First, F must be independent of φ. Second, there must be a particular relation between F and G. With these restrictions

$$n(\kappa,t)=\frac{qm\omega_cE_\kappa}{\kappa}\int_0^\infty dr\,r\int_0^{2\pi}d\varphi'\,\frac{\partial F}{\partial(\frac{1}{2}r^2)}\sum_n\frac{nJ_n(\kappa r)}{\omega-n\omega_c+i\gamma_1}\exp(-i\omega t+in\varphi'+i\kappa r\sin\varphi'+\textstyle\int_0^t\gamma d\tau),$$

$$\int_0^\infty dr\,rG(\tfrac{1}{2}r^2,\varphi)=\frac{qm\omega_cE_\kappa}{\kappa}\int_0^\infty dr\,r\frac{\partial F}{\partial(\frac{1}{2}r^2)}\sum_n\frac{nJ_n(\kappa r)}{\omega-n\omega_c+i\gamma_1}\exp(-i\omega t_1+in\varphi-in\omega_ct_1).$$

The equations for $n(\kappa,t)$ and for f are identical in form with that obtained from the linearized Vlasov equation, with the substitution of F for f_0. Viewed from the x-v_x-v_y phase space, F is just the spatial average of f. As long as only the original instability frequency is present, a modified linear dispersion relation is valid, and f is of the usual linearized form. Any other functional form of $f(\frac{1}{2}r^2,\varphi,\xi)$ will lead to a density perturbation with frequency contributions at all the cyclotron harmonics, but donimantly for those values of n such that the resonant denominator $|\omega-n\omega_c+i\gamma_1|$ is smallest.

We have now essentially proven our original hypothesis of cyclotron harmonic generation. As the electric field grows, the $\frac{1}{2}r^2$ and φ of a particle have an oscillation plus a net drift. Examining the equation for W we see that nonlinear orbit effects will become important when the change in kr or the change in φ is of order π. We can obtain a conservative upper bound on the electric field required for this effect by approximating all cosines and sines by 1, and the time integral by $2\pi/\omega_c$. Then $qE2\pi\kappa/m\omega_c^2=\pi$ or, alternatively, $2q\Phi/m\langle v^2\rangle=1/\kappa^2R^2$, where R^2 is the mean-square orbit radius. More careful analysis, given elsewhere, yields a slightly smaller energy ratio.[2] For flute modes, κ^2R^2 is usually much greater than 1 so that nonlinear effects are indeed important.

If the plasma contains several linearly unstable wavelengths with comparable energies, the effect of each k component is less, and it is uncertain, by simply examining the Hamiltonian, whether cyclotron generation will take place. The computer simulation studies indicate that the effect is still there but not as dominant. If there is a component of k parallel to the magnetic field, and $k_\parallel/k_\perp \ll 1$, particles would still have the above type of perpendicular motion and cyclotron generation should still occur.

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SPIN RELAXATION AND SELF-DIFFUSION IN LIQUID CRYSTALS*

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The frequency and temperature dependence of proton relaxation times have been measured for the nematic liquid-crystal and isotropic liquid phases of *p*-azoxyanisole and *p*-azoxyphenetole as well as for the "neat" mesophase of sodium stearate. Self-diffusion coefficients were determined by the proton-spin-echo method. The anomalous effects found are interpreted in terms of collective long-range-order fluctuations in the nematic region and a residual order in the isotropic liquid.

In this Letter we report a study of the frequency and temperature dependence of proton spin-lattice (T_1) and rotating frame ($T_{1\rho}$) relaxation times for three liquid crystals [*p*-azoxyanisole (PAA), *p*-azoxyphenetole (PAP), and anhydrous sodium stearate (NaSt)] in the nematic and isotropic-liquid regions. Earlier[1-3] it was suggested that thermal fluctuations of the nematic order might contribute to the nuclear spin relaxation rates in nematic liquids in addition to translational diffusion which contributes to the relaxation in ordinary liquids. The observed values of T_1 and $T_{1\rho}$ reported here are shown to be a result of the former relaxation mechanism. The anomalous values of $T_{1\rho}$ persist up to 15°K above the nematic-isotropic liquid transition temperature (T_M) demonstrating the existence of nematic clusters in the isotropic liquid. Measurements of self-diffusion coefficients, hitherto not reported for a liquid crystal, are given for the isotropic-liquid phase of PAA and the "neat" mesophase of NaSt.

Theory. – The anisotropic nematic phase is characterized by the existence of long-range order in the orientation of the principal molecular axes. The centers of gravity of the molecules are not fixed, and in addition, each molecule is free to rotate around the principal axis, the average direction of which will be specified by a unit vector $\vec{n}$. Since $\vec{n}$ is normally nearly parallel to the direction of the applied magnetic field $\vec{H}_0$ a rotation about $\vec{n}$ does not greatly reduce the magnetic dipolar interaction between the close pairs of benzene-ring protons in PAA and PAP. This residual interaction gives rise to the well-known characteristic doublet spectrum in the nematic region. Thermal fluctuations in the nematic long-range order, however, produce a space and time dependence of $\vec{n}$,

$$\vec{n} = \vec{n}^0 + \delta\vec{n}(\vec{r}, t), \tag{1}$$

which modulates the dipolar interaction between the proton pairs on the benzene ring and gives rise to spin relaxation. The relevant terms in the dipolar-interaction Hamiltonian up to the lowest order in $\delta\vec{n}$ expressed in the laboratory frame are

$$H(t) = \frac{3}{2}\frac{\gamma^2\hbar^2}{R^3}\{6n_z{}^0\delta n_z(t)[\tfrac{2}{3}I_{1z}I_{2z} - \tfrac{1}{6}(I_{1+}I_{2-} + I_{1-}I_{2+})] + \{n_z{}^0[\delta n_x(t) - i\delta n_y(t)] + (n_x{}^0 - in_y{}^0)\delta n_z(t)\}[I_{1z}I_{2+} + I_{1+}I_{2z}] + \text{c.c.} + \{n_x{}^0[\delta n_x(t) + i\delta n_y(t)] + n_y{}^0[\delta n_x(t) - i\delta n_y(t)]\}I_{1+}I_{2+} + \text{c.c.}\}, \tag{2}$$

where R is the proton pair distance and c.c. stands for the complex conjugate of the term preceding it. As suggested by de Gennes,[2] the orientational order fluctuations can be treated in the long-wavelength limit by the elastic continuum theory of Frank.[4] Introducing Fourier components,

$$\vec{n}_q(t) = \frac{1}{V}\int \vec{n}(\vec{r}, t)e^{i\vec{q}\cdot\vec{r}}dV, \tag{3}$$

one finds that the free energy of deformation ΔF of a nematic-liquid crystal is

$$\Delta F = \tfrac{1}{2}\sum_q\{K_{11}(n_{q_{x'}}q_{x'} + n_{q_{y'}}q_{y'})^2 + K_{22}(n_{q_{x'}}q_{y'} - n_{q_{y'}}q_{x'})^2 + K_{33}(n_{q_{x'}}{}^2q_{z'}{}^2 + n_{q_{y'}}{}^2q_{z'}{}^2) + \Delta\chi H_0{}^2(n_{q_{x'}}{}^2 + n_{q_{y'}}{}^2)\}, \tag{4}$$

where the K_{ii} are the Frank elastic constants, $\Delta\chi = \chi_\perp - \chi_\parallel$ is the anisotropic part of the diamagnetic susceptibility, and the "saddle splay" term[4] is set equal to zero. To illustrate simply the general features of the nematic phase we set $K_{11} = K_{22} = K_{33} = K$. In the Landau-Khalatnikov approximation,[5] where each long-wavelength Fourier component $\vec{n}_q$ of the orientational order fluctuation relaxes exponentially towards equilibrium with a q-dependent time constant τ_q, one has

$$\tau_q{}^{-1} = (1/\eta)(Kq^2 + \Delta\chi H^2), \tag{5}$$

where η is an orientational average of the six Leslie viscosity coefficients.[6] The relaxation times T_1 and $T_{1\rho}$ associated with the order waves are determined by the spectral densities of the autocorrelation functions of the space parts of $H(t)$.[7] The autocorrelation functions are constructed by summing over all values of q and hence are not simple exponential functions of time. In the approximation that $n_z{}^0 = 1$, the spectral density $J^{(1)}(\omega_0)$ of $\langle\delta\vec{n}\cdot\delta\vec{n}(t)\rangle_{\text{av}}$ at frequency $\omega_0 = \gamma H_0$ is the only nonzero term in the expressions for T_1 and $T_{1\rho}$. One obtains

$$J^{(1)}(\omega_0) = \frac{1}{V}\int\int_{-\infty}^{\infty}\rho(q)\langle|n_q|^2\rangle_{\text{av}}e^{-t/\tau_q}e^{-i\omega_0 t}d^3\vec{q}dt, \tag{6}$$

where $\rho(q)$ is the density of order wave states. The ensemble average of $|n_q|^2$ may be readily seen to be

$$\langle|n_q|\rangle_{\text{av}} = \frac{kT}{(Kq^2 + \Delta\chi H_0{}^2)V}, \tag{7}$$

and Eq. (6) may be written as follows:

$$J^{(1)}(\omega_0)=\frac{kT\eta^{1/2}}{2\pi^2K^{3/2}}\int_0^\infty\frac{x^{1/2}dx}{\omega_0^{\,2}+(x+r)^2}\tag{8}$$

$$=\frac{kT\eta^{1/2}}{2\pi K^{3/2}(\omega_0^{\,2}+r^2)^{1/4}}\frac{\sin\{\frac{1}{2}\tan^{-1}(\omega_0/r)\}}{\sin[\tan^{-1}(\omega_0/r)]},\tag{9}$$

where $r=\Delta\chi H_0^{\,2}/\eta$ and ρ has been set equal to $V/8\pi^3$. Equation (9) reduces in the limit $r\ll\omega_0$ to the result given by Pincus,[3]

$$J^{(1)}(\omega_0)\propto\omega_0^{\,-1/2},$$

whereas in the opposite limit that $r\gg\omega$,

$$J^{(1)}(\omega_0)\propto\omega_0^{\,-1}.$$

From the well-known expressions[7] for T_1 and $T_{1\rho}$ one obtains

$$T_1^{\,-1}=\tfrac{2}{5}T_{1\rho}^{\,-1}=\frac{9\gamma^4\hbar^2}{8R^6}J^{(1)}(\omega_0).\tag{10}$$

Thus one expects T_1 and $T_{1\rho}$ to depend on ω_0 and $T_1\neq T_{1\rho}$. For the general case where $n_z^{\,0}<1$ and the elastic moduli K_{ll} are retained, the spectral densities $J^{(0)}(2\omega_1)$ and $J^{(2)}(2\omega_0)$ are nonzero; and T_1 and $T_{1\rho}$ depend on the order parameter $\frac{1}{2}[(3n_z^{\,0})^2-1]$ and $T_{1\rho}$ depends on $\omega_1=\gamma H_1$. The autocorrelation function $\langle\delta n\delta n(\tau)\rangle_{\rm av}$, for values of τ not too short, goes as $\tau^{-1/2}$ which is markedly different from the usual behavior in liquids.

Experimental. – Proton T_1 and $T_{1\rho}$ measurements were performed on carefully evacuated samples at $\omega_0/2\pi=42$ and 7 MHz and $\omega_1/2\pi=33$ and 21 kHz using a conventional NMR spectrometer. Diffusion coefficients along $\vec{H}_0$ were determined using the single-shot, variable-gradient, spin-echo method.

The results for PAA and PAP are shown in Figs. 1 and 2, respectively. In both liquids $T_{1\rho}$ is much shorter than T_1 in the nematic range and T_1 at 7 MHz is shorter than T_1 at 42 MHz. The usual relaxation-rate theory[7] for liquids yields

$$T_1^{\,-1}=T_{1\rho}^{\,-1}=C\tau_c,\tag{11}$$

where C is a constant and τ_c the correlation time ($\omega_0\tau_c\ll1$). In PAA $T_{1\rho}$ is smaller than T_1 in the isotropic liquid up to $T=T_M+15°{\rm K}$ demonstrating the presence of nematic short-range-order clusters.[8] The results given in Fig. 3 clearly show that the total relaxation rate in the nematic phase is of the form $A+B(\omega)$, i.e., a sum of a frequency-independent relaxation rate A and a frequency-dependent part $B(\omega)$ which is associated with the fluctuations in the nematic order previously discussed. For perfect nematic ordering parallel to the applied field, $B(\omega)=(9\gamma^4\hbar^2/8R^6)J^{(1)}(\omega_0)$ with $J^{(1)}(\omega_0)$ given by Eq. (9). However, the nematic order parameter $\frac{1}{2}[(n_z^{\,0})^2-1]$ is about 0.7, $J^{(2)}(2\omega_0)$ contributes to $T_1^{\,-1}$, and $J^{(0)}(2\omega_1)$ and $J^{(2)}(2\omega_0)$ contribute to $T_{1\rho}^{\,-1}$. From Fig. 3 one finds $A\approx0.8\ {\rm sec}^{-1}$ for PAA and $0.55\ {\rm sec}^{-1}$ for PAP, whereas $B(\omega)$ varies as $\omega_0^{\,-n}$ with the same factor of proportionaltiy for PAA and PAP and $\frac{1}{2}<n<1$.

The temperature dependence of T_1 in the nematic phases of PAA and PAP follows that given by Eq. (9): $T_1\propto T^{-1}\eta^{-1/2}$, except in the vicinity of T_M. The decrease in T_1 near T_M may be due to the presence of liquidlike regions in the nematic phase for which the self-diffusion coefficient D is practically the same ($\sim10^{-5}\ {\rm cm}^2\ {\rm sec}^{-1}$) as in the isotropic liquid where it is given by $D=D_0$

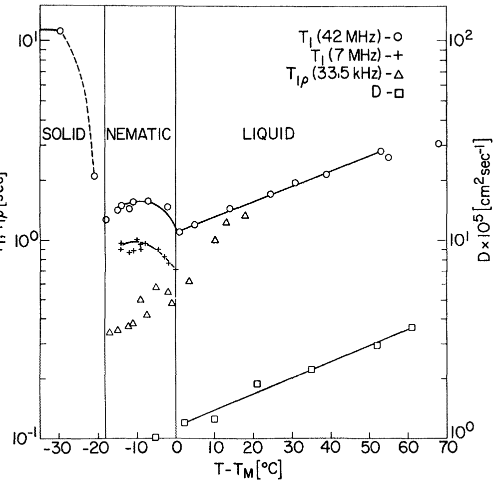

FIG. 1. Proton relaxation times T_1 and $T_{1\rho}$ and the self-diffusion coefficient D for PAA versus $T-T_M$.

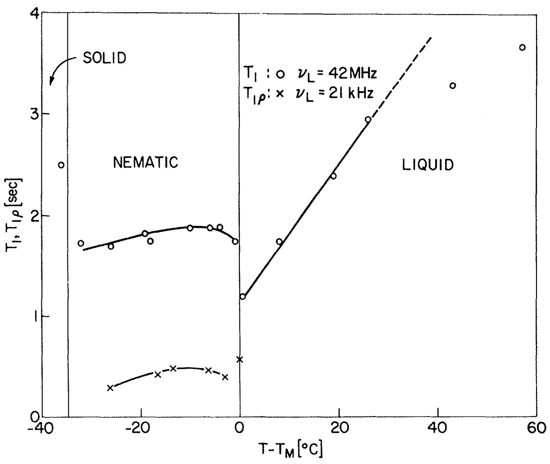

FIG. 2. Proton relaxation times T_1 and $T_{1\rho}$ vs $T-T_M$ for PAP.

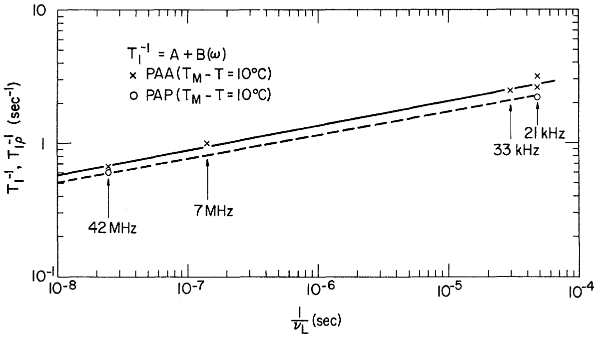

FIG. 3. T_1 and $T_{1\rho}$ vs $\nu_L{}^{-1} = 2\pi/\omega_0$ for PAA and PAP.

$\times \exp(-\Delta E/RT)$ with $\Delta E = 7.3$ kcal mole^{-1} and $D_0 = 7.7 \times 10^{-2}$ cm^2 sec^{-1} (Fig. 1). On account of the dipolar fine structure and short T_2 of the -CH_3 group protons it is difficult to measure D in the ordered regions, but its value appears to be quite different from D in the isotropic-liquidlike defect region at the same temperature.

In the isotropic liquid, T_1 is determined by translational diffusion except close to the melting point where the frequency dependence of T_1 suggests the presence of an additional contribution arising from the existence of nematic clusters.

The reorientation times for molecules within such clusters are determined by the rotational diffusion time of the cluster as a whole or by the lifetime of such a cluster, whichever is shorter. These correlation times have to be shorter than 10^{-4} sec in view of the disappearance of the nematic doublet fine structure in the isotropic liquid.

In contrast to PAA and PAP, NaSt exhibits a variety of solid-solid and mesomorphic phase changes.[9] The intramolecular dipolar interactions are here averaged out by rotations around the longitudinal hydrocarbon-chain axis and the relaxation rates should be at higher temperatures determined by the diffusion-modulated interchain interactions rather than by order fluctuations. Measurements of the proton-spin-lattice relaxation time and the self-diffusion coefficient in the high-temperature smectic "neat" phase (stable between 224 and 294°C) have indeed shown that T_1 is determined by translational diffusion. The self-diffusion coefficient parallel to H_0 is rather large (~10^{-6} cm^2/sec) and its temperature dependence is given by $D = D_0 \exp(-\Delta E/RT)$ with $D_0 = 2$ cm^2 sec^{-1} and $\Delta E = 14$ kcal mole.

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