

even a few tenths of a millimeter from the intense beam. This is consistent with a very local mechanism for the streaming. Similar responses to other types of perturbations have been observed microscopically.⁸

We have also observed protoplasmic streaming in the whorled leaf cells of *Nitella*. In these cells the flow pattern seems to follow the leaflike contour of the cells, and the maximum velocity was determined to be 55–60 $\mu\text{m}/\text{sec}$. This flow is also reversibly quenched by para-chloromercuribenzoate.

We believe that the technique of laser-light-scattering spectroscopy is ideally suited to the measurement of flow patterns within cells. Some of the advantages which we have found this technique to have in comparison with microscopy are as follows: (1) It is objective; i.e., all motion within the scattering region is viewed, rather than just the motion of selected particles. (2) The information is directly interpretable in terms of velocities. (3) It is exceedingly fast. Complete velocity distributions (spectra) are obtained in a few seconds. (4) Any desired component of the velocity can be measured just by changing the orientation of the cell with respect to the scatter-

ing vector. (5) The motion of submicroscopic particles can readily be observed. This technique may have a great role to play in the elucidation of the mechanism of protoplasmic streaming and in the study of other phenomena in which protoplasmic movement is an important factor.

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Nuclear Spin-Lattice Relaxation in Liquid Crystals by Fluctuations in the Nematic Director

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We show that a finite cutoff of the hydrodynamic modes (order fluctuations) in the nematic liquid-crystalline phase explains the measured spin-lattice relaxation in this phase. A calculation of T_1 based upon such a cutoff and a fit to the data of MBBA (4-*n*-methoxybenzylidene-4'-*n*-butylaniline) show this cutoff to be 1 molecular length. At T_{10} frequencies, far from the cutoff, order fluctuations are shown to be the dominant relaxation mechanism. This is done by comparing the predicted angular dependence of T_{10} for these modes with that measured in MBBA.

The published measurements¹⁻¹³ of spin-lattice relaxation in nematic liquid crystals have not lent themselves to a single interpretation. For example, one compound, PAA (*p*-azoxyanisole) has been shown to exhibit a $\nu^{1/2}$ frequency dependence characteristic of thermal fluctuations of the director, whereas the compound MBBA (4-*n*-

methoxybenzylidene-4'-*n*-butylaniline) has not shown this dependence over the same frequency range.¹¹ It has not been clear why one compound should obey one mechanism while another compound in the same phase appears to obey another.

In this paper we shall show that this behavior can be explained by a cutoff of the collective or-

der fluctuations at the molecular level, where the dispersion relations for these modes are expected to break down. The frequency dependence of T_1 is calculated for an arbitrary cutoff and fitted to the data of MBBA. The best fit gives a value for the cutoff of 1 molecular length.

In addition, it is shown that at frequencies far removed from the cutoff frequency (as is obtained by $T_{1\rho}$ measurements) MBBA does indeed follow the order-fluctuation mechanism. This is done by measuring the angular dependence of $T_{1\rho}$ in the nematic phase of MBBA and comparing it with a calculation based on fluctuations of the director.

In this Letter we outline the calculation of T_1 and $T_{1\rho}$ in the nematic liquid-crystalline phase. This calculation includes the angular dependence of T_1 and $T_{1\rho}$ as well as the cutoff. The calculation is based upon the magnetic dipole interaction between two like spin- $\frac{1}{2}$ nuclei with a fixed separation distance and also applies to the quadrupole interaction of spin-1 nuclei with an elec-

tric field gradient of fixed magnitude coming from within the molecule. In our discussion we shall only refer to the dipole interaction.

The calculation is greatly simplified because of the rapid rotation ($\tau_c \approx 10^{-10}$ sec) of the rodlike molecules about their long axes. This motionally averages the dipole interactions in such a way that all the spin interactions in the molecule are effectively along the direction of the molecular axis. Rapid fluctuations of the molecular axis about the director further average the interaction. The much slower thermal fluctuations of the director $\delta\vec{N}$ about some average direction \vec{N}_0 are the modes we ultimately consider. It is these thermal fluctuations that provide the relaxation mechanism.¹⁴⁻¹⁶

For the situation described above, the spin-lattice relaxation is related to the spectral densities of the correlation functions, $J_h(p\omega)$, by the following expressions¹⁷:

$$T_1^{-1} = \frac{9}{8}\gamma^4\hbar^2r^{-6}[J_1(\omega_0) + J_2(2\omega_0)], \quad (1)$$

and

$$T_{1\rho}^{-1} = \frac{9}{8}\gamma^4\hbar^2r^{-6}\left[\frac{5}{2}J_1(\omega_0) + \frac{1}{4}J_2(2\omega_0) + \frac{1}{4}J_0(2\omega_1)\right], \quad (2)$$

where

$$J_h(p\omega) = \int_{-\infty}^{\infty} \langle F_h(0)F_h^*(t) \rangle \exp(-ip\omega t) dt, \quad (3)$$

and where the $F_h(t)$ are the time-dependent spherical harmonic functions:

$$F_0(t) = 1 - 3n^2; \quad F_1(t) = (l + im)n; \quad F_2(t) = (l + im)^2, \quad (4)$$

with l , m , and n the direction cosines of the molecular axis (time-averaged direction of the dipolar interaction) with respect to the laboratory coordinate system (x, y, z) in which the z axis is in the direction of the applied magnetic field \vec{H}_0 .

In general, the vector \vec{N}_0 will be parallel to \vec{H}_0 as a result of the anisotropy of the diamagnetic susceptibility. With the application of competing electric fields, the use of thin films, or perhaps even the rotation of very viscous nematic liquid crystals, the direction of \vec{N}_0 can be oriented away from the direction of \vec{H}_0 . Under these circumstances, we must make a transformation of the direction cosines to a frame (primed frame) where the z' axis is parallel to \vec{N}_0 . In terms of the Euler angles (φ, θ, ψ) the transformed spherical harmonic functions become

$$F_0(t) = \frac{1}{2}(3\cos^2\theta - 1)F_0'(t) + 3i\sin\theta\cos\theta e^{i\psi}F_1'(t) + \text{c.c.} + \frac{3}{4}\sin^2\theta e^{2i\psi}F_2'(t) + \text{c.c.}; \quad (5a)$$

$$F_1(t) = e^{i\varphi}\left[\frac{1}{2}(i\sin\theta\cos\theta)F_0'(t) + \frac{1}{2}e^{i\psi}(1 + \cos\theta)(2\cos\theta - 1)F_1'(t) + \frac{1}{2}e^{-i\psi}(1 - \cos\theta)(1 + 2\cos\theta)F_1'^*(t) + \frac{1}{4}i\sin\theta[-e^{2i\psi}(1 + \cos\theta)F_2'(t) + e^{-2i\psi}(1 - \cos\theta)F_2'^*(t)]\right]; \quad (5b)$$

$$F_2(t) = e^{2i\varphi}\left[\frac{1}{2}(1 - \cos^2\theta)F_0'(t) - ie^{i\psi}\sin\theta(1 + \cos\theta)F_1'(t) - ie^{-i\psi}\sin\theta(1 - \cos\theta)F_1'^*(t) + \frac{1}{4}e^{2i\psi}(1 + \cos\theta)^2F_2'(t) + \frac{1}{4}e^{-2i\psi}(1 - \cos\theta)^2F_2'^*(t)\right], \quad (5c)$$

where the F_h' have the same functional form as Eqs. (5) except that the direction cosines are primed and describe the molecular axis relative to \vec{N}_0 . The instantaneous preferred direction of orientation of the molecular axis $\vec{N}(\vec{r}, t)$ will thermally fluctuate about \vec{N}_0 . Explicitly, the expression

$$\vec{N}(\vec{r}, t) = \vec{N}_0 + \delta\vec{N}_0(\vec{r}, t) \quad (6)$$

describes the orientational order fluctuation at time t at position \vec{r} in the nematic phase. In order to

include this motion in the spectral densities we make a second infinitesimal transformation of the spherical harmonic functions $F_h'(t)$ from \vec{N}_0 to $\vec{N}(\vec{r}, t)$. This transformation has been described in a previous publication¹⁶ where it was shown that the correlation functions become

$$\langle F_1'(0)F_1'^*(t) \rangle = S^2 \langle \delta \vec{N}(\vec{r}, 0) \delta \vec{N}^*(\vec{r}, t) \rangle, \quad (7a)$$

and

$$\langle F_0'(0)F_0'^*(t) \rangle = \langle F_2'(0)F_2'^*(t) \rangle = 0, \quad (7b)$$

where S is the degree of molecular order. In calculating the correlation functions $\langle F_h(0)F_h^*(t) \rangle$ it is therefore only necessary to retain the terms containing $\langle F_1'(0)F_1'^*(t) \rangle$. By making use of this fact and the cylindrical symmetry about \vec{H}_0 and \vec{N}_0 , the correlation functions become

$$\langle F_h(0)F_h^*(t) \rangle = f_h(\theta) \langle F_1(0)F_1^*(t) \rangle, \quad (8)$$

where

$$f_0(\theta) = 18(\cos^2\theta - \cos^4\theta) \quad (8a)$$

$$f_1(\theta) = \frac{1}{2}(1 - 3\cos^2\theta + 4\cos^4\theta), \quad (8b)$$

$$f_2(\theta) = 2(1 - \cos^4\theta). \quad (8c)$$

With the use of the dispersion relation $i\omega(q) = Kq^2/\eta$ for the order modes¹⁸ where K is the appropriate deformation constant and η the viscosity, the spectral density is calculated in the usual fashion with the only modification being the cutoff in the modes near the molecular length. That is, instead of integrating over all of the hydrodynamic modes, we integrate up to the wave vector q_c . The spectral densities may then be expressed as¹⁶

$$J_h(p\omega) = f_h(\theta) [4S^2V/(2\pi)^3] \int_0^{q_c} \int_{-\infty}^{\infty} (kT/Kq^2V) \exp(-t/\tau_q) 4\pi q^2 dq \exp(-ip\omega t) dt,$$

where kT/Kq^2V is the thermal amplitude of the modes, V the volume, $[V/(2\pi)^3] 4\pi q^2 dq$ the number of states in a shell of volume $4\pi q^2 dq$, and $\tau_q^{-1} = Kq^2/\eta$. The result can be expressed in closed form and becomes

$$J_h(p\omega) = C f_h(\theta) (p\omega)^{-1/2} g(a), \quad (9)$$

where

$$g(a) = \pi - \frac{1}{2} \ln |(a^2 + 2^{1/2}a + 1)/(a^2 - 2^{1/2}a + 1)| - \tan^{-1}(1 + 2^{1/2}a) - \tan^{-1}(2^{1/2}a - 1), \quad (10)$$

where $a = p^{1/2}(\omega/\omega_c)^{1/2}$; ω is frequency of the NMR measurement and is ω_1 for the case of $T_{1\rho}$; $\omega_c = Kq_c^2/\eta$ and is the cutoff frequency. The constant C is given explicitly as

$$C = 2^{1/2} S^2 k T \eta^{1/2} / \pi^2 K^{3/2}.$$

To determine T_1^{-1} and $T_{1\rho}^{-1}$ Eqs. (1) and (2) are used and become¹⁹

$$T_1^{-1} = A g(a) \omega^{-1/2} [(\frac{1}{2} + 2^{1/2}) - \frac{3}{2} \cos^2\theta + (2 - 2^{1/2}) \cos^4\theta] + B, \quad (11)$$

$$T_{1\rho}^{-1} = A_\rho g(a) \omega_1^{-1/2} \{ (9/2^{3/2}) (\cos^2\theta - \cos^4\theta) + [(\frac{5}{4} - 2^{-3/2}) - \frac{15}{4} \cos^2\theta + (5 - 2^{-3/2} \cos^4\theta) (\omega_1/\omega_0)^{1/2}] \} + B_\rho, \quad (12)$$

where A and A_ρ are constants obtained from Eqs. (1), (2), (8), and (9). The constants B and B_ρ are contributions of other relaxation mechanisms at frequencies above the cutoff, i.e., where $g(a) \rightarrow 0$. These expressions are easily modified for the quadrupolar case by replacing $\gamma^4 \hbar^2 / r^6$ by $e^4 q^2 Q^2 / 4$, where q is the electric field gradient and Q is the quadrupole moment. It is not clear, however, that the magnitude of q will not be modulated in the nematic phase.

To compare Eq. (10) with experiment we have used the measurements of Vilfan, Blinc, and Doane¹¹ of the frequency dependence of T_1^{-1} in MBBA shown in Fig. 1. The fitting parameter is $\nu_c = \omega_c / 2\pi$. The best fit gives a value of 80 ± 20 MHz for ν_c . For MBBA at room temperature, $K \approx 6.0 \times 10^{-7}$ dyn.^{20,21} For the value of η we take the value of γ_1 measured by Meiboom²² as 0.5 P. Taking $q_c = 2\pi/\lambda_c$ we obtain $\lambda_c = 31 \pm 5$ Å

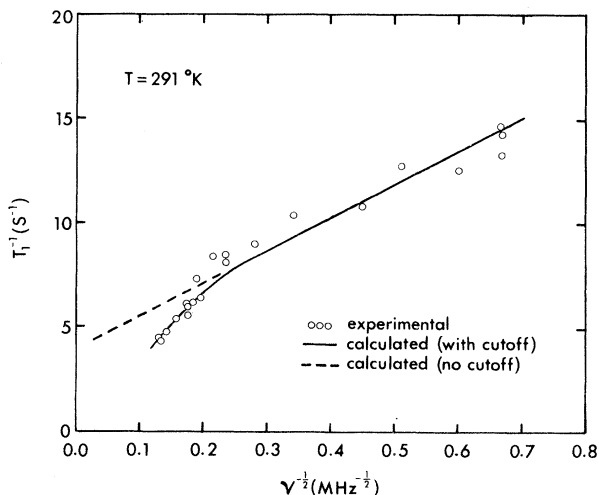


FIG. 1. Frequency dependence of T_1 in MBBA (from data of Ref. 11).

which is within error of being the molecular length for MBBA (28 Å).

At $T_{1\rho}$ frequencies, $\omega_c \gg \omega_1$ so that the relaxa-

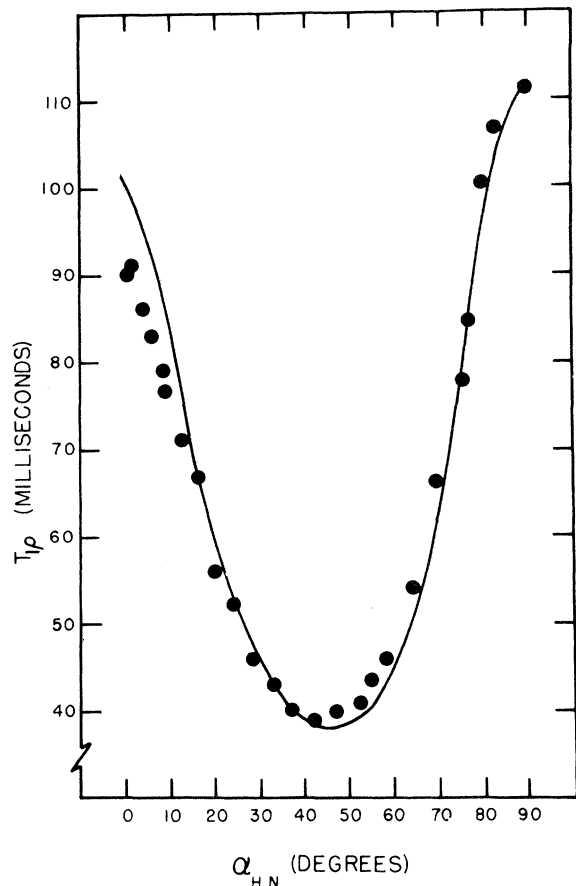


FIG. 2. Orientational dependence of $T_{1\rho}$ in MBBA for $\omega_1 \approx 40$ kHz and $\omega_0 = 30$ MHz. The solid line is Eq. (12).

tion time is not influenced by the cutoff, and, therefore, should follow the angular dependence of Eq. (12). The angular dependence of $T_{1\rho}$ in MBBA oriented in an electric field is shown in Fig. 2. The angular dependence of T_1 in MBBA was also measured at 30 MHz which is so close to ω_c that $g(a)$ is small, resulting in only a small angular variation in T_1 . The form of T_1 agrees well, however, with Eq. (11). In contrast, PAA does not show a cutoff behavior, as ω_c is near 200 MHz which is far above the range of frequencies in which T_1 has been measured in PAA.

It would be interesting to test the concept of a cutoff in systems where there exists short-range smectic-A order. Such order should also cut off these modes. In particular, one might use this technique to determine the size of the short-range smectic-A order.

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Anisotropy in the *B* Phase of He³

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The magnetic anisotropy of the *B* phase (assumed to be a Balian-Werthamer phase) is investigated within the Landau-Ginzburg theory. The anisotropy is determined by the action of the dipolar energy and the magnetic field on a single vector \vec{n} and it is shown that walls will induce variations in \vec{n} on a scale of $R_C \sim 0.1$ cm. In the presence of a field H this characteristic length becomes $R_C H_B / H$, where H_B is of the order of 100 Oe.

The discovery¹ of the new superfluid phases of He³ has generated considerable excitement because of the anisotropic nature of the states involved. These phases are undoubtedly BCS-type states made up of Cooper pairs with the orbital and spin angular momenta equal to 1.² The *A* phase has attracted most attention because in it each pair has $m_L = 1$ along some axis \vec{l} and $m_s = 0$ along some other axis \vec{k} .³⁻⁵ These axes, along with the phase and magnitude of the order parameter, characterize the state of the *A* phase. It has been shown that \vec{l} acts as an anisotropy axis for propagation of the various types of sound waves⁴ and superfluid flow.^{3,5} It has also been shown⁶ that \vec{l} will be oriented perpendicular to the surface of any walls so that the *A* phase should exhibit textures, that is, gradual variations of \vec{l} which are determined by the shape of the sample, the applied fields, and any imposed currents. In this sense this phase is similar to a liquid crystal. In the same context little attention has been

paid to the *B* phase because it is generally believed to be isotropic. Although in many respects this statement is true it is not so for the magnetic properties of the *B* phase,^{7,8} and we shall show that there are a number of theoretical reasons which make the *B* phase attractive from the point of view of studying textures and singularities of the order parameter with nuclear magnetic resonance techniques.

The *B* phase is believed to be the Balian-Werthamer state⁹ in which each pair has $\vec{J} = \vec{L} + \vec{S} = 0$, but with the spin variables rotated (arbitrarily) relative to the orbital variables. The state is therefore specified by a rotation matrix which we write in terms of the axis of rotation \vec{n} and the angle of rotation θ . Thus introducing the notation used previously¹⁰ to specify the order parameter, namely that

$$\langle a_{\vec{k}\beta\alpha} - \vec{k}_\gamma \rangle \propto \sum_{\alpha i} d_{\alpha i} \hat{k}_\alpha (\sigma^i \sigma^Y)_{\beta\gamma}, \quad (1)$$

we write

$$d_{\alpha i} = (\Delta/\sqrt{3}) [\delta_{\alpha i} \cos\theta + n_\alpha n_i (1 - \cos\theta) + \epsilon_{\alpha i j} n_j \sin\theta]. \quad (2)$$