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Citation: *The Journal of Chemical Physics* **76**, 253 (1982); doi: 10.1063/1.442772

View online: <http://dx.doi.org/10.1063/1.442772>

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Molecular motion in anisotropic medium. I. The effect of the dipolar interaction on nuclear spin relaxation

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The diffusion equation in the presence of a restoring potential is solved and the result is applied to dipolar NMR relaxation in liquid crystal solvents. The potential imparted by the solvent is approximated by a series of rotation matrices of rank two. The solution of the diffusion equation is expressed as an infinite series of rotation matrices. It is then shown that only the terms of rank two of this series are necessary to compute the dipolar spectral densities. This theory predicts the spectral densities to be different for different z -projection numbers, even in the case of extreme narrowing.

I. INTRODUCTION

The theory underlying intramolecular relaxation in multispin systems is well developed^{1,2} and has been shown to be a very powerful tool for the study of anisotropic reorientation of molecules in liquids. However, in the case of spin systems consisting of several identical nuclei, only one spectral line is observable and the information that can be derived from it is rather limited. To a lesser extent this is also the case of partially degenerate spin systems like AX_n ($n \geq 2$) where two or more transitions are found to be degenerate. It has already been pointed out³ that the study of these systems can be done in an anisotropic medium, where molecular ordering prevents the complete averaging of the dipolar interactions thus completely or partially lifting the degeneracy of these systems.

The presence of the surrounding liquid crystal phase, however, affects the microdynamical behavior of the molecules which are subjected to a restoring torque that tends to bring them back to their equilibrium positions. In isotropic liquids, the diffusion model of Favro⁴ has been the most widely used so far. However, this model is no longer valid in the anisotropic environment where the ordering has to be taken into account. The relevant equation for diffusion in the presence of an ordering potential was derived by Favro.⁵ Simplified forms of this equation were solved by Nordio^{6,7} for rod-like molecules. Later, Freed and co-workers extended in the formalism describing the theory of relaxation in liquid crystals to include director fluctuations.⁸⁻¹²

This paper deals with the diffusion of a molecule experiencing a general second order potential. In this way it extends the work of Nordio which was limited to problems of cylindrical symmetry. The diffusion equation is not symmetrized prior to its numerical solution, thereby providing an alternate approach to the one generally used.¹⁰ This leads to an increased computational difficulty since it involves the diagonalization of a general complex matrix, but directly yields the coefficients of the expansion of the conditional probability. Finally, spectral densities coherent with the ones used in a previous work¹ are presented, thus allowing practical com-

parisons to be made with relaxation matrices presented elsewhere.³

II. POTENTIAL AND TIME-INDEPENDENT PROBABILITY

In solution in a liquid crystal, the molecules are subjected to a potential which can be written¹⁰

$$\frac{V}{kT} = \lambda + \sum_{lkm} \bar{a}_{km}^l D_{km}^l(\Omega) . \quad (1)$$

The D_{km}^l are the rotation matrices of order l ,¹³ Ω refers to the three Euler angles which carry the molecular frame into a frame with the z axis aligned along the director of the liquid crystal phase.

Symmetry of the molecular orientations around the director implies that the averages taken over the last Euler angle vanish unless $m=0$ in the sum given by Eq. (1) which becomes

$$\frac{V}{kT} = \lambda + \sum_{lk} \bar{a}_{k0}^l D_{k0}^l(\Omega) . \quad (2)$$

The solute molecules under magnetic field ordering have no preference for alignment parallel or antiparallel to the director axis. This limits the sum in Eq. (2) to the even values of l . One usually considers only the terms of highest symmetry, keeping only the terms for which $l=2$. This includes the Maier Saupe potential¹⁴ which has been widely used in liquid crystal studies. Furthermore, it has been shown in the case of cylindrically symmetric molecules, that the experimental spectra are not very sensitive to the inclusion of the next higher order terms for which $l=4$.⁹ We will thus approximate the potential created by the nematic phase by the following sum:

$$\frac{V}{kT} = \lambda + \sum_k a_k D_{k0}^2(\Omega) . \quad (3)$$

The probability associated with this potential is

$$P(\Omega) = e^{-V/kT} / \int e^{-V/kT} d\Omega , \quad (4)$$

which at second order is equal to

$$P(\Omega) = \frac{1}{8\pi^2} \left[1 + \sum_k \beta_k D_{k0}^2(\Omega) + \sum_k \gamma_k D_{k0}^4(\Omega) \right] , \quad (5)$$

where β_k and γ_k are given by

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$$\begin{aligned}\beta_k &= -K \left[a_k + \frac{1}{2} \sqrt{\frac{2}{7}} \sum_i a_{k-i} a_i c(2, 2, 2 | k-l, l) \right], \\ \gamma_k &= K \frac{1}{2} \sqrt{\frac{18}{35}} \sum_i a_{k-i} a_i c(2, 2, 4 | k-l, l), \\ K &= \left[1 + \frac{1}{10} \sum_i (-1)^i a_i a_{-i} \right]^{-1},\end{aligned}\quad (6)$$

where $c(l, l', l'' | m, m')$ is the Clebsch-Gordan coefficient for the addition of two angular momenta (l, m) and (l', m') yielding $(l'', m + m')$.

In the NMR spectrum, the magnitude of the splitting constants resulting from the residual dipolar couplings can be related to parameters characterizing the ordering relative to the magnetic field.¹⁵ The probability given in Eq. (5) allows us to compute similar parameters, with the difference that they characterize ordering relative to the director axis of the liquid crystal phase. If the solvent molecules are assumed to be fully oriented by the magnetic field, then there would be no director fluctuations, and the two kinds of ordering parameters should agree in value. For simplicity this assumption is made in our derivation.

A commonly used potential is the Maier-Saupe potential.¹⁴ In this case, Eq. (3) becomes

$$V/kT = \lambda + a_0 D_{00}^2, \quad (7)$$

yielding through the use of Eq. (5):

$$S_{zz} = \langle D_{00}^2 \rangle = -\frac{1}{5} \left[a_0 - \frac{a_0^2}{7} - \frac{a_0^3}{10} \right]. \quad (8)$$

As director fluctuations become important, they would tend to reduce the ordering relative to the magnetic field (i.e., the parameter obtained from the residual dipolar coupling constant) as compared with the ordering relative to the director axis [i.e., the parameter obtained through Eq. (8)]. The effective S_{zz} parameter measured from relaxation data will represent a composite of director ordering and projections on to the magnetic field. Thus, a breakdown in our assumption of the director axis and magnetic field axis being coincident might be expected to yield an effective S_{zz} which is slightly larger than the corresponding value for dipolar splittings.

III. DIFFUSION EQUATION AND CONDITIONAL PROBABILITY

The equation for diffusion in the presence of a potential V was derived by Favro⁵

$$\begin{aligned}-\frac{d}{dt}P(\Omega, t | \Omega') &= \left[\mathbf{M} \cdot \mathbf{R} \cdot \mathbf{M} - \mathbf{M} \cdot \mathbf{R} \cdot \mathbf{M} \frac{V}{kT} \right] P(\Omega, t | \Omega').\end{aligned}\quad (9)$$

$P(\Omega, t | \Omega')$ is the conditional probability for finding the laboratory frame in the orientation Ω at time t , when its orientation at time 0 was Ω' . \mathbf{M} is the quantum mechanical angular momentum operator in the molecular frame and \mathbf{R} is the diffusion tensor. This differential equation is subject to the initial condition

$$P(\Omega, 0 | \Omega') = \delta(\Omega - \Omega') \quad (10)$$

The operators of Eq. (9) act on Ω and we develop P in an expansion of rotation matrices

$$P(\Omega, t | \Omega') = \sum_{lmn} \beta_{lmn}^l(\Omega', t) D_{lmn}^l(\Omega), \quad (11)$$

$$\beta_{lmn}^l(\Omega', t) = \sum_{l', m', n'} \alpha_{lmn}^{l' m' n'}(t) D_{l' m' n'}^{l'}(\Omega), \quad (12)$$

where $\alpha_{lmn}^{l' m' n'}(t)$ and $\beta_{lmn}^l(\Omega', t)$ are unknown functions of time. The action of the operator \mathbf{M} on the rotation matrices can be defined by

$$\begin{aligned}M^2 D_{lmn}^l(\Omega) &= l(l+1) D_{lmn}^l(\Omega), \\ M^z D_{lmn}^l(\Omega) &= m D_{lmn}^l(\Omega), \\ M^\pm D_{lmn}^l(\Omega) &= \eta_{lm}^\pm D_{l, m \pm 1, n}^l(\Omega),\end{aligned}\quad (13)$$

where $\eta_{lm}^\pm = [l(l+1) - m(m \pm 1)]^{1/2}$. Using these relations, Eq. (11), and projecting on the rotation matrices yields the following formulation for Eq. (9):

$$-\frac{d}{dt} \beta_{lmn}^l = \sum_{l', m', n'} \Gamma_{lmn}^{l' m' n'} \beta_{l' m' n'}^{l'}. \quad (14)$$

As the operators of Eq. (9) only act on the two first Euler angles, the matrix Γ of Eq. (14) is found to be block diagonal, factorization occurring for the n index corresponding to the last Euler angle.

Equation (14) can thus be written in condensed matrix notation

$$-\frac{d}{dt} \beta_n = \Gamma_n \beta_n. \quad (15)$$

Γ_n mixes only the β_{lmn}^l with the $\beta_{l' m' n'}^{l'}$. Its matrix elements are found to be

$$\begin{aligned}\Gamma_{\mu n}^{\lambda l} = & \delta_{l\lambda} \Gamma_1 + c(2, l, \lambda | \mu - m, m) c(2, l, \lambda | 0, n) \Gamma_2 \\ & + c(2, l, \lambda | 0, n) [c(2, l, \lambda | \mu - m - 1, m + 1) \eta_{lm}^+ \Gamma_3 + c(2, l, \lambda | \mu - m - 1, m - 1) \eta_{lm}^- \Gamma_4],\end{aligned}\quad (16)$$

with

$$\begin{aligned}\Gamma_1 &= \delta_{m+2, \mu} B^+ \eta_{lm}^+ \eta_{l, m+1}^+ + \delta_{m+1, \mu} D^+ \eta_{lm}^+ (2m+1) + \delta_{m, \mu} [A l(l+1) + (C-A)m^2] + \delta_{m-1, \mu} D^- \eta_{lm}^- (2m-1) + \delta_{m-2, \mu} B^- \eta_{lm}^- \eta_{l, m-1}^-, \\ \Gamma_2 &= B^+ \eta_{2, \mu-m-2}^+ \eta_{2, \mu-m-1}^+ a_{\mu-m-2} + D^+ \eta_{2, \mu-m-1}^+ (2\mu-m-1) a_{\mu-m-1} + [6A + (C-A)(\mu-m)^2 + Cm(\mu-m)] a_{\mu-m} \\ &+ D^- \eta_{2, \mu-m+1}^- (2\mu-m+1) a_{\mu-m+1} + B^- \eta_{2, \mu-m+2}^- \eta_{2, \mu-m+1}^- a_{\mu-m+2}, \\ \Gamma_3 &= \eta_{2, \mu-m-2}^+ B^+ a_{\mu-m-2} + (\mu-m-1) D^+ a_{\mu-m-1} + \frac{1}{2} A \eta_{2, \mu-m}^+ a_{\mu-m}, \\ \Gamma_4 &= \eta_{2, \mu-m+2}^- B^- a_{\mu-m+2} + (\mu-m+1) D^- a_{\mu-m+1} + \frac{1}{2} \eta_{2, \mu-m}^- A a_{\mu-m}.\end{aligned}\quad (17)$$

In these formulas when an index goes beyond its allowed range, the corresponding term is set to zero, i.e.,

$$a_i = 0 \text{ if } i > 2 \text{ or } i < -2. \quad (18)$$

The constants A , B , C , and D are given by

$$\begin{aligned} A &= \frac{1}{2}(R_{xx} + R_{yy}), \\ B &= \frac{1}{4}(R_{xx} - R_{yy}) + (i/2)R_{xy}, \\ C &= R_{zz}, \\ D &= \frac{1}{2}(R_{xx} - iR_{yz}). \end{aligned} \quad (19)$$

Each Γ_n matrix can be diagonalized

$$\Gamma_n = \mathbf{B}_n \cdot \Lambda_n \cdot \mathbf{C}_n. \quad (20)$$

\mathbf{B}_n is the matrix formed by arranging the eigenvectors of Γ_n by columns. Λ_n is the diagonal matrix formed by the eigenvalues λ_{kn} of Γ_n and \mathbf{C}_n is the inverse of \mathbf{B}_n . The solution of Eq. (9) can then be written

$$\beta_n(t) = \mathbf{B}_n \cdot e^{-\Lambda_n t} \cdot \mathbf{C}_n \cdot \beta_n(0). \quad (21)$$

If we define a time-dependent coefficient d by

$$d_{m' n'}^{l' l''}(t) = \sum_k b_{mkn}^l e^{-\lambda_{kn} t} c_{km' n'}^{l' l''}, \quad (22)$$

where b_{mkn}^l is the (l, m) , k element of \mathbf{B}_n and c_{kmn}^l the k , (l, m) element of \mathbf{C}_n it is then possible to write an expression for the α appearing in the solution Equation (12) of the diffusion equation as follows:

$$\alpha_{m' n'}^{l' l''}(t) = \sum_{l''', m'''} d_{m' n'}^{l' l''}(t) \alpha_{m'' n''}^{l''' l'''}(0). \quad (23)$$

The initial condition given in Eq. (10) yields the following equation for the value of the α at time 0:

$$\alpha_{m' n'}^{l' l''}(0) = \delta_{l' l''} \delta_{-m' m''} \delta_{-n' n''} (-1)^{m' n'} \frac{5}{8\pi^2}. \quad (24)$$

This indicates that the α are null whenever $n + n'$ is non-zero. One can thus write the value of these α at time t

$$\alpha_{m' n'}^{l' l''}(t) = \frac{5}{8\pi^2} (-1)^{m' n'} d_{m' n'}^{l' l''}(t). \quad (25)$$

This represents the solution of Eq. (9) in terms of an infinite series of rotation matrices. We have written a FORTRAN program that yields the values of the α given in Eq. (24) for the values of $l = l' = 2$. As will be shown later, these are the only coefficients needed for the computation of the spectral densities. Diagonalization and inversion of the complex matrices Γ_n and \mathbf{B}_n are done by using standard mathematical subroutines from I. M. S. L.¹⁶ It is found that it is necessary to carry out the development in Eq. (12) up to order four in l and l' . It takes approximately 40 s to obtain the α of Eq. (24) from the initial parameters on the PDP 11/70.

IV. DIPOLAR SPECTRAL DENSITIES

In the case of dipolar relaxation, the terms needed to compute the Redfield matrix elements are the spectral densities,¹

$$\begin{aligned} J_{ij k l}^n(\omega) &= \xi_{ij} \xi_{kl} \int_0^\infty \langle Y_n^2[\Phi_{ij}^{lab}(0)] Y_n^2[\Phi_{kl}^{lab}(t)] \rangle e^{-i\omega\tau} d\tau. \end{aligned} \quad (26)$$

The Y_n^2 are the second order spherical harmonics and are functions of the two polar angles Φ_{ij}^{lab} that characterize the ij th internuclear vector in the laboratory frame. The ξ_{ij} are constants equal to $\sqrt{(6\pi/5)} (\gamma_i \gamma_j \hbar / r_{ij}^3)$. These spectral densities can be expressed in terms of the internuclear vector orientation Φ_{ij}^{mol} in the molecular frame, and in terms of the ensemble average of the rotation matrices

$$\begin{aligned} J_{ij k l}^n(\omega) &= \xi_{ij} \xi_{kl} \sum_{mm'} Y_n^2[\Phi_{ij}^{mol}] Y_n^2[\Phi_{kl}^{mol}] \\ &\times \int_0^\infty \langle D_{mn}^2[\Omega(\tau)] D_{m' n'}^2[\Omega(0)] \rangle e^{-i\omega\tau} d\tau. \end{aligned} \quad (27)$$

$\Omega(\tau)$ refers to the three Euler angles that carry the molecular frame to the laboratory frame at time τ . The ensemble average in Eq. (27) can be written as

$$\langle \rangle = \iint D_{mn}^2(\Omega) D_{m' n'}^2(\Omega') P(\Omega, \tau | \Omega') P(\Omega') d\Omega d\Omega'. \quad (28)$$

Assuming the absence of director fluctuations, the director axis is taken as the laboratory frame z axis and the conditional probability and the time independent probability contained in this equation are given by Eqs. (4) and (9), respectively.

The product of these probabilities can be expanded in terms of the rotation matrices according to

$$\begin{aligned} P(\Omega') P(\Omega, \tau | \Omega') &= \sum_{l m n} \sum_{l' m' n'} P_{l m n}^{l' m' n'}(\tau) D_{l m n}^l(\Omega) D_{l' m' n'}^{l'}(\Omega'). \end{aligned} \quad (29)$$

The orthogonality of the rotation matrices then implies that Eq. (28) becomes

$$\begin{aligned} \langle D_{mn}^2(\tau) D_{m' n'}^2(0) \rangle &= (-1)^{m+n+m'+n'} \left(\frac{8\pi^2}{5} \right)^2 p_{-m-n, -m'-n'}^2(\tau). \end{aligned} \quad (30)$$

Thus of all the terms that form the expansion in Eq. (29) only 5⁴ at most are necessary to compute the spectral densities. This number is reduced further by the fact that the p are null if $n + n'$ is not equal to zero. In fact multiplication of the two series given in Eqs. (5) and (11) yields

$$\begin{aligned} 8\pi^2 p_{mn m' n'}^2(\tau) &= \alpha_{mn m' n'}^2(\tau) + \sum_j c(j, 2, 2 | -n, 0) \\ &\times \sum_q c(j, 2, 2 | n' - q, q) \beta_q \alpha_{mn m' n' - q n}^2(\tau) + \sum_j c(j, 4, 2 | -n, 0) \\ &\times \sum_q c(j, 4, 2 | n' - q, q) \gamma_q \alpha_{mn m' n' - q n}^2(\tau). \end{aligned} \quad (31)$$

The time dependence of the α occurs through the exponentials of Eq. (22). After Fourier transformation in Eq. (27) they will yield Lorentzian functions. Thus introducing

$$\begin{aligned} \tilde{d}_{m' n'}^{l' l''}(\omega) &= \sum_k b_{mkn}^l c_{km' n'}^{l' l''} \frac{\lambda_{kn}}{\lambda_{kn}^2 + \omega^2}, \\ \tilde{\alpha}_{m' n'}^{l' l''}(\omega) &= \frac{5}{8\pi^2} (-1)^{m' n'} \tilde{d}_{m' n'}^{l' l''}(\omega). \end{aligned} \quad (32)$$

The formulas in Eqs. (30) and (31) will yield the Fourier

transform of the ensemble average of the rotation matrices at the frequency ω by simply changing α to $\tilde{\alpha}$. In particular, when the extreme narrowing condition can be used, the formulas become ω independent and one can simply write

$$\hat{d}_{m m'}^{l l'} = \sum_k b_{m k n}^l c_{m' k n}^{l'} \frac{1}{\lambda_{k n}} \quad (33)$$

thus yielding through Eqs. (27), (30), (31), and (25) a frequency-independent spectral density.

In the case of isotropic liquids, extreme narrowing implies equality of the spectral densities corresponding to different z -projection numbers (i. e., the n and n' indices of $J_{ij}^{n n'}(\omega)$ given by Eq. (26). This is no longer the case in partially ordered systems, where for each pair of m and m' indices in Eq. (30) there are three different values of p corresponding to the values of $|n| = 0, 1$, and 2 . This implies, through Eq. (27) that the J 's themselves will be different for different values of n , even though one may be in a motional regime which would otherwise correspond to extreme narrowing.

V. CONCLUSION

The formula given in this paper allows one to compute the spectral densities which are necessary in the relaxation matrix formalism developed by Redfield.¹⁶ Contrary to the isotropic liquid case, the diffusion equation in ordered liquids can no longer be solved in closed form and must be solved numerically. As a result of the solute molecule assuming a preferential ordering relative to the director axis, the spectral densities differ for $|m| = 0, 1$, and 2 , the three different z -projection numbers, even though the motion would otherwise justify the extreme narrowing approximation.

This theory and its implications have been experi-

mentally verified and the results appear in the adjoining papers.^{18,19}

ACKNOWLEDGMENT

Support for this work was provided by the Public Health Service on Grant GM 08521 from the National Institute of General Medical Sciences.

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