

Theory for spin-lattice relaxation in nematic liquid crystals*

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A theory is developed for spin-lattice relaxation in the nematic phase which includes both local and collective motion. It is found that the frequency dependence of the relaxation rate T_1^{-1} depends on the correlation time for the motion at the local molecular level, τ_c . When $\omega\tau_c \ll 1$, where ω is the Larmor frequency, the theory gives the $\omega^{1/2}$ law characteristic of *p*-azoxyanisole (PAA). When $\omega\tau_c \lesssim 1$, the theory gives the more complex frequency dependence observed in the more viscous compound 4-*n*-methoxybenzylidene-4'-*n*-butylaniline (MBBA). A correlation is drawn between τ_c and the retarded relaxation time observed in electric dipole studies which corresponds to reorientation of the long molecular axis. The dependence of T_1^{-1} on the orientation of the director in the magnetic field is included in the calculation. A model is presented to include intermolecular effects on T_1 .

I. INTRODUCTION

Measured values of T_1 in the nematic phase at normal NMR frequencies can range from 100 msec to several seconds, depending upon the compound.¹ There appears to be a direct correlation between these values and the viscosity of the nematic sample. Those compounds which have a rotational viscosity coefficient γ_1 near 1.0 P and larger show values of T_1 significantly shorter than the less viscous nematics, where $\gamma_1 \lesssim 0.1$ P. Not only is the magnitude of T_1 different, but its dependence on frequency, temperature, and orientation in the magnetic field can also be strikingly different.

An example of a compound which has a relatively low viscosity is PAA (*p*-azoxyanisole).² Although this compound has not turned out to have been the most desirable one to study, it has been the compound most accessible to most workers and the one most thoroughly investigated.^{1,3-8} The characteristic frequency dependence $T_1^{-1} = AS^2\omega^{-1/2} + B$ for this compound has been well established by the field-cycling work of Wölfel, Noack, and Stohrer.⁴ The relative contributions of the *intra*- and *inter*-molecular mechanisms have likewise been well established by the isotopic substitution experiments of Fung, Wade, and Orwoll.⁵ The latter study has been most helpful in that it shows that the principal contributor to T_1 in PAA, in particular to the *B* term in the equation above, is *intra*-molecular. In addition, the work also shows a frequency dependence for the *inter*-molecular contributions.

In contrast to PAA is the compound MBBA (4-*n*-methoxybenzylidene-4'-*n*-butylaniline) which has a much larger viscosity² and significantly shorter T_1 . The frequency dependence described above is not realized in the nematic phase of this compound. Vilfan *et al.*³ has shown this dependence to

be rather complex when measured over a wide range of frequencies. They have suggested a diffusion mechanism for this behavior.⁹

In this paper we will present a theory for T_1 in nematics which can explain the frequency dependence of both PAA and MBBA and in which only one parameter need be adjusted to make the fit. This parameter is related to the viscosity and is the correlation time for the local molecular motion. The theory is really nothing more than a more complete version of previous theories^{1,10-16} for proton relaxation in nematics. It has been our hope to present a more exact treatment of the local and collective fluctuations of the system. In general, our treatment results in three contributions to the relaxation rate: a long-range term arising from the collective modes of the nematic, a local term owing to diffusion only, and a cross-correlation term which includes the effects of both motions. It is the last term which appears to be important in MBBA.

To give the theory more applicability, we have calculated the dependence of T_1 on the orientation of the director in the magnetic field. T_1 data from rotating nematic samples is used to provide checks on this calculated angular dependence.

Finally, an *inter*-molecular contribution is calculated. This theory requires a more specific and detailed model of the local molecular environment. A model resembling that of vacancy diffusion is presented.

II. THEORY

In this section we will show a calculation of the spin-lattice relaxation rate in the nematic phase for two interacting dipolar spins of the same nuclear species. We will begin by regarding the internuclear separation distance r as fixed and develop a theory in which the nuclear spins are

members of the same molecule. Later, we will show a model in which the theory can be adopted to the *intermolecular* case, where the two spins belong to different molecules.

It is convenient to start with the familiar expression which relates the relaxation rate to the spectral densities¹⁷

$$T_1^{-1} = \frac{3}{2}(\gamma^4 \hbar^2 / r^6) I(I+1) [J_1(\omega) + J_2(2\omega)], \quad (1a)$$

where

$$J_p(\rho\omega) = \int_{-\infty}^{\infty} \langle F_p(t) F_p^*(t+\tau) \rangle e^{-i\rho\omega\tau} d\tau, \quad (1b)$$

and where $F_p(t)$ are the time-dependent spherical harmonic functions of order 2 which describe the internuclear vector in the laboratory frame in which the z axis is parallel to the direction of the applied magnetic field \vec{H} .

Fundamental to the nematic phase is the concept

$$f = \frac{1}{8} \begin{pmatrix} 8 - 24 \sin^2 \theta_0 + 18 \sin^4 \theta_0 & 144(\sin^2 \theta_0 - \sin^4 \theta_0) & 9 \sin^4 \theta_0 \\ 2(\sin^2 \theta_0 - \sin^4 \theta_0) & 8 - 20 \sin^2 \theta_0 + 16 \sin^4 \theta_0 & 2 \sin^2 \theta_0 - \sin^4 \theta_0 \\ 2 \sin^4 \theta_0 & 16(2 \sin^2 \theta_0 - \sin^4 \theta_0) & 8 - 8 \sin^2 \theta_0 + \sin^4 \theta_0 \end{pmatrix}. \quad (2b)$$

The primed spherical harmonic functions now describe the internuclear vector in the frame of the director \vec{N}_0 .

It is to our interest to include both the local diffusional motion of the molecules and the long-range collective motion of the fluctuating director in the T_1 calculation. To do this, we follow a procedure that we developed earlier¹¹ of making an additional

of the director \vec{N}_0 , which is the preferred direction of orientation of the long axis of the molecules. In the typical T_1 measurement, \vec{N}_0 will be parallel to \vec{H} . However, when the samples are slowly rotated or when thin films are used, it is possible to alter the direction of \vec{N}_0 to a fixed angle θ_0 relative to \vec{H} . This angular dependence gives added versatility to T_1 measurements in liquid crystals. We therefore start the calculation with a transformation of the spherical harmonics from \vec{H} to \vec{N}_0 , where the fixed angle between the two directions is given by θ_0 [see Fig. 1(a)]. Taking advantage of the cylindrical symmetry of the nematic phase about \vec{N}_0 , we obtain for the transformed correlation functions

$$\langle F_p(t) F_p^*(t+\tau) \rangle = \sum_{q=0}^2 f_{pq}(\theta_0) \langle F'_q(t) F'_q{}^*(t+\tau) \rangle, \quad (2a)$$

where

infinitesimal coordinate transformation from \vec{N}_0 to a time-dependent $\vec{N}(t)$ which fluctuated about \vec{N}_0 (see Fig. 1). Furthermore, we assume that the azimuthal angle of $\vec{N}(t)$ is slowly varying compared to the polar angle and can be neglected here in the thermal averages. This assumption or approximation is probably equivalent to the "one-elastic-constant" assumption we make below. We then obtain

$$\begin{aligned} \langle F_p(t) F_p^*(t+\tau) \rangle &= \sum_{q=0}^2 f_{pq} \langle F'_q(t) F'_q{}^*(t+\tau) \rangle \\ &+ \{ f_{p1} [\langle F''_0(t) F''_0{}^*(t+\tau) \rangle + \langle F''_2(t) F''_2{}^*(t+\tau) \rangle] / 4 + (18f_{p0} + 4f_{p2}) \langle F''_1(t) F''_1{}^*(t+\tau) \rangle \} \langle \delta\theta(t) \delta\theta(t+\tau) \rangle, \end{aligned} \quad (3)$$

where the double-primed spherical harmonics now describe the internuclear vector in the frame of $\vec{N}(t)$. The correlation function $\langle \delta\theta(t) \delta\theta(t+\tau) \rangle$, which for small fluctuations can be written¹¹ $\langle \delta\vec{N}(t) \cdot \delta\vec{N}^*(t+\tau) \rangle$, gives the contribution of the order or director fluctuations to T_1 . It is noted from Eq. (3) that we have taken the local fluctuations to be uncorrelated with the long-range motion, which is a practice we have used and argued

in the past.¹¹ It will be seen that in the model we have adopted for the *intermolecular* case, the uncoupling of the local diffusive motion from the long-range order fluctuations, is strictly true. In the *intramolecular* case, on the other hand, this separation may be reasonable only when there is a large disparity in time scales between the two motions. This point will be discussed later.

Equation (3) can be put in a more useful form by

the application of a theorem of Khinchin¹⁸ to the double-primed correlation functions. If we assume that the local motion in the *intra*- as well as the *intermolecular* case can be adequately described by a single correlation time τ_c , then we can write

$$\langle F_p''(t)F_p''^*(t+\tau) \rangle = \langle F_p''(t) \rangle^2 + \langle |F_p''(t)|^2 \rangle e^{-|\tau|/\tau_c}. \quad (4)$$

The terms independent of τ go to zero in the Fourier integral and the averages $\langle F_p'' \rangle = 0$ for $p = 1, 2$, because of rotations about the molecular axis.

The application of Eq. (4) to Eq. (3) and then to Eq. (1) will then give rise to a relaxation rate which is the sum of three contributions,

$$T_1^{-1} = (T_1^{-1})_a + (T_1^{-1})_b + (T_1^{-1})_c, \quad (5)$$

where each rate is calculated from the respective correlation functions corresponding to the following motions:

(a) Long-range or collective fluctuations, where

$$\langle F_p''(t)F_p''^*(t+\tau) \rangle_a = \frac{1}{4}f_{p1} \langle F_0''(t) \rangle^2 \langle \delta \vec{N}(t) \cdot \delta \vec{N}(t+\tau) \rangle. \quad (6a)$$

(b) Local or diffusion motion, where

$$\langle F_p''(t)F_p''^*(t+\tau) \rangle_b = \sum_{q=0}^2 f_{pq} \langle |F_q''(t)|^2 \rangle e^{-|\tau|/\tau_c}. \quad (6b)$$

(c) Cross terms between the above two motions, where

$$\begin{aligned} \langle F_p''(t)F_p''^*(t+\tau) \rangle_c = & \left\{ \frac{1}{4}f_{p1} [\langle |F_0''(t)|^2 \rangle + \langle |F_2''(t)|^2 \rangle] \right. \\ & \left. + (18f_{p0} + 4f_{p2}) \langle |F_1''(t)|^2 \rangle \right\} \\ & \times \langle \delta \vec{N}(t) \cdot \delta \vec{N}(t+\tau) \rangle e^{-|\tau|/\tau_c}. \end{aligned} \quad (6c)$$

The first term in Eq. (5), which is the long-range-fluctuation term, has been considered in previous publications^{1,10,11} for the *intramolecular* case. We will show in this paper how it can also be made to apply to the *intermolecular* case. The correlation function in Eq. (6a) is calculated by regarding $\delta \vec{N}(t)$ as a superposition of plane waves.¹⁹ Thus

$$\delta \vec{N}(\vec{r}, t) = V^{-1/2} \sum_{\vec{q}} \delta \vec{N}_{\vec{q}} e^{i\vec{q} \cdot \vec{r}}, \quad (7)$$

where V is the volume of the sample and \vec{q} the wave vector. Following de Gennes²⁰ and applying the continuum elastic theory for the nematic phase and the equipartition theorem, the thermal amplitudes of the modes become

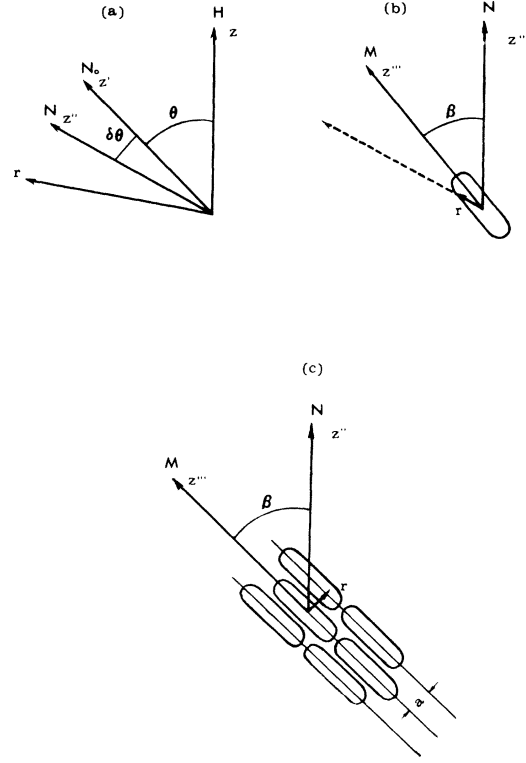


FIG. 1. Diagrams illustrating the z axes of the reference frames used in the theory. (b) *Intermolecular* case, where the interacting spins are members of the same molecule; (c) *intermolecular* case, where the two spins belong to different molecules.

$$\langle |\delta N_{qx}|^2 \rangle = kT / (K_{11}q_x^2 + K_{33}q_z^2) V, \quad (8)$$

$$\langle |\delta N_{qy}|^2 \rangle = kT / (K_{22}q_x^2 + K_{33}q_z^2) V,$$

where K_{11} , K_{22} , and K_{33} are the splay, twist, and bend deformation constants, respectively. De Gennes²⁰ has calculated the dispersion relations for these collective modes to be

$$\tau_{qx}^{-1} = (K_{11}q_x^2 + K_{33}q_z^2) / \eta_x, \quad \tau_{qy}^{-1} = (K_{22}q_x^2 + K_{33}q_z^2) / \eta_y, \quad (9)$$

where η_x and η_y are viscosity coefficients and are combinations of Leslie's viscosity coefficients used to describe the hydrodynamics of the nematic phase.

Except in the vicinity of a smectic phase transition, it is a reasonable approximation to set $K_{11} \approx K_{22} \approx K_{33} = K$. For the purposes of this paper it is also convenient to lump the viscosities into one quantity η . Making the above approximations¹⁵ greatly simplifies the calculation as well as the end result and the theory remains valid for a wide range of nematics.

Applying only Eq. (6a), Eq. (1b) becomes

$$[J_p(p\omega)]_a = \frac{f_{p1} \langle F_0''(t) \rangle^2}{4} \times \int_{-\infty}^{\infty} \int_0^{q_c} \langle |\delta \vec{N}_{\vec{q}}|^2 \rangle e^{-|\tau|/\tau_{\vec{q}}} e^{-i p \omega \tau} d\tau \times \frac{V}{(2\pi)^3} 4\pi q^2 dq, \quad (10)$$

where $\langle |\delta \vec{N}_{\vec{q}}|^2 \rangle = 2kT/Kq^2V$ and $\tau_{\vec{q}}^{-1} = Kq^2/\eta$ for the single-deformation-constant approximation. The integration limit q_c is to account for the long-range mode being cut off near the molecular size. Carrying out the above integration yields

$$(T_1^{-1})_a = \frac{1}{4} A \langle F_0'' \rangle^2 \omega^{-1/2} [f_{11} u(\omega) + (f_{21}/\sqrt{2}) u(2\omega)], \quad (11a)$$

where

$$A = \frac{9}{8} \gamma^4 \hbar^2 k T \eta^{1/2} / \pi \sqrt{2} \gamma^6 K^{3/2}, \quad (11b)$$

and $u(p\omega)$ is a factor which results from the cut-off of the collective modes. At normal NMR frequencies the cutoff factor can be approximated by

$$u(p\omega) \approx 1 - (2\sqrt{2}/\pi)(p\omega/\omega_c)^{1/2}, \quad (12)$$

where $\omega_c = Kq_c^2/\eta$ and $\omega_c \gg \omega$. Since the last term of Eq. (12) represents only a minor correction,¹⁶ we will ignore it altogether, that is, we will disregard the cutoff by taking $u(p\omega) = 1$. An exact expression for $u(p\omega)$ can be found in previous publications.¹⁶

The second term of Eq. (5) is just the familiar Bloombergen contribution,^{17,21} except in this case it is modified to accommodate the anisotropy characteristic of the liquid crystal. Equations (6b) and (1) give

$$(T_1^{-1})_b = \frac{9\gamma^4 \hbar^2}{8\gamma^6} \sum_{q=0}^2 \langle |F_q''|^2 \rangle \left(f_{1q} \frac{2\tau_c}{1 + (\omega\tau_c)^2} + f_{2q} \frac{2\tau_c}{1 + (2\omega\tau_c)^2} \right). \quad (13)$$

Finally, we consider the cross terms of Eq. (6c), which, as will be shown later, can be significant contributors to T_1 in the nematic phase. These terms have unfortunately been neglected in previous studies. From Eq. (6c) the spectral density of Eq. (1b) is written

$$[J_p(p\omega)]_c = C_p \int \langle \delta \vec{N}(\vec{r}, t) \cdot \delta \vec{N}(\vec{r}, t + \tau) \rangle \times e^{-|\tau|/\tau_c} e^{-i p \omega \tau} d\tau, \quad (14a)$$

where

$$C_p = \frac{1}{4} f_{p1} [\langle |F_0''(t)|^2 \rangle + \langle |F_2''(t)|^2 \rangle] + (18f_{p0} + 4f_{p2}) \langle |F_1''(t)|^2 \rangle. \quad (14b)$$

Again using the single-deformation-constant approximation,

$$[J_p(p\omega)]_c = (kT\eta^{1/2}\tau_c^{1/2}/\sqrt{2}\pi K^{3/2}) C_p g(p\omega\tau_c), \quad (15a)$$

where the function

$$g(x) \equiv \{[1 + (1 + x^2)^{1/2}]/(1 + x^2)\}^{1/2}. \quad (15b)$$

Applying Eq. (1a), the relaxation rate becomes

$$(T_1^{-1})_c = A\tau_c^{1/2} [C_1 g(\omega\tau_c) + C_2 g(2\omega\tau_c)]. \quad (16)$$

A. Intramolecular contribution

Here we apply Eqs. (11), (13), and (16) to the case where the spins are members of the same molecule. The parameter τ_c in this case corresponds to the anisotropic rotational diffusion of the molecular long axis about the director \vec{N} . Measured values of the order parameter²² indicate that this motion can be appreciable. That is, the molecular long axis can swing to angles approaching 40° away from its preferred direction \vec{N} . Dipole-relaxation studies²³ give a value $\tau_c = 3 \times 10^{-11}$ sec. Rotation of the molecule about the long axis occurs at a similar rate. Utilization of Eqs. (11), (13), and (16) requires the calculation of the averages $\langle |F_p''(t)|^2 \rangle$ and $\langle F_p''(t) \rangle^2$. This requires a further transformation of the double-primed spherical harmonics $F_p''(t)$ from the director \vec{N} to the frame of \vec{M} , the frame fixed by the molecular long axis [Fig. 1(b)]. Considering only the long axis of the molecule to be preferentially ordered, that is, that on the average there is cylindrical symmetry about the director \vec{N} , the transformation gives

$$\langle |F_p''(t)|^2 \rangle = \sum_{q=0}^2 M_{pq} \langle |F_q''|^2 \rangle, \quad (17a)$$

where

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

in which the direction cosines l , m , and n describe the internuclear vector in a frame where \vec{M} establishes the z direction, and

$$M_{pq} = \langle f_{pq}(\beta(t)) \rangle. \quad (17b)$$

The order parameter S is defined in terms of $\langle \cos^2\beta \rangle$ according to the expression $\langle \cos^2\beta \rangle = \frac{1}{3}(2S + 1)$. While it is not possible to relate $\langle \cos^4\beta \rangle$ to S with an exact expression, a very close approximation can be made. Using a familiar trigonometric identity, one can write

$$\langle \cos^4\beta \rangle = \langle \cos^2\beta \rangle + \frac{1}{8} \langle \cos 4\beta \rangle - \frac{1}{8}. \quad (18)$$

Because of the factor $\frac{1}{8}$, it is a good approximation in Eq. (18) to replace $\langle \cos 4\beta \rangle$ by $\frac{1}{15}(16S - 1)$,

which is correct for perfect order and for the isotropic case. With this substitution,

$$\langle \cos^4 \beta \rangle \simeq \frac{1}{5} (4S + 1). \quad (19)$$

The matrix in Eq. (17) can now be expressed as

$$M = \frac{1}{5} \begin{pmatrix} 4S + 1 & 12(1 - S) & 3(1 - S) \\ \frac{1}{6}(1 - S) & 3S + 2 & \frac{1}{2}(1 - S) \\ \frac{2}{3}(1 - S) & 8(1 - S) & 3S + 2 \end{pmatrix}. \quad (20)$$

The averages $\langle F_p''(t) \rangle^2$ give a much simpler result,

$$\langle F_0''(t) \rangle^2 = S^2 \langle F_0'''(t) \rangle^2 \quad \text{and} \quad \langle F_1''(t) \rangle^2 = \langle F_2''(t) \rangle^2 = 0. \quad (21)$$

To illustrate the use of the above formalism we will make application to the specific case where the internuclear vector is parallel to the molecular axis. We have chosen this case since rapid rotational diffusion about the molecular axis could time average all *intramolecular* interactions to be parallel to \vec{M} . In addition, it often happens that the dominant interaction is along \vec{M} . In this case $|F_0'''|^2 = 4$ and $F_1''' = F_2''' = 0$. Writing only the case where $\theta_0 = 0$, Eqs. (5), (11), (13), and (16) for the *intramolecular* case become

$$T_1^{-1} = A \tau_c^{1/2} \left[\frac{S^2}{(\omega \tau_c)^{1/2}} + \frac{2(1 - S)}{15} d \tau_c^{1/2} \left(\frac{1}{1 + (\omega \tau_c)^2} + \frac{4}{1 + (2\omega \tau_c)^2} \right) + \frac{2S + 1}{3} g(\omega \tau_c) + \frac{8(1 - S)}{15} g(2\omega \tau_c) \right], \quad (22)$$

where $d = (2\sqrt{2} \pi / kT)(K^3 / \eta)^{1/2}$. For $\theta \neq 0$, T_1^{-1} can be found in the same manner. If $\omega \tau_c \sim 1$, it is noted that this is a rather complicated frequency dependence. It will be shown later that Eq. (22) will fit the measured frequency-dependence data of MBBA with τ_c the only fitting parameter. The center term on the right-hand side of Eq. (22) is the Bloombergen term we have generalized to include anisotropic liquids. It reduces to the familiar Bloombergen equation for normal liquids when $S = 0$. In addition, the angular dependence of this contribution will vanish at $S = 0$, as it should. The last term of Eq. (22) is the cross term and can become dominant for $\omega \tau_c \gtrsim 1$. To illustrate the angular dependence we apply Eqs. (5), (11), (13), and (16) to the special case when $\omega \tau_c \ll 1$ and again where the internuclear vector is parallel to \vec{M} . The theory gives

$$T_1^{-1} = \alpha_0 + \alpha_1 \sin^2 \theta_0 + \alpha_2 \sin^4 \theta_0, \quad (23)$$

with

$$\alpha_0 = A \tau_c^{1/2} \left[S^2 / (\omega \tau_c)^{1/2} + \frac{2}{3}(1 - S) d \tau_c^{1/2} + \frac{1}{15\sqrt{2}}(2S + 13) \right], \quad (23a)$$

$$\alpha_1 = A \tau_c^{1/2} \left[S^2 (2\sqrt{2} - \frac{5}{2}) / (\omega \tau_c)^{1/2} + S d \tau_c^{1/2} + \frac{1}{10\sqrt{2}}(7 + 8S) \right], \quad (23b)$$

$$\alpha_2 = A \tau_c^{1/2} [S^2 (2 - \sqrt{2}) / (\omega \tau_c)^{1/2}]. \quad (23c)$$

Note that for $\theta_0 = 0$,

$$T_1^{-1} = AS^2 \omega^{-1/2} + B, \quad (24)$$

where B is a frequency-independent term, which is the form observed in PAA.

B. Intermolecular contribution

In this section we develop a model in which the two spins in question belong to two different molecules, as illustrated in Fig. 1(c). We imagine that the molecules remain in a fixed preferred position for a period of time τ_d . In this position let the distance of closest approach between two spins be a . While in this preferred position, $\vec{N}(t)$ fluctuates about \vec{N}_0 . These fluctuations and their influence on T_1 can be taken into account through Eqs. (11) and (16). When the molecule carrying one of the two spins diffuses we consider it to jump to a new preferred position which is a distance R away. If $R \gg a$ (a fraction of a molecular length would be large enough) then such a jump would suddenly "turn off" the two-spin interaction. The molecule jumping into position in the vacancy would turn it back on again. It would not be necessary for the molecule to diffuse to interrupt the spin interaction. Since the strength varies as r^{-3} , the mere appearance of a large local strain which would occur in the vicinity of a vacancy could abruptly reduce the spin interaction. Assuming a single correlation time τ_d for this jump motion,²⁴ we can apply this model to Eqs. (11), (13), and (16) to calculate the relaxation rate.

The above model requires the degree of parallel orientation to be larger over small volumes than the long-range degree of order. High local order is apparently in accord with electric-dipole relaxation work.²³

The averages $\langle |F_p''(t)|^2 \rangle$ involve the long-range average. The model used is illustrated in Fig. 1(c), where two neighboring molecules take on a

preferred position relative to one another and their long axes fluctuate together until a vacancy appears and the interaction is interrupted. As described earlier, the spin interaction could be interrupted by the spin-containing molecule jumping into the vacancy or by a large local strain. With this model we can use the time averages of Eq. (20). Since the molecules can rotate rapidly about their long axis ($\tau_c \ll \tau_d$), the shortest average spin-interaction distance is the distance a [see Fig. 1(c)] between the long molecular axes. Taking the internuclear vector perpendicular to the molecular axis, $|F_0''|^2 = |F_2''|^2 = 1$ and $|F_1''|^2 = 0$. Equation (5) for the *intermolecular* case becomes

$$T_1^{-1} = A \tau_d^{1/2} \left[\frac{S^2}{4(\omega \tau_d)^{1/2}} + \frac{d\tau_d^{1/2}}{15} \left(\frac{2(1-S)}{1+(\omega \tau_d)^2} + \frac{8+7S}{1+(2\omega \tau_d)^2} \right) + \frac{2+S}{6} g(\omega \tau_d) + \frac{8(1-S)}{15} g(2\omega \tau_d) \right]. \quad (25)$$

III. EXPERIMENTAL DETAILS

Several aspects of the theory in Sec. II, e.g., the frequency dependence, can be checked with data already present in the literature. Other aspects, such as the angular dependence, require more precise data. In a computer-controlled experiment we were able to obtain relaxation rates accurate to within 1%.

These data were taken using a Brüker pulsed NMR spectrometer model B-KR322S, a Biomation transient recorder, model 802, and a Nicolet NIC-80 minicomputer. A $\frac{1}{2}\pi$, τ_1 , $\frac{1}{2}\pi$, τ_2 pulse sequence was used, with τ_2 greater than five times the relaxation time. The signal after the second $\frac{1}{2}\pi$ pulse was subtracted digitally from the signal after the first pulse; then the portion of this new curve lying between two adjustable cursors was integrated to get a value $M(\tau_1)$ for the change in magnetization. The subtraction removed errors due to slow changes in the zero level of our signal, while the integration averaged out high-frequency noise. This sequence was repeated a number of times for signal averaging; then the delay was changed under minicomputer control and $M(\tau_1')$ obtained.

The number of delays used was generally five, varying from delays of 40 msec to about twice the relaxation time. These values of $M(t)$ were then used to find the best χ^2 fit to the functional form $M(t) = e^{A-Bt}$, where $B = T_1^{-1}$ and the errors were taken to be a fixed amount. The values of M were available for plotting on semilogarithmic paper so that we could look for curvature in the plot and check for the occasional bad point. The instrumental sources of error that occurred were (a) a pulse not equal to $\frac{1}{2}\pi$ (small problem); (b) magnet

off resonance; (c) drift in amplifier gain; and (d) improper placement of cursors.

Items (b) and (c) limited the allowable duration of the experiment. Long-term averaging was of little use if the gain changed by a few percent.

Item (d) is an important consideration. For MBBA a change of 8% in the relaxation rate was easy to get by moving the cursors further down the free induction decay (FID) or by including the area of the whole signal, which would be equivalent to finding the relaxation time of the center of the spectrum. A 15- μ sec segment of the FID as close as possible to the pulse was generally used. The cursors were picked so as to be usable at all frequencies.

The samples of PAA were prepared by repeatedly cooling to a solid phase and heating back to liquid, and then sealing under vacuum. An open sample of PAA could absorb enough oxygen to reduce T_1 by 10% in the course of a day.

The temperature of the sample was monitored by a thermocouple mounted inside the probe. Air flowed over heater wires and through the probe, and over the sample and thermocouple. As the thermocouple was not in direct contact with the sample, the nematic-isotropic transition point was used to calibrate the system, using the approximation that the difference between sample and thermocouple temperatures was proportional to the difference between thermocouple and ambient (18°C) temperatures. This relationship was checked by putting another thermocouple inside the sample. It was found that the temperature of the sample increased when it was rotated and thus the temperature dependences were done separately for the stationary and rotating experiments.

IV. COMPARISON WITH DATA

A. Frequency dependence

As mentioned in Sec. I, the frequency dependence $T_1^{-1} = AS^2\omega^{-1/2} + B$ is well established in the literature for the nematic phase of PAA.^{4,8} After subtracting the *intermolecular* contributions of the isotropic substitution experiments,⁵ the expression still holds. We therefore use Eq. (23a) to obtain a value of τ_c for the local motion. The value obtained depends on the value used for the internuclear separation distance r and the degree of molecular order. For the strongest two-spin interaction in PAA,²² the value of r is 2.45 Å. Using a value of 0.55 for the degree of order and the isotropic substitution data,⁵ we obtain a value of $\tau_c \approx 1 \times 10^{-10}$ sec. While the condition $\omega \tau_c \ll 1$ is valid in PAA at normal NMR frequencies, it is seen that an increase in τ_c of an order of magni-

tude or greater would invalidate this condition and the $\omega^{-1/2}$ law would no longer be expected to hold. We might expect this to happen in MBBA, where the rotational viscosity increases by a factor of 10. In this case, if the *intramolecular* contribution is still the dominant mechanism, we should use Eq. (22) to predict the frequency dependence. Figure 2 shows the data of Blinc, Vilfan, and Rutar.⁹ We have fitted Eq. (22) to these data. The fitting parameters are A and τ_c . At high frequencies T_1^{-1} is independent of τ_c , allowing A and τ_c to be adjusted independently. We used the calculated value of $d = 7.6 \times 10^4$, where we took $K = 5 \times 10^{-7}$ dyn,²⁰ and $\gamma_1 = 1$ P.² The best fit, shown as the solid line in Fig. 2, gave a value of $\tau_c = 4.5 \times 10^{-9}$ sec, which is about that expected from the PAA data and the change in viscosity. From the fitted value of $A = 5.2 \times 10^4$ sec^{-3/2}, the calculated internuclear separation distance r was 2.6 Å, which is reasonable. A value of 0.6 is assumed for the degree of order.

We found it interesting to also attempt a fit of Eq. (25) from the *intermolecular* model to the MBBA data. The dashed line in Fig. 2 shows the best fit of this equation, where three parameters, A , τ_d , and d , were adjusted. The *intermolecular* theory did not work nearly as well, since the calculated value of d would not give a reasonable fit and had to be adjusted. The value of $\tau_d = 6 \times 10^{-9}$ sec turned out to be slightly larger than the value obtained from the *intramolecular* fit. The value of d , on the other hand, was significantly reduced, giving a value of $K \sim 1 \times 10^{-7}$ dyn. Likewise, the fitted value of $A = 1 \times 10^5$ sec^{-3/2} gave 3.4 Å, which is smaller than expected for the distance

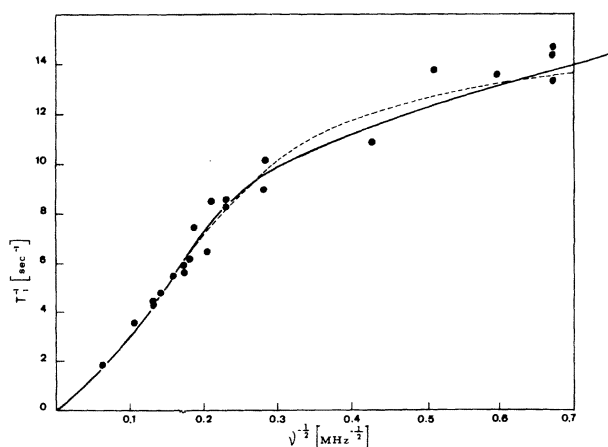


FIG. 2. Frequency dependence of T_1^{-1} in the nematic phase of MBBA. The solid and dashed lines are fits to the theory, as explained in the text. The data were taken from Refs. 8 and 9.

between adjacent molecular axes. These values could be improved by recognizing that there are six neighboring molecules instead of one, which could improve the values for the *intermolecular* separation distance as well as the value K . However, the fit is not as satisfying as in the *intramolecular* case.

B. Temperature dependence and value of τ_c

Figure 3 shows detailed measurement of the relaxation rate in PAA at three different frequencies measured when the sample was rotating and again when stationary in the magnetic field. With the use of Eq. (23a) and the data for the stationary sample, τ_c was obtained. The value of A in Eq. (24) can be obtained from the slope of the $\omega^{-1/2}$ dependence, B from the projected intercept, and the value of S from the literature²² and from measured splittings. Again taking the value of r to be 2.45 Å gives the values for τ_c plotted in Fig. 4. An activation energy of 8.5 kcal/mole is obtained from the temperature dependence. This value is similar to that measured for viscosity.² The value of $\tau_c = 1.2$

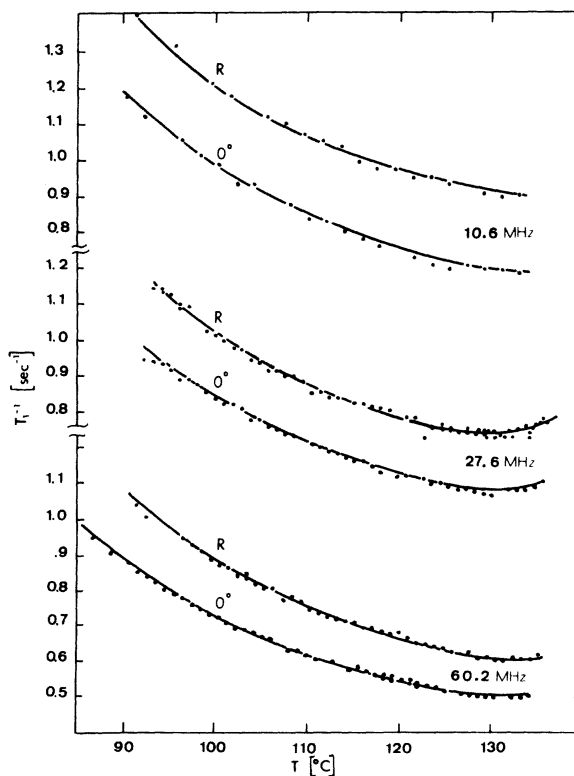


FIG. 3. Spin-lattice relaxation rate for protons in the nematic phase of PAA in rotating samples (R) and stationary samples (0°) at selected frequencies. These data extend from the isotropic-nematic transition at 136°C into the supercooled region terminating near 90°C.

$\times 10^{-10}$ sec at 125 °C can be compared with the electric-dipole relaxation value²³ of τ_D measured in PAA at the same temperature through the relation¹⁷ $\tau_D = 3\tau_c$.

Dipole-relaxation experiments²³ in PAA at 125 °C give two values for τ_D for the rotational motion of the long molecular axis $\tau_{D1} = 2.5 \times 10^{-11}$ and $\tau_{D2} = 4.3 \times 10^{-9}$ sec. The latter time is identified with an end-for-end flip of the molecule. The spin-lattice relaxation value of $3\tau_c$ determined above lies between these two values of τ_D . We suggest that the rapid fluctuations of the long axis which correspond to τ_{D1} serve to time average the spin interactions along the nematic director. Motion related to τ_{D2} , on the other hand, is the local motion primarily responsible for relaxing the spins. Our value of $3\tau_c$ may be smaller than τ_{D2} because the degree of order on the local level is greater than the long-range order.²³ A larger value for the degree of order used in Eq. (23a) would give a value of $3\tau_c$ closer to τ_{D2} . It could also be that fluctuations of the long molecular axis to large angles rather than a complete end-for-end flip may be sufficient to perturb the spin interactions. Such motion could occur more frequently.

C. Angular dependence

The angular dependence of Eq. (23) can be tested from the data of Fig. 3 for rotating and nonrotating samples. When a bulk nematic sample in a magnetic field \vec{H} is rotated about an axis perpendicular to \vec{H} at a sufficiently rapid rate, the director will become uniformly distributed throughout the x, z plane, where the y and z axes of the rectangular coordinate frame are established by the

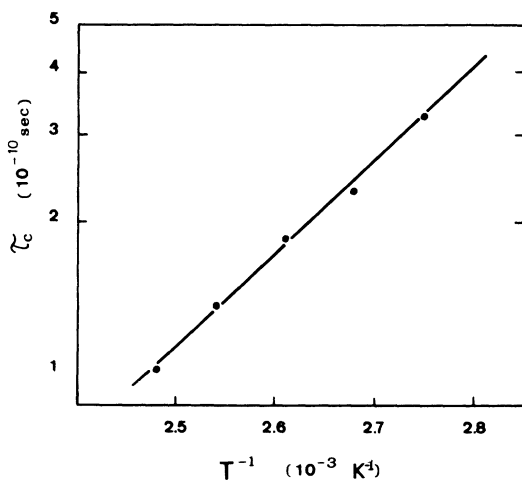


FIG. 4. Temperature dependence of the correlation time τ_c of the long molecular axis in the nematic phase of PAA as determined from T_1 data.

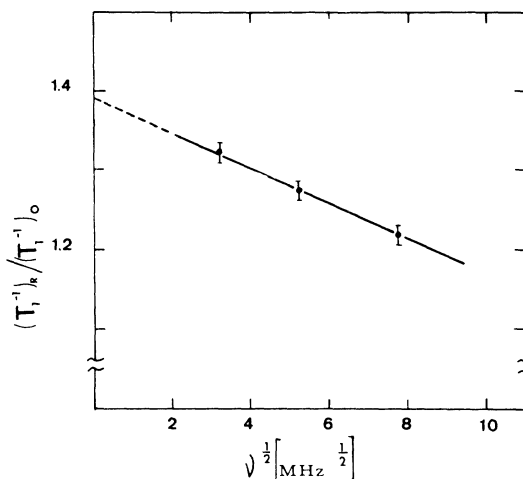


FIG. 5. Frequency dependence of the ratio $(T_1^{-1})_R / (T_1^{-1})_0$ at 125 °C in PAA.

axis of rotation of the sample and the direction of the magnetic field, respectively.²⁵ The sample rotation frequency Ω must be fast enough such that $\Omega > \Delta\chi H^2 / \gamma$, where $\Delta\chi$ is the anisotropy of the diamagnetic susceptibility. The value of the relaxation rate when the sample is rotating, $(T_1^{-1})_R$, depends upon the angular dependence. Equation (23) gives the form of this dependence, in which case $(T_1^{-1})_R$ becomes²⁵

$$(T_1^{-1})_R = \alpha_0 + \frac{1}{2}\alpha_1 + \frac{3}{8}\alpha_2. \quad (26)$$

An interesting quantity is the ratio $(T_1^{-1})_R / (T_1^{-1})_0$, where $(T_1^{-1})_0$ is the rate at $\theta = 0$. The theory of Sec. II predicts that in PAA this ratio will be near the value

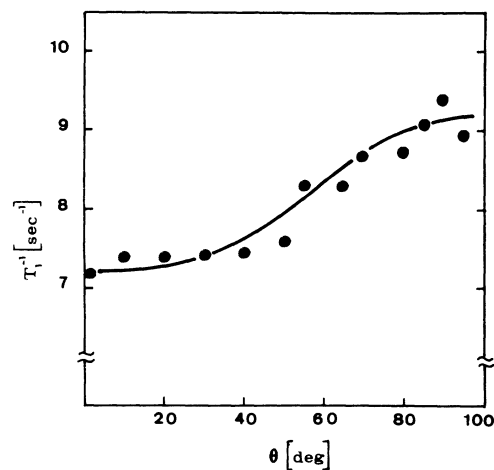


FIG. 6. Angular dependence of T_1^{-1} obtained from thin films of MBBA at 35 °C and at a frequency of 8.0 MHz. The solid line is a trace through the points to aid the eye.

of 1.38. More precisely, this ratio is predicted to be frequency dependent. In the case where $\omega\tau_c \ll 1$ Eqs. (23) for the *intramolecular* case give the ratio to be of the form

$$(T_1^{-1})_R / (T_1^{-1})_0 \approx 1.384 + C\omega^{1/2}, \quad (27)$$

where C is a constant determined from the constant terms in Eqs. (23). As is seen in Fig. 5, Eq. (27) predicts the ratio $(T_1^{-1})_R / (T_1^{-1})_0$ with surprising accuracy, particularly with regard to the intercept value of 1.38. Based strictly on the *intramolecular* contribution, however, Eqs. (23) would predict the constant C to be positive instead of its observed value, which is negative. This implies that the *intermolecular* contribution T_1^{-1} in PAA has little angular dependence, that is, its contribution to α_1 and α_2 of Eq. (26) is small. Such a result would force the value of C to be negative and yet maintain the intercept value of 1.38. If the *intermolecular* contributions were isotropic at all frequencies, rotating the sample would be an easy way to separate the two mechanisms.

The angular dependence in MBBA was not nearly as satisfying. These results are shown in Fig. 6. Thin films were used so that the surface alignment could be used to compete with the field in the alignment of the director. A stack of 35 films with an average spacing of 10 μm was used. The glass surfaces were treated in the usual fashion²⁰ for homeotropic alignment. Since the critical bending field was less than the NMR field strength, there was some distortion of the director, particularly at angles near 45°, which could be observed by the free induction decay. While these data are not sufficiently reliable to accurately test the angular dependence, they do show a marked dependence in the predicted direction. On the other

hand, the magnitude of the dependence is about a factor of 2 less than expected for both the *intra-* and *intermolecular* mechanisms. (Please note that the solid curve in Fig. 6 is not the theoretical curve.) If the *intramolecular* contribution holds in MBBA, this could mean that one cannot assume the local and collective modes to be totally independent. It could also be a result of the one-elastic-constant assumption.

V. SUMMARY

The frequency dependence of proton spin-lattice relaxation in nematics depends strongly on the local motion. This dependence can be explained in PAA as well as in MBBA by the adjustment of the correlation time τ_c for rotational diffusion of the molecular long axis. This correlation time appears to be related to the long correlation time observed in electric-dipole-relaxation studies corresponding to large reorientation of the molecular long axis. From this argument, the relaxation process in MBBA appears to be predominantly *intramolecular*, as it has been found to be in PAA. The values for τ_c and the rotational viscosity coefficient γ_1 appear to be correlated²⁶ and can be used as a guide to predict the frequency dependence of T_1 .

The calculated angular dependence appears to work well when $\omega\tau_c \ll 1$.

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¹ An excellent collection of references on spin-lattice relaxation in nematic liquid crystals can be found in Ref. 4.

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