Molecular dynamics in lipid bilayers

Anisotropic diffusion in an odd restoring potential

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ABSTRACT Recent ^{2}H nuclear magnetic resonance spin relaxation studies have questioned the influence of restoring potential parity on the description of lipid or molecular reorientational dynamics. In biomembranes the polar head groups of lipid and sterol constituents are expected to associate with the aqueous interface; therefore, realistic descriptions of molecular reorientation in bilayer systems should use an odd restoring potential. The multiexponential correlation functions and related spectral density functions for small-step anisotropic diffusion in a pseudo-restoring potential of the form $U(\beta) = -\lambda \cos\beta$ are evaluated as a function of molecular ordering $\langle P_2(\cos\beta)\rangle$. From analysis of these results the single exponential approximation used in previous investigations is found to overestimate the decay rate at lower order, but is reliable for $\langle P_2(\cos\beta)\rangle > 0.6$. The exception to this trend is the decay constant for the $G_{11}(\Omega; t)$ correlation function, which is not accurately portrayed by the first-order approximations. A second-order single exponential approximation is presented, and is shown to be equivalent to the weighted sum of the multidecay constants. In general, the potential parity is found to have only minor effects on the spin relaxation rates obtained to describe molecular reorientation in lipid bilayers.

INTRODUCTION

Nuclear magnetic resonance (NMR) has been used in the investigation of structural and dynamical properties of lipid phases. In addition to being a major component of biological membranes, lipids may also prove important in understanding the properties of liquid-crystalline phases. Deuterium (^{2}H) NMR spin relaxation studies are an important experimental tool in the elucidation of motions in lipid and model membrane systems (Brown, 1982; Jarrell et al., 1988; Auger et al., 1990; Bonmatin et al., 1990; Mayer et al., 1990; Stohrer et al., 1991; Winsborrow et al., 1991; Trouard et al., 1992), because segmental and molecular motions in lipid systems occur on the time scale of the Larmor frequency. Investigation of relaxation rates can provide information concerning the mechanism, rate, and amplitude of these dynamic processes. A wide variety of motional models have been proposed, and in general can be described as: (*a*) internal or segmental motions, (*b*) molecular reorientations, (*c*) collective order fluctuations, and (*d*) vesicle tumbling (Brown, 1982; Brown et al., 1990; Brown and Söderman, 1990; Halle, 1991).[1] Unfortunately, the importance and relative contributions of these motions are still open to debate.

It has long been recognized that spin relaxation is dependent on the angle between the motional symmetry axis and the static magnetic field, and provides an additional test of proposed models. This angular dependence or anisotropy of relaxation has not been exploited extensively in lipid systems because of averaging from lateral diffusion over the curved lipid surface (Brown and Davis, 1981). Recent investigations using physically oriented lipid samples on glass substrates have allowed spin relaxation as a function of the angle between the director axis of the lipid phase and external magnetic field to be determined (Jarrell et al., 1988; Bonmatin et al., 1990; Stohrer et al., 1991; Winsborrow et al., 1991; Trouard et al., 1992). Spin-lattice relaxation studies of selectively deuterated 1,2-Dimyristoyl-*sn*-glycero-3-phosphocholine and 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine revealed a weak angular dependence (Jarrell et al., 1988). In contrast, spin-lattice relaxation rates of oriented cholesterol/phospholipid bilayers revealed significant angular anisotropy in both the acyl chain of the lipid and the labeled cholesterol molecule (Bonmatin et al., 1990; Trouard et al., 1992). Combined studies of angular dependent spin-lattice (R_{1Z}), quadrupolar order (R_{1Q}) relaxation rates, and the derived spectral densities, $J_1(\omega_0)$ and $J_2(2\omega_0)$, have been undertaken on oriented glycolipids (Winsborrow et al., 1991) and perdeuterated phospholipid bilayers (Trouard et al., 1992). These investigations may provide a crucial test of proposed models for lipid and membrane dynamics.

Diffusion models have been used previously to describe NMR relaxation in liquid crystalline phases including lipid bilayers (Brown, 1982; Brown et al., 1990; Trouard et al., 1992).[1] Recent investigations of lipid dynamics using spin relaxation have raised the question concerning the effects of the restoring potential parity in a small-step rotational diffusion description of molecular reorientation (Halle, 1991; Trouard et al., 1992).[1] In biomembranes the polar head group of the lipid and sterol constituents effectively associates with the aqueous interface. Therefore, molecular reorientations in the liquid crystalline lamellar phase using diffusion models are more realistically described using an odd restoring potential. This odd parity reflects the tendency of the head groups to align along the bilayer normal with the head group at the aqueous interface. Procedures for the evaluation of the diffusion equation in the presence

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[1] Trouard, T. P., T. M. Alam, J. Constantin, and M. F. Brown, manuscript submitted for publication.

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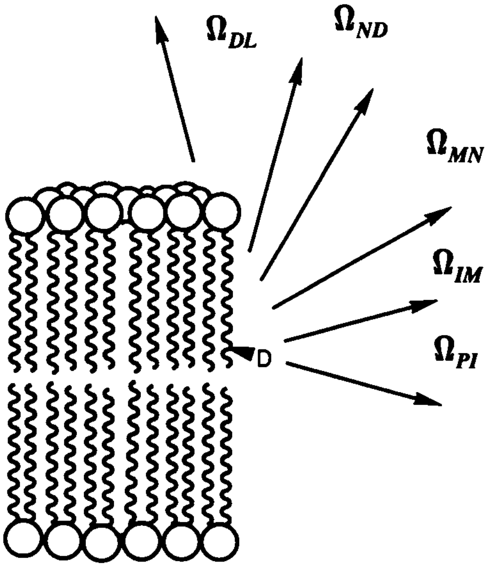

FIGURE 1 Conceptual diagram of the transformations used in the formulation of the anisotropic rotational diffusion model. The transformation of the electric field gradient (EFG) tensor into the laboratory frame through Euler angles $\Omega_{\mathrm{PL}} \equiv (\alpha_{\mathrm{PL}}, \beta_{\mathrm{PL}}, \gamma_{\mathrm{PL}})$ is accomplished by five intermediate transformations specifically useful to the model discussed. The Euler angles Ω_{PI} describe the transformation from the principal axis system (PAS) of the static EFG tensor to an intermediate motional coordinate system; Ω_{IM} describes the transformation from the intermediate frame to the molecular axis system; Ω_{MN} describes the rotation from the molecular frame to the instantaneous director $\mathbf{n}(t)$; Ω_{ND} represents the transformation from the instantaneous director to the average director or macroscopic bilayer normal $\mathbf{n}_0$; and Ω_{DM} describes the fixed transformation from the average director to the laboratory frame (i.e., static external magnetic field), in which $(\alpha_{\mathrm{DL}}, \beta_{\mathrm{DL}}) \equiv (\phi, \theta)$.

of a restoring pseudo-potential have been presented (Polnaszek and Freed, 1975; Moro and Nordio, 1983; Vold and Vold, 1988), but have only been discussed for even potentials of the form $U(\beta) = -\lambda \cos^{2n} \beta$. In this paper, solutions for rotational diffusion in a restoring pseudo-potential of the form $U(\beta) = -\lambda \cos \beta$ are investigated. The multiexponential correlation functions as a function of the second rank order parameter $\langle P_2(\cos \beta) \rangle = \langle D^{(2)}_{00}(\beta) \rangle$ are evaluated, allowing a direct comparison to previous results for even restoring potentials (Vold and Vold, 1988). Earlier lipid studies (Halle, 1991)[1] comparing anisotropic diffusion in an odd or even restoring potentials have used short-time or first-order single exponential approximations for the correlation function (Moro and Nordio, 1983; Szabo, 1984). By direct comparison to the weighted sum of the multiexponential solutions from this study, the accuracy and the range of molecular order for which these approximations are valid are addressed. These results allow a critical evaluation concerning the effects of even and odd restoring potentials in the description of lipid dynamics.

THEORY

Spin relaxation and spectral densities

For an isolated deuterium nucleus, fluctuations of the quadrupolar interaction yield a time-dependent perturbation that governs nuclear spin relaxation. Spin-lattice relaxation and quadrupolar order decay rates are obtained using standard ^{2}H NMR relaxation theory (Abragam, 1961; Slichter, 1990; Vold and Vold, 1991) and are given by

$$R_{1\mathrm{Z}} = {}^3\!/\!_4\pi^2\chi^2[J_1(\omega_0) + 4J_2(2\omega_0)], \tag{1}$$

$$R_{1\mathrm{Q}} = {}^9\!/\!_4\pi^2\chi^2 J_1(\omega_0), \tag{2}$$

where $\chi \equiv e^2qQ/h$ is the static quadrupolar coupling constant, ω_0 is the nuclear Larmor frequency, and $J_m(m\omega_0)$ are the spectral densities of motion. The spectral densities are Fourier transform partners of the autocorrelation functions $G_m(t)$ describing the fluctuations of the quadrupolar interaction, and are given by

$$J_m(m\omega_0) = \mathrm{Re} \int_{\infty}^{-\infty} G_m(t) e^{-im\omega_0 t}\, \mathrm{d}t. \tag{3}$$

The electrical field gradient (EFG)[2] tensor components in the principal axis system (PAS) can be transformed to the laboratory frame using the second-rank rotation matrices $D^{(2)}_{sm}(\Omega_{\mathrm{PL}})$ (Brink and Satchler, 1968).

It is convenient to describe the reorientational dynamics of membrane constituents in terms of a series of individual intermediate frames, in which Ω_{PL} is replaced by various Euler angles using the closure property of the rotation group (Brink and Satchler, 1968). A set of intermediate frames that has proven useful in the description of lipid bilayer dynamics (Brown, 1982; Trouard et al., 1992) is illustrated schematically in Fig. 1, and is expressed by

$$D^{(2)}_{sm}(\Omega_{\mathrm{PL}}; t) = \sum_r \sum_q \sum_p \sum_n D^{(2)}_{sr}(\Omega_{\mathrm{PI}}; t) D^{(2)}_{rq}(\Omega_{\mathrm{IM}}; t) \times D^{(2)}_{qp}(\Omega_{\mathrm{MN}}; t) D^{(2)}_{pn}(\Omega_{\mathrm{ND}}; t) D^{(2)}_{nm}(\Omega_{\mathrm{DL}}). \tag{4}$$

The Euler angles Ω_{PI} specify the rotation from the PAS (P) of the static EFG tensor to an internal or intermediate (I) motional frame; Ω_{IM} defines the transformation from the intermediate motional frame to the molecular (M) axis system; Ω_{MN} expresses the rotation from the molecular frame to the axis system of the instantaneous director $\mathbf{n}(t)$; Ω_{ND} represents the transformation from the instantaneous director to the average director $\mathbf{n}_0$ (i.e., macroscopic bilayer normal); and, finally, Ω_{DL} describes the fixed transformation from the average director (D) to the laboratory frame (L) (i.e., the static external magnetic field). In the latter transformation, $(\alpha_{\mathrm{DL}}, \beta_{\mathrm{DL}}) \equiv$

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[2] *Abbreviations used in this paper:* EFG, electrical field gradient; PAS, principal axis system.

(ϕ, θ), which are the spherical polar angles describing the orientation of the magnetic field in the bilayer frame.

A major contribution to the observed spin relaxation in bilayers is lipid or molecular reorientation. As detailed previously (Trouard et al., 1992),[1] internal or segmental motions may preaverage the static EFG tensor resulting in a residual or effective EFG tensor that is modulated by the time-dependent transformation Ω_{MD} from the molecular diffusion tensor to the average macroscopic bilayer normal. Assuming an axially symmetric static EFG tensor ($\eta = 0$), plus the absence of instantaneous director fluctuations, the spectral densities are defined by[1]

$$\begin{aligned} J_m(m\omega_0) = \sum_r \sum_q \sum_n & |\langle D^{(2)}_{0r}(\Omega_{\mathrm{PI}})\rangle|^2 |D^{(2)}_{rq}(\Omega_{\mathrm{IM}})|^2 \\ & \times [\langle |D^{(2)}_{qn}(\Omega_{\mathrm{MD}})|^2\rangle - |\langle D^{(2)}_{qn}(\Omega_{\mathrm{MD}})\rangle|^2 \delta_{q0}\delta_{n0}] \\ & \times j_{qn}(m\omega_0) |D^{(2)}_{nm}(\Omega_{\mathrm{DL}})|^2, \end{aligned} \tag{5}$$

where the reduced spectral densities for molecular anisotropic diffusion (vide infra) are denoted by $j_{qn}(m\omega_0)$. Rotational symmetry about both the diffusion tensor and the average director z-axes has been assumed (Trouard et al., 1992).[1] The molecular reorientation is described by the spectral density component $J_{qn}(\Omega_{\mathrm{MD}}; m\omega_0)$ or the correlation function $G_{qn}(\Omega_{\mathrm{MD}}; t)$, which can be factored into time-dependent components given by products of the reduced correlation functions $g_{qn}(\Omega_{\mathrm{MD}}; t)$ or reduced spectral densities $j_{qn}(\Omega_{\mathrm{MD}}; m\omega_0)$ and the time-independent mean-squared fluctuations, $g_{qn}(\Omega_{\mathrm{MD}}; 0)$:

$$\begin{aligned} G_{qn}(\Omega_{\mathrm{MD}}; t) & \equiv g_{qn}(\Omega_{\mathrm{MD}}; 0) g_{qn}(\Omega_{\mathrm{MD}}; t) \\ & = \{\langle |D^{(2)}_{qn}(\Omega_{\mathrm{MD}})|^2\rangle - |\langle D_{qn}(\Omega_{\mathrm{MD}})\rangle|^2 \delta_{q0}\delta_{n0}\} \\ & \quad \times g_{qn}(\Omega_{\mathrm{MD}}; t), \end{aligned} \tag{6}$$

$$\begin{aligned} J_{qn}(\Omega_{\mathrm{MD}}; m\omega_0) & \equiv g_{qn}(\Omega_{\mathrm{MD}}; 0) j_{qn}(m\omega_0) \\ & = \{\langle |D^{(2)}_{qn}(\Omega_{\mathrm{MD}})|^2\rangle - |\langle D^{(2)}_{qn}(\Omega_{\mathrm{MD}})\rangle|^2 \delta_{q0}\delta_{n0}\} \\ & \quad \times j_{qn}(m\omega_0). \end{aligned} \tag{7}$$

The products of the rotation matrices are evaluated in terms of their Clebsch-Gordan series (Brink and Satchler, 1968) expansions:

$$\begin{aligned} D^{(j_1)*}_{m_1'm_1}(\Omega) D^{(j_2)}_{m_2'm_2}(\Omega) = (-1)^{m_1-m_1'} \sum_j (2j+1) & \\ \times \begin{pmatrix} j_1 & j_2 & j \\ -m_1' & m_2' & m' \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j \\ -m_1 & m_2 & m \end{pmatrix} D^{(j)*}_{m'm}(\Omega), & \end{aligned} \tag{8}$$

where

$$\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \tag{9}$$

denotes a Wigner 3-j symbol, and $\Omega \equiv (\alpha, \beta, \gamma)$ are generalized Euler angles. The value of j in Eq. 9 satisfies the triangle condition $\Delta(j_1\, j_2\, j)$ (Brink and Satchler, 1968).

Evaluation of spectral density functions for a general potential of mean torque

Evaluation of the $J_{qn}(\Omega_{\mathrm{MD}}; m\omega_0)$ or $G_{qn}(\Omega_{\mathrm{MD}}; t)$ in Eqs. 6 and 7 is governed by the potential used. A general potential of mean torque may be defined by (Zannoni, 1985)

$$U(\cos\beta) = \sum_i a_i P_i(\cos\beta), \tag{10}$$

where $\Omega = (0, \beta, 0)$ is a general Euler angle, $P_i(\cos\beta)$ is a Legendre polynomial of rank i, and a_i is the relative weight. Approximating the potential in this manner allows the relevant order parameters to be evaluated using the Boltzmann expression[1]

$$\begin{aligned} \langle D^{(i)}_{00}(\Omega)\rangle & = \langle P_i(\cos\beta)\rangle \\ & = \frac{\int_0^\pi P_i(\cos\beta) e^{-\mathrm{U}(\cos\beta)/\mathrm{kT}} \sin\beta \, \mathrm{d}\beta}{\int_0^\pi e^{-\mathrm{U}(\cos\beta)/\mathrm{kT}} \sin\beta \, \mathrm{d}\beta}. \end{aligned} \tag{11}$$

In general the spectral density component $J_{qn}(\Omega_{\mathrm{MD}}; m\omega_0)$ in Eq. 7 is a function of both even and odd rank order parameters. To evaluate Eq. 7, the rotational diffusion equation for a given potential of mean torque $U(\beta)$ must be solved (Polnaszek and Freed, 1975; Nordio and Segre, 1979; Moro and Nordio, 1983; Vold and Vold, 1988). The reduced correlation function can be written as an infinite sum of exponentials taking the form (Nordio and Segre, 1979)

$$g_{qn}(\Omega_{\mathrm{MD}}; t) = e^{-q^2(\mathrm{D}_\parallel - \mathrm{D}_\perp)\mathrm{t}} \sum_{i=1}^{\infty} b^{(i)}_{qn} e^{-\alpha^{(i)}_{pn}\mathrm{D}_\perp \mathrm{t}}, \tag{12}$$

or equivalently the reduced spectral densities can be written as an infinite series of Lorentzians

$$j_{qn}(\Omega_{\mathrm{MD}}; m\omega_0) = \sum_{i=1}^{\infty} b^{(i)}_{qn} \frac{\tau^{(i)}_{qn}}{1 + [m\omega_0 \tau^{(i)}_{qn}]^2}, \tag{13}$$

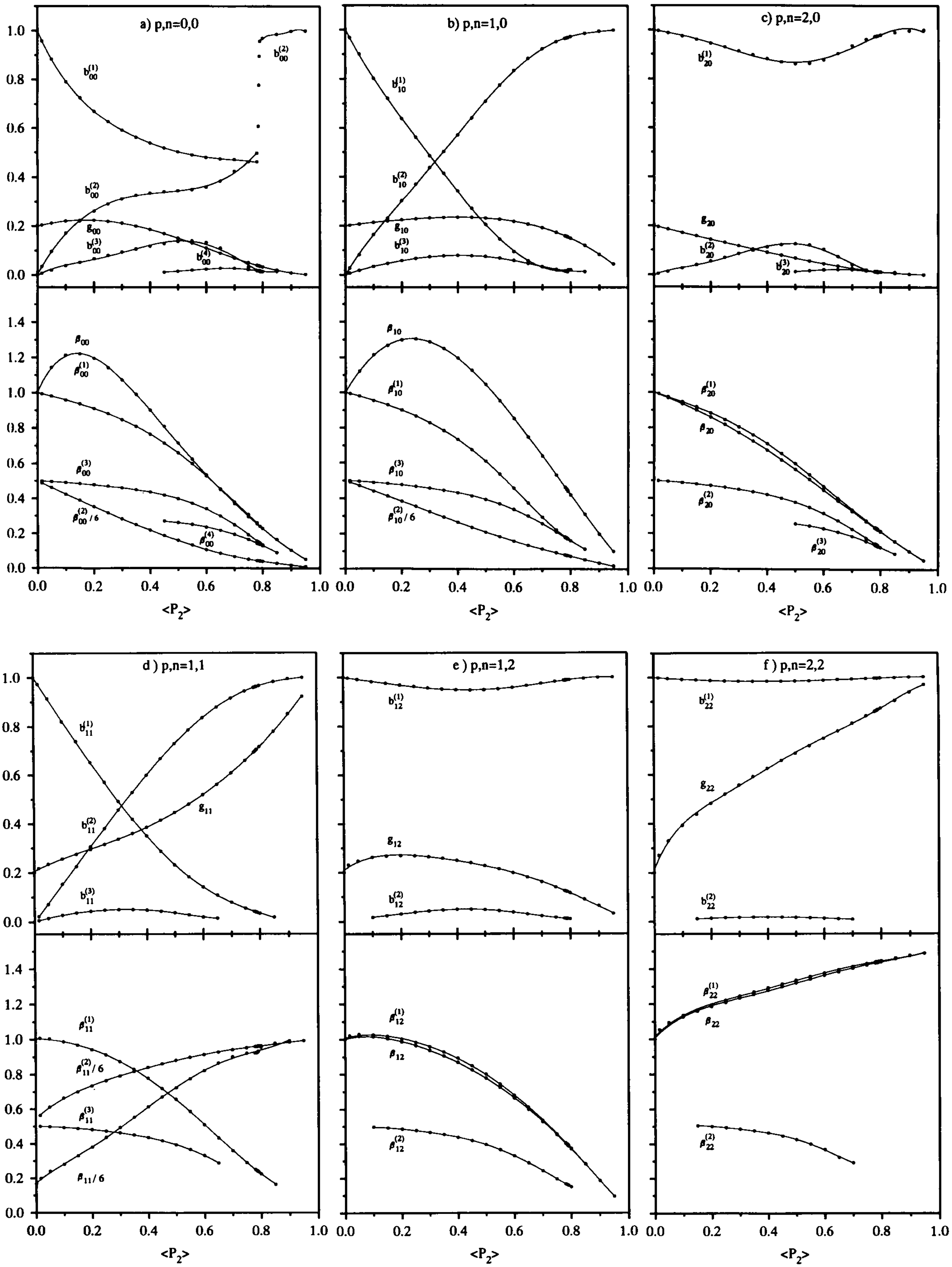
in which $b^{(i)}_{qn}$ and $\tau^{(i)}_{qn}$ are the relative weight and the correlation time for ith relaxation component, respectively.

Evaluation of odd restoring potential

The correlation function $G_{qn}(\Omega_{\mathrm{MD}}; t)$ is given by the matrix elements of the exponential symmetrized diffusion operator $\hat{\mathbf{R}}$

$$G_{qn}(\Omega_{\mathrm{MD}}; t) = \langle f^{(2)}_{qn}(\Omega_{\mathrm{MD}}) | e^{-\hat{\mathrm{R}}\mathrm{t}} | f^{(2)}_{qn}(\Omega_{\mathrm{MD}})\rangle, \tag{14}$$

where $f^{(i)}_{qn}(\Omega_{\mathrm{MD}})$ is the normalized nonorthogonal basis set defined by Moro and Nordio (1983). The matrix elements of the symmetrized diffusion operator are given by


a) p,n=0,0
b) p,n=1,0
c) p,n=2,0
d) p,n=1,1
e) p,n=1,2
f) p,n=2,2
$b_{00}^{(1)}$
$b_{00}^{(2)}$
g_{00}
$b_{00}^{(3)}$
$b_{00}^{(4)}$
β_{00}
$\beta_{00}^{(1)}$
$\beta_{00}^{(3)}$
$\beta_{00}^{(2)}/6$
$\beta_{00}^{(4)}$
$b_{10}^{(1)}$
$b_{10}^{(2)}$
g_{10}
$b_{10}^{(3)}$
β_{10}
$\beta_{10}^{(1)}$
$\beta_{10}^{(3)}$
$\beta_{10}^{(2)}/6$
$b_{20}^{(1)}$
g_{20}
$b_{20}^{(2)}$
$b_{20}^{(3)}$
$\beta_{20}^{(1)}$
β_{20}
$\beta_{20}^{(2)}$
$\beta_{20}^{(3)}$
$b_{11}^{(1)}$
$b_{11}^{(2)}$
g_{11}
$b_{11}^{(3)}$
$\beta_{11}^{(1)}$
$\beta_{11}^{(2)}/6$
$\beta_{11}^{(3)}$
$\beta_{11}/6$
$b_{12}^{(1)}$
g_{12}
$b_{12}^{(2)}$
$\beta_{12}^{(1)}$
β_{12}
$\beta_{12}^{(2)}$
$b_{22}^{(1)}$
g_{22}
$b_{22}^{(2)}$
$\beta_{22}^{(1)}$
β_{22}
$\beta_{22}^{(2)}$
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
<P$_2$>

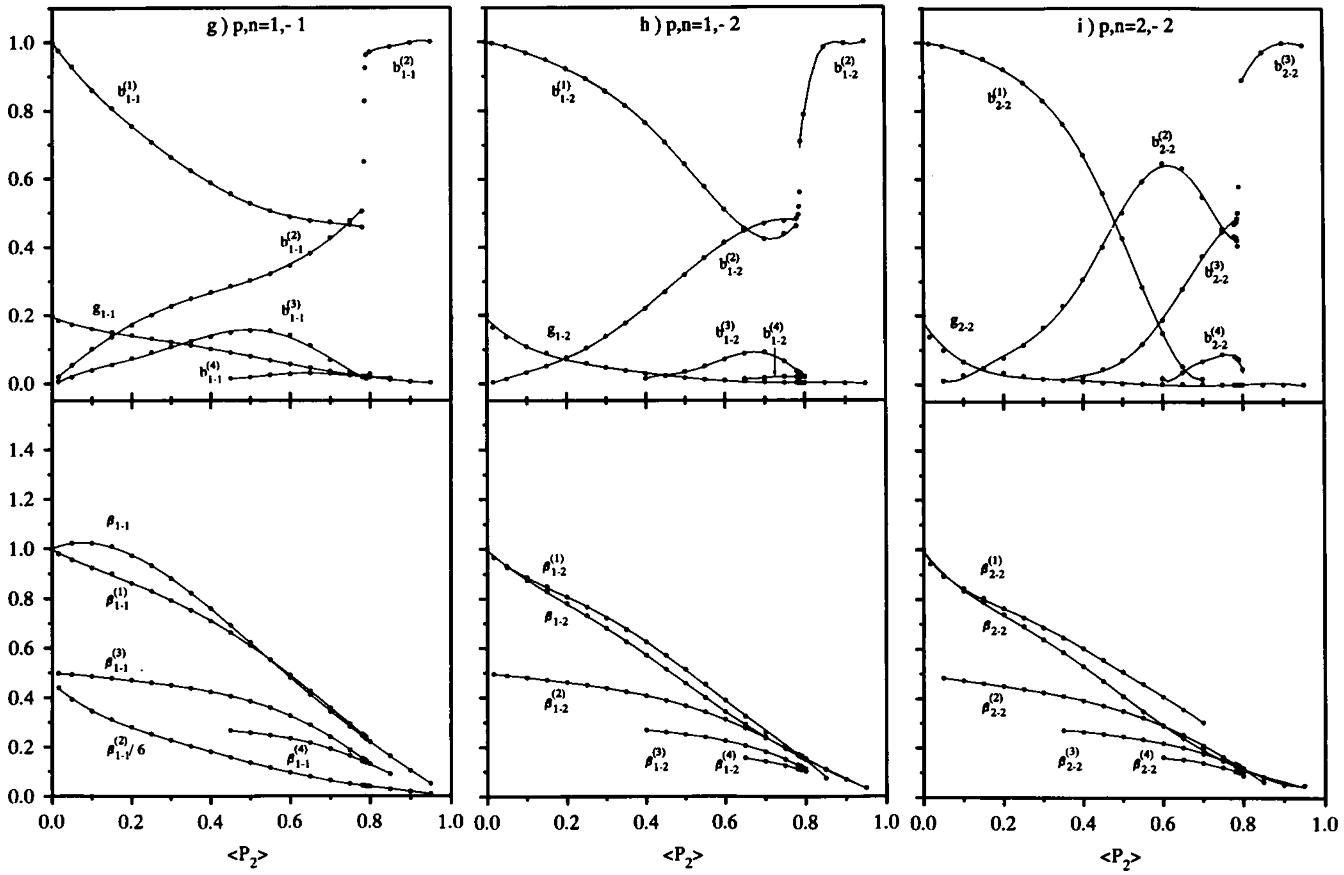


FIGURE 2 Mean squared amplitudes (g_{qn}), relative weights ($b^{(i)}_{qn}$), decay constants ($\beta^{(i)}_{qn} = 6/\alpha^{(i)}_{qn}$), and weighted average decay constants (β_{qn}) as a function of the order parameter $\langle P_2(\cos\beta_{\text{MD}})\rangle$, for the multiexponential correlation functions and spectral densities (Eqs. 12 and 13) describing rotational diffusion for an isotropic diffusion tensor in a restoring potential $U(\beta) = -\lambda\cos\beta$. Solid points represent values calculated as described in Theory. Curves are the power series representations, $\Sigma_{\text{n}}\, a_{\text{n}}\langle P_2(\cos\beta_{\text{MD}})\rangle^{\text{n}}$, given in Table 1.

$$\begin{aligned}\langle f^{(i)}_{qn}(\Omega_{\text{MD}})|\,\hat{\mathbf{R}}\,|f^{(j)}_{qn'}(\Omega_{\text{MD}})\rangle &= \delta_{nn'}N^{-1/2}_{iiqn}N^{-1/2}_{jjqn}\sum_k b^{(ij,qn)}_k\langle P_k(\cos\beta_{\text{MD}})\rangle\\ &\quad\times\{q^2D_\parallel + {}^1\!/\!_2[i(i+1)+j(j+1)\\ &\quad - 2q^2 - k(k+1)]D_\perp\},\end{aligned} \tag{15}$$

where N_{ijqn} are normalization factors,

$$N_{ijqn} = \langle D^{(i)}_{qn}(\Omega_{\text{MD}})|\,D^{(j)}_{qn}(\Omega_{\text{MD}})\rangle, \tag{16}$$

and the coefficients $b^{(ij,qn)}_k$ are defined by (see Eq. 8)

$$b^{(ij,qn)}_k = (-1)^{n-q}(2k+1)\begin{pmatrix} i & j & k\\ -q & q & 0\end{pmatrix}\begin{pmatrix} i & j & k\\ -n & n & 0\end{pmatrix}. \tag{17}$$

The use of the nonorthogonal basis set $f^{(i)}_{qn}(\Omega_{\text{MD}})$ requires the evaluation of the overlap matrix **S**, defined by (Vold and Vold, 1988)

$$\begin{aligned}\langle f^{(i)}_{qn}(\Omega_{\text{MD}})|\,S\,|f^{(j)}_{qn}(\Omega_{\text{MD}})\rangle &= N^{-1/2}_{iiqn}N^{-1/2}_{jjqn}[\langle D^{(i)}_{qn}(\Omega_{\text{MD}})|\,D^{(j)}_{qn}(\Omega_{\text{MD}})\rangle\\ &\quad - \langle D^{(i)}_{qn}(\Omega_{\text{MD}})\rangle\langle D^{(j)}_{qn}(\Omega_{\text{MD}})\rangle].\end{aligned} \tag{18}$$

The correlation functions for anisotropic diffusion in an odd restoring potential were evaluated by direct diagonalization of the symmetrized diffusion operator (Eq. 15) after transformation. The resulting correlation functions are then described by the infinite sum

$$G_{qn}(\Omega_{\text{MD}};t) = g_{qn}(\Omega_{\text{MD}};0)\sum_{i=1}^{\infty} b^{(i)}_{qn}e^{-\lambda^{(i)}_{qn}t}, \tag{19}$$

where $\lambda^{(i)}_{qn}$ is the ith eigenvalue of the infinite symmetric matrix $\hat{\mathbf{R}}$, $b^{(i)}_{qn}$ is the relative weight of the ith relaxation mode (Vold and Vold, 1988), and $g_{qn}(\Omega_{\text{MD}};0)$ is defined in Eq. 6. The anisotropy of the rotational diffusion tensor is commonly defined using $\eta_{\text{D}} = D_\parallel/D_\perp$, where $D_\parallel$ and $D_\perp$ are the principal values of the axially symmetric tensor. In the limit of an isotropic diffusion tensor (i.e., $\eta_{\text{D}} = 1$), $\lambda^{(i)}_{qn} = \alpha^{(i)}_{qn}D_\perp$. Determination of the eigenvalues for an arbitrary anisotropic diffusion tensor ($\eta_{\text{D}} \neq 1$) is not required (Vold and Vold, 1988). Inspection of Eq. 15 reveals that the resulting eigenvalues for the isotropic case simply need to be shifted for an arbitrary anisotropic diffusion tensor.

Single exponential approximations

Szabo (1984) presented a number of useful approximations for the infinite sum of exponentials in the correlation function defined by Eq. 12. A single exponential approximation that was linear at short times with analytical solutions in terms of the order parameters $\langle D^{(j)}_{00}(\Omega_{\mathrm{MD}})\rangle = \langle P_j(\cos\beta_{\mathrm{MD}})\rangle$ has been discussed for an arbitrary potential $U(\beta)$, (Szabo, 1984).[1] The single exponential of this first-order approximation decays with the correlation time τ_{qn} and represents the weighted sum of correlation times in the infinite exponential or Lorentzian series (Eqs. 12 and 13). The single exponential correlation time is defined by

$$\frac{1}{\tau_{qn}} = [\alpha_{pn} + (\eta_{\mathrm{D}} - 1)q^2]D_\perp, \tag{20}$$

where α_{qn} is approximated by

$$\alpha_{qn} = \frac{\mu_{qn}}{\{\langle |D^{(2)}_{qn}(\Omega_{\mathrm{MD}})|^2\rangle - |\langle D^{(2)}_{qn}(\Omega_{\mathrm{MD}})\rangle|^2\delta_{q0}\delta_{n0}\}} \tag{21}$$

and the approximation coefficient μ_{qn} is defined as (see Eq. 6.27 in Szabo [1984])

$$\mu_{qn} = \left\langle\left(\frac{\partial D^{(2)}_{qn}(\beta_{\mathrm{MD}})}{\partial\beta_{\mathrm{MD}}}\right)^2\right\rangle + \left\langle\frac{q^2 + n^2 - 2qn\cos\beta_{\mathrm{MD}}}{\sin^2\beta_{\mathrm{MD}}}\,|D^{(2)}_{\mathrm{qn}}(\beta_{\mathrm{MD}})|^2\right\rangle, \tag{22}$$

where the mean-squared amplitudes and approximation coefficient can be written using algebraic expansions of the Clebsch-Gordan coefficients (Buckmaster et al., 1972) denoted by $c^{(j)}_q$

$$\langle |D^{(2)}_{qn}(\beta_{\mathrm{MD}})|^2\rangle = {}^1\!/_5 + \sum_{j=1}^{4} c^{(j)}_q c^{(j)}_n \langle P_j(\cos\beta_{\mathrm{MD}})\rangle, \tag{23}$$

$$\begin{aligned}\mu_{qn} = {}^6\!/_5 &+ 5c^{(1)}_q c^{(1)}_n \langle P_1(\cos\beta_{\mathrm{MD}})\rangle \\ &+ 3c^{(2)}_q c^{(2)}_n \langle P_2(\cos\beta_{\mathrm{MD}})\rangle \\ &- 4c^{(4)}_q c^{(4)}_n \langle P_4(\cos\beta_{\mathrm{MD}})\rangle,\end{aligned} \tag{24}$$

where

$$c^{(1)}_n = \frac{n}{\sqrt{10}}, \tag{25}$$

$$c^{(2)}_n = \frac{(n^2 - 2)}{\sqrt{14}}, \tag{26}$$

$$c^{(3)}_n = \frac{(5n^3 - 17n)}{6\sqrt{10}}, \tag{27}$$

$$c^{(4)}_n = \frac{(35n^4 - 155n^2 + 72)}{12\sqrt{70}}. \tag{28}$$

Expressions for the mean-squared amplitudes, $g_{qn}(0)$, and μ_{qn} for a general potential of mean torque are detailed in Tables V and VI of an unpublished paper.[1] For an isotropic diffusion tensor this expression is equivalent to diagonal elements of the symmetrized diffusion operator for $i = j = 2$ defined in Eq. 15. Inspection of Eq. 33 in Moro and Nordio (1983) and Eq. B19 of an unpublished paper[1] along with the recursion relations of the 3-j symbols reveals the equivalence.

This single exponential approximation is known to perform well except for the case $q = n$. In particular, $q = n = 1$ fails as a result of odd and even rank elements of the symmetrized diffusion operator being connected (Moro and Nordio 1983). In this situation a simple diagonalization of a two-by-two matrix for the diffusion operator evaluated in an orthonormal basis set, provides a second-order approximation (α'_{qn}), and for $\eta_{\mathrm{D}} = 1$ is given by

$$\alpha'_{qn}D_\perp = \frac{\hat{\mathbf{R}}_{11}\hat{\mathbf{R}}_{22} - \kappa^2\hat{\mathbf{R}}^2_{12}}{\hat{\mathbf{R}}_{11} + \kappa^2(\hat{\mathbf{R}}_{11} - 2\hat{\mathbf{R}}_{12})}, \tag{29}$$

where

$$\kappa^2 = \frac{(\langle D^{(1)}_{qn}(\Omega_{\mathrm{MD}})|D^{(2)}_{qn}(\Omega_{\mathrm{MD}})\rangle)^2}{\langle D^{(1)}_{qn}(\Omega_{\mathrm{MD}})|D^{(1)}_{qn}(\Omega_{\mathrm{MD}})\rangle\langle D^{(2)}_{qn}(\Omega_{\mathrm{MD}})|D^{(2)}_{qn}(\Omega_{\mathrm{MD}})\rangle} \tag{30}$$

and

$$\hat{\mathbf{R}}_{\mathrm{ij}} = \frac{\langle D^{(i)}_{qn}(\Omega_{\mathrm{MD}})|\hat{\mathbf{R}}|D^{(j)}_{qn}(\Omega_{\mathrm{MD}})\rangle}{N_{ijqn}}. \tag{31}$$

For the $G_{11}(\Omega_{\mathrm{MD}}; t)$ correlation function, with $\eta_{\mathrm{D}} = 1$, the different matrix elements are easily obtained:

$$\frac{\hat{\mathbf{R}}_{11}}{D_\perp} = \frac{4 + 3\langle P_1(\cos\beta_{\mathrm{DM}})\rangle - \langle P_2(\cos\beta_{\mathrm{DM}})\rangle}{2 + 3\langle P_1(\cos\beta_{\mathrm{DM}})\rangle + \langle P_2(\cos\beta_{\mathrm{DM}})\rangle}, \tag{32}$$

$$\frac{\hat{\mathbf{R}}_{12}}{D_\perp} = \frac{9\langle P_1(\cos\beta_{\mathrm{DM}})\rangle + 5\langle P_2(\cos\beta_{\mathrm{DM}})\rangle - 4\langle P_3(\cos\beta_{\mathrm{DM}})\rangle}{3\langle P_1(\cos\beta_{\mathrm{DM}})\rangle + 5\langle P_2(\cos\beta_{\mathrm{DM}})\rangle + 2\langle P_3(\cos\beta_{\mathrm{DM}})\rangle}, \tag{33}$$

$$\begin{aligned}\kappa^2 = 21[3\langle P_1(\cos\beta_{\mathrm{DM}})\rangle &+ 5\langle P_2(\cos\beta_{\mathrm{DM}})\rangle \\ &+ 2\langle P_3(\cos\beta_{\mathrm{DM}})\rangle]^2 \times [(10 + 15\langle P_1(\cos\beta_{\mathrm{DM}})\rangle \\ &+ 5\langle P_2(\cos\beta_{\mathrm{DM}})\rangle)(14 + 7\langle P_1(\cos\beta_{\mathrm{DM}})\rangle \\ &+ 5\langle P_2(\cos\beta_{\mathrm{DM}})\rangle + 28\langle P_3(\cos\beta_{\mathrm{DM}})\rangle \\ &+ 16\langle P_4(\cos\beta_{\mathrm{DM}})\rangle)]^{-1},\end{aligned} \tag{34}$$

where the $\hat{\mathbf{R}}_{22}$ element is given by Eq. 15 or 20.

RESULTS AND DISCUSSION

Solutions to Eqs. 14–19 were obtained using a FORTRAN program running on a 5000/25 work station

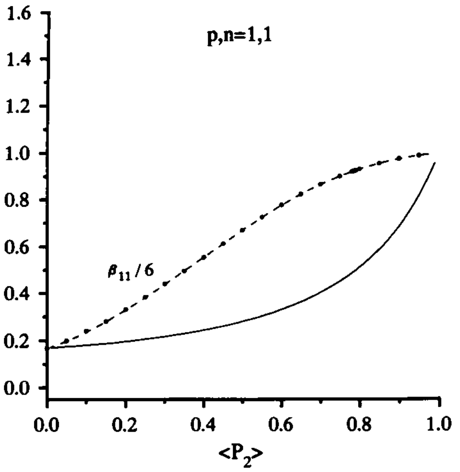


FIGURE 3 Weighted average decay constants $\beta_{11}^{(i)} = 6/\alpha_{11}^{(i)}$ (●) as a function of order parameter $\langle P_2(\cos \beta_{MD})\rangle$. Curves represent first- (——) and second-order (- - -) single exponential approximations to the correlation functions.

(Digital Equipment Corp., Marboro, MA). The details of the diagonalization and transformation have been described (Vold and Vold, 1988). The original basis set consisted of 64 normalized, nonorthogonal functions, but in general, smaller basis sets were sufficient in obtaining nonvariant diffusion time constants and relative weights. The program allowed the dimensions of the basis sets to be altered until no significant changes in the dominant eigenvalues or relative weights were observed. The infinite summation in Eq. 19 was truncated to include only those components with >1% relative contribution (i.e., $b_{qn}^{(i)} > 0.01$). The resulting initial amplitudes, $g_{qn}(\Omega_{MD};\ 0)$, relative weights, $b_{qn}^{(i)}$, and decay rates, $\alpha_{qn}^{(i)}$, are given graphically in Fig. 2 as a function of the restoring potential order. To maintain consistency with previous investigations, a decay time constant $\beta_{qn}^{(i)} = 6/\alpha_{qn}^{(i)}$ is shown in Fig. 2. This $\beta_{qn}^{(i)}$ is equivalent to $b_{qn}^{(i)}$ in Fig. 2 of Vold and Vold (1988). The weighted sum of these decay times, defined as β_{qn}, is also presented in Fig. 2. The correlation function in Eq. 19 was evaluated for an odd restoring potential with molecular order ranging from 0.001 to 0.95, in 0.05 steps. A sharp transition was observed in several of the reorientational modes at approximately $\langle P_2(\cos \beta_{MD})\rangle = 0.8$, requiring evaluation of additional $\langle P_2(\cos \beta_{MD})\rangle$ values in this region. For low order, $\langle P_2(\cos \beta_{MD})\rangle = 0.0$–$0.25$, four to six basis functions were required to obtain convergence of the relative amplitudes and decay times to four significant digits. Between $\langle P_2(\cos \beta_{MD})\rangle$ of 0.25 and 0.65, 8–12 basis functions were required. For intermediate order, $\langle P_2(\cos \beta_{MD})\rangle = 0.65$–$0.85$, 14–20 basis functions were adequate. Above $\langle P_2(\cos \beta_{MD})\rangle = 0.90$, the overlap matrix proved difficult to evaluate consistently for large basis set size. A similar situation was noted in the study of the Maier-Saupe potential (Vold and Vold, 1988): 6–10 basis functions were used to evaluate the correlation function in this region.

Inspection of Fig. 2, *A–C*, of this paper and Fig. 2 of Vold and Vold (1988) reveals that the mean square amplitudes for the odd restoring potential are approximately the same as the even Maier-Saupe potential for the $G_{00}(\Omega_{MD};\ t)$, $G_{10}(\Omega_{MD};\ t)$, $G_{20}(\Omega_{MD};\ t)$ correlation functions. Significant differences in the mean squared amplitude for the $G_{11}(\Omega_{MD};\ t)$, $G_{22}(\Omega_{MD};\ t)$, $G_{12}(\Omega_{MD};\ t)$ correlation functions (Fig. 2, *D–F*) in odd and even restoring potentials have been noted previously.[1] The amplitudes within the odd potential are greater, and for intermediate ordering are approximately a factor of two larger. The additional $G_{1\text{-}1}(\Omega_{MD};\ t)$, $G_{2\text{-}2}(\Omega_{MD};\ t)$, $G_{1\text{-}2}(\Omega_{MD};\ t)$ correlation functions, shown in Fig. 2, *G–I*, contribute little to the overall correlation functions or spectral densities in Eqs. 6 and 7 because of the vanishing mean-squared amplitudes, except at low molecular ordering. All previous comparisons between odd and even restoring potentials have used single exponential approximations, suggesting only small differences in the decay rates common to both potentials (Halle, 1991).[1] Inspection of Fig. 2 reveals that the multiexponential behavior of the correlation functions is extremely rich, with several differences between the even and odd potentials. The simplest correlation functions, $G_{22}(\Omega_{MD};\ t)$ and $G_{12}(\Omega_{MD};\ t)$, are single exponentials over the entire range of $\langle P_2(\cos \beta_{MD})\rangle$ investigated, with a minor ($b_{qn}^{(2)} \sim 0.03$) second exponential between $\langle P_2(\cos \beta_{MD})\rangle$ of 0.25 and 0.7 (Fig. 2, *E* and *F*). This behavior is reminiscent of that observed for the even Maier-Saupe restoring potential, with the dominant decay constant for these correlation functions being approximately the same. The correlation function $G_{20}(\Omega_{MD};\ t)$ in Fig. 2*C* is dominated by a single exponential, with two additional exponentials contributing up to 10% relative amplitude. For the Maier-Saupe restoring potential $G_{20}(\Omega_{MD};\ t)$ is predominantly single exponential, switching between different time constants from high to low ordering (see Fig. 2 *C* of Vold and Vold [1988]). The dominant decay constant is slightly greater than that observed in the Maier-Saupe potential. The correlation functions $G_{10}(\Omega_{MD};\ t)$, $G_{11}(\Omega_{MD};\ t)$, $G_{00}(\Omega_{MD};\ t)$ are triexponential, with a minor fourth exponential contributing to $G_{00}(\Omega_{MD};\ t)$ (Fig. 2, *A*, *B*, and *D*). These higher order exponentials contrast to the single and biexponential correlation functions observed for the even Maier-Saupe restoring potential. In these correlation functions the dominant decay constant diminishes faster with increasing molecular order than observed in the Maier-Saupe potential. This difference accounts for the minor variation in the weighted average decay constant β_{qn} between odd and even restoring potentials noted earlier.[1] The $G_{1\text{-}1}(\Omega_{MD};\ t)$, $G_{1\text{-}2}(\Omega_{MD};\ t)$, $G_{2\text{-}2}(\Omega_{MD};\ t)$ correlation functions are all described by four exponentials with a relative contribution of >1%

TABLE 1 Expansion coefficients for the correlation and spectral density functions†

	a_0	a_1	a_2	a_3	a_4	a_5	a_6	Range	R*
Mean squared amplitude									
g_{00}	0.200	0.279	−0.788	−0.268	0.770	−0.193		0.00–0.95	0.99999
g_{10}	0.200	0.157	−0.211	0.345	−0.675	0.182		0.00–0.95	0.99997
g_{20}	0.200	−0.297	0.107	−0.228	0.330	−0.111		0.00–0.95	0.99999
g_{11}	0.202	0.636	−1.448	3.529	−3.049	1.138		0.00–0.95	0.99997
g_{12}	0.204	0.886	−3.984	7.635	−7.402	2.670		0.00–0.95	0.99954
g_{22}	0.213	2.788	−13.003	40.337	−65.771	52.283	−16.874	0.00–0.95	0.99978
g_{1-1}	0.198	−0.502	1.658	−3.805	3.741	−1.295		0.00–0.95	0.99982
g_{1-2}	0.195	−1.188	4.112	−8.098	7.854	−2.887		0.00–0.95	0.99879
g_{2-2}	0.191	−1.840	7.666	−15.605	15.023	−5.456		0.00–0.95	0.99395
Relative weights									
$b_{00}^{(1)}$	1.002	−2.675	7.276	−13.243	13.693	−5.763		0.00–0.78	0.99997
$b_{00}^{(2)}$ ‡	0.001	2.106	−4.923	5.226	−2.915	1.555		0.00–0.78	0.99973
$b_{00}^{(2)}$ ‡	−279.55	1038.4	−1067.0	−288.89	1033.4	−435.59		0.79–0.95	0.99999
$b_{00}^{(3)}$	−0.003	0.719	−4.155	15.198	−22.819	11.173		0.00–0.80	0.99624
$b_{00}^{(4)}$	5.003	−53.192	234.64	−549.13	718.79	−497.71	142.01	0.45–0.85	0.99484
$b_{10}^{(1)}$	1.002	−2.298	4.085	−10.592	13.076	−5.170		0.00–0.79	0.99998
$b_{10}^{(2)}$	−0.003	1.962	−4.075	11.818	−14.514	5.822		0.00–0.95	0.99998
$b_{10}^{(3)}$	0.000	0.413	−0.898	2.068	−3.786	2.299		0.00–0.85	0.99801
$b_{20}^{(1)}$	0.998	−0.198	−0.005	−3.166	8.247	−4.946		0.00–0.95	0.99417
$b_{20}^{(2)}$	−0.002	0.484	−2.986	13.862	−24.326	13.438		0.00–0.79	0.99874
$b_{20}^{(3)}$	−2.500	21.778	−75.239	128.74	−108.49	35.898		0.50–0.85	0.99834
$b_{11}^{(1)}$	1.000	−1.769	−0.034	0.652	1.280	−1.180		0.00–0.85	0.99999
$b_{11}^{(2)}$	−0.004	1.541	−0.065	0.828	−2.698	1.404		0.00–0.95	0.99999
$b_{11}^{(3)}$	−0.003	0.426	−1.606	4.496	−7.936	5.176		0.00–0.65	0.99974
$b_{12}^{(1)}$	0.999	−0.146	−0.165	0.504	0.255	−0.456		0.00–0.95	0.99876
$b_{12}^{(2)}$	0.005	0.109	0.134	0.040	−1.412	1.188		0.10–0.80	0.99834
$b_{22}^{(1)}$	1.000	−0.093	0.146	−0.115	0.194	−0.133		0.00–0.95	0.99971
$b_{22}^{(2)}$	0.000	0.093	−0.190	0.324	−0.551	0.341		0.15–0.70	0.99999
$b_{1-1}^{(1)}$	1.001	−1.631	3.113	−7.508	10.746	−5.473		0.00–0.78	0.99997
$b_{1-1}^{(2)}$ ‡	0.016	0.744	1.438	−8.558	12.783	−5.663		0.00–0.78	0.99983
$b_{1-1}^{(2)}$ ‡	−160.20	594.78	−606.81	−173.71	598.04	−251.19		0.79–0.95	0.99999
$b_{1-1}^{(3)}$	−0.028	1.156	−6.629	22.748	−33.669	16.782		0.00–0.79	0.99840
$b_{1-1}^{(4)}$	2.801	−21.515	64.157	−92.404	64.553	−17.583		0.45–0.85	0.86161
$b_{1-2}^{(1)}$	1.000	−0.176	−1.829	6.609	−16.728	13.053		0.00–0.80	0.99996
$b_{1-2}^{(2)}$ ‡	−0.015	0.653	−2.724	10.993	−13.284	4.645		0.00–0.78	0.99993
$b_{1-2}^{(2)}$ ‡	−418.86	1444.3	−1369.1	−373.40	1175.7	−457.61		0.79–0.95	0.99999
$b_{1-2}^{(3)}$	−10.912	98.237	−346.81	598.82	−503.45	164.53		0.40–0.80	0.99801
$b_{1-2}^{(4)}$	138.57	−875.97	2195.3	−2723.7	1670.8	−404.68		0.65–0.80	0.99980
$b_{2-2}^{(1)}$	1.000	−0.011	−3.818	17.666	−48.296	38.273		0.00–0.70	0.99999
$b_{2-2}^{(2)}$	0.095	−3.167	39.499	−199.08	505.76	−596.80	259.06	0.05–0.79	0.99944
$b_{2-2}^{(3)}$ ‡	−4.085	36.551	−124.07	196.23	−139.62	34.969		0.35–0.79	0.99945
$b_{2-2}^{(3)}$ ‡	−9.908	20.091	−1.797	−1.681	−16.927	11.196		0.80–0.95	0.99999
$b_{2-2}^{(4)}$	1513.9	−10923.	31463.	−45236.	32469.	−9308.1		0.60–0.80	0.99865
Decay constants									
$\beta_{00}^{(1)}$	1.000	−0.355	−0.571	1.119	−4.002	2.901		0.00–0.78	0.99999
$\beta_{00}^{(2)}$	3.014	−5.003	4.264	−11.303	15.941	−6.859		0.00–0.95	0.99999
$\beta_{00}^{(3)}$	0.495	0.053	−1.261	3.855	−5.938	2.617		0.00–0.80	0.99996
$\beta_{00}^{(4)}$	2.127	−14.344	43.792	−65.485	47.590	−13.771		0.45–0.85	0.99971
$\beta_{10}^{(1)}$	1.000	−0.360	−1.001	2.979	−8.302	6.005		0.00–0.79	0.99999
$\beta_{10}^{(2)}$	3.014	−5.003	4.264	−11.303	15.941	−6.859		0.00–0.95	0.99999
$\beta_{10}^{(3)}$	0.493	0.091	−1.617	5.079	−7.963	3.941		0.00–0.85	0.99999
$\beta_{20}^{(1)}$	1.002	−0.602	0.791	−4.432	4.814	−1.569		0.00–0.95	0.99999
$\beta_{20}^{(2)}$	0.494	0.055	−1.518	4.860	−7.941	4.036		0.00–0.79	0.99999
$\beta_{20}^{(3)}$	−1.568	15.562	−51.977	86.104	−71.169	23.105		0.50–0.85	0.99999
$\beta_{11}^{(1)}$	1.003	−0.040	−1.223	−0.079	−0.853	1.294		0.00–0.85	0.99998
$\beta_{11}^{(2)}$	3.345	7.374	−13.650	21.001	−18.780	6.739		0.00–0.95	0.99996
$\beta_{11}^{(3)}$	0.501	−0.057	−0.228	0.160	−0.552	−0.218		0.00–0.65	0.99999
$\beta_{12}^{(1)}$	1.004	0.473	−3.037	4.681	−5.422	2.311		0.00–0.95	0.99997
$\beta_{12}^{(2)}$	0.488	0.266	−2.430	7.074	−10.806	5.523		0.10–0.80	0.99999
$\beta_{22}^{(1)}$	1.007	1.756	−6.082	13.043	−13.001	4.796		0.00–0.95	0.99955
$\beta_{22}^{(2)}$	0.409	1.667	−10.420	28.980	−38.927	19.193		0.15–0.70	0.99962
$\beta_{1-1}^{(1)}$	0.998	−0.836	1.447	−3.883	2.606	−0.337		0.00–0.78	0.99998

TABLE 1 (continued)

	a_0	a_1	a_2	a_3	a_4	a_5	a_6	Range	R*
Decay constants (continued)									
$\beta^{(2)}_{1\text{-}1}$	2.678	−7.397	17.856	−35.669	35.718	−13.222		0.00–0.95	0.99998
$\beta^{(3)}_{1\text{-}1}$	0.493	0.038	−1.416	4.495	−6.985	3.269		0.00–0.79	0.99998
$\beta^{(4)}_{1\text{-}1}$	0.308	0.586	−4.662	12.094	−13.761	5.423		0.45–0.85	0.99992
$\beta^{(1)}_{1\text{-}2}$	1.000	−1.529	5.273	−15.448	17.944	−7.463		0.00–0.80	0.99993
$\beta^{(2)}_{1\text{-}2}$	0.494	−0.081	−.764	2.492	−4.464	2.334		0.00–0.95	0.99999
$\beta^{(3)}_{1\text{-}2}$	−0.426	6.563	−23.718	41.554	−35.756	11.707		0.40–0.80	0.99999
$\beta^{(4)}_{1\text{-}2}$	112.55	−726.96	1868.6	−2383.4	1507.3	−377.87		0.65–0.80	0.99999
$\beta^{(1)}_{2\text{-}2}$	0.997	−2.262	9.740	−27.915	35.636	−17.053		0.00–0.70	0.99987
$\beta^{(2)}_{2\text{-}2}$	0.493	−0.208	−0.116	0.647	−2.043	1.126		0.05–0.85	0.99981
$\beta^{(3)}_{2\text{-}2}$	−1.144	13.318	−48.433	85.482	−73.972	24.828		0.35–0.95	0.99944
$\beta^{(4)}_{2\text{-}2}$	538.80	−3894.9	11239.0	−16178.0	11616.0	−3328.8		0.60–0.80	0.99999
Average decay constants									
β_{00}	1.003	3.539	−17.464	26.972	−20.013	5.975		0.00–0.95	0.99998
β_{10}	1.000	2.791	−7.222	3.678	0.113	−0.363		0.00–0.95	0.99999
β_{20}	1.000	−0.635	−0.065	−1.688	2.095	−0.710		0.00–0.95	0.99999
β_{11}	0.998	3.584	6.529	2.390	−15.027	7.544		0.00–0.95	0.99999
β_{12}	1.003	0.398	−3.157	5.246	−5.804	2.318		0.00–0.95	0.99998
β_{22}	1.007	1.665	−5.737	12.159	−11.870	4.293		0.00–0.95	0.99965
$\beta_{1\text{-}1}$	1.001	0.638	−4.700	4.645	−1.757	0.172		0.00–0.95	0.99999
$\beta_{1\text{-}2}$	0.997	−1.453	3.237	−9.113	10.247	−3.928		0.00–0.95	0.99998
$\beta_{2\text{-}2}$	0.993	−2.057	6.536	−16.935	18.254	−6.778		0.00–0.95	0.99987

* Coefficient of linear regression.

‡ Power expansion given for 2 different ranges of molecular ordering. † Correlation and spectral density functions (Eqs. 12 and 13) describe rotational diffusion for an isotopic diffusion tensor in a restoring potential $U(\beta_{MD}) = -\lambda \cos \beta_{MD}$, expressed as a power series, $\Sigma_n a_n\langle P_2(\cos \beta_{MD})\rangle^n$.

(Fig. 2, *G–I*). While this multiexponential behavior of the later terms is indeed interesting, the effect on observable spin relaxation will be negligible due to the vanishing mean-squared amplitudes. For the Maier-Saupe potential these terms have no counterpart as a result of the symmetry $G_{qn}(\Omega_{MD};\, t) = G_{q-n}(\Omega_{MD};\, t) = G_{-qn}(\Omega_{MD};\, t)$ inherent in even restoring potentials. The observation that the dominant decay constants are approximately the same would suggest that any variation in the resulting spectral densities $J_{qn}(m\omega_0)$ arises from differences in the initial amplitudes. In the intermediate ordering regime the initial amplitudes for the $G_{11}(\Omega_{MD};\, t)$, $G_{22}(\Omega_{MD};\, t)$, $G_{12}(\Omega_{MD};\, t)$ correlation functions were found to be significantly larger, but the summation in Eq. 5 along with the symmetry properties of the even potential effectively removes these differences.[1] The similarity of spin relaxation results in the different potentials is reminiscent of earlier studies considering the influence of the restoring potential shape (even) on the observed relaxation (Vold and Vold, 1988). The distinction between odd and even restoring potential at low molecular ordering awaits experimental investigation.

The weighted average decay constant β_{qn} shown in Fig. 2 can be used to assess the single exponential approximation used in previous studies (Halle, 1991).[1] The behavior of the first-order approximations as a function of molecular order for an odd restoring potential is given in Fig. 9 of an unpublished paper.[1] Inspection of the weighted average β_{qn} ($=6/\alpha_{qn}$) reveals that, for the first-order approximation, α_{qn} is overestimated at low order. For molecular order $\langle P_2(\cos \beta_{MD})\rangle > 0.6$, the agreement between the first-order approximation and weighted average improves. For the $G_{11}(\Omega_{MD};\, t)$ correlation function the approximation proves unsatisfactory at all values of molecular order, as was expected from previous discussions (Moro and Nordio, 1983). A comparison between the weighted average decay constant and the first- and second-order single exponential approximations (see Theory section) is shown in Fig. 3 for the $G_{11}(\Omega_{MD};\, t)$ term. It is evident that the second-order approximation more accurately reflects the results from evaluation of the multiexponential correlation functions. Similar improvement for all the correlation functions at low order can be obtained using the approximation given in Eq. 29.

The calculated curves in Fig. 2 for $b^{(i)}_{qn}$, $\beta^{(i)}_{qn}$, β_{qn}, and g_{qn} were obtained from fits of the exact calculated points, to the polynomial $\Sigma_n a_n\langle P_2(\cos \beta_{MD})\rangle^n$. These regression coefficients are given in Table 1, allowing the different functions to be easily calculated given the ordering potential $\langle P_2(\cos \beta_{MD})\rangle$. In turn, these correlation functions can be used to calculate the spin-lattice relaxation and quadrupolar order decay using Eqs. 1–3, and provide a complementary source of information to Table I of Vold and Vold (1988). These results for rotational diffusion are easily extended to the anisotropic viscosity model of Polnaszek and Freed (1975), but were not pursued in this investigation.

CONCLUSIONS

This evaluation of anisotropic diffusion in an odd restoring potential is revelant for NMR relaxation and fluorescent depolarization investigations of dynamics of lipid bilayers, proteins in membranes, and other macromolecular systems. While it has been argued that the potential has little effect on the observed spin relaxation in lipid bilayers[1] in the case of a single exponential approximation, these multiexponential solutions have allowed a more critical evaluation. The dominant decay constants are similar between odd and even potentials, and in the intermediate order regime, $\langle P_2(\cos \beta_{MD}) \rangle \sim 0.6$–$0.8$, the differences in mean-squared amplitude are effectively removed via summation within the spectral densities. It is true that at extremely low order significant differences exist as a result of potential parity, yet these limits are not commonly observed experimentally in lipid bilayers. These findings suggest that motional rates obtained from the wealth of studies during the past decade using an even Maier-Saupe potential will remain essentially unchanged. The ability of the multiexponential correlation functions to successfully explain the small but significant frequency dependence observed in angular anisotropic R_{1Z} and R_{1Q} investigations (Winsborrow et al., 1991; Trouard et al., 1992) is presently being pursued.

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REFERENCES

Abragam, A. 1961. Principles of Nuclear Magnetism. Oxford Science Publications, Oxford, UK. 599 pp.

Auger, M., D. Carrier, I. C. P. Smith, and H. C. Jarrell. 1990. Elucidation of motional modes in glycerolipid bilayers. A ^{2}H NMR relaxation and line-shape study. *J. Am. Chem. Soc.* 112:1373–1381.

Bonmatin, J.-M., I. C. P. Smith, H. C. Jarrell and D. J. Siminovitch. 1990. Use of a comprehensive approach to molecular dynamics in ordered lipid systems: cholesterol reorientation in oriented lipid bilayers. A ^{2}H NMR relaxation case study. *J. Am. Chem. Soc.* 112:1697–1704.

Brink, D. M., and G. R. Satchler. 1968. Angular Momentum. Oxford University Press, Oxford, UK. 160 pp.

Brown, M. F. 1982. Theory of spin-lattice relaxation in lipid bilayers and biological membranes. ^{2}H and ^{14}N quadrupolar relaxation. *J. Chem. Phys.* 77:1576–1598.

Brown, M. F., and J. H. Davis. 1981. Orientation and frequency dependence of the deuterium spin-lattice relaxation in multilamellar phospholipid dispersions: implications for dynamical models of membrane structure. *Chem. Phys. Lett.* 79:431–435.

Brown, M. F., and O. Söderman. 1990. Orientational anisotropy of nuclear spin relaxation in phospholipid membranes. *Chem. Phys. Lett.* 167:158–164.

Brown, M. F., A. Salmon, U. Henriksson, and O. Söderman. 1990. Frequency dependent ^{2}H NMR relaxation rates of small unilamellar phospholipid vesicles. *Mol. Phys.* 69:379–383.

Buckmaster, H. A., R. Chatterjee, and Y. H. Shing. 1972. The application of tensor operators in the analysis of EPR and ENDOR spectra. *Physica Status Solidi A: Applied Research.* 13:13–50.

Halle, B. 1991. ^{2}H NMR relaxation in phospolipid bilayers. Toward a consistent molecular interpretation. *J. Phys. Chem.* 95:6724–6733.

Jarrell, H. C., I. C. P. Smith, P. A. Jovall, H. H. Mantsch, and D. J. Siminovitch. 1988. Angular dependence of ^{2}H NMR relaxation rates in lipid bilayers. *J. Chem. Phys.* 88:1260–1263.

Mayer, C., G. Grobner, K. Muller, K. Weisz, and G. Kothe. 1990. Orientation-dependent deuteron spin-lattice relaxation times in bilayer membranes: characterization of the overall lipid motion. *Chem. Phys. Lett.* 165:155–161.

Moro, G., and P. L. Nordio. 1983. A modified Wigner function set for the Smoluchowski operator representation in anisotropic liquids. *Chem. Phys. Lett.* 96:192–199.

Nordio, P. L., and U. Segre. 1979. Rotational dynamics. *In* The Molecular Physics of Liquid Crystals. G. R. Luckhurst and G. W. Gray, editors. Academic Press Inc., New York. 411–449.

Polnaszek, C. F., and J. H. Freed. 1975. Electron spin resonance studies of anisotropic ordering, spin relaxation, and slow tumbling in liquid crystalline solvents. *J. Phys. Chem.* 79:2283–2306

Slichter, C. P. 1990. Principles of Magnetic Resonance. Springer-Verlag New York Inc., New York. 655 pp.

Stohrer, J., G. Gröbner, D. Reimer, K. Weisz, C. Mayer, and G. Kothe. 1991. Collective lipid motions in bilayer membranes studied by transverse deuteron spin relaxation. *J. Chem. Phys.* 95:672–678.

Szabo, A. 1984. Theory of fluorescence depolarization in macromolecules and membranes. *J. Chem. Phys.* 81:150–167.

Trouard, T. P., T. M. Alam, J. Zajicek, and M. F. Brown. 1992. Angular anisotropy of ^{2}H NMR spectral densities in phospholipid bilayers containing cholesterol. *Chem. Phys. Lett.* 189:67–75.

Vold, R. R., and R. L. Vold. 1988. Nuclear spin relaxation and molecular dynamics in ordered systems: models for molecular reorientation in thermotropic liquid crystals. *J. Chem. Phys.* 88:1443–1457.

Vold, R. R., and R. L. Vold. 1991. Deuterium relaxation in molecular solids. *In* Advances in Magnetic and Optical Resonance. Warren. Academic Press Inc., New York. 85–171.

Winsborrow, B. G., I. C. P. Smith, and H. C. Jarrell. 1991. Dynamics of glycolipids in the liquid-crystalline state. *Biophys. J.* 59:729–741.

Zannoni, C. 1985. Quantitative description of orientational order: rigid molecules. *In* Nuclear Magnetic Resonance of Liquid Crystals. J. W. Emsley, editor. D. Reidel, Hingham, MA. 1–34.