sum_{lmn} \frac{2l+1}{8\pi^2}\,\overline{T}^l_{mn}(g_0)\,\Gamma_{lm}(t)\,T^l_{mn}(g) \tag{6}$$

$$\Gamma_{lm}(t) = \exp\left\{[m^2 - l(l+1)]\int_0^t D_{xx}(t)\,dt - m^2\int_0^t D_{zz}(t)\,dt\right\} \tag{7}$$

For the simplest case, when the tensor D_{ij} is spherically symmetric $[D_{ii}(t) = D(t),\ i = x, y, z]$, we have

$$\Gamma_{lm}(t) = \exp\left[-l(l+1)\int_0^t D(t)\,dt\right] \tag{8}$$

When $t \to \infty$ integral $\int_0^t D(t)\,dt \to Dt$, where D is the coefficient of rotational diffusion, and $W(g(t), g(0))$ in (6) transforms into a fundamental solution of the rotational diffusion equation (4). Now we shall set about calculating $D(t)$.

3. For the sake of simplicity, let us assume that the molecule participating in the Brownian motion is a spherical top with moment of inertia I. This assumption reduces the problem of the random rotation of a molecule with three degrees of freedom (the center of mass of the molecule is assumed fixed) to one-dimensional problem with an angular parameter ξ.

The quasicrystal model of rotational Brownian motion is constructed using the assumption that the angular displacement ξ can be represented as the superposition of statistically independent displacements $\xi_i(\nu_i, t)$ analogous to normal coordinates (modes) in solids. For modes with frequencies ν_i less than some critical frequency ν', the displacements ξ_i satisfy the equation

$$\ddot{\xi}_i + \beta\dot{\xi}_i = (1/I)\, M_i(t) \tag{9}$$

where $M_i(t)$ is rapidly fluctuating force affecting the molecule and β is a friction coefficient similar for all modes with $\nu_i < \nu'$. For modes with frequencies ν_i greater than ν' but less than the finite frequency ν_{D}, the ξ_i satisfy the equation

$$\ddot{\xi}_i + \beta_i\dot{\xi}_i + \nu_i^2\xi_i = (1/I)\, M_i(t) \tag{10}$$

It is apparent that the rotational motion described by Eq. (9) is rotational diffusion. Equation (10) describes forced rotational oscillations with damping. The finite frequency ν_{D} for the solid coincides with the Debyl characteristic frequency for orientational oscillation. We assume that

$$\beta_s = 2\gamma\nu_s \tag{11}$$

where γ is a parameter of the theory. For the sake of simplicity, assume also that the density of normal modes $\rho(\nu_i)$ satisfies the Debye parabolic law:

$$\rho(\nu_i) = 3\nu_i^2/\nu_{\mathrm{D}}^3 \tag{12}$$

The important feature of (12) is that $\rho(\nu_i)$ is monotone decreasing to zero as $\nu_i \to 0$. In a solid (in a molecular crystal) $\rho(\nu_i)$ in the form of (12) is unapplicable since in this form, as was shown by Anselm and Porfirieva(22) sheer orientational oscillations with small frequencies are not present. In the liquid, however, due to the presence of rotational reorientation (diffusion), the existence of orientational oscillations with small frequencies does not cause any problem. Hence in liquids the distribution (12) may be expected to reflect at least qualitatively the frequency distribution of orientational oscillation. The solution of Eqs. (9) and (10) can be obtained from Chandrasekhar(23) and Wang and Uhlenbeck.(24) The correlation function for angular velocity for (10) is

$$\langle \omega_i(0)\, \omega_i(t) \rangle_T = (\kappa T/I)\, e^{-\beta_i t/2}[\cos \nu_1 t - (\beta_i/2\nu_1) \sin \nu_1 t] \tag{13}$$

where $\nu_1 = (\nu_i^2 - \frac{1}{4}\beta_i^2)^{1/2}$. Correspondingly, for Eq. (9) we have

$$\langle \omega_i(0) \omega_i(t) \rangle_T = (\kappa T/I) e^{-\beta t} \tag{14}$$

The parameter ν' differentiates between diffusional and oscillational modes. For $\nu' = \nu_{\mathrm{D}}$ rotational motion is of a pure diffusional character, for $\nu' = 0$ it has a damped rotational oscillational character.

Averaging expressions (13) and (14) according to the Debye distribution gives

$$\begin{aligned}\langle \omega_i(0)\, \omega_i(t) \rangle_T &= \int_0^\infty \rho(\nu_i) \langle \omega_i(0)\, \omega_i(t) \rangle \, d\nu_i \\ &= \frac{\kappa T}{I} \left[\left(\frac{\nu'}{\nu_{\mathrm{D}}} \right)^3 e^{-\beta t} + \frac{3}{\nu_{\mathrm{D}}^3} \int_{\nu'}^{\nu_{\mathrm{D}}} (\cos \nu_1 t - \Gamma \sin \nu_1 t)\, e^{-\Gamma \nu_1 t} \nu_i^2 \, d\nu_i^2 \right]\end{aligned} \tag{15}$$

where Γ is determined from the relationship $\gamma \nu_i = \Gamma \nu_1$; moreover,

$$1 + \Gamma^2 = (1 - \gamma^2)^{-1} \tag{16}$$

From Eqs. (2) and (5) we obtain for $D(t)$

$$D(t) = (\kappa T/I)[(\nu'/\nu_{\mathrm{D}})^3 (1/\beta)(1 - e^{-\beta t}) + 3(\Gamma/\nu_{\mathrm{D}}\gamma)^3\, G(t)] \tag{17}$$

where

$$G(t) = G(\nu', t) - G(\nu_{\mathrm{D}}, t) \tag{18}$$

$$\begin{aligned} G(\nu, t) = \frac{e^{-\nu\gamma t}}{(1 + \Gamma^2)t} \Bigg\{ \frac{\nu\gamma}{\Gamma} \left[\left(\Gamma \sin \left(\frac{\nu\gamma}{\Gamma} t \right) + \cos \left(\frac{\nu\gamma}{\Gamma} t \right) \right] \\ + \frac{1}{(1 + \Gamma^2)t} \left[2\Gamma \cos \left(\frac{\nu\gamma}{\Gamma} t \right) - (1 - \Gamma^2) \sin \left(\frac{\nu\gamma}{\Gamma} t \right) \right] \Bigg\} \end{aligned} \tag{19}$$

From (17) it is seen that when $t \rightarrow 0$, $D(t) \rightarrow 0$. When t increases, $D(t)$ oscillates, asymptotically approaching the magnitude D^* determined by the relation

$$D^* = (\kappa T/\beta I)(\omega'/\omega_{\mathrm{D}})^3 \tag{20}$$

For $\omega' = \omega_{\mathrm{D}}$, D^* coincides with the rotational diffusion coefficient. It is worth noting that $D(t) \rightarrow 0$ when $t \rightarrow 0$ or $t \rightarrow \infty$. For intermediate values of the argument $G(t)$ oscillates.

Relations (6), (7), and (17)–(19) determine the required orientational probability distribution of the Brownian particle (molecule) for the quasicrystal model of rotational Brownian motion. The calculation of correlation functions, using the distribution obtained, for random functions of orientation and their Fourier transforms can be performed on a computer.

4. The quasicrystal model considered in this paper is believed to be the most realistic of all the existing models of Brownian rotational motion and should be of extreme importance for the consideration of a number of phenomena in liquids, including nuclear magnetic and dielectric relaxation, slow neutron scattering, and the Mössbauer effect. Reconsideration of these phenomena with the aid of the present theory could lead to new, interesting results.

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