

Rev. Lett. 26, 1616 (1971).

<sup>5</sup>E. Valeo, C. Oberman, and F. W. Perkins, Phys. Rev. Lett. 28, 340 (1972); D. F. DuBois and M. V. Goldman, Phys. Rev. Lett. 28, 218 (1972).

<sup>6</sup>N. Rynn, Rev. Sci. Instrum. 35, 40 (1964).

<sup>7</sup>E. L. Gonztou, *Microwave Measurements* (McGraw-Hill, New York, 1957), p. 404.

<sup>8</sup>The measured temperature increase due to classical heating is small and does not affect classical power losses appreciably.

<sup>9</sup>F. W. Perkins and J. Flick, Phys. Fluids 14, 2012 (1971).

<sup>10</sup>J. M. Dawson and C. Oberman, Phys. Fluids 5, 517 (1962), and 6, 394 (1963).

## Dynamical Behavior of a Nematic Liquid Crystal just above the Nematic-Isotropic Transition from Spin-Lattice Relaxation

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We report here the proton spin-lattice relaxation time  $(T_1)_{CF}$  measured in *p*-methoxybenzylidene *p*-*n* butylaniline at two frequencies in a temperature range of about 25°C just above the nematic-isotropic transition. We have determined the correlation time for critical fluctuations,  $\tau_{CF}$ , using a simple extension of the Bloembergen-Purcell-Pound theory which relates  $\tau_{CF}$  and  $(T_1)_{CF}$ . The temperature dependence  $\tau_{CF}$  is in good agreement with the de Gennes theory and with experimental results of Stinson and Litster.

The dynamical behavior of a nematic liquid crystal just above the nematic-isotropic transition temperature  $T_c$  is of great interest from both experimental and theoretical standpoints. Experimental studies show clearly that this is a weak first-order transition<sup>1</sup> (low latent heat) while both the static and dynamical behaviors of the isotropic phase close to  $T_c$  demonstrate characteristics of a second-order transition<sup>2</sup> having a critical temperature  $T^* < T_c$ ;  $T^*$  is usually within 1°C of  $T_c$ . This behavior strongly suggests that this phase would be about to undergo a second-order transition at  $T^*$  with the lowering of temperature unless it were intercepted by a first-order transition at  $T_c$ . As a result, many characteristics of the low-temperature phase persist above  $T_c$ , although to a lesser extent, just as in a magnetic transition.<sup>3</sup> For example, the long-range order characteristic of the nematic phase persists no longer above  $T_c$  but the short-range order does. Suggestions of the existence of this short-range order were made earlier by Blinc *et al.*<sup>4</sup> and by Weger and Cabane.<sup>5</sup> Litster and Stinson<sup>6</sup> and, more recently, Chu, Bak, and Lin<sup>7</sup> have demonstrated the short-range-order effects in a nematic system very convincingly. Theories<sup>2,8,9</sup> based on Landau's theory of second-order transitions<sup>10</sup> have been very successful in explaining these re-

sults.

We report in this Letter studies on the dynamical behavior of the nematic liquid crystal *p*-methoxybenzylidene *p*-*n* butylaniline (MBBA) in the isotropic phase close to  $T_c$  from proton spin-lattice relaxation. Our results are in good agreement with the Landau-de Gennes theory<sup>2,8</sup> and with experimental results of Stinson and Litster,<sup>6</sup> obtained by a light-scattering technique. Attempts were made earlier, with limited success, to correlate the dynamical behavior and the nuclear relaxation time  $T_1$  or  $T_2$  (or linewidth).<sup>4,11</sup> The main problem of such a correlation is to determine the true contribution of critical fluctuations characteristic of dynamical behavior to the total spin relaxation time  $T_1$  or  $T_2$  which is measured experimentally. Since even in the nematic phase many aspects of molecular dynamics are close to those of an isotropic liquid, such as rotation about the molecular axis and random translational motion of the centers of gravity of molecules, it is expected that the experimental  $T_1$  should not be solely due to critical fluctuations, but rather should have two contributions in general. As a result, we can write

$$(1/T_1)_{\text{expt}} = (1/T_1)_{CF} + (1/T_1)_0, \quad (1)$$

where the subscripts CF and 0 denote, respec-

tively, contributions to the experimental  $1/T_1$  from critical fluctuations and other sources expected to be present. A similar separation is also possible for  $T_2$ . Neither of the above two contributions may be negligible in comparison with the other in the neighborhood of  $T_c$ ; but it can be safely assumed that  $(1/T_1)_{CF} \ll (1/T_1)_0$  both at  $T = T^*$  and at some  $T \equiv T_0 > T_c$ .  $T_0$  must be determined experimentally and is expected to be 20 to 30°C above  $T_c$ . As we shall see later, it is convenient to determine  $(1/T_1)_0$  at  $T^*$ . A reliable value of  $(1/T_1)_0$  at  $T^*$  can be obtained by extrapolating the plot of  $(1/T_1)_{\text{expt}}$  versus  $T$  made from close measurements just above  $T_c$ . Then, with a reasonable assumption on the  $T$  dependence of  $(1/T_1)_0$ ,  $(1/T_1)_{CF}$  versus  $T$  can be determined using Eq. (1). Extending the Bloembergen-Purcell-Pound (BPP) theory,<sup>12,13</sup> we show below that  $(1/T_1)_{CF}$  is given by Eq. (4), according to which  $(1/T_1)_{CF}$  is maximum for  $\omega\tau_{CF} \approx 0.62$ , where  $\tau_{CF}$  is the correlation time of critical fluctuations and  $\omega$  is the operating angular frequency. Hence the separation of  $(1/T_1)_{CF}$  from  $(1/T_1)_{\text{expt}}$  becomes unambiguous if  $(1/T_1)_{CF}$  shows a maximum.

According to the theory<sup>2</sup> of the dynamical behavior, any traceless second-rank tensor quantity can describe the short-range order and its fluctuations. The dipole interaction is such a tensor, which is most convenient for our purpose since proton relaxation is expected to be of dipolar origin. Then, following the BPP theory,<sup>13</sup> we can write

$$\langle F^{m*}(t)F^m(0) \rangle = \langle |F^m(0)|^2 \rangle \exp(-|t|/\tau_{CF}), \quad (2)$$

where the  $F^m$  are dipole-interaction tensor components in spherical harmonics; the components  $m = \pm 1$  and  $\pm 2$  contribute to  $T_1$ , while in  $T_2$  an additional contribution comes from the component  $m = 0$ . Equation (2) follows also from the de Gennes theory<sup>2</sup> which further states

$$\tau_{CF} = \tau_{CF}^0 \exp(W/T)/(T - T^*)^\gamma, \quad (3)$$

where  $W$  is activation energy of viscosity or molecular self-diffusion, and  $\gamma$  is an unknown parameter to be determined experimentally. In the mean-field theory such as that of Maier and Saupe,<sup>14</sup>  $\gamma = 1$ . We then get<sup>13</sup>

$$\left(\frac{1}{T_1}\right)_{CF} = C \left( \frac{\tau_{CF}}{1 + \omega^2\tau_{CF}^2} + \frac{4\tau_{CF}}{1 + 4\omega^2\tau_{CF}^2} \right), \quad (4)$$

where  $C$  is a constant, independent of  $T$ , involving dipole-interaction parameters.

To determine  $(1/T_1)_{CF}$  from  $(1/T_1)_{\text{expt}}$ , we measured  $T_1$  for protons in MBBA at close  $T$  inter-

vals in a range of about 25°C above  $T_c$  ( $\approx 43^\circ\text{C}$ ) using the three-pulse null methods<sup>15</sup> at two radio frequencies, 14 and 60 MHz. The null point was determined by observing the echo signal with a homodyning rf background to maintain linearity. Further improvement was achieved using least-squares fits with a linear relation for echo amplitudes versus time, by means of a desk computer. Such a linear relation was found to be pretty good for echoes around the null point as shown by the correlation coefficient (usually much better than 0.99) of the least-squares fits. At least two to three points on each side of the null point giving the best least-squares fits were used. Errors in such fits were within 1 to 2%. Data points shown in Fig. 1 are averages of six measurements, three for sample temperatures varying from low to high, and three from high to low; the error bar included in the figure shows a typical error of such averages. Since we are interested here in absolute values of  $T_1$ , a few checks were made to ensure the correct  $180^\circ$  adjustment for the first pulse by measuring  $T_1$  with the three-pulse growth method.<sup>15</sup> Agreement between the two methods was good within experimental error, suggesting that the  $180^\circ$  adjustment was acceptable, and no correction factor was introduced. The temperature gradient over the sample volume was better than  $0.25^\circ\text{C}$  which was the limit of our measuring equipment.

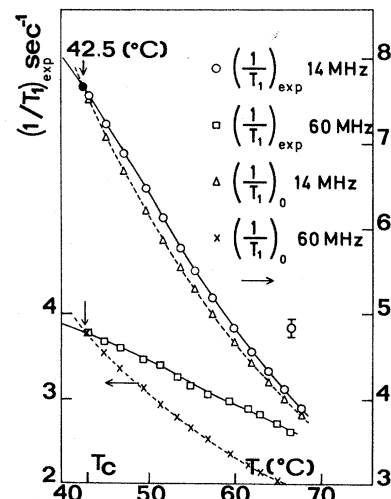


FIG. 1.  $(1/T_1)_{\text{expt}}$  versus  $T$  for protons in MBBA. Both 14- and 60-MHz data are shown. The left ordinate is for 60-MHz data and the right one for 14-MHz data. The dashed lines show computed curves obtained using Eq. (5) for best  $T^*$  (marked). The points indicated on the dashed lines, corresponding to experimental points, were used to compute  $(1/T_1)_{CF}$  following Eq. (1) (see text for details).

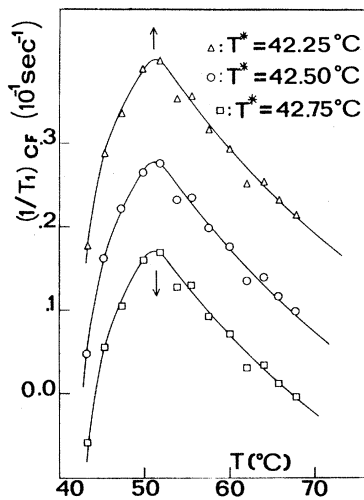


FIG. 2.  $(1/T_1)_{CF}$  versus  $T$  for various choices of  $T^*$  as obtained from 14-MHz measurements. Vertical scales for the two extreme lines are shifted as shown by arrows, each by one division.

First, let us consider our 14-MHz data as shown in Fig. 1.  $(1/T_1)_0$  at  $T^*$  is determined by extrapolating the curve of  $(1/T_1)_{\text{expt}}$  versus  $T$  since, as we have discussed earlier,  $(1/T_1)_0 = (1/T_1)_{\text{expt}}$  at  $T = T^*$  can be found from other sources<sup>5</sup> but, as will be discussed below, we can determine it independently.

We have assumed here the  $T$  dependence of  $(1/T_1)_0$  to be

$$(1/T_1)_0 = K \exp(W/T), \quad (5)$$

where  $K$  is a constant independent of  $T$ , and  $W$  is the activation energy of molecular self-diffusion. Such a relation follows from the BPP theory<sup>13</sup> when the relaxation process is governed by diffusion effects, as in a simple liquid, and when  $\omega\tau \ll 1$ , where  $\tau$  is the correlation time for this process and is  $\propto 1/D$  ( $D$  is the coefficient of molecular self-diffusion). We have also measured  $D$  by the spin-echo technique in the same temperature range of  $T_1$ , yielding  $D = D_0 \exp(-W/T)$ , with  $W = (3.00 \pm 0.01) \times 10^3 \text{°K}$ . With this value of  $W$  and units  $(1/T_1)_0$  at  $T^*$  as described earlier,  $K$  was determined.

Then, using Eqs. (5) and (1), we determine  $(1/T_1)_{CF}$  as a function of  $T$ , which shows a clear maximum (at 51°C) as is expected from Eq. (4). The maximum does not shift in  $T$  with reasonable choices of  $T^*$ . We have tried different  $T^*$  starting from 39°C to 42.75°C at intervals of 0.25°C without noticing any appreciable shift of the maximum. Three such choices of  $T^*$  are shown in

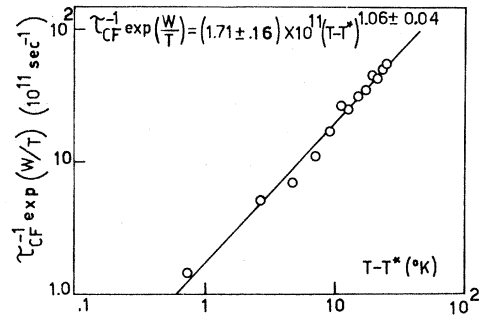


FIG. 3. Log-log plot of  $\tau_{CF}^{-1} \exp(W/T)$  versus  $T - T^*$  with  $T^* = 42.5^\circ\text{C}$  and  $W = 3.0 \times 10^3 \text{°K}$  for 14-MHz measurements. Solid line, least-squares fit using the relation  $\tau_{CF}^{-1} \exp(W/T) = (\tau_{CF}^0)^{-1} (T - T^*)^\gamma$ , which follows from Eq. (3).

Fig. 2. Using  $\omega\tau_{CF} = 0.62$ , we compute  $\tau_{CF}$  at 51°C. Then, using  $(1/T_1)_{CF}$  as determined above and Eq. (4),  $\tau_{CF}$  at other temperatures can be obtained unambiguously.  $\tau_{CF}$  values thus determined for various choices of  $T^*$  have been fitted with Eq. (3) by the method of least squares. The best fits are obtained for  $T^* = 42.5^\circ\text{C}$  with  $\gamma = 1.06 \pm 0.04$ , and the results are shown in Fig. 3.

To have an additional check on our observations, we measured  $T_1$  at 60 MHz, another frequency available with our spectrometer. Experimental results are shown in Fig. 1. From these data,  $(1/T_1)_{CF}$  was determined as a function of  $T$  following the procedure described already with  $T^* = 42.5^\circ\text{C}$  obtained from the 14-MHz data. No maximum was observed for  $(1/T_1)_{CF}$  versus  $T$  in the range of our study, as is expected. Even then, an independent set of  $\tau_{CF}$  versus  $T$  could be obtained from these data using one point coincident with Eq. (4); the coincidence was made unambiguous using  $\tau_{CF}$  for this point determined from 14-MHz data. The least-squares fits of this set of  $\tau_{CF}$  with Eq. (3) yield  $\gamma = 0.97 \pm 0.06$ , in good agreement with the 14-MHz data and suggesting the essential correctness of our approach.

Values of  $(1/T_1)_{CF}$  determined at two frequencies suggest that the factor  $C$  in Eq. (4) is frequency dependent. This frequency dependence is of opposite nature to that observed for  $(1/T_1)_0$ . Neither of these frequency dependences is yet understood properly. Limitations in applying the BPP theory to details were also noticed earlier, even for simple liquids, but the general features are right.<sup>13</sup> In view of this fact, the general agreement of our experiment and a simple extension of the BPP theory seems good. It is particularly gratifying to note the good agreement be-

tween the  $\tau_{CF}$  determined by us and those by Stinson and Litster, not only in their  $T$  dependence but also in their magnitudes (our values are about a factor of 2 shorter).

In conclusion, we would like to point out that assuming the experimental  $T_1$  or  $T_2$  to be totally due to critical fluctuations, as has been done by Cabane and Clark<sup>11</sup> for *p*-azoxyanisole (PAA), may not be completely justified even for N<sup>14</sup> resonance for reasons noted earlier. The omission of other sources of  $T_2$  may be the reason for missing the  $T$ -dependent exponential part of  $\tau_{CF}$  ( $\tau$  in their notation). In fact, some doubt has also been expressed by Dong, Forbes, and Pintar<sup>16</sup> in a recent study on the same system. Our preliminary study on PAA shows that  $(1/T_1)_0$  for protons is more complex than that observed in MBBA, and studies are under way to understand the sources. It is to be noted that although our sample is not very pure ( $T_c \approx 43^\circ\text{C}$ ), we expect that impurities do not have appreciable effect on our observations except on enhancing the  $(1/T_1)_0$  part of Eq. (1). In fact, it has been shown earlier<sup>6,17</sup> that  $\tau_{CF}$  does not depend sensitively on impurities. Purer samples will improve the determination of the  $(1/T_1)_{CF}$  from  $(1/T_1)_{\text{expt}}$ .

Finally, we would like to point out the important advantage of using proton resonance in the type of studies reported here. As we have noted earlier, the main problem here is to determine  $(1/T_1)_{CF}$  from  $(1/T_1)_{\text{expt}}$  unambiguously. Such an unambiguous determination is possible when  $(1/T_1)_{CF}$  shows a maximum as expected from Eq. (4). For this purpose, it is essential to vary the experimental frequency, which can be done con-

veniently with proton resonance.

<sup>1</sup>I. G. Chistyakov, Usp. Fiz. Nauk **89**, 563 (1966) [Sov. Phys. Usp. **9**, 551 (1967)].

<sup>2</sup>P. G. de Gennes, Mol. Cryst. Liquid Cryst. **12**, 193 (1971).

<sup>3</sup>H. E. Stanley, *Introduction to Phase Transition and Critical Phenomena* (Clarendon, Oxford, England, 1971), Chap. 1.

<sup>4</sup>R. Blinc, D. E. O'Reilly, E. M. Peterson, J. Lahajnar, and I. Levstek, Solid State Commun. **6**, 839 (1968); R. Blinc, D. L. Hogenboom, D. E. O'Reilly, and E. M. Peterson, Phys. Rev. Lett. **23**, 969 (1969).

<sup>5</sup>M. Weger and B. Cabane, J. Phys. (Paris) **30**, C4 (1969).

<sup>6</sup>J. D. Litster and T. W. Stinson, J. Appl. Phys. **41**, 996 (1970); T. W. Stinson and J. D. Litster, Phys. Rev. Lett. **25**, 503 (1970).

<sup>7</sup>B. Chu, C. S. Bak, and F. L. Lin, Phys. Rev. Lett. **28**, 1111 (1972).

<sup>8</sup>P. G. de Gennes, Phys. Lett. **30A**, 454 (1969).

<sup>9</sup>C. Fan and M. J. Stephen, Phys. Rev. Lett. **25**, 500 (1970).

<sup>10</sup>L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, England, 1969), Chap. XIV.

<sup>11</sup>B. Cabane and W. G. Clark, Phys. Rev. Lett. **25**, 91 (1970).

<sup>12</sup>N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

<sup>13</sup>A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, England, 1961), Chap. VIII.

<sup>14</sup>W. Maier and A. Saupe, Z. Naturforsch. **15a**, 287 (1960).

<sup>15</sup>T. Ghose, S. K. Ghosh, and D. K. Ray, Nuovo Cimento **5**, 1771 (1957).

<sup>16</sup>R. Y. Dong, W. F. Forbes, and M. M. Pintar, J. Chem. Phys. **55**, 145 (1971).

<sup>17</sup>J. D. Litster, private communication.