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Dynamics of a Liquid Crystal by Deuterium NMR: The Analysis of Director Fluctuations and Reorientation of Molecules

Ronald Y. Dong*

Department of Physics and Astronomy, Brandon University, Brandon, Manitoba R7A 6A9, Canada, and Physics Department, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Xiaodong Shen

Physics Department, Univerisity of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

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The zero-frequency spectral densities $J_0(0)$ data[1] for the liquid crystal *p*-(methoxybenzylidine)-*p*-*n*-butylaniline (MBBA) is quantitatively interpreted using a model that includes director fluctuations and rotational diffusion of symmetric rotors in a nematic phase. The contribution to $J_0(0)$ from director fluctuations has mainly a second-order component, whereas the first-order contribution to $J_1(\omega)$ is suppressed in the megahertz region (Larmor frequencies are 15.3 and 46 MHz) due to the high-frequency cutoff, which is estimated to be around 3−10 MHz for MBBA. A global target approach is used in the analysis of all the available spectral densities. As a result, motional parameters and a molecular prefactor for director fluctuations are obtained in the nematic phase of MBBA.

Introduction

Director fluctuations are unique and important[2,3] sources of nuclear spin relaxation in liquid crystals. These fluctuations involve collective motions of a large number of molecules. Studies of director fluctuations can provide information on molecular properties such as elastic constants and viscosities. This dynamic process was first used to explain light scattering experiments in liquid crystals by Chatelain.[4] de Gennes[5] was first to recognize that director fluctuations consist of long-range collective modes of motion in liquid crystals. This hydrodynamic description in the nematic phase was soon confirmed by new light scattering experiments.[6,7] The first variable frequency proton T_1 study[8] indicated that the usual Lorentzian frequency dependence expected from the BPP theory[9] was not obeyed. This led Pincus[10] to derive a $\omega^{-1/2}$ frequency relation for the nuclear spin−lattice relaxation rate. Lubensky[11] noted the square of the nematic order parameter in the spin−lattice relaxation rate. Following that, many proton NMR studies were reported by Doane and Visintainer,[12] Brochard,[13] and Blinc et al.[14] These earlier proton relaxation experiments already showed that the proton relaxation behavior in liquid crystals was more complex than originally anticipated by the Pincus theory. In particular, molecular rotations and translational self-diffusion have also been shown to cause spin relaxation in liquid crystals as in normal liquids.

The reorientation of molecules in liquid crystals can be described by the rotational diffusion model.[15,16] The model assumes a stochastic Markov process for molecular reorientation in which each molecule moves in time as a sequence of small angular steps caused by collisions with its surrounding molecules and under the influence of the potential of mean torque set up by them. Nordio and co-workers[16] considered reorientation of cylindrical, rigid molecules in uniaxial phases. Each molecule is characterized by a rotational diffusion tensor, normally defined in a frame fixed on the molecule. A number of models of increasing complexity have been proposed.[17−21] Recently, we have examined[22,23] how an asymmetric rotational diffusion tensor for solvent molecules may influence the relaxation data of 50.7 and 40.8 in their uniaxial phases by solving the full rotational diffusion equation as described by Tarroni and Zannoni.[19] When couplings between director fluctuations and molecular reorientations are considered,[24,25] a "small" cross term contribution exists in $J_1(\omega)$.

When using a small angle (θ) approximation, where θ is the angle between the instantaneous director and its equilibrium orientation, it is well-known that director fluctuations contribute a frequency term in the spectral density $J_1(\omega)$ and have zero contributions in $J_2(2\omega)$ and $J_0(\omega)$. However, angular excursions of the local director can have large amplitudes and high-order terms of θ can now contribute to $J_2(2\omega)$ and $J_0(\omega)$. Second-order director fluctuations ($\propto\theta^2$) have been considered by Vold et al.[26] and van der Zwan et al.[27] The frequency dependence in J_2 is calculated to be generally small, whereas J_0 is predicted to be quite large as $\omega \rightarrow 0$.[26] Since director fluctuations contain many long wavelength modes which are effective for spin relaxation in the kilohertz region, the influence of director fluctuations for solvent spins in liquid crystals can best be studied using the field cycling technique.[28]

Although director fluctuations normally give small contributions in the megahertz region, there are at least two liquid crystals 50.7[22] and 40.8[23,29] in which director fluctuations have been used to account for part of $J_1(\omega)$. For these two liquid crystals, the high-frequency cutoffs appear to be on the order of 10^2 MHz, while for *p*-(methoxybenzylidine)-*p*-*n*-butylaniline (MBBA or 10.4), there is no detectable contribution from director fluctuations to the deuteron spin−lattice relaxation in the megahertz regime.[30] The same conclusion was made by Vilfan et al.[31] on the basis of their proton NMR study. Recent published data[1] show, however, that there is a substantial contribution from director fluctuations to $J_0(0)$. The data are analyzed here using a global target approach.[32] We believe that a possible explanation of the different behaviors among the studied liquid crystals of the *n*0.*m* series may be due to their high-frequency cutoffs, since the prefactors *A* for these liquid crystals are comparable. The paper is organized into a theory section, which summarizes theoretical spectral densities neces-

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sary for interpreting our data. This is followed by a section on results and discussion, and a brief summary.

Theory

Standard theories[2,3] of spin relaxation by director fluctuations in nematics are based on the notion that the mean-square amplitude $\langle\theta^2\rangle$ of the director's displacement is small such that terms of this and higher orders can be neglected. Recently, second-order contributions from director fluctuations are predicted[26,27,33] in $J_0(0)$, $J_1(\omega)$, and $J_2(2\omega)$. When treating deuterons residing on the rigid part of a molecule, e.g., the methine deuteron in MBBA, the spectral densities are calculated as follows:

$$\begin{aligned} J_{2\mathrm{DF}}(\omega) &= J_{0\mathrm{DF}}(\omega)/3 \\ &= 4(q_{\mathrm{CD}})^2 A^2 \mathrm{S}_0{}^2 [d^2_{00}(\beta_{\mathrm{M,Q}})]^2 L(\omega) \end{aligned} \tag{1}$$

where $q_{\mathrm{CD}} = e^2qQ/h$ is the quadrapolar coupling constant, $\beta_{\mathrm{M,Q}}$ is the angle between the C−D bond and the molecular z_{M} axis, and

$$L(\omega) = \int_0^{q_c} \mathrm{d}q \int_0^{q_c} \frac{q^2 + q'^2}{(q^2 + q'^2)^2 + (\eta/K)^2\omega^2} \mathrm{d}q' \tag{2}$$

with $q_c = (\eta/K)^{1/2}\omega_c{}^{1/2}$, ω_c is the high-frequency cutoff, K is the average elastic constant, and η is the average viscosity. S_0 is a nematic order of the molecule relative to the local director and is related to the usual nematic order parameter $\langle P_2\rangle$ according to[26]

$$S_0 = \langle P_2\rangle/(1 - 3\alpha) \tag{3}$$

where the parameter $\alpha = kTq_c/2\pi^2K$ is a measure of the magnitude of director fluctuations. The prefactor is[3]

$$A = \frac{3kT}{4\sqrt{2}\pi}(\eta/K^3)^{1/2} = 3\pi\alpha/\sqrt{8\omega_c} \tag{4}$$

By integrating over a circle in q, q' space rather than a square, Vold et al.[26] obtained from eq 2

$$L(\omega) = \frac{\pi}{8}\ln[1 + (\omega_c/\omega)^2] \tag{5}$$

This gives

$$J_{0\mathrm{DF}}(\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}})^2 A^2 \frac{\langle P_2\rangle^2}{(1 - 3\alpha)^2}[\mathrm{d}^2_{00}(\beta_{\mathrm{M,Q}})]^2 \frac{1}{\pi}\ln[1 + (\omega_c/\omega)^2] \tag{6}$$

$$J_{2\mathrm{DF}}(2\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}})^2 A^2 \frac{\langle P_2\rangle^2}{(1 - 3\alpha)^2}[d^2_{00}(\beta_{\mathrm{M,Q}})]^2 \frac{1}{3\pi}\ln[1 + (\omega_c/2\omega)^2] \tag{7}$$

To get the zero-frequency component $J_{0DF}(0)$, one needs to introduce[25,26] a low-frequency cutoff in order to remove its divergence as $\omega \to 0$. This cutoff frequency can arise from bulk susceptibility effects. However, this procedure does not allow one to write down an analytical expression for $J_{0DF}(0)$. A less exact procedure[26] is to replace the lower limit in the mode expression by a finite wave number q_1 and gives

$$J_{0\mathrm{DF}}(\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}})^2 A^2 \frac{\langle P_2\rangle^2}{(1 - 3\alpha)^2}[d^2_{00}(\beta_{\mathrm{M,Q}})]^2 \frac{1}{\pi}\ln\left[\frac{1 + (\omega_c/\omega)^2}{1 + (\omega_1/\omega)^2}\right] \tag{8}$$

where ω_1 may be estimated from the magnetic coherence length ξ in the presence of the magnetic field,[34] i.e., $\omega_1 = K/\eta\xi^2$ and

$$\xi = \left(\frac{K}{\Delta\chi}\right)^{1/2}\frac{1}{B} \tag{9}$$

with $\Delta\chi$ being the diamagnetic susceptibility anisotropy and B the applied magnetic field. When second-order contributions are included in $J_{1DF}(\omega)$, Joghems et al.[33] found that it has a correction factor $(1 - 4\alpha)$, which reduces to 1 when α is very small. Thus,

$$J_{1\mathrm{DF}}(\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}})^2 A\langle P_2\rangle^2[d^2_{00}(\beta_{\mathrm{M,Q}})]^2 \frac{(1 - 4\alpha)}{(1 - 3\alpha)^2} U(\omega_c/\omega)/\sqrt{\omega} \tag{10}$$

where the $U(\omega_c/\omega)$ function[25] accounts for the cutoff of coherence modes at high frequencies,

$$U(x) = \frac{1}{2\pi}\ln\left[\frac{x - \sqrt{2x} + 1}{x + \sqrt{2x} + 1}\right] + \frac{1}{\pi}[\tan^{-1}(\sqrt{2x} - 1) + \tan^{-1}(\sqrt{2x} + 1)] \tag{11}$$

and $\omega_c = 4\pi^2K/\eta\lambda_c{}^2$ with the cutoff wavelength λ_c typically the order of the molecular length.

For C−D bonds located in the flexible chain, the effect of director fluctuations is made smaller as a result of additional averaging within the chain from conformational changes. It has been recognized[35] in earlier deuterium NMR studies of MBBA that the spin−lattice relaxation rates for the chain deuterons should scale with the square of their quadrupolar splittings if the spin relaxation is caused only by director fluctuations. Indeed the quadrupolar splitting can give the segmental order parameter of the C−D bond at carbon site i, which is defined by

$$Si^{(i)}_{\mathrm{CD}} = \langle\langle P_2(\cos\Theta^{(i)})\rangle\rangle \tag{12}$$

where $\Theta^{(i)}$ is the angle between the ith C−D bond and the equilibrium director; $\langle\langle\ \rangle\rangle$ denotes both the conformational average and overall motional average. In uniaxial phases like the nematic, the above equation can be expressed as[3]

$$\begin{aligned} S^{(i)}_{\mathrm{CD}} &= \langle\langle P_2[(\beta^{(i)}_{\mathrm{M,Q}})]P_2[\cos(\theta)]\rangle\rangle \\ &= \overline{d^2_{00}(\beta^{(i)}_{\mathrm{M,Q}})}\,\langle P_2\rangle \end{aligned} \tag{13}$$

where $\overline{d^2_{00}(\beta^{(i)}_{\mathrm{M,Q}})}$ denotes the conformational average over the $\beta^{(i)}_{\mathrm{M,Q}}$ angle of the particular C−D bond with respect to the molecular z_{M} axis, and θ is the angle between the z_{M} axis and the equilibrium director. The assumption was made for the last step in eq 13 that the motional modes for the internal chain motions and for the molecular reorientation are decoupled. With this simplifying assumption, the geometric factor in eqs 6−8 and 10 must involve an additional average due to internal motions and together with $\langle P_2\rangle$ can be replaced by the segmental order parameter (or in terms of the quadrupolar splitting) of the ith deuterons. Thus, director fluctuations contribute to the chain deuterons according to

$$J_{0\mathrm{DF}}^{(i)}(\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}}^{(i)})^2 \frac{A^2}{(1-3\alpha)^2}(S_{\mathrm{CD}}^{(i)})^2 \frac{1}{\pi}\ln\left[\frac{1+(\omega_{\mathrm{c}}/\omega)^2}{1+(\omega_1/\omega)^2}\right] \quad (14)$$

$$J_{1\mathrm{DF}}^{(i)}(\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}}^{(i)})^2 \frac{A}{(1-3\alpha)^2}(S_{\mathrm{CD}}^{(i)})^2 (1-4\alpha)U(\omega_{\mathrm{c}}/\omega)/\sqrt{\omega} \quad (15)$$

$$J_{2\mathrm{DF}}^{(i)}(2\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}}^{(i)})^2 \frac{A^2}{(1-3\alpha)^2}(S_{\mathrm{CD}}^{(i)})^2 \frac{1}{3\pi}\ln[1+(\omega_{\mathrm{c}}/2\omega)^2] \quad (16)$$

It is noted that in all these equations for director fluctuations, the contributions to J_0, J_1, and J_2 are all related to the high-frequency cutoff ω_{c}. The ω_{c} value depends on molecular properties and perhaps also on the detailed molecular structure. Thus, it is expected to change from sample to sample. When the Larmor frequency $\omega_0 \ll \omega_{\mathrm{c}}$, like the case in 5O.7 and 4O.8, the cutoff function of eq 11 approaches unity and the differences in ω_{c} of different samples become immaterial in $J_1(\omega)$. As the cutoff frequency drops below the Larmor frequency, the cutoff function approaches zero and the negative cross term (see below) can in fact cancel the $J_{1\mathrm{DF}}$. The total director fluctuation contribution to J_1 may even become negative. In addition, the $J_{2\mathrm{DF}}(2\omega)$ is small because of its second-order nature and can be neglected in the megahertz region. Thus, it may be difficult to study director fluctuations in the megahertz regime using only the spectral densities J_1 and J_2. The zero-frequency component $J_0(0)$ becomes a unique and useful tool in studying director fluctuations in this case.

In a stochastic Markovian process, to describe the molecular reorientation of an asymmetric molecule in an uniaxial medium, one must find the conditional probability by solving a symmetrized form of the rotational diffusion equation. The symmetrized rotational diffusion operator $\hat{\Gamma}$ in ref 19 is given in terms of $\epsilon = (D_x - D_y)/(D_x + D_y)$ and $\eta = D_z/\rho$, with $\rho = (D_x + D_y)/2$. D_x, D_y, and D_z are the principal elements of a rotational diffusion tensor, defined by a set of molecular axes, and ϵ, an asymmetry parameter of the rotational diffusion tensor, is zero in the special case of uniaxial molecules. In general, the orientational correlation functions can be written as a sum of decaying exponentials,[16,19]

$$G_{mnn'}^{\mathrm{L}}(t) = \sum_K (\beta_{mnn'}^{\mathrm{L}})_K \exp[(\alpha_{mnn'}^{\mathrm{L}})_K t] \quad (17)$$

where m and n (n') represent the projection indices of a rank L tensor in the laboratory and molecular frames, respectively; $(\alpha_{mnn'}^{\mathrm{L}})_K/\rho$, the decay constants, are the eigenvalues of the Γ matrix, and $(\beta_{mnn'}^{\mathrm{L}})_K$, the relative weights of the exponentials, are the corresponding eigenvectors.

The spectral densities in a deuteron NMR experiment ($L = 2$) are the Fourier transform of the time correlation functions ($m = 0, 1, 2$) to give

$$J_{m\mathrm{R}}(\mathrm{m}\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}})^2 \sum_n \sum_{n'} d_{n,0}^2(\beta_{\mathrm{M,Q}}) d_{n'0}^2(\beta_{\mathrm{M,Q}}) \times \sum_K \frac{{(\beta_{mnn'}^2)_K}^2 {(\alpha_{mnn'}^2)_K}^2}{{(\alpha_{mnn'}^2)_K}^2 + m^2\omega^2} \quad (18)$$

where the subscript R is used to denote molecular rotation. For the methine deuteron, one may use the above equation to give $J_{m\mathrm{R}}^{(0)}(m\omega)$ with $\beta_{\mathrm{M,Q}} = 67°$ (the molecular z_{M} axis is taken to be along the para axis of the butyl ring) and $q_{\mathrm{CD}} = 185$ kHz. For the deuterons in the chain, a decoupled model[36] is used to describe correlated internal rotations in the flexible butyl chain, and there are 27 different conformations.[30] The spectral densities can be written on the basis of these models:

$$J^{(i)}{}_{m\mathrm{R}}(\mathrm{m}\omega) = \frac{3\pi^2}{2}(q_{\mathrm{CD}}^{(i)})^2 \sum_n \sum_{n'} \sum_{k=1}^{27} \left(\sum_{l=1}^{27} d_{n,0}^2(\beta_{\mathrm{M,Q}}^{(i)l}) \times \exp[-in\alpha_{\mathrm{M,Q}}^{(i)l}]\, x_l^{(1)}\, x_l^{(k)} \right) \times \left(\sum_{l'=1}^{27} d_{n'0}^2(\beta_{\mathrm{M,Q}}^{(i)l'}) \times \exp[-in'\alpha_{M,Q}^{(i)l'}]\, x_{l'}^{(1)}\, x_{l'}^{(\mathrm{k})} \right) \sum_K \frac{(\beta^2{}_{mnn'})_K\,[(\alpha^2{}_{mnn'})_K + |\lambda_k|]}{[(\alpha^2{}_{mnn'})_K + |\lambda_k|]^2 + m^2\omega^2} + \frac{3\pi^2}{2}(q_{\mathrm{CD}}^{(i)})^2 \delta_{m0} \langle P_2\rangle^2 \sum_{k=1}^{27} \left| \sum_{l=1}^{27} d_{00}^2(\beta_{\mathrm{M,Q}}^{(i)l}) x_l^{(1)}\, x_l^{(k)} \right|^2 / |\lambda_k| \quad (19)$$

where $q_{\mathrm{CD}}^{(i)} = 165$ kHz, $\beta_{\mathrm{M,Q}}^{(i)l}$ and $\alpha_{\mathrm{M,Q}}^{(i)l}$ are the polar angles of the C_i−D bond of the comformer l in the molecular frame, and λ_k and $\vec{x}^{(k)}$ are the eigenvalues and eigenvectors from diagonalizing a symmetrized transition rate matrix. The rate matrix describing conformational changes in the butyl chain contains jump constants k_1, k_2, and k_3 for one-, two-, and three-bond motions[36] in the chain. Furthermore, if director fluctuations are slow in comparison with molecular rotations, couplings between these two motions produce[24,25] a small cross term contribution to $J_1(\omega)$. Following Freed,[25] this negative cross term for the methine deuteron can be shown as

$$J_{1\mathrm{CR}}^{(0)}(\omega) = -\frac{3\pi^2}{2}(q_{\mathrm{CD}})^2 \frac{A}{(1-3\alpha)^2}\langle P_2\rangle^2 [d_{00}^2(\beta_{\mathrm{M,Q}})]^2 \frac{\sqrt{8\omega_{\mathrm{c}}}}{\pi} \sum_K b_K \times \frac{(\alpha_{100}^2)_K}{{(\alpha_{100}^2)_K}^2 + \omega^2} \quad (20)$$

where the subscript CR is to denote the cross term and $b_K = (\beta_{100}^2)_K/(\beta_{100}^2)_1$ are relative weights of exponentials that describe the molecular reorientation. For the methylene deuterons on the chain,

$$J_{1\mathrm{CR}}^{(i)}(\omega) = -\frac{3\pi^2}{2}(q_{\mathrm{CD}}^{(i)})^2 \frac{A}{(1-3\alpha)^2}(S_{\mathrm{CD}}^{(i)})^2 \frac{\sqrt{8\omega_{\mathrm{c}}}}{\pi} \sum_K b_K \frac{(\alpha_{100}^2)_K}{{(\alpha_{100}^2)_K}^2 + \omega^2} \quad (21)$$

Here cross terms from second-order director fluctuations are neglected. Finally, the calculated spectral densities for the ith deuterons are obtained from

$$J_1^{(i)}(\omega) = J_{1\mathrm{R}}^{(i)}(\omega) + J_{1\mathrm{DF}}^{(i)}(\omega) + J_{1\mathrm{CR}}^{(\mathrm{i})}(\omega) \quad (22)$$

$$J_2^{(i)}(2\omega) = J_{2\mathrm{R}}^{(i)}(2\omega) + J_{2\mathrm{DF}}^{(i)}(2\omega) \quad (23)$$

$$J_0^{(i)}(0) = J_{0\mathrm{R}}^{(\mathrm{i})}(0) + J_{0\mathrm{DF}}^{(i)}(0) \quad (24)$$

where $i = 0, 1, 2$, and 3, with $i = 0$ denoting the methine site.

Our experiments consist of measurements of the spin−spin relaxation rate[1] $1/T_2$ at 46 MHz and measurements of the

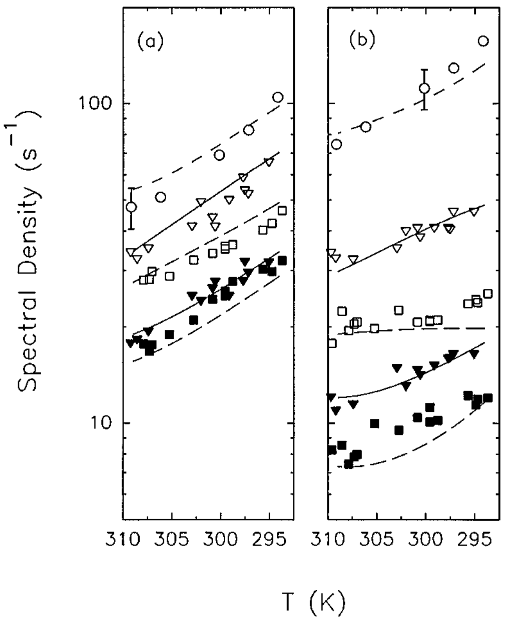

Figure 1. Plots of experimental (symbols) and calculated (lines) spectral densities of MBBA by using $\omega_c = 10$ MHz. Parts a and b are for C_0 and C_1, respectively. The circles denote the spectral densities $J_0(0)$, the open symbols denote $J_1(\omega_0)$, while the closed symbols denote $J_2(2\omega_0)$. The triangles represent the data at 15.3 MHz, while the squares represent data at 46 MHz. Solid and long dashed lines denote calculated spectral densities at 15.3 and 46 MHz, respectively.

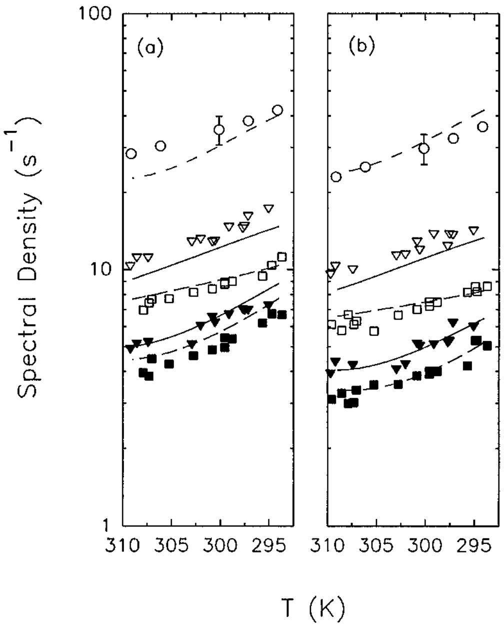

Figure 2. Plots of experimental (symbols) and calculated (lines) spectral densities of MBBA by using $\omega_c = 10$ MHz. Parts a and b are for C_2 and C_3, respectively. The symbols are the same as those in Figure 1.

Zeeman and quadrupolar spin−lattice relaxation rates[30] $1/T_{1Z}$ and $1/T_{1Q}$ at 15.3 and 46 MHz. From the spin relaxation theory for deuteron ($I = 1$), these are related to the spectral densities $J_m(m\omega)$ by[37]

$$T_2^{(i)-1} = \frac{3}{2}J_0^{(i)}(0) + \frac{3}{2}J_1^{(i)}(\omega_0) + J_2^{(i)}(2\omega_0) \tag{25}$$

$$T_{1Z}^{(i)-1} = J_1^{(i)}(\omega_0) + 4J_2^{(i)}(2\omega_0) \tag{26}$$

$$T_{1Q}^{(i)-1} = 3J_1^{(i)}(\omega_0) \tag{27}$$

where ω_0 is the Larmor frequency.

Results and Discussion

The spectral densities $J_m^{(i)}(m\omega_0)$ at two different Larmor frequencies, reproduced in Figures 1 and 2, are those reported before.[1,30] The analysis of quadrupolar splittings[30] used the internal energies $E_{tg} = 2550$ J/mol and $E_{gg} = 6000$ J/mol to give the model parameters (X_a, $\lambda_c = X_c/X_a$, $\langle P_2\rangle$, and $S_{xx} - S_{yy}$) needed in our analysis. In particular, the order parameter tensor of the average conformer allows us to adopt a biaxial orienting potential (specified by a_{20}, a_{22})[19] for solving the rotational diffusion equation. We analyze the spectral densities of methine C_0 and methylene C_i ($i = 1, 2, 3$) deuterons using a global target approach,[32] that is, treating the spectral density data at different temperatures and at both Larmor frequencies in the same fitting procedure. Smoothed lines of data were used to obtain the $J_0^{(i)\exp}(0)$, $J_1^{(i)\exp}(\omega_0)$ and $J_2^{(i)\exp}(2\omega_0)$ values at six different temperatures. Now, individual target analysis (i.e., minimization at a single temperature) must first be performed before the global procedure in order to get some ideas on temperature relations of the model parameters. The global target analysis takes advantage of the fact that target parameters of the model vary smoothly with temperature. This was found[38] particularly useful when the parameters of the model were highly correlated and/or affected by large statistical errors. An optimization routine[39] (AMOEBA) is used to minimize the sum squared percent error F,

$$F = \sum_k \sum_{\omega_0} \sum_i \sum_m \left[\frac{J_m^{(i)\mathrm{calc}}(m\omega_0) - J_m^{(i)\exp}(m\omega_0)}{J_m^{(i)\exp}(m\omega_0)} \times 100\right]_k^2 \tag{28}$$

where the sum k is over six different temperatures, and $m = 0$, 1, or 2. The fitting quality Q is given by the percentage mean squared deviation,

$$Q = \frac{\sum_k \sum_{\omega_0} \sum_i \sum_m [J_m^{(i)\mathrm{calc}}(m\omega_0) - J_m^{(i)\exp}(m\omega_0)]_k^2}{\sum_k \sum_{\omega_0} \sum_i \sum_m [J^{(i)\exp}{}_m(m\omega_0)\,]_k^2} \times 100\% \tag{29}$$

It is believed that the motional biaxiality for the MBBA molecule is very small. Therefore, $D_x = D_y$ is set in our minimization. From the individual target analysis, it is clear that the diffusion constants and the jump constants k_1 and k_3 all obey simple Arrhenius-type relations, giving

$$D_x = D_x^0 \exp(-E_a^{Dx}/RT) \tag{30}$$

$$D_z = D_z^0 \exp(-E_a^{Dz}/RT) \tag{31}$$

$$k_1 = k_1^0 \exp(-E_a^{k1}/RT) \tag{32}$$

$$k_3 = k_3^0 \exp(-E_a^{k3}/RT) \tag{33}$$

where the global parameters are the pre-exponentials D_x^0, D_z^0, k_1^0, and k_3^0, and their corresponding activation energies E_a^{Dx}, E_a^{Dz}, E_a^{k1}, and E_a^{k3}. When such a relation does not exist for a target parameter like k_2 and the prefactor A of director fluctuations, it is still possible to introduce an interpolating relation linking its values at various temperatures. As k_2 and $A_{DF}(=A\langle P_2\rangle^2)$ are weakly temperature dependent, we model them by

$$k_2 = k_2' - k_2''(T - T_{\max}) \tag{34}$$

$$A_{\mathrm{DF}} = A_{\mathrm{DF}}' - A_{\mathrm{DF}}''(T - T_{\max}) \tag{35}$$

where the temperature $T_{\max}$ is the highest temperature used in the global analysis, and the global parameters k_2', k_2'', A_{DF}', and A_{DF}'' are optimized. Thus there are 12 global parameters (two from each of eqs 30−35) for the global fit.

TABLE 1: Comparisons of Activation Energies E_a (in kJ/mol) and Fitting Results Using Different High-Frequency Cutoffs for MBBA in our Calculations

ω_c (MHz)	$E_a^{k_1}$	$E_a^{k_3}$	E_a^{Dx}	E_a^{Dz}	F	Q
3	103	80.0	49.9	45.0	10 600	0.95%
10	102 ± 2	78 ± 2	50.0 ± 0.8	44.3 ± 0.6	9 600	0.97%
13	100	77.2	49.2	44.0	9 000	0.97%
20	95.9	75.1	47.8	43.4	7 900	0.99%

TABLE 2: Calculated Spectral Densities for C_0-C_3 Deuterons Due to Director Fluctuations and Molecular Reorientation in the Global Minimization with a High-Frequency Cutoff $\omega_c = 10$ MHz; The Numbers (in s^{-1}) within Parentheses Are for 46 MHz, While Those without Parentheses Are for 15.3 MHz, and the Temperature Is 300 K

C_i	$J_0(0)$	$J_{0DF}(0)$	$J_1(\omega)$	$J_{1DF}(\omega)$	$J_{1CR}(\omega)$	$J_2(2\omega)$	$J_{2DF}(2\omega)$
C_0	74.59	26.16	53.17	2.46	−4.17	26.2	0.04
	(74.59)	(26.16)	(38.54)	(0.3)	(−2.0)	(21.75)	(0.00)
C_1	102.7	58.29	40.38	5.47	−9.29	14.34	0.09
	(102.7)	(58.29)	(19.75)	(0.68)	(−4.5)	(8.60)	(0.01)
C_2	30.42	18.43	12.21	1.73	−2.94	6.63	0.03
	(30.42)	(18.43)	(9.12)	(0.21)	(−1.4)	(5.72)	(0.00
C_3	31.62	20.11	11.1	1.89	−3.21	4.97	0.03
	(31.62)	(20.11)	(7.48)	(0.23)	(−1.5)	(3.93)	(0.00)

TABLE 3: Motional Parameters Derived from a Global Analysis of Spectral Densities Using $\omega_c = 10$ MHz

T (K)	k_1 ($\times 10^{11}$ s^{-1})	k_2 ($\times 10^{10}$ s^{-1})	k_3 ($\times 10^{12}$ s^{-1})	D_x ($\times 10^{7}$ s^{-1})	D_z ($\times 10^{9}$ s^{-1})	A($\times 10^{-5}$ $s^{1/2}$)
309	10.5	1.51	2.58	6.24	3.66	1.9 ± 0.4
306	7.12	1.65	1.92	5.16	3.09	1.76
303	4.79	1.80	1.41	4.24	2.60	1.70
300	3.20	1.94	1.04	3.48	2.18	1.71
297	2.12	2.09	0.76	2.84	1.82	1.76
294	1.39	2.24	0.55	2.31	1.52	1.78

TABLE 4: Comparisons of *A* Values in 1O.4, 5O.7, and 4O.8 at Different Reduced Temperature T_{red} ($=T/T_C$); The *A* Values in Refs 22 and 23 Were Incorrectly Reported Due to Unfortunate Numerical Errors

T_{red}	10.4	T_{red}	50.7[22]	T_{red}	40.8[23]
0.988	1.93×10^{-5}	0.993	1.27×10^{-5}	0.995	9.72×10^{-6}
0.979	1.76×10^{-5}	0.979	6.06×10^{-6}	0.981	5.27×10^{-6}
0.969	1.70×10^{-5}	0.964	3.42×10^{-6}	0.966	3.85×10^{-6}
0.96	1.71×10^{-5}	0.95	1.81×10^{-6}	0.952	2.98×10^{-6}
0.95	1.76×10^{-5}	0.936	1.14×10^{-6}	0.938	2.54×10^{-6}
0.94	1.78×10^{-5}			0.924	2.38×10^{-6}
	$T_C = 312.6$ K		$T_C = 350.6$ K		$T_C = 351.8$ K

We analyze the deuteron data at four carbon sites (C_0, C_1, C_2, C_3). At each site, there are two experimental J_1 and two experimental J_2 values from the two Larmor frequencies, but only one $J_0(0)$ value due to the zero-frequency component being independent of the Larmor frequency. So we have a total of 120 spectral densities from six temperatures to derive 12 global parameters for a given ω_c value. For convenience, the diffusion and jump rate pre-exponentials were not used as global parameters. Rather eqs 30−33 were rewritten in terms of the activation energies and the diffusion and jump constants D_x', D_z', k_1', k_3' at 309 K ($T_{\max}$), giving the set of global parameters used in our minimization. Initial values at the chosen temperature (309 K) were first obtained by an individual target analysis.

We assume for simplicity that ω_c is constant in the nematic phase of MBBA. The assumption is probably good for the temperature range studied here. Several high-frequency cutoff values, between 3 and 20 MHz, were tested (Table 1); these fits between the calculated and experimental spectral density data are in general acceptable, since Q values are all less than 1%. The derived activation energies vary slightly with ω_c. At $\omega_c = 3$ MHz, a better Q value of 0.95% was obtained, whereas at $\omega_c = 20$ MHz, a better F value of 7900 was achieved. Thus, it is reasonable to estimate the ω_c value for MBBA to be around 3−10 MHz. We note that the E_a^{Dx} is a little larger than E_a^{Dz}, indicating the spinning motion of the MBBA molecule is less hindered than the tumbling motion. This was not achieved when a global target analysis was carried out[32] using only the $J_1(\omega)$ and $J_2(2\omega)$ data. Without loss of generality, we take $\omega_c = 10$ MHz in the following discussion. From the global minimization, the predicted site dependences of the spectral densities and director fluctuation contributions are listed in Table 2 for one temperature. Director fluctuations mainly have effects on the zero-frequency spectral densities. They account for 35% of the methine $J_0(0)$ and over 50% for the methylene (C_1-C_3) $J_0^{(i)}(0)$. Their total first-order contributions ($J_{1DF}^{(i)}$ plus negative $J_{1CR}^{(i)}$) to $J_1^{(i)}(\omega)$ are small but negative; the biggest effects occur at the chain deuterons, where the director fluctuation contributions amount to about 10% of $J_1^{(i)}(\omega)$. The second-order contributions of $J_{2DF}^{(i)}$ to $J_2^{(i)}(2\omega)$ are indeed very small and less than 1%. Indeed the observed frequency dependences in $J_2^{(i)}(2\omega)$ are mainly due to "slow" molecular rotations. The model parameters (3 k's, 2 D's and A) for $\omega_c = 10$ MHz at each chosen temperature are summarized in Table 3. The activation energies (Table 1) and the pre-exponentials ($k_1^0 = 1.75 \times 10^{29}$ s^{-1}, $k_3^0 = 4.3 \times 10^{25}$ s^{-1}, $D_x^0 = 1.74 \times 10^{16}$ s^{-1}, and $D_z^0 = 1.13 \times 10^{17}$ s^{-1}) are used to plot the theoretical spectral density curves in Figures 1 and 2. The $J_2^{(i)}$ values at 46 MHz show deviations at C_0 to C_2. Although there are some systematic deviations between experimental and calculated spectral densities, the overall fits are quite satisfactory. It is interesting to note that a comparison of the rate and diffusion constants with those reported before[32] shows reasonable agreements. In Table 4, we list the prefactor A values for the different samples of the *n*0.*m* series. It is noted that the prefactor A obtained for MBBA is larger than that of 50.7[22] and 40.8[23], yet there is negligible contribution from director fluctuations to J_1 of MBBA at the same Larmor frequencies. This is of course due to the lower high-frequency cutoff in MBBA. Using typical values of $K = 5 \times 10^{-12}$ N and $\eta = 6.5 \times 10^{-2}$ Pa s, $A = 1.6 \times 10^{-5}$ s$^{1/2}$ is calculated from eq 4 at 300 K. Thus, the derived A values appear to agree with the theory. The calculated cross term $J_{1CR}^{(i)}$ has absolute values slightly larger than $J_{1DF}^{(i)}$, contrary to the prediction that the cross term should be "small". Therefore, the controversy with the cross term remains to be explored with proper theoretical models. As seen in Table 4, the temperature dependence of A in MBBA differs from those of 50.7 and 40.8. It is not clear at present why the differences exist. The error limit for a particular global parameter was estimated by varying the one under consideration while keeping all other global parameters identical to those for the minimum F, to give an approximate doubling in the F value. Thus the error bar for D_x^0 is given by (1.25−2.54) × 10^{16} s^{-1}, while that of D_z^0 is (0.88−1.53) × 10^{17} s^{-1}. Similarly, k_1^0 varies from 0.85×10^{29} s^{-1} to 5.2×10^{29} s^{-1} and k_3^0 varies from 1.8×10^{25} s^{-1} to 4.3×10^{26} s^{-1}. Finally, the error bars for the derived activation energies are indicated in Table 1 for $\omega_c = 10$ MHz. These activation energies are fairly well-defined by the global target analysis.

Summary

We explore in the present study the applicability of director fluctuations up to second-order contributions as well as the rotational diffusion model of Tarroni and Zannoni (in the limit of $D_x = D_y$) for both the deuteron spin−spin and spin−lattice relaxation in the nematic phase of MBBA. Our T_1 and T_2 data support the idea that MBBA has a relatively low value for the high-frequency cutoff (around 3−10 MHz). We find that director fluctuations have larger effects on $J_0^{(i)}(0)$ (35%−50%) than on $J_1^{(i)}(\omega)$ (<10%). The derived A values are quite reasonable, ranging between 1.7×10^{-5} and 1.9×10^{-5} s$^{1/2}$. The fits to the available experimental spectral densities between 293 and 310 K in MBBA are on the whole very satisfactory with an overall quality Q factor of about 1%.

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References and Notes

(1) Dong, R. Y. *Chem. Phys. Lett.* **1996**, *251*, 387.

(2) Vold, R. L.; Vold, R. R. In *The Molecular Dynamics of Liquid Crystals*; Luckhurst, G. R., Veracini, C. A., Eds.; Kumer Academic: Dordrecht, 1994.

(3) Dong, R. Y. *Nuclear Magnetic Resonance of Liquid Crystals*; Springer-Verlag: New York, 1994. Wade, C. G. *Annu. Rev. Phys. Chem.* **1977**, *28*, 47.

(4) Chatelain, P. *Acta Crystallogr.* **1948**, 1, 315.

(5) de Gennes, P. G. *Compt. Rend.* **1968**, *226B*, 15.

(6) Orsay Liq. Crys. Group, *Phys. Rev. Lett.* **1969**, *22*, 1361; *J. Chem. Phys.* **1969**, *51*, 816.

(7) Haller, I.; Litster, J. D. *Phys. Rev. Lett.* **1970**, *25*, 1550.

(8) Weger, M.; Cabane, B. *J. Phys. (Paris), Colloq.* **1969**, *30*, C4−72.

(9) Bloembergen, N.; Purcell, E. M.; Pound, R. V. *Phys. Rev.* **1948**, *73*, 679.

(10) Pincus, P. *Solid State Commun.* **1969**, *7*, 415.

(11) Lubensky, T. *Phys. Rev. A* **1970**, *2*, 2497.

(12) Doane, J. W.; Visintainer, J. J. *Phys. Rev. Lett.* **1969**, *23*, 1421. Doane, J. W.; Tarr, C. E.; Nickerson, M. A. *Phys. Rev. Lett.* **1974**, *33*, 620.

(13) Brochard, F. *J. Phys. (Paris)* **1973**, *34*, 411.

(14) Blinc, R.; Vilfan, M.; Luzar, M.; Seliger, J.; Zagar, V. *J. Chem. Phys.* **1978**, *68*, 303.

(15) Freed, J. H. *J. Chem. Phys.* **1964**, 41, 2077; Huntress, W., Jr. *Adv. Magn. Reson.* **1970**, *4*, 1.

(16) Nordio, P. L.; Busolin, P. *J. Chem. Phys.* **1971**, *55*, 5485. Nordio, P. L.; Rigatti, G.; Segre, U. *Mol. Phys.* **1973**, *25*, 129.

(17) Bernassau, J. M.; Black, E. P.; Grant, D. M. *J. Chem. Phys.* **1982**, *76*, 253

(18) Bulthuis, J.; Plomp, L. *J. Phys.* (Paris) **1990**, *51*, 2581

(19) Tarroni, R.; Zannoni, C. *J. Chem. Phys.* **1991**, *95*, 4550.

(20) Berggren, E.; Tarroni, R.; Zannoni, C. *J. Chem. Phys.* **1993**, *99*, 6180.

(21) Berggren, E.; Zannoni, C. *Mol. Phys.* **1995**, *85*, 299.

(22) Dong, R. Y.; Shen, X. *J. Chem. Phys.* **1996**, *105*, 2106; *Phys. Rev. E.* **1994**, *49*, 538.

(23) Dong, R. Y. *J. Phys. Chem.* **1996**, *100*, 15663.

(24) Ukleja, P.; Pirs, J.; Doane, J. W. *Phys. Rev. A* **1976**, *14*, 414.

(25) Freed, J. H. *J. Chem. Phys.* **1977**, *66*, 4183.

(26) Vold, R. L.; Vold, R. R.; Warner, M. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 997.

(27) van der Zwan, G.; Plomp, L. *Liq. Cryst.* **1989**, *4*, 133.

(28) Noack, F. *Progr. NMR Spectrosc.* **1986**, *18*, 171. Schweikert, K. H.; Noack, F. *Mol. Cryst. Liq. Cryst.* **1992**, *212*, 33.

(29) Barbara, T. M.; Vold, R. R.; Vold, R. L.; Neubert, M. E. *J. Chem. Phys.* **1985**, *82*, 1612.

(30) Dong, R. Y.; Friesen, L.; Richards, G. M. *Mol. Phys.* **1994**, *81*, 1017.

(31) Vilfan, M.; Blinc, R.; Doane, J. W. *Solid State Commun.* **1972**, *11*, 1073

(32) Dong, R. Y. *Mol. Phys.* **1996**, *88*, 979.

(33) Joghems, E. A.; van der Zwan, G. *J. Phys. II* **1996**, *6*, 845.

(34) de Gennes, P. G. in *Proceeding of the 2nd International Liquid Conference*; Brown, G. H., Ed.; Gordon & Breach: New York, 1969; p 531.

(35) Dong, R. Y.; Lewis, J.; Tomchuk, E.; Bock, E. *J. Chem. Phys.* **1978**, *69*, 5314.

(36) Dong, R. Y. *Phys. Rev. A* **1991**, *43*, 4310.

(37) Jacobsen, J. P.; Bildsoe, H. K.; Schumburg, K. *J. Magn. Reson.* **1976**, *23*, 153. Ahmad, S. B.; Packer, K. J.; Ramsden, J. M. *Mol. Phys.* **1977**, *33*, 857. Vold, R. R.; Vold, R. L. *J. Chem. Phys.* **1977**, *66*, 4018.

(38) Arcioni, A.; Bertinelli, F.; Tarroni, R.; Zannoni, C. *Chem. Phys.* **1990**, *143*, 259.

(39) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge University: Cambridge, UK, 1986.