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PRETRANSITIONAL PHENOMENA IN THE ISOTROPIC PHASE OF A NEMATIC LIQUID CRYSTAL*

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(Received 7 July 1970)

We have observed a divergence of the magnetic birefringence, and a critical increase and slowing of the fluctuations in order in the isotropic phase of a nematic liquid crystal. Our results are quantitatively described by a mean-field model except for a critical region close to the ordering temperature where the fluctuations are so large that the mean-field approximation fails.

In this Letter we report the results of an experimental study of pretransitional phenomena in the isotropic phase of the nematic liquid crystal *p*-methoxy benzylidene *p*-*n*-butylaniline (MBBA).[1] As the temperature of a liquid crystal is lowered there is a phase change from an isotropic liquid state to a state (also liquid) with long-range orientational order of the molecules. In the ordered phase of a nematic liquid the centers of mass of the molecules remain as randomly distributed as in the isotropic phase, and the molecules align with their long axes parallel. The anisotropy of the molecules in a nematic material is uniaxial; the electric polarizability is usually greater parallel to the long axis of the molecule.[2] The degree of order may therefore be determined by measuring the anisotropy of the dielectric constant, and optical methods are ideal for this purpose. The diamagnetic susceptibility is also usually greater along the axis of the molecule and it is possible to align molecules in the isotropic phase with a magnetic field. The magnetically induced birefringence (Cotton-Mouton effect) then is proportional to the alignment produced. In addition, from the intensity and spectrum of scattered light one may obtain the mean squared amplitude and time dependence of fluctuations in the order.

In the isotropic phase of MBBA we have accurately measured the magnetic birefringence as a function of temperature. We have also measured the intensity and spectrum of light scattered by anisotropic fluctuations in the dielectric constant. We observed a divergence of the Cotton-Mouton coefficient, and a divergence and critical slowing of the fluctuations in order as the phase transition was approached. This behavior is similar to that of materials in the vicinity of a critical point.[3] Although the nematic-isotropic transition is first order[2] (as shown by a latent heat and volume discontinuity), our measurements demonstrate that over a wide temperature range the liquid crystal behaves as if it were going to undergo a second-order phase transition at a critical point.

We provide a theoretical interpretation of our data using a phenomenological model due to Landau[4] and its extension by de Gennes[5] to describe dynamical behavior. We find that this mean-field model adequately describes the behavior over most of the temperature range, but that close to the phase transition there is a critical region where the mean-field approximation fails.

We now discuss our experimental results using the Landau model. We take the ordered nematic liquid crystal as optically uniaxial and so it is necessary to specify only the birefringence and the direction of the optic axis. Except for gradient terms (which we shall see later are negligible) the free energy is independent of the orientation of the optic axis. Therefore for purposes of the Landau model we may specify an order parameter[6] $Q=\frac{3}{2}\langle\cos^2\theta-\frac{1}{3}\rangle$, where θ is the angle between the long axis of a molecule and the local optic axis. For a completely aligned material ($Q=1$) let ϵ_p and ϵ_t be the dielectric constants parallel and transverse to the optic axis. Then the Cartesian dielectric tensor is $\epsilon_{\alpha\beta}=\bar{\epsilon}\delta_{\alpha\beta}$

$+Q(\frac{1}{3}\Delta\epsilon)(3n_\alpha n_\beta-\delta_{\alpha\beta})$, where n_α, n_β are the Cartesian components of a unit vector parallel to the optic axis, $\bar{\epsilon}=\frac{1}{3}(2\epsilon_t+\epsilon_p)$, and $\Delta\epsilon=\epsilon_p-\epsilon_t$. Following Landau, we write the free-energy density in the vicinity of the phase transition as

$$\Phi=\Phi_0+\tfrac{1}{2}AQ^2-\tfrac{1}{3}BQ^3+\tfrac{1}{4}CQ^4-\tfrac{1}{3}\Delta\chi H^2Q+\cdots. \quad (1)$$

In the model the coefficient of the quadratic term is taken to be $A=a(T-T_c^*)$. The anisotropy in the diamagnetic susceptibility is $\Delta\chi=\chi_p-\chi_t$. Minimizing the free energy with respect to Q gives the equation of state,

$$AQ-BQ^2+CQ^3-\tfrac{1}{3}\Delta\chi H^2=0. \quad (2)$$

Identical results may be obtained from the Maier-Saupe mean-field theory of nematic liquid crystals.[6]

The equilibrium value of Q is the root of Eq. (2) corresponding to the lower minimum of the free energy. If the coefficient B were zero the system would have a second-order transition to an ordered phase at $T=T_c^*$. The cubic term in Eq. (1) means that in zero field a first-order transition to a state of finite Q will occur at $T_K=T_c^*+2B^2/9aC$. The discontinuity in order parameter at T_K is $Q_K=2B/3C$, and the latent heat is $\frac{1}{2}T_KQ_K^2$.

We now analyze our birefringence measurements to establish all of the parameters in the free-energy expression, Eq. (1), and then proceed to check the consistency of the model by comparing its predictions with our measurements of the intensity and spectrum of the scattered light. This represents the first quantitative application of the mean-field model to interpret experimental measurements in the isotropic phase of a liquid crystal.

The order produced by a magnetic field in the isotropic phase ($T>T_K$) may be calculated to a first approximation from Eq. (2) as $Q=\Delta\chi H^2/3A$. The magnetic field determines the optic axis, and the magnetically induced birefringence (for $Q\ll 1$) is

$$\Delta n=(\epsilon_{zz})^{1/2}-(\epsilon_{xx})^{1/2}$$
$$=\Delta\epsilon\Delta\chi H^2/6(\bar{\epsilon})^{1/2}a(T-T_c^*). \quad (3)$$

In Fig. 1 we present our measured values of $H^2/\Delta n$; the temperature dependence over most of the range is clearly linear in agreement with Eq. (3). [The transition temperature T_K often varies from sample to sample of liquid crystal. This is probably caused by impurities resulting from hydrolysis of the MBBA into its amine and aldehyde constituents. Data are shown for two samples; it is apparent that the behavior is identical except for a shift in temperature scale. Although T_c^* shows considerable variation from sample to sample, the other coefficients in Eq. (1) remain constant within the sensitivity of our measurements.] From the slope of the plots (45×10^{12} G^2/°K) we may estimate the coefficient a. For MBBA[7] $\bar{\epsilon}=2.605$, Δn at T_K is 0.133, and $\Delta\chi=1.25\times10^{-7}$ erg G^{-2} cm^{-3}. Taking $Q_K=0.40$[6] we estimate $\Delta\epsilon=1.09$ and $a=0.062$ J cm^{-3} °K^{-1}. This gives a latent heat of 1.6 J cm^{-3}, which compares favorably with the value 1.5 J cm^{-3} measured for MBBA.[7] Extrapolation of the solid lines in Fig. 1 gives T_c^* for each sample; we also measured T_K for each and find $T_K-T_c^*=1.0$°K for both samples. From these results and the relations given earlier (with $Q_K=0.40$) we estimate $B=0.47$ J cm^{-3} and $C=0.79$ J cm^{-3}.

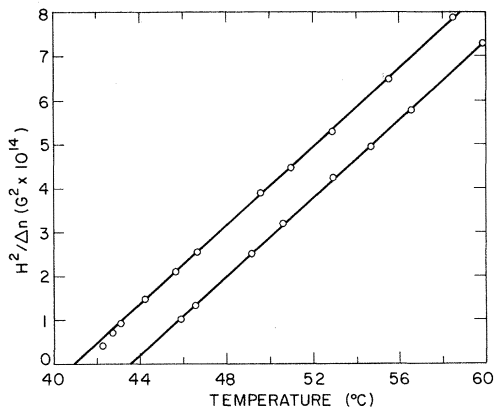

FIG. 1. The reciprocal of the Cotton-Mouton coefficient is shown as a function of temperature for two samples of MBBA. The solid lines are a fit to the mean-field result of Eq. (3).

Our measured temperature dependence of the intensity of light scattered by fluctuations in the order parameter in the isotropic phase is shown in Fig. 2. If $\vec{k}$ is the wave vector of the incident light, then the light is scattered through an angle θ by a Fourier component of the fluctuations in the dielectric constant whose wave vector is $q=2k\sin\frac{1}{2}\theta$. The intensity of scattered light which is polarized parallel to the incident light is proportional to $\langle\delta\epsilon_{zz}^2(q)\rangle$, while $\langle\delta_{xz}^2(q)\rangle$ gives the scattered intensity polarized perpendicular to the incident polarization.

In the long-wavelength limit for an illuminated volume V the free-energy expression [Eq. (1), with no applied field] leads to the result[8]

$$\langle Q^2(q)\rangle=kT/VA(1+\xi^2q^2)$$
$$=kT/Va(T-T_c^*)(1+\xi^2q^2). \quad (4)$$

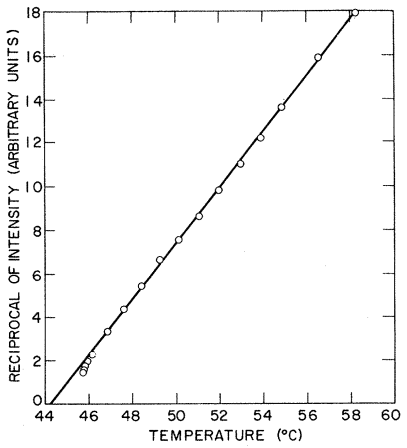

FIG. 2. The reciprocal of the intensity of light scattered by fluctuations in the isotropic phase of MBBA. The solid line is a fit to the mean field result of Eq. (4).

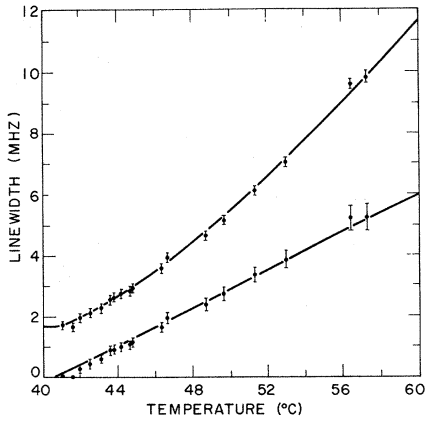

FIG. 3. The half-width of the Lorentzian spectrum of light scattered by fluctuations in the isotropic phase of MBBA. The upper curve is the raw data and includes the instrumental half-width of 1.65 MHz; the solid line is a fit of a $(T-T_c^*)^{4/3}$ power law (see Ref. 9). The lower curve shows the results corrected for the temperature dependence of the transport coefficient ν, as described in the text. (The relaxation time for the fluctuations is $\tau = 1/\Gamma$.)

Here ξ is the correlation length for the fluctuations, and in the Landau theory[8] varies as $\xi = \xi_0[(T/T_c)-1]^{-1/2}$. Since fluctuations in the isotropic phase involve all orientations of the optic axis with equal probability, we average Eq. (4) over all angles to obtain

$$\langle \delta\epsilon_{zz}{}^2(q)\rangle = (4/3)\langle \delta\epsilon_{xz}{}^2(q)\rangle = (4/45)\Delta\epsilon^2\langle Q^2(q)\rangle. \quad (5)$$

A reasonable estimate for ξ (we take $\xi_0 = 15$ Å, about the maximum dimension of a molecule) shows the ξ^2q^2 term in Eq. (4) to be negligible for visible light. Our experiments confirm this and justify the omission of gradient terms from Eq. (1). We measured the intensity ratio for polarized and depolarized components of the scattered light to be 1.35 ± 0.06, as predicted by Eq. (5). The temperature dependence of the intensity shown in Fig. 2 is linear over a wide temperature range as predicted by Eq. (4).

In an earlier publication[9] we reported measurements of the relaxation time for fluctuations of the order parameter in the isotropic phase of MBBA. We observed a critical slowing down as the ordering temperature was approached, and de Gennes has extended the Landau theory to explain our results. In de Gennes' theory[5] the relaxation time for long-wavelength fluctuations is $\tau = \nu/A$, where ν is a transport coefficient. We found our measurements of the relaxation time could be fitted by a power law of the form $\tau \sim (T-T_c^*)^{-4/3}$ as shown in the upper curve of Fig. 3 ($\tau = 1/\Gamma$). To interpret these data properly it is necessary to know the temperature dependence of ν. We might reasonably expect this transport coefficient to be proportional to the shear viscosity of the isotropic liquid.[5] In this isotropic phase of *p*-azoxyanisole (a nematic liquid crystal similar to MBBA) the shear viscosity varies as $\exp(W/kT)$ with $W/k \simeq 2800°K$.[10] Assuming this temperature dependence for ν in MBBA, we obtain from our relaxation-time measurements the linear variation of A with temperature shown as the lower curve of Fig. 3. Although the experimental uncertainties are large, the result is consistent with our birefringence and intensity measurements.

A careful examination of Figs. 1 and 2 shows close to T_K a departure from the $(T-T_c^*)^{-1}$ dependence that is predicted by the mean-field model for the Cotton-Mouton coefficient and the intensity of the scattered light. This occurs where the precision of our measurements is highest and is definitely a real effect. Analogous observations have been made in many other substances[3] that the mean-field approximation does not correctly describe the detailed behavior in the critical region. The approximation fails because it does not include the effects of the large fluctuations as the phase transition is approached. At the transition temperature T_K, two equal minima in the free energy (corresponding to $Q=0$ and $Q = Q_K$) are separated by a free-energy maximum which we estimate below to be $\sim kT$. This explains why we observed no superheating or supercooling of the phase transition and also means

that close to T_K large fluctuations and departures from the mean-field results [e.g., Eq. (3)] are to be expected. However, we may use the mean-field approximation to estimate the temperature at which these departures may be observable.

To discuss these effects in a liquid crystal we use the fact that fluctuations are correlated over a finite range $\xi = \xi_0[(T/T_c^*)-1]^{-1/2}$. The increase in free energy associated with a fluctuation $Q(\vec{r})$ at a point is then approximately given by

$$\delta\Phi = v^*[\tfrac{1}{2}AQ^2 - \tfrac{1}{3}BQ^3 + \tfrac{1}{4}CQ^4 - \tfrac{1}{3}\Delta\chi H^2 Q], \qquad (6)$$

where $v^* \simeq (4\pi/3)\xi^3$ is the correlation volume. We take the probability of a fluctuation to be proportional to $\exp(-\delta\Phi/kT)$ and expand the exponential for cubic and quartic terms of Eq. (6). We obtain thereby the approximate result in zero field[11]:

$$\langle Q^2(q)\rangle = \frac{kT}{VA}\left[1 - \frac{3CkT}{v^*A^2} + \frac{5B^2kT}{v^*A^3} + \cdots\right]. \qquad (7)$$

We find that Eq. (3) should also be multiplied by the correction factor given in brackets in Eq. (7). Since the two free-energy minima (for $Q = Q_K$ and 0) at T_K are separated by a barrier $v^*(B^4/324C^3) \simeq 0.6kT$, we expect the approximations used to derive Eq. (7) will fail very close to T_K. However the result should still serve to indicate where departures from the mean-field results may first be observed. With $\xi_0 = 15$ Å we calculate that the Cotton-Mouton coefficient and the intensity of the scattered light should be 6% larger than the mean-field result when $T = T_K + 1$°K. This is in good agreement with our experimental results.

Our conclusions are as follows: We have observed a divergence in the magnetic birefringence and fluctuations in the order parameter, as well as a critical slowing of these functions, in the isotropic phase of a nematic liquid crystal. These pretransitional phenomena are analogous to the behavior of substances (e.g., ferromagnets) in the vicinity of a critical point. Our measurements may be consistently and quantitatively interpreted using the mean-field approximation, except for a critical region very close to the phase transition. This model provides a more detailed description than the Frenkel concept of heterophase fluctuations[12] and could be used to interpret other observations[13,14] of pretransitional phenomena in liquid crystals. It seems reasonable that the behavior we have observed is typical of nematic liquid crystals, and it would be interesting to learn the results of similar studies of smectic and cholesteric materials.

The model we have used to interpret our results also predicts non-Gaussian fluctuations within a correlation volume. Unfortunately it would be difficult to observe this in the statistics of the scattered radiation. The only sufficiently coherent sources available (visible light) probe many correlation volumes and the central-limit theorem dictates that the scattered light will be Gaussian. We estimate that departures from Gaussian statistics in the fluctuations within a coherence volume v^* will be reduced in the scattered light by a factor v^*/V, where V is the illuminated volume.

We appreciate helpful discussions with P. G. de Gennes, M. J. Freiser, and M. J. Stephen.

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*Research supported by the Advanced Projects Research Agency under contract No. SD-90.

†National Science Foundation Predoctoral Fellow.

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