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Nuclear magnetic resonance study of soft-mode dynamics in the nematic phase of p-azoxyanisole

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The critical slowing down of the optical soft mode, or the order-parameter fluctuation, in the nematic phase of methyl-deuterated p-azoxyanisole is detected for the first time by combining the proton spin-lattice relaxation times in the laboratory and in the rotating frames. Freed's recent theory of spin relaxation by quasicritical order-parameter fluctuations is used to satisfactorily interpret our NMR measurements. The present study confirms the mean-field prediction of symmetry in critical order-parameter fluctuations at isotropic-nematic transitions.

I. INTRODUCTION

In investigating the dynamic properties of the Maier-Saupe model of nematic liquid crystals, Blinc *et al.*[1] demonstrated the existence of soft modes, the condensation of which leads to an isotropic-nematic transition at a temperature T_c. The symmetry-recovering Goldstone mode in the nematic phase corresponds to order-director fluctuations[2-5] which are well-studied by NMR. The diffusive optical soft modes in the nematic phase describe fluctuations in the magnitude of the nematic order parameter and condense at the stability limit $T^\dagger$ of the nematic phase. In the isotropic phase, the soft modes, which describe the well-studied short-range orientational-order fluctuations,[6] condense at the corresponding stability limit T^* of the isotropic phase. Since $T^\dagger$ is always greater than T^*, the isotropic-nematic transition will be of first order with $T^* < T_c < T^\dagger$. As pointed out by Blinc *et al.*,[7] the nematic optical soft mode may be observable, for example, by NMR relaxation techniques.

This paper reports for the first time on an NMR study of the nematic soft modes. Freed's[4] recently developed theory of spin relaxation by quasicritical order-parameter fluctuations below T_c is tested by the present NMR study of soft-mode dynamics in the nematic phase of methyl-deuterated p-azoxyanisole (PAA-d_6).

II. THEORY

In this section, we outline the relevant section of Freed's paper[4] which is required for the interpretation of our NMR measurements. Consider the relation between the isotropic and nematic phase-stability limits by examining the orientational free-energy fluctuations. Below T_c, the difference (ΔF) in free-energy density between the nematic and the isotropic states is given by

$$\Delta F = \tfrac{1}{2}\tilde{A}Q^2 - \tfrac{1}{3}\tilde{B}Q^3 + \tfrac{1}{4}\tilde{C}Q^4 , \tag{1}$$

where the magnetic field term is neglected, $Q(\vec{r})$ is the local orientation order parameter and $\tilde{A} = a(T - T^*)$ in the mean-field approximation. When ΔF is minimized with respect to Q, one obtains the nematic value Q_N given by

$$Q_N = (\tilde{B}/2\tilde{C})[1 + (1 - 4\tilde{A}\tilde{C}/\tilde{B}^2)^{1/2}] . \tag{2}$$

At T_c, the free-energy densities of the nematic and isotropic phases are equal (i.e., $\Delta F = 0$) and hence $Q_N = 2\tilde{B}/3\tilde{C}$ and $\tilde{A} = 2\tilde{B}^2/9\tilde{C} = a(T_c - T^*)$. In the nematic phase $Q = Q_N + \Delta Q$, where ΔQ is the fluctuation in the magnitude of the orientation order of the molecules. Keeping the lowest-order terms in ΔQ, this gives

$$\Delta F_N \simeq \tfrac{1}{2}\bar{A}\Delta Q^2 \tag{3}$$

where ΔF_N is the free-energy-density deviation in the nematic phase from the equilibrium value of $\frac{1}{2}\tilde{A}Q_N^2 - \frac{1}{3}\tilde{B}Q_N^3 + \frac{1}{4}\tilde{C}Q_N^4$ and $\bar{A} = \tilde{A} - 2\tilde{B}Q_N + 3\tilde{C}Q_N^2$. Now for small $\tilde{A}$ (viz., $|T - T^*| < |T_c - T^*|$), one may expand the expression for Q_N [Eq. (2)] to lowest order in $\tilde{A}$ to obtain $\bar{A} \simeq 3a(T^\dagger - T)$ with $T^\dagger - T_c = \frac{1}{2}(T_c - T^*)$. By including the lowest-order space variation of Q in Eq. (3), one obtains the free-energy-density deviation in terms of the Fourier components $\Delta Q_{\vec{q}}$ of ΔQ:

$$\Delta F_N = \frac{V}{2} \sum_q (\bar{A} + L_N q^2)\, |\Delta Q_{\vec{q}}|^2 , \tag{4}$$

where L_N is a nematic elastic coupling constant between neighboring molecules. From the equipartition theorem,

$$\langle |\Delta Q_{\vec{q}}|^2 \rangle = kT/\bar{A}V(1 + \bar{\xi}^2 q^2) , \tag{5}$$

where V is the volume and $\bar{\xi} = (L_N/\bar{A})^{1/2}$ is the coherence length of the nematic order-parameter fluctuations. Now

$$\Delta \dot{Q}_{\vec{q}} = -\bar{\tau}_q^{-1} \Delta Q_{\vec{q}} = -\frac{1}{\nu_N} \frac{\partial \Delta F_N}{\partial \Delta Q_{\vec{q}}} \tag{6}$$

where ν_N is a nematic viscosity or diffusion constant and $\bar{\tau}_q = \nu_N/\bar{A}(1+\bar{\xi}^2 q^2)$. The coherence length $\bar{\xi}$ is proportional to $(T^\dagger - T)^{-1/2}$ in the mean field approximation.

The theory of nuclear-spin relaxation arising from fluctuations in the magnetic dipolar interaction of a spin-$\frac{1}{2}$ pair gives the following spin-lattice relaxation rate in the laboratory frame:

$$(T_1)^{-1} = (9\gamma^4\hbar^2/8r^6)[J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)], \tag{7}$$

and in the rotating frame

$$(T_{1\rho})^{-1} = (9\gamma^4\hbar^2/8r^6)[\tfrac{5}{2}J^{(1)}(\omega_0) + \tfrac{1}{4}J^{(2)}(2\omega_0) + \tfrac{1}{4}J^{(0)}(2\omega_1)], \tag{8}$$

where r is a fixed internuclear distance, ω_1/γ is the rotating field B_1, and all other symbols have their usual meaning. In treating quasicritical order-parameter fluctuations below T_c, Freed has extended the Landau-deGennes mean-field theory[7] which has been successfully applied to the isotropic phase, where fluctuations in both magnitude and orientation of the single-molecule orienting potential were considered. For a spin-$\frac{1}{2}$ pair with $\vec{r}$ parallel to the long molecular axis, Freed has obtained the following spectral densities[4]:

$$J^{(M)}(M\omega_0) = \frac{M^2}{3\sqrt{2}\,\pi}\,\frac{kT\,\nu_N^{1/2}\bar{\tau}_0^{1/2}}{L_N^{3/2}}[\kappa(0,M)]^2 \times[1+(1+M^2\omega_0^2\bar{\tau}_0^2)^{1/2}]^{-1/2}, \tag{9}$$

$$J^{(0)}(2\omega_1) = \frac{\sqrt{2}}{\pi}\,\frac{kT\,\nu_N^{1/2}\bar{\tau}_0^{1/2}}{L_N^{3/2}}[\kappa(0,0)]^2 \times[1+(1+4\omega_1{}^2\bar{\tau}_0{}^2)^{1/2}]^{-1/2}, \tag{10}$$

where $\bar{\tau}_0$ is $\bar{\tau}_{q=0}$ and the $\kappa(0,M)$'s are given in terms of the nematic order parameter $S(\equiv Q_N)$ and its small fluctuating component S_1 as below:

$$\begin{aligned} \kappa(0,0) &= \tfrac{1}{5} + \tfrac{1}{2}(S+S_1) - (S+S_1)^2 \simeq \tfrac{1}{5} + \tfrac{1}{2}S - S^2, \\ \kappa(0,1) &= \tfrac{1}{5}, \\ \kappa(0,2) &= \tfrac{1}{5} - \tfrac{1}{4}(S+S_1) \simeq \tfrac{1}{5} - \tfrac{1}{4}S. \end{aligned} \tag{11}$$

The effect of these $\kappa(0,M)$ coefficients is to reduce the importance of the order-parameter fluctuations as the ordering increases. Indeed far below T_c, order-director fluctuations are important. It suffices to state that when the director is along the external magnetic field B_0, the order-director fluctuations give a nonzero $J^{(1)}(\omega_0)$ only and hence

$$T_1/T_{1\rho} = \tfrac{5}{2}. \tag{12}$$

III. EXPERIMENTAL PROCEDURE

Since the theory is applicable to a spin-$\frac{1}{2}$ pair, we have chosen to examine the phenyl protons of an extremely pure methyl-deuterated p-azoxyanisole sample which has a clearing temperature $T_c = (136.5 \pm 0.3)$ °C. The sample was sealed in a vacuum after degassing by the freeze-melt method. The inversion-recovery method was used to determine the proton T_1 at $\omega_0/2\pi = 60$ MHz, while the proton $T_{1\rho}$ measurements were performed at the same Larmor frequency with a spin-locking field B_1 of 10 G. Both the T_1 and the $T_{1\rho}$ measurements were made on the same sample with a Bruker SXP4-100 MHz pulsed spectrometer with an experimental error of less than 5%. The temperatures at the sample were maintained by an air flow with a temperature gradient across the sample of around 0.5 °C. Care was taken to avoid heating of the sample by the B_1 field pulse.

IV. RESULTS AND DISCUSSION

Figure 1 shows the proton T_1 and $T_{1\rho}$ measurements in the nematic phase of PAA-d_6 as a function of temperature. As reported earlier,[5] the proton T_1 is independent of temperature in the nematic phase. However, the proton $T_{1\rho}$ remains constant until 130 °C and decreases monotonically until T_c is reached. PAA-d_6 has two phenyl rings and therefore four identical sets of orthoproton pairs. Since the proton $T_{1\rho}$ of PAA (Ref. 8) is dominated by the order-director fluctuations in the nematic phase, it would show the quasicritical order-parameter fluctuations by a decrease in its magnitude as T_c is approached. The critical tem-

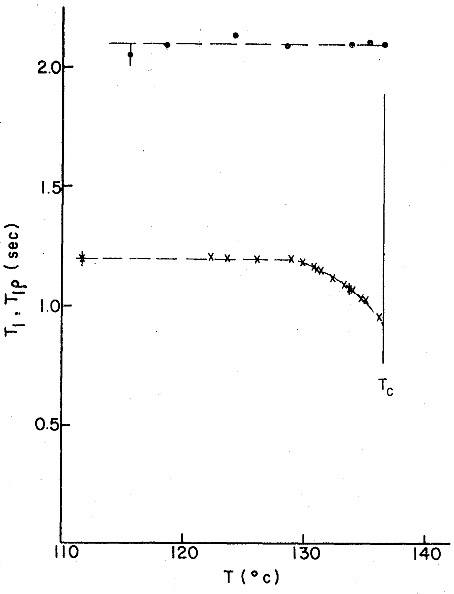

FIG. 1. Proton T_1 (●) and $T_{1\rho}$ (×) in the nematic phase of PAA-d_6 vs temperature at 60 MHz and B_1 = 10 G.

perature dependence of the proton $T_{1\rho}$ arises from the spectral density $J^{(0)}(2\omega_1)$ because $\omega_1 < \bar{\tau}_0^{-1} \ll \omega_0$. In this limit, Eq. (10) becomes

$$J^{(0)}(2\omega_1) \propto [\kappa(0,0)]^2 \nu_N \bar{\xi}/L_N^2 \tag{13}$$

which is independent of B_1 and acquires a critical dependence on temperature through the coherence length $\bar{\xi}$. $\kappa(0,0)$ reduces the importance of order-parameter fluctuations as S increases from a value of ~0.4 at T_c to a value of 0.76 at which it vanishes.

Since the measured T_1 and $T_{1\rho}$ contain both intermolecular and intramolecular contributions, the intermolecular contribution must be subtracted from the experimental relaxation rates before comparison with Freed's theory. The intermolecular contribution $(T_1)_r^{-1}$ to the proton T_1 of PAA-d_6 has been determined by an isotope dilution experiment[9] at 120 °C. The intermolecular contribution arises from magnetic dipolar interactions between the phenyl protons of neighboring molecules and gives $(T_1)_r^{-1}/(T_1)_a^{-1} = 0.29$ at 60 MHz, where $(T_1)_a^{-1}$ is the spin-lattice relaxation rate due to magnetic dipolar interactions between protons within a PAA-d_6 molecule. Thus

$$(T_1)^{-1} = (T_1)_a^{-1} + (T_1)_r^{-1} = 1.29 (T_1)_a^{-1}. \tag{14}$$

Because a detailed temperature study was not performed we assume that the ratio $(T_1)_a/(T_1)_r$ is temperature insensitive and obtain $(T_1)_a = 2.71$ s for all temperatures in the nematic phase. The intermolecular contribution to the proton $T_{1\rho}$ of PAA-d_6 has not been determined experimentally. However, there is evidence from the low-field T_1 study[10] and the $T_{1\rho}$ angular-dependence study[8] in the nematic phase of PAA that the intramolecular contribution from order-director fluctuations are predominant. We therefore assume that the main contribution to the $T_{1\rho}$ of PAA-d_6 arises from intramolecular interactions, i.e., $T_{1\rho} = (T_{1\rho})_a$. This assumption appears justified by the fact that the experimental ratio of $(T_1)_a/(T_{1\rho})_a$ below 130 °C, where order-director fluctuations are responsible for spin relaxation, is 2.3 ± 0.1 in close agreement with the theoretical value of Eq. (12). Above 130 °C, this ratio increases leading us to assume that quasicritical order-parameter fluctuations are indeed responsible for spin relaxation both in the laboratory and rotating frames. With these assumptions and using Eqs. (9) and (10) to combine Eqs. (7) and (8), we obtain

$$\begin{aligned}(T'_{1\rho})_a^{-1} &= (T_{1\rho})_a^{-1} - f(s)(T_1)_a^{-1} \\ &= (9\gamma^4\hbar^2/32r^6) J^{(0)}(2\omega_1),\end{aligned} \tag{15}$$

where

$$f(s) = \frac{\frac{5}{2} + (1 - \frac{5}{4}S)^2/\sqrt{2}}{1 + 4(1 - \frac{5}{4}S)^2/\sqrt{2}}.$$

Note that when $S = 0.8$ $[f(s) = \frac{5}{2}]$, Eq. (15) again reduces to Eq. (12) as expected at temperatures far from T_c where order-parameter fluctuations are replaced by order-director fluctuations. The calculated values of $(T'_{1\rho})_a$ from Eq. (15) (see Table I) show the quasicritical temperature behavior of order-parameter fluctuations, that is, the critical slowing down of the optical soft mode. The S values in Table I are from NMR measurements[11] of PAA. Combining Eqs. (13) and (15) by using $\nu_N \propto e^{W/T}$, where W is the thermal activation energy in °K, and the mean-field critical exponent for $\bar{\xi}$, one obtains

$$(T'_{1\rho})_a^2 e^{2W/T} [\kappa(0,0)]^4 \propto T^\dagger - T. \tag{16}$$

This equation must be obeyed by $(T'_{1\rho})_a$ if it is governed by order-parameter fluctuations. The quantity on the left-hand side of Eq. (16) is tabulated in Table I with $W = 5900$ °K for PAA (Ref. 12) and plotted versus temperature in Fig. 2. The larger error bars at lower temperatures are due to the diminishing $J^{(0)}(2\omega_1)$. The solid line of Fig. 2 represents a fit to the $(T'_{1\rho})_a$ data between 405 °K and T_c by a least-squares linear-regression program. It appears that quasicritical order-param-

TABLE I. $(T'_{1\rho})_a$, $[\kappa(0,0)]^4 e^{(2W/T)} (T'_{1\rho})_a^2$, and $[\kappa(0,0)]^3 e^{(3W/2T)} (T'_{1\rho})_a^{3/2}$ calculations at different temperatures in PAA-d_6.

T (°K)	$T_{1\rho}$ (s)	S	$f(S)$	$(T'_{1\rho})_a$ (s)	$[\kappa(0,0)]^4 (T'_{1\rho})_a^2 e^{2W/T}$ ($\times 10^{10}$ s^2)	$[\kappa(0,0)]^3 (T'_{1\rho})_a^{3/2} e^{3W/2T}$ ($\times 10^7$ $s^{3/2}$)
403	1.18 ± 0.02	0.52	1.921	7.21	34.9 ± 6.3	45.4 ± 6.3
404	1.15	0.51	1.890	5.81	23.5 ± 3.7	33.8 ± 4.1
405	1.13	0.495	1.844	4.89	18.1 ± 2.5	27.7 ± 2.9
406	1.11	0.475	1.784	4.12	14.4 ± 1.8	23.3 ± 2.2
407	1.08	0.46	1.739	3.52	11.0 ± 1.2	19.1 ± 1.7
408	1.03	0.435	1.666	2.81	7.8 ± 0.8	14.7 ± 1.1
409	0.96	0.41	1.596	2.21	5.2 ± 0.5	10.9 ± 0.7
409.5	0.91 ± 0.02	0.40	1.568	1.92	4.0 ± 0.4	8.9 ± 0.6

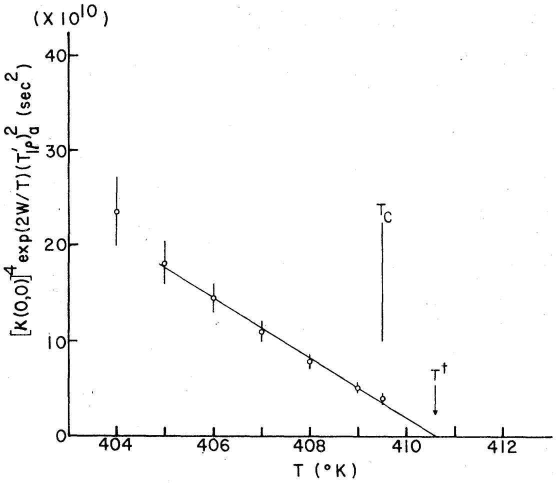

FIG. 2. Plot of $[\kappa(0,0)]^4(T'_{1\rho})_a^2 e^{2W/T}$ vs temperature in the nematic phase of PAA-d_6.

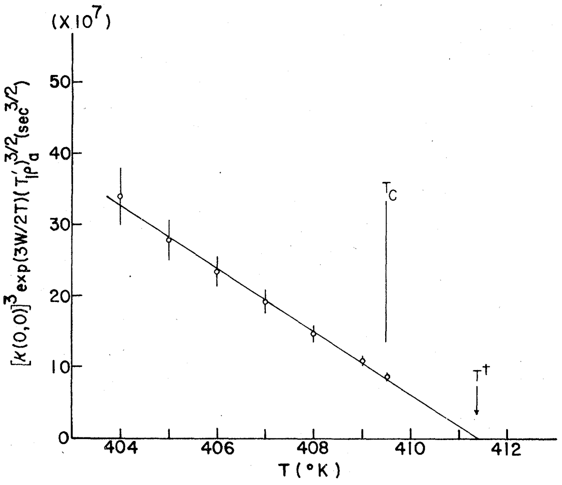

FIG. 3. Plot of $[\kappa(0,0)]^3(T'_{1\rho})_a^{3/2}e^{3W/2T}$ vs temperature in the nematic phase of PAA-d_6.

eter fluctuations do exist up to 5 °K below T_c and the critical temperature $T^\dagger$ at which a second-order phase transition would occur is at 410.6 °K. Thus $T^\dagger - T_c = (1.1 \pm 0.5)$ °K as compared with $T_c - T^* \simeq 3$ °K[6] in close agreement with the mean-field prediction of Sec. II. However as seen in Fig. 2, data over a wider temperature range show a systematic curvature. When the additional point at 404 °K is included in the above fitting process, the probability for goodness of fit by a χ^2 analysis decreases from 90% to 40%. To see if the mean-field critical exponent of ξ is indeed appropriate for order-parameter fluctuations, we try $\xi \propto (T^\dagger - T)^{-2/3}$ in Eq. (13) to give

$$(T'_{1\rho})_a^{3/2} e^{3W/2T}[\kappa(0,0)]^3 \propto T^\dagger - T\,. \qquad (17)$$

The exponent-$\frac{2}{3}$ is chosen because it is appropriate for most known second-order transitions (e.g., superfluid helium). The quantity on the left-hand side of Eq. (17) is again tabulated in Table I and plotted versus temperature in Fig. 3. The solid line represents a least-squares fit to the $(T'_{1\rho})_a$ data between 404 °K and T_c. A χ^2 analysis shows that the fit has a probability of 98% to be good as compared with a value of only 40% in the mean-field approximation. $T^\dagger$ is found in this case to be 411.4 °K giving $T^\dagger - T_c = (1.9 \pm 0.5)$ °K. It seems therefore that the critical exponent, $-\frac{2}{3}$, instead of the mean-field value of $-\frac{1}{2}$ used for ξ, can better fit the data over a larger temperature range, while over a smaller temperature range, we are unable to distinguish between the two critical exponents.

In conclusion, the quasicritical order-parameter fluctuation or the critical slowing down of the nematic optical soft mode has been identified through the spectral density $J^{(0)}(2\omega_1)$ in the nematic phase of PAA-d_6 by combining the proton T_1 and $T_{1\rho}$ measurements at 60 MHz just below T_c. It is essential in evaluating $J^{(0)}(2\omega_1)$ to know the intermolecular contribution to both the proton T_1 and $T_{1\rho}$ since Freed's theory is derived for interactions between a spin-$\frac{1}{2}$ pair within a single molecule. Certain assumptions were made in this respect but they appear to be reasonable. It is shown here that Freed's theory for spin relaxation by order-parameter fluctuations below T_c is satisfactory, and that a symmetry exists for the critical order-parameter fluctuations at T_c as predicted by the mean-field theory. Current work suggests that the isotropic-nematic transition obeys the mean-field theory over a sufficiently small temperature range (~5 °C) below T_c. However over a wider temperature range, the critical exponent for ξ is found to be $-\frac{2}{3}$ rather than the mean-field value of $-\frac{1}{2}$. This would imply that the isotropic-nematic transition is similar to most known second-order transitions in which the mean-field approximation fails. The observation is indeed interesting and hence an independent determination of the critical temperature $T^\dagger$ should be undertaken to choose the appropriate critical exponent for ξ over the wider temperature range.

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