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Thermal Fluctuations and Proton Spin-Lattice Relaxation in Nematic Liquid Crystals†

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Abstract—Measurements of the spin-lattice relaxation time T_1 in both nematic and isotropic phases of normal (PAA) and methyl-deuterated (PAA-CD_3) p-azoxyanisole are reported and discussed. For both materials, T_1 varies linearly with temperature in the isotropic phase, just above the transition. In order to explain this behaviour two processes are discussed: diffusion and thermal fluctuations in the local order parameter. It is shown crudely that diffusion, in this region, is to be expected as a " correlated " process. Recent measurements of D are criticized within this context, but no definite conclusion can be drawn. A simple theoretical approach of the fluctuations in the order parameter is proposed which accounts for the observed behaviour of $T_1(T)$. In the nematic phase of PAA-CD_3, T_1 does not depend on temperature. The frequency dependence is the same as for PAA. Our results show the relative importance of short range phenomena and allow us to question the meaningfulness of earlier discussions of experimental data on the unique basis of Pincus's formula.

1. Introduction

Recent developments on the continuum theory of liquid crystals have led to important studies of the thermal fluctuations in the orientational order of the molecules. It has been recognized that these fluctuations are very large for long wavelengths and therefore give rise to some important phenomena. Light scattering, for instance, is controlled by these fluctuations. We also expect that they contribute to the nuclear spin-lattice relaxation through the modulation of the dipole-dipole interaction of the spins located on one molecule. This is most strongly suggested by the fact that the

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calculated(1) spectrum of the fluctuations possesses a branch in the radio frequency region.

This contribution to the nuclear spin relaxation has been derived theoretically by Pincus(2) from the results of Ref. 1. Assuming that orientational and diffusive motions of the liquid crystal molecules are uncoupled, he starts with the following correlation function:

$$G(t) = (2\pi)^{-3} \int \mathrm{d}\mathbf{q} \left(\frac{k_B T}{K q^2}\right) e^{-(K/\eta) q^2 t}\, e^{-D q^2 t} \tag{1}$$

considering only the dipole-dipole interaction of a proton pair located on one molecule. His final result may be written:

$$T_1 \propto \frac{K}{TS} \left[\omega \left(D + \frac{K}{\eta}\right)\right]^{1/2}. \tag{2}$$

In these formulae K is some average of the Frank elastic constants,(3) S is the degree of order, η is some average of the viscosity coefficients appearing in the hydrodynamic theory of Leslie,(4) D is the diffusion constant and q is a fluctuation mode wavevector.

Expression (2) or an extension of it,(5) has been contrasted to some experimental data but conclusions of different authors do not agree very well.(5–8) The frequency dependence of the spin-lattice relaxation time T_1 given by (2) is found to be in good agreement with experiments, except at very low frequencies, where this formula cannot be valid because it gives infinitely high relaxation rates. On the contrary, the temperature dependence of T_1 predicted by the expression above does not at all follow the experimental data.(7–9)

We felt that discussion of the mentioned experimental results on the basis of expression (2) should not allow definitive conclusions on the validity of the theory. As already stated, the model used by Pincus considers only two spins located on the axis of the elongated molecule and it is the relaxation of this pair, arising from the modulation of the dipole-dipole interaction through thermal fluctuations of the director $\mathbf{n}(\mathbf{r})$, which is calculated. If we look at the *p*-azoxyanisole molecule it appears clearly that benzene ring protons satisfy rather well this model (cross interactions are here relatively weak) but protons of the methyl groups are in a very different situation. Furthermore, it is expected that the contribution of these protons to the overall (measured) relaxation time is rather important.

In order to test this argument and discuss more closely the validity of the theory, measurements of the proton spin-lattice relaxation time were performed with methyl-deuterated *p*-azoxyanisole (PAA-CD_3). The experimental results are presented here together with some new data on normal PAA. Both nematic and isotropic phases are considered.

2. Experimental

The measurements were made with a Brüker B-KR 321 s variable-frequency pulsed NMR spectrometer. The data were obtained by employing the 180°–90° pulse sequence method in the usual manner. For the measurements and stabilization of temperature a Brüker B-ST 100/700 apparatus has been used.

All samples of PAA used were highly purified by zone refining, degassed by repeated freezing and melting under vacuum and then sealed in evacuated ($p \lesssim 10^{-4}$ mm Hg) glass containers. The PAA-CD_3 was synthetized in our laboratory and purified by a double recrystallization from ethanol. Evacuated samples were then prepared as for PAA.

PAA-CD_3, which is PAA with the CH_3 groups replaced by CD_3, was prepared according to a known(10) two steps procedure used for synthetizing *p*-azoxyanisole. It consists essentially in the reduction of the corresponding nitroderivative. In the first step, deuterated nitroanisole was prepared according to the following scheme:

$$CD_3ONa + Cl(C_6H_4)NO_2 \rightarrow CD_3O(C_6H_4)NO_2 + NaCl$$

The CD_3ONa has been obtained from the reaction of pure sodium with CD_3OD. In the second step of the preparation, reduction of $CD_3O(C_6H_4)NO_2$ by sodium methylate was accomplished.

3. Results and Discussion: Nematic Phase

Our measurements of the nuclear spin-lattice relaxation time T_1 in the nematic phase of PAA agree rather well with those of Doane *et al.*,(7,9) already published, therefore they will not be reproduced here.

Figure 1 shows a part of our experimental data on T_1 in both nematic and isotropic phases of PAA-CD_3. This material has nearly the same macroscopic properties as PAA, namely, the same temperature range for the nematic phase. In the nematic phase of

PAA-CD_3 the T_1 values are lower than those found for PAA in the same conditions. The frequency dependence of T_1 is the same as before but there is no dependence on temperature (Fig. 1) within the experimental error.

These results show, first, the correctness of our feeling on the relative importance of the methyl protons' contribution to the relaxation. As a consequence, we can say that earlier discussions of experimental values of T_1 as a function of temperature on the basis of Pincus's formula are not meaningful. Second, the disagreement between predictions of (2) and experience remains, although it is not so striking as before.† But even in the present case, one might not have the right to compare directly theory and experimental results. Before doing that we must be sure that the spectral density $J(\omega)$ contains no contribution, at the nuclear Larmor frequency, coming from short or medium range phenomena. Rotation of methyl groups in PAA around their symmetry axes is one of these phenomena and we have seen how much it influences the character of the curve $T_1(T)$.

A better way to test Pincus's result (2) would be to carry out T_1 measurements at lower frequencies. But in choosing the frequency range of the experiments we have to remember that expression (2) predicts infinitely high relaxation rates when ω vanishes and this cannot be valid.

For many short range phenomena, the spectral density is constant up to frequencies of the order of the inverse of the characteristic time of the motion. This implies that at low enough frequencies these short range phenomena will contribute to the relaxation rate $T_1^{-1}(\omega)$ with a constant term. In fact, reported measurements on several

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† After this work was presented, it came to the author's attention a paper by Doane *et al.*, *Chem. Phys. Lett.* **6**, 291 (1970), which slightly modifies Pincus's expression (2): in place of S one must put S^2. This modification seems to give qualitative agreement with the data in fig. 1. A rigorous comparison between theory and experimental results cannot be made until the functions $D(T)$, $K(T)$ and $\eta(T)$ be known exactly. Note that $K(T)$ is some average of the Frank coefficients $K_{ii}(i = 1,2,3)$ and $\eta(T)$ is an orientational average of the Leslie viscosity coefficients. Another paper by T. C. Lubensky, *Phys. Rev.* **A2**, 2497 (1970), gives by a somewhat different technique, $1/T_1 \sim \omega_D^2 t_c + 1/T_1'$ where $\omega_D^2 t_c$ is the corrected Pincus's result and $1/T_1'$ represents fluctuations in the magnitude of S and short distance variations in the direction of preferred order.

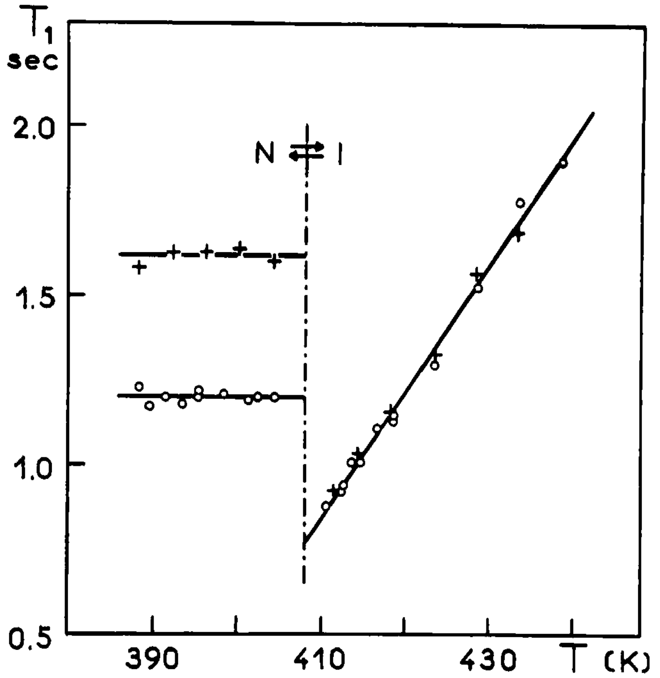

Figure 1. Temperature dependence of the proton spin-lattice relaxation time in PAA-CD_3; data for two frequencies: ○, 24 MHz; +, 56 MHz. The straight line $T_1(T)$ referring to the isotropic phase (I) fits the data for 24 MHz; the other points are simply superimposed.

nematic liquid crystals show that $T_1^{-1} \sim A + B(\omega)$. But we cannot assign a definite meaning to the constant A until a correction to the Pincus's formula is introduced in order to allow realistic predictions for vanishing frequencies. Our work is at present oriented towards the solution of these problems. In particular, we should like to know whether diffusion is the dominant process contributing to the values of T_1 found for PAA-CD_3. This is strongly suggested when the results in Fig. 1 are contrasted with recent measurements of D published by Blinc *et al.*,(11) at least if the measured diffusion coefficients really refer to the translational motion of the molecules. The same type of measurements performed with PAA-CD_3 would allow one to stress or discard this interpretation.

4. Results and Discussion: Isotropic Phase

Let us consider first the case of PAA-CD_3. As shown in Fig. 1, in the region just above the nematic-isotropic transition T_1 depends on temperature according to the following expression:

$$T_1 \sim T_1^* + \alpha \Theta \tag{3}$$

where T_1^* and α are constants and Θ is some temperature. Our experiments prove that for PAA-CD_3 T_1^* and α do not depend on the frequency (within the 10–60 MHz range studied).

Two kinds of phenomena can in principle be expected to contribute to relaxation in the isotropic phase, just above the transition. One is self-diffusion and the other is the fluctuation in some parameter characterizing the strong local order of the fluid in this region of temperature.

Very few measurements of the self-diffusion coefficient D have been published(5,11) and it has been argued that D behaves as in normal liquids, i.e.

$$D = D_0 \exp(-\Delta E/kT) \tag{4}$$

This is to be expected far enough above the transition but is very questionable if the region just above T_c is considered. In this region, which has a 20–30 degrees temperature range, many experimental results suggest the existence of a very strong short range molecular order. This means that inside a region of linear dimensions ξ motions of different molecules are strongly correlated (ξ is the correlation length). In a rather crude approximation, we can expect that under the influence of a driving force F the molecules move together with a mean velocity v so that the mobility $\mu = D/kT = v/F$ is given by $\mu \sim 1/\eta\xi$ (Stokes). It follows that $D\eta \sim \xi^{-1}$ and we expect diffusion to be a " correlated " process.

In this case expression (4) is not applicable just above the nematic-isotropic transition. A close examination of the published(5,11) experimental values of D shows that extrapolation into this region of the high temperature behavior may be inadequate. Unfortunately, the number of published experimental points up to 30 degrees above T_c is very few and their dispersion too great so that no definite conclusion can be drawn on this point.

If expression (4) was valid and nuclear relaxation was essentially due to diffusion, then our empirical formula (3) would be in fault. On the other hand, we have not yet a model for " correlated " diffusion detailed enough to allow a comparison between theory and our experimental results. For this reason we turn now to the analysis of the second process mentioned above which is also expected to contribute to relaxation.

Fluctuations in the local order referred to above are believed to be the fundamental cause of many special phenomena which appear just above the transition temperature T_c. We shall consider that the interaction responsible for spin-lattice relaxation is modulated by these fluctuations. The relevant correlation function is boldly assumed to be of the form:

$$G(t) = (2\pi)^{-3} \int \mathrm{d}\mathbf{q} G(q, 0) \exp(-t/\tau) \tag{5}$$

where $G(q, 0)$, is the mean square fluctuation of the q-mode and the integral is extended over a region of dimension ξ^{-1} (ξ is the correlation length). $G(q, 0)$ is calculated from the free energy density in the usual manner.(12) As stated by De Gennes(13) the free energy density $g(\mathbf{r})$, in the isotropic phase, near T_c, may be written as a power series expansion in some appropriate order parameter $Q(\mathbf{r})$

$$\begin{aligned} g(\mathbf{r}) &= g_0 + aQ(\mathbf{r})^2 + bQ(\mathbf{r})^3 + \cdots \\ &\quad + c[\nabla Q(\mathbf{r})]^2 \end{aligned} \tag{6}$$

where g_0 is independent of Q. We are disregarding a term imposed by the external field always present in our NMR experiments.

In the following discussion we neglect all terms of order higher than two, in the expression (6), although the term of order Q^3 has in this case a precise meaning: it states the fact that nematic-isotropic transition is first order. Further, we suppose that the contribution to fluctuations of the two remaining terms (i.e. those other than g_0) are comparable in magnitude. This enables us to follow the Landau treatment of the second order phase transitions. Then, starting from Eq. (6), taking the Fourier components and using the equipartition theorem, the thermal amplitude of the fluctuations in the order parameter is readily seen to be

$$\begin{aligned} G(q, 0) &= \frac{k_B T}{2(a + cq^2)} \\ &= \frac{k_B T}{2c} \cdot \frac{1}{q^2 + \xi^{-2}} \quad (q \ll \xi^{-1}). \end{aligned} \tag{7}$$

By substitution of (7) in (5) and integration one obtains readily the explicit form of the correlation function.

Now, as $1/T_1 \propto J(\omega)$, in order to get T_1 we have to calculate the component $J(\omega)$ at the nuclear Larmor frequency of the Fourier transform of the correlation function (5). We obtain:

$$J(\omega) \simeq \frac{1}{6\pi^2}\frac{k_B T}{c}\tau\xi^{-1} \tag{8}$$

if $q^2\xi^2 \ll 1$ and $\omega < 1/\tau$ as expected in the present case.

From a simple (assumed) transport equation[13,14] one obtains $\tau = 1/\Gamma a$ where Γ is a transport coefficient (dimensionally it is the inverse of a viscosity). Equation (7) shows that $\xi^2 = c/a$ and within the framework of the Landau theory we expect[15]

$$\begin{aligned} &a \sim \Theta^{r} \\ &c \sim \Theta^{r-2v} \end{aligned} \tag{9}$$

with $\Theta = T - T^*$. This temperature T^* must be slightly below the first order transition temperature T_c.[13,16] From (8) and (9) we find

$$T_1 \propto \frac{1}{T}\left(\frac{1}{\tau}\right)\Theta^{r-3v} \tag{10}$$

This result is to be contrasted with experimental data. First we note that this theory does not give the constant term T_1^* appearing in the empirical relation (3). Disregarding this, we may put $1/T \simeq 1/T_c$ and $1/\tau \sim \Theta^{4/3}$ according to recent light scattering measurements of Litster *et al.*[17] for MBBA (*p*-methoxybenzylidene-*p*-*n*-butylaniline) whose structure is rather similar to that of PAA. Then, if (10) is to agree with results in Fig. 1, one must write

$$\gamma - 3\nu + 4/3 \simeq 1$$

A possible solution of this equation is given by $\nu = \frac{1}{2}$ and $\gamma \simeq 1.17$, in rather good agreement with the expected values.

These results do not exclude the possibility of some contribution of the self-diffusion to the relaxation. Further work is needed before the complete solution of this problem is to be given.

Let us finally return to the case of normal PAA. Figures 2 and 3 show the results of our measurements in the isotropic phase of this material.

In this case the temperature dependence of T_1 (Fig. 2) is still given

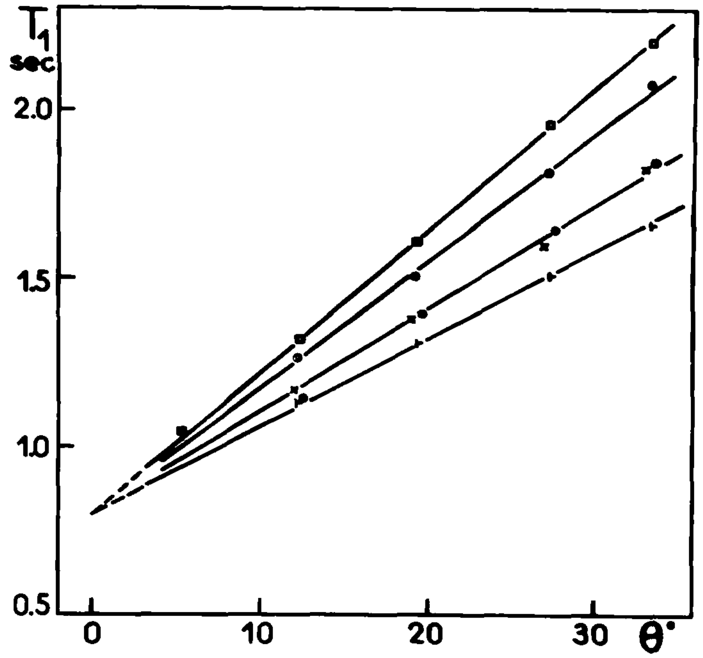

Figure 2. Temperature dependence of the proton spin-lattice relaxation time in the isotropic phase of PAA. Very pure samples: ○, 12 MHz; □, 36 MHz. Thermal degraded sample (after several tens of hours of usage): ●, 12 MHz; ×, 48 MHz; ⊢, 60 MHz. The value $T_c - T^*$ has not been measured in these experiments.

by expression (3) but the coefficient α is now frequency dependent. Thus T_1 depends on the frequency in the peculiar manner shown by Fig. 3 and varies linearly with temperature $\Theta = T - T^*$, all lines diverging from the point (T^*, T_1^*). The observed frequency dependence of T_1 must be attributed to the motion of methyl protons. However, the form of the curves $T_1(\omega)$ is not yet fully understood.

Thermal degradation, even in highly purified materials, is generally observed when liquid crystals are used for a long time especially in the isotropic phase. We have shown (Fig. 2) that this degradation only affects the coefficient $\alpha(\omega)$ by a factor independent of frequency. This factor essentially gives the thermal history of the sample.

5. Concluding Remarks

Considerable progress has been achieved in this two year period

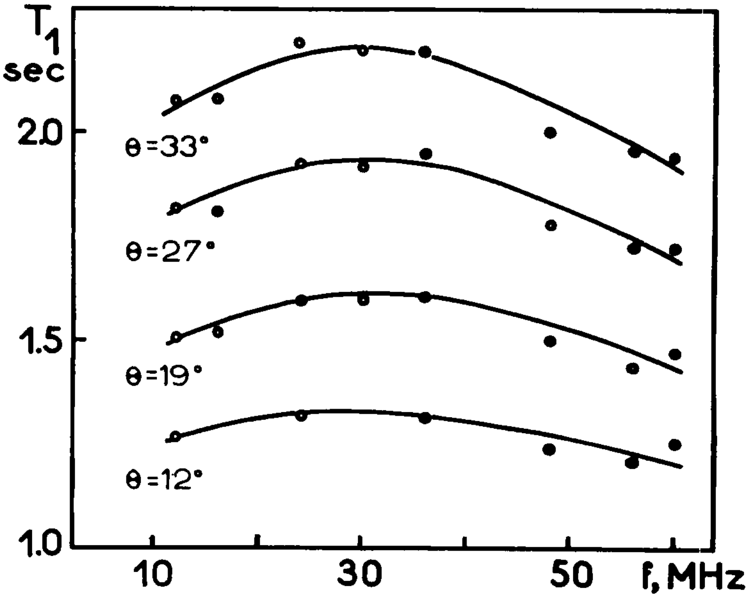

Figure 3. Frequency dependence of the proton spin-lattice relaxation time in the isotropic phase of PAA.

of research in understanding the mechanisms of the nuclear magnetic relaxation in liquid crystals. However, the essential problems are still to be resolved. The theoretical approaches of De Gennes and Pincus are simple approximations and we dont know yet the exact experimental conditions for their validity. The relative importance of long range fluctuations and short range phenomena is not fully established within the frequency range of the usual NMR experiments. A more recent problem concerns the nature of the self-diffusion process. A diffusion coefficient *D* independent of temperature (process with no activation energy) has been measured for the nematic phases of PAA and anisalazin,(11) but the precise meaning of this is not clear.

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