Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Ronald Y. Dong (1997): Detection of Second-Order Director Fluctuations by Deuteron Spin-Spin Relaxation at a Standard High Field, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 431-440

To link to this article: http://dx.doi.org/10.1080/10587259708039453

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 431–440
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DETECTION OF SECOND-ORDER DIRECTOR FLUCTUATIONS BY DEUTERON SPIN-SPIN RELAXATION AT A STANDARD HIGH FIELD

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Abstract We report on the measurements of deuteron spin-spin relaxation time T_2 in the nematic phase of MBBA and 5CB using the quadrupolar echo pulse train in a magnetic field of 7 T. The spectral densities $J_0^{(i)}(0)$ at different carbon sites were derived from the T_2 and T_1 measurements. Using a model that combined rotational diffusion motion of individual molecules and their internal bond rotations, the spectral densities $J_1^{(i)}(\omega_0)$ and $J_2^{(i)}(2\omega_0)$ could be interpreted, while the measured $J_0^{(i)}(0)$ were too large. It is argued that second-order director fluctuations contribute in part to the $J_0^{(i)}(0)$ spectral densities. Thus T_2 measurements at a standard high magnetic field can be used to gain insights on director fluctuations.

INTRODUCTION

It is well known[1,2] that director fluctuations are an important source of nuclear spin relaxation in liquid crystals. Deuterium nuclear magnetic resonance has been used to examine both solvent and solute spins in liquid crystals.[3] The detection of director fluctuations by means of deuteron spin-lattice relaxation in mesogens at conventional NMR frequencies has met[4–6] with limited success. Here we report on how deuteron spin-spin relaxation time (T_2) may be used to detect higher-order director fluctuations at a standard high field. The liquid crystals chosen have deuteron spin-lattice relaxation rates which are not influenced by director fluctuations in the MHz region. The director fluctuations mode spectrum depends on many factors which include the viscoelastic properties of the medium, molecular length, domain size, temperature and degrees of ordering in the sample. In the small angle (θ) approximation, director fluctuations contribute[7–9] a frequency term to the spectral density $J_1(\omega)$, and have zero contributions to $J_0(\omega)$ and $J_2(2\omega)$. To explain the observed frequency dependence in J_2 for strongly ordered solutes in liquid crystals, second-order director fluctuations ($\propto \theta^2$) have been considered.[10–12] The calculated frequency dependence in J_2 was generally too small. Recently Joghems et al.[13] argued that there is an over-estimation of director fluctuations on $J_1(\omega)$ unless a second-order contribution is also included. Therefore, director fluctuations make contributions to all spectral densities when the small angle approximation is removed. The paper is organized into an experimental section, basic theory and finally results and discussion.

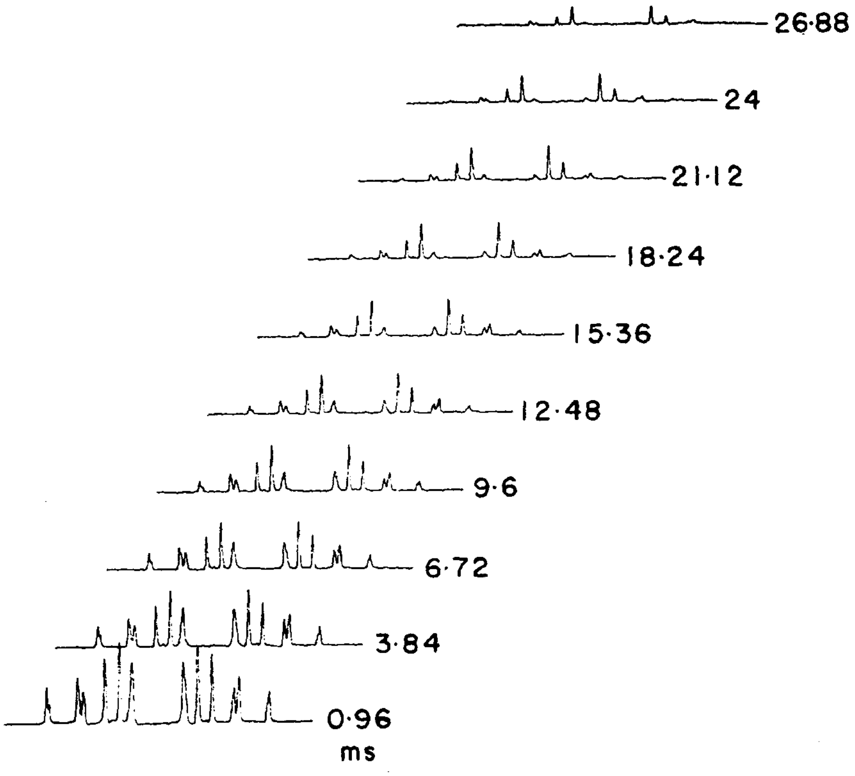

FIGURE 1 Stacked plot of a quadrupolar echo pulse train experiment in 5CB-d_{15} at 46 MHz with $2\tau = 0.32$ *ms*.

EXPERIMENTAL METHOD

Two nematic liquid crystals used in our previous T_1 studies[14,15] are used here, i.e., 4-n-pentyl-d_{11}-4′-cyanobiphenyl-d_4 (5CB-d_{15}) and p-methoxy-d_3-benzylidene-d_1-p-n-butyl-d_9-aniline (MBBA-d_{13}). For these compounds, the director is aligned along the magnetic field. A quadrupolar echo pulse train,[16] $90_x - \tau - 90_y - (2\tau - 90_y)_n -$, with an eight step phase cycling scheme was used to measure T_2 at 46 MHz. Typical 90° pulse length was about 4 μs. Free induction decays (FIDs) after the last 90° pulse for different n were recorded with quadrature detection and then fast Fouriertransformed to obtain deuterium spectra (see Figure 1). At 46 MHz, FID signals were averaged over 8 scans in 5CB and 24 scans or less in MBBA with a repetition time 400 *ms* or longer. Each T_2 experiment consisted of 32 different n (e.g., $n = 1, 3, 6, 9, \cdots 96$) values and sample heating was found to be minimal ($< 0.5°$). A plot of the peak intensity of a quadrupolar doublet versus $2n\tau$ was used to determine T_2. Ahmad et al.[16] have shown that the measured T_2 depends on the pulse spacing. Two limiting cases could be considered. When the pulse spacing $\tau << 1/\nu_Q$ with $2\nu_Q = \Delta\nu$ being the quadrupolar splitting of the deuteron in question, the deuteron spin relaxes as if the splitting is absent. This limit is not feasible experimentally because of rather large quadrupolar splittings in liquid crystals and overheating of the sample by the rf pulse train. At other limit ($\tau > 1/\nu_Q$), the two lines of the doublet relax independently and the spin-spin relaxation rate $R_2 = (T_2)^{-1}$ obeys:

$$R_2 = \frac{3}{2} J_0(0) + \frac{3}{2} J_1(\omega_0) + J_2(2\omega_0) \tag{1}$$

where $\omega_0/2\pi$ is the Larmor frequency.

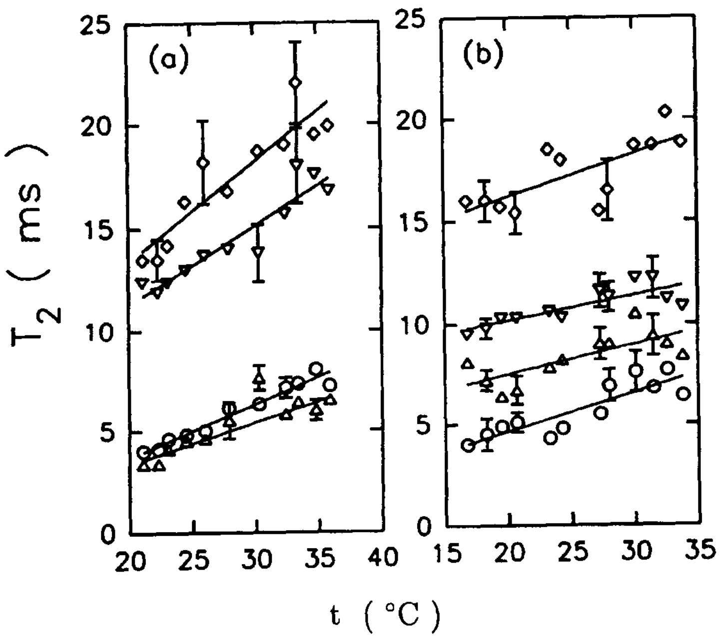

FIGURE 2 Plots of T_2 versus the temperature at 46 MHz for (a) MBBA: ○ and △ denote C_0 and C_1, while ▽ and ◇ denote C_2 and C_3; (b) 5CB: ○ and △ denote C_1 and C_2, while ▽ and ◇ denote C_3 and C_4.

Due to the smaller quadrupolar splittings of the methyl groups and ring deuterons, we only measured T_2 for the methine (C_0) and the methylene deuterons at carbons C_1, C_2 and C_3 in the butyl chain of MBBA, and in 5CB the methylene deuterons of the pentyl chain. The pulse spacing τ was set at 120 μs in MBBA and 160 μs in 5CB to satisfy the $\tau > 1/\nu_Q$ condition for all the deuterons under study. These T_2 values are shown for both samples as a function of temperature in Figure 2. The errors in our T_2 measurements were estimated to be ± 10% (for C_2 and C_3 deuterons in MBBA the errors were probably a bit worse due to severe spectral overlaps). To determine $J_0(0)$ from Equation (1), previous measured J_1 and J_2 values in 5CB[14] and MBBA[15] were used. Because of experimental uncertainties in J_1 and J_2 values, the derived $J_0(0)$ can have fairly large errors.

THEORY

We first outline the spin relaxation theory[1-3] of director fluctuations. When fluctuations in the orientation of director include terms up to second-order ($\propto \theta^2$), all spectral densities $J_0(0), J_1(\omega_0)$ and $J_2(2\omega_0)$ become non-zero.[10-13] Vold et al.[11] and van der Zwan et al.[12] found for the ith deuteron(s)

$$\begin{aligned} J^{(i)}_{2,DF}(\omega) &= J^{(i)}_{0,DF}(\omega)/3 \\ &= \frac{1}{3\pi}\ K^{(i)}_Q A^2 S_0^2 \left[d^2_{00}(\beta^{(i)}_{M,Q})\ \right]^2\ \ln\left[1 + (\omega_c/\omega)^2\right] \end{aligned} \qquad (2)$$

where $K_Q = \frac{3\pi^2}{2}\ (q_{CD})^2$ and q_{CD} is the quadrupolar coupling constant (e^2qQ/h), $\beta_{M,Q}$ is the angle between the C-D bond and the molecular z_M axis, S_0 is the nematic order parameter of the molecule relative to the local director, A is the standard prefactor[1] for director fluctuations

$$A = \frac{3kT}{4\sqrt{2}\ \pi}\ \left(\frac{\eta}{K^3}\right)^{1/2} \qquad (3)$$

and ω_c, an upper cut-off frequency, is given in terms of the cut-off wave vector q_c by $\omega_c = Kq_c^2/\eta$. K is the average elastic constant, and η the average viscosity. Now Equation (2) gives a $J^{(i)}_{0,DF}(\omega)$ expression which unfortunately diverges as $\omega \to 0$. To remove the divergence, a low frequency cut-off is required.[9] An analytical expression for $\omega \to 0$ is obtained[11] by using a less exact procedure:

$$J^{(i)}_{0,DF}(\omega) = K^{(i)}_Q A^2 S_0^2 \left[d^2_{00}(\beta^{(i)}_{M,Q})\right]^2\ \frac{1}{\pi}\ \ln\left(\frac{1 + (\omega_c/\omega)^2}{1 + (\omega_1/\omega)^2}\right) \qquad (4)$$

where the frequency ω_1 may be estimated in the presence of the magnetic field, i.e., $\omega_1 = K/\eta\xi^2$ where the magnetic coherence length $\xi = (\mu_0 K/\triangle\chi\ B^2)^{1/2}$ with

$\Delta\chi$ being the anisotropic part of the molecular diamagnetic susceptibility. Now the spectral density $J_1(\omega)$ is given by

$$J^{(i)}_{1,DF}(\omega) = K^{(i)}_Q \, AS_0^2 \left[d^2_{00}(\beta^{(i)}_{M,Q})\right]^2 \, (1-4\alpha)U(\omega_c/\omega)/\, \omega^{1/2} \tag{5}$$

where the cut-off function $U(x)$ is[9] to limit coherent modes in the director fluctuation spectrum by a low cut-off wavelength, the factor (1-4α) is needed[13] when second-order director fluctuations are taken in account, and $\alpha = kTq_c/2\pi^2K$, is a measure of the magnitude of director fluctuations. In the small angle approximation, $\alpha \rightarrow 0$ and Equation (7) reduces to the familiar $J_1(\omega)$ expression.[1] The nematic order parameter w.r.t. local director is given by $S_0 = S/(1-3\alpha)$, where the order parameter S can be derived from $\Delta\nu$ using

$$\Delta\nu = \left| \frac{3}{2} q_{CD} d^2_{00}(\beta_{M,Q})S \right| \tag{6}$$

The theory outlined above has ignored any internal bond rotations. Thus far the effects of chain flexibility on director fluctuations have not been addressed theoretically. Nonetheless, the autocorrelation function for a particular deuteron may be written as

$$G^{DF}_{m_L}(t) = K_Q(S_{CD})^2 < \{D^{2*}_{m_L0}[\Omega(0)] - < D^{2*}_{m_L0} >\}\{D^2_{m_L0}[\Omega(t)] - < D^2_{m_L0} >\} > \tag{7}$$

where the Euler angles, $\Omega(t)$, describe the orientation of the instantaneous director in the laboratory frame at time t and S_{CD}, the order parameter of the C-D bond, is given by $S_{CD} = 2\,\Delta\,\nu/3q_{CD}$. Fourier-transforming Equation (7) gives the corresponding spectral densities of motion. Thus one would expect a linear relation[8,17] between $J^{(i)}_{0,DF}(0)$ and $(S^{(i)}_{CD})^2$.

In the present study, Nordio's model[18] is used to describe molecular reorientation and a decoupled model[19] to describe correlated internal rotations in the flexible chain of 5CB and MBBA. The approach was successful in interpreting the frequency and temperature dependences of $J_1(\omega)$ and $J_2(2\omega)$ for 5CB[14] and MBBA.[15] The derived model parameters can be used to predict the contribution to $J^{(i)}_{0,MR}(0)$ of the methylene deuterons due to molecular external/internal rotations, i.e.,

$$\begin{aligned} J^{(i)}_{0,MR}(0) = {} & K^{(i)}_Q \sum_{m_M} \sum_{n=1}^{N} c_{0m_M} \left| \sum_{l=1}^{N} d^2_{m_M0}\left(\beta^{(i)l}_{M,Q}\right) \exp\left(-im_M\alpha^{(i)l}_{M,Q}\right) x_l^{(1)} x_l^{(n)} \right|^2 \\ & \times \sum_j a^{(j)}_{0m_M} / \left[\left(\tau^{(j)}_{0m_M}\right)^{-1} + |\lambda_n| \right] \end{aligned}$$

$$+ \quad K_Q^{(i)} S^2 \sum_{n=1}^{N} \left| \sum_{l=1}^{N} d_{00}^2 \left(\beta_{M,Q}^{(i)l} \right) x_l^{(1)} x_l^{(n)} \right|^2 / \, |\lambda_n| \tag{8}$$

where $\beta_{M,Q}^{(i)l}$ and $\alpha_{M,Q}^{(i)l}$ are the polar angles of the C_i-D bond of the conformer l in the molecular (x_M, y_M, z_M) frame, λ_n and $\vec{x}^{(n)}$ are the eigenvalues and eigenvectors from diagonalizing a symmetrized $N \times N$ transition rate matrix and N is the number of conformers available to the chain[14] (N is equal to 27 in MBBA and 81 in 5CB). The rate matrix describing conformational changes in the chain contains jump constants k_1, k_2 and k_3 for one-, two- and three-bond motions.[19] The orientational correlation times $\tau_{0m_M}^{(j)}$ are given by

$$\left(\tau_{0m_M}^{(j)} \right)^{-1} = \frac{6 D_\perp}{b_{0m_M}^{(j)}} + m_M^2 \left(D_\parallel - D_\perp \right) \tag{9}$$

where $D_\parallel$ and $D_\perp$ refer to rotational diffusion constants of the 'average' molecule about its z_M axis and of the z_M axis, respectively. The z_M axis is taken to be along the para axis of the biphenyl ring or the aniline ring. The term which contains S^2 in Equation (8) represents a cross-term between the overall reorientation and internal bond rotations. The a, b and c coefficients are given in terms of S by Vold et al.[20] For the methine deuteron in MBBA, only molecular reorientation contributes. Thus

$$J_{0,MR}^{(0)}(0) = K_Q^{(0)} \sum_{m_M} c_{0m_M} \left[d_{m_M 0}^2 \left(\beta_{M,Q}^{(0)} \right) \right]^2 \sum_j a_{0m_M}^{(j)} \, \tau_{0m_M}^{(j)} \tag{10}$$

where $\beta_{M,Q}^{(0)}$ is taken to be 67°, $q_{CD}^{(0)} = 185$ kHz, for the methylene deuterons $q_{CD} = 165$ kHz. Since the experimental $J_0^{(i)}(0)$ values are larger than the calculated $J_{0,MR}^{(i)}(0)$, we propose that the excess zero frequency spectral densities $J_{0,EX}^{(i)}(0)$

$$J_{0,EX}^{(i)}(0) = J_0^{(i)}(0) - J_{0,MR}^{(i)}(0) \tag{11}$$

are due to second-order director fluctuations, since there is no first-order contribution to $J_0(0)$.

RESULTS and DISCUSSION

The experimental $J_0^{(i)}(0)$ are plotted at several temperatures for MBBA in Figure 3(a) and for 5CB in Figure 3(b). The model parameters $D_\parallel, D_\perp, k_1, k_2$ and k_3 needed to evaluate $J_{0,MR}^{(i)}(0)$ in Equations (8) and (10) were those determined before[14,15] based on fitting the experimental $J_1(\omega)$ and $J_2(2\omega)$ at 15 and 46 MHz using molecular external and internal rotations and no director fluctuations. For example, the

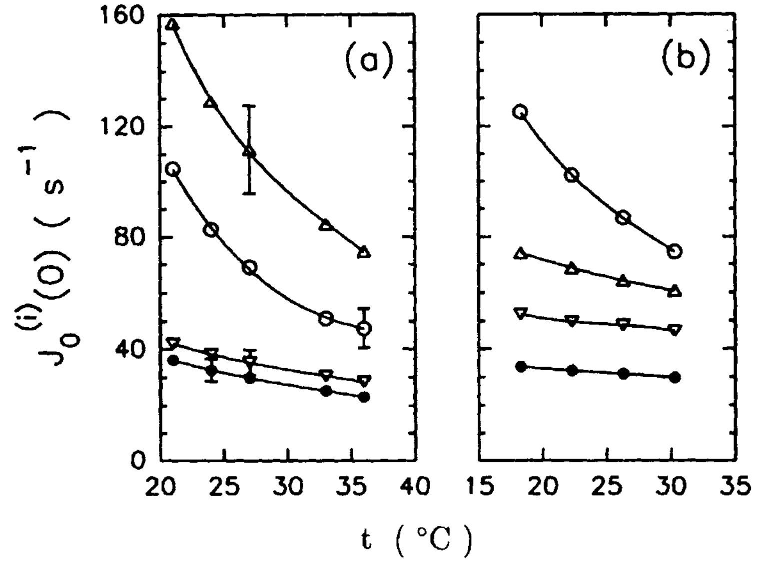

FIGURE 3 Plots of derived $J_0(0)$ versus the temperature for (a) MBBA: o and △ denote C_0 and C_1, while ▽ and • denote C_2 and C_3; (b) 5CB: o and △ denote C_1 and C_2, while ▽ and • denote C_3 and C_4.

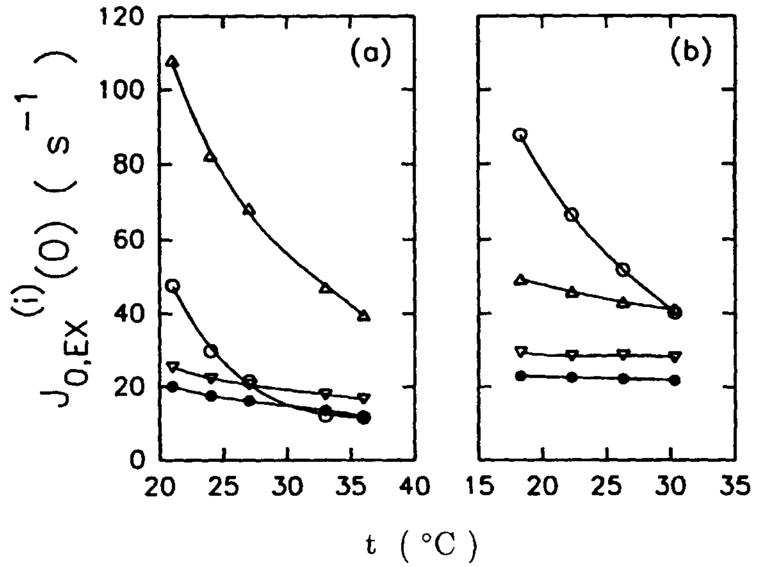

FIGURE 4 Plots of derived $J_{0,EX}(0)$ versus the temperature for (a) MBBA: o and △ denote C_0 and C_1, while ▽ and • denote C_2 and C_3; (b) 5CB: o and △ denote C_1 and C_2, while ▽ and • denote C_3 and C_4.

model parameters determined for 5CB at 26.3° C are $D_{\|} = 1.04 \times 10^9\text{s}^{-1}, D_{\perp} = 4.56 \times 10^7\text{s}^{-1}, k_1 = 2.57 \times 10^{11}\text{s}^{-1}, k_2 = 1.48 \times 10^{12}\text{s}^{-1}$ and $k_3 = 100k_2$. Putting the calculated $J^{(i)}_{0,MR}(0)$ into Equation (11), we compute $J^{(i)}_{0,EX}(0)$ plotted at different temperatures for MBBA in Figure 4(a) and 5CB in Figure 4(b). In both liquid crystals, $J^{(i)}_{0,EX}(0)$ depends on the carbon site and shows temperature dependences similar to the experimental $J^{(i)}_0(0)$, i.e., they increase with decreasing temperature. To demonstrate that director fluctuations make contributions to $J^{(i)}_{0,EX}(0)$, we plot the 'normalized' ratio $J^{(i)}_{0,EX}(0)/J^{(1)}_{0,EX}(0)$ versus $(S^{(i)}_{CD})^2$ at two different temperatures for MBBA and 5CB in Figure 5. The normalized ratio was chosen[17] for clarity in data presentations. Although the fairly large uncertainty in $J^{(i)}_{0,EX}(0)$ prevents a definite conclusion, it can be seen that the experimental data at least qualitatively support $J^{(i)}_{0,EX}(0) \equiv J^{(i)}_{0,DF}(0) \propto [S^{(i)}_{CD}]^2$ in 5CB and MBBA.

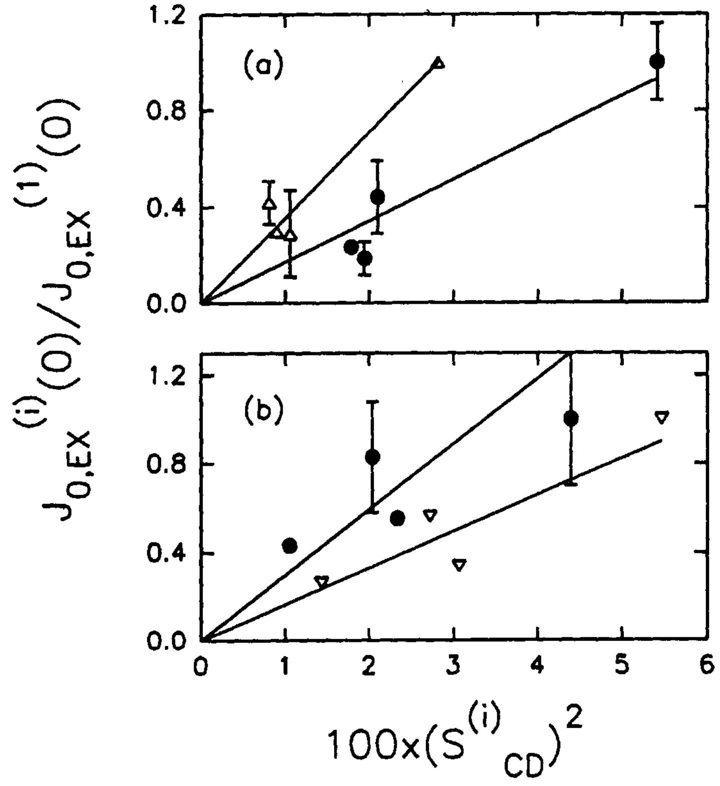

FIGURE 5 Plots of $J^{(i)}_{0,EX}(0)/J^{(1)}_{0,EX}(0)$ versus the square of $S^{(i)}_{CD}$ in the nematic phase of (a) MBBA: △ and • denote 36° and 21° C, respectively; (b) 5CB: • and ▽ denote 26.3° and 18.3°, respectively.

To further test the above proposal, we examine whether Equation (4) can predict the correct order of magnitude for $J^{(0)}_{0,DF}(0)$ and $J^{(1)}_{0,DF}(0)$ in MBBA and for $J^{(1)}_{0,DF}(0)$ in 5CB, noting that the C_1-D bond makes a fixed angle ($\beta^{(1)}_{M,Q} = 107.5°$) with respect to the z_M axis. The calculations for MBBA were presented elsewhere;[17] at 27°C, $J^{(0)}_{0,DF}(0)$ and $J^{(1)}_{0,DF}(0)$ were computed as 42 s^{-1} and 60.9 s^{-1} in reasonable agreement with the experimental values ($J^{(0)}_{0,EX}(0) = 22\ s^{-1}, J^{(1)}_{0,EX}(0) = 68\ s^{-1}$). A similar calculation is carried out here at 26.3°C for 5CB. Using $K = 6.8 \text{ x } 10^{-12}$N, $\eta = 6.3 \text{ x } 10^{-2}$ Pa s and $\Delta\chi = 10^{-6}$ SI units for 5CB[21] and B = 7 T, we find that $\xi = 0.42\ \mu m$ and $\omega_1 = 618\ s^{-1}$. For a cut-off wavelength of 25 Å (about the length of a molecule), $\omega_c = 5 \times 10^8 s^{-1}$. Now $S = 0.51$, $\alpha = 0.077$ and $A = 9.9 \times 10^{-6} s^{1/2}$ at 26.3°C. Substituting these into Equation (4), we find $J^{(1)}_{0,DF}(0) \simeq 20\ s^{-1}$. This is smaller than the experimental value ($J^{(1)}_{0,EX}(0) = 51.9\ s^{-1}$) by a factor of 2.5. Given the large uncertainty in the 'experimental' value (see Figure 5(b)) and in the material parameters, the agreement is fairly reasonable.

In conclusion, we believe that second-order director fluctuations can be detected using deuteron T_2 measurements in a standard high field strength of 7 T. This is possible for the two liquid crystals studied, since their spin-lattice relaxation times T_{1Z} and T_{1Q} are independent of director fluctuations at this field strength. In comparing MBBA and 5CB, the 5CB T_2 data seems to show larger scatterings when compared with the theory.

ACKNOWLEDGMENTS

The financial support of the Natural Sciences and Engineering Council of Canada is gratefully acknowledged. We thank Mr. N. Finlay for technical support.

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