ISOTROPIC-NEMATIC PHASE TRANSITION IN LIQUID CRYSTALS*

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The molecular-field description of the isotropic-nematic phase transition in liquid crystals is investigated. It is found that the effects of fluctuations may be observable, and the first corrections due to fluctuations to the light scattering and magnetic birefringence in the isotropic phase are determined. The effects of applied fields on the phase transition are investigated. It is found that if the molecules prefer to line up transverse to an applied field there is a critical field above which the phase transition is second order.

An appropriate order parameter[1] to describe the degree of order in a nematic liquid crystal where the molecules have axial symmetry is

$$\Delta_{ij}=\langle\delta_{ij}-3n_in_j\rangle, \tag{1}$$

where n_i are the components of a unit vector giving the direction of the axis of a molecule and the average is over all the molecules in a small but macroscopic volume. Any traceless symmetric second-rank tensor[2] can be used in place of (1); the most appropriate one depends on the problem being considered. Close to the isotropic-nematic phase transition we suppose, in accordance with the usual assumptions of molecular-field theory, that the free energy per unit volume F can be expanded in a power series in Δ_{ij}:

$$F=F_0+\tfrac{1}{2}A\Delta_{ij}^2+\tfrac{1}{3}B\Delta_{ij}\Delta_{jk}\Delta_{ki}+\tfrac{1}{4}C\Delta_{ij}^2\Delta_{kl}^2+\tfrac{1}{2}D(\nabla_i\Delta_{kl})^2+\tfrac{1}{6}\chi_a\Delta_{ij}H_iH_j+\tfrac{1}{6}\alpha_a\Delta_{ij}E_iE_j. \tag{2}$$

In (2) A, B, C, and D are constants.[3] We assume that $A=A'(T-T_c^*)$, where T_c^* is a temperature slightly below the actual transition temperature T_K, and the remaining constants B, C, D are positive and temperature independent. The orienting effects of magnetic and electric fields are described by the last two terms in (2). χ_a and α_a are the anisotropy in the magnetic and electric susceptibilities per unit volume and are positive if the molecules prefer to be parallel to the applied fields and are negative if the molecules prefer to lie transverse to the fields.

It is convenient to write Δ_{ij} in the form

$$\Delta_{ij}=\Delta(\vec{r})[\delta_{ij}-3n_i(\vec{r})n_j(\vec{r})], \tag{3}$$

where n_i are the components of a unit vector specifying the orientation of the molecules at $\vec{r}$, and $\Delta(\vec{r})$ is the fraction of molecules at $\vec{r}$ lined up along $\vec{n}$. Equation (3) is not the most general form of Δ_{ij} but assumes that the liquid crystal is uniaxial. Substituting (3) in (2) and neglecting the fields we find

$$F=F_0+3A\Delta^2-2B\Delta^3+9C\Delta^4+3D(\nabla\Delta)^2+9D\Delta^2(\nabla_in_k)^2. \tag{4}$$

The last term in (4) is the elastic energy associated with changes in molecular orientation and is equivalent to the free-energy expression of Oseen[4] and Frank[5] in the case of nonpolar nematic crystals when all the elastic constants are equal. Following Saupe[6] we may identify $18D\Delta^2$ with the Frank elastic constants K. However, care must be exercised in using this result. For example, the intensity of light scattered by the orientation fluctuations of molecules in the nematic phase is proportional to kT/Dq^2 (where q is the momentum transfer and k is Boltzmann's constant) and then varies slowly with temperature. If the amount of order is not taken into account the light scattering intensity[7] is proportional to kT/Kq^2. Then K cannot simply be replaced by $18D\Delta^2$, but the fact that the dielectric anisotropy is also proportional to Δ must be included.

The amount of order Δ in a uniform system is determined by minimizing the free energy

$$\bar{F}=F_0+3A\Delta^2-2B\Delta^3+9C. \tag{5}$$

The cubic term in Δ, as discussed by Landau,[8] leads to a first-order phase transition. The values of Δ minimizing $\bar{F}$ are

$$\Delta=0,\quad T>T_K; \tag{6a}$$

$$\Delta=\frac{B}{12C}[1+(1-24\beta)^{1/2}],\quad T<T_K, \tag{6b}$$

where $\beta = AC/B^2$. The transition temperature T_K is given by

$$\frac{T_K - T_c^*}{T_c^*} = \frac{B^2}{27A'CT_c^*}, \tag{7}$$

and the latent heat per unit volume, L, of the transition is

$$L = (A'B^2/27C^2)T_K. \tag{8}$$

The validity of the molecular-field description of the phase transition can be estimated, as suggested by Ginzburg,[9] by examining the fluctuations around the solutions (6). In the present case the Ginzburg criterion (apart from a numerical factor) may be put in the form

$$h\xi^3 \gg kT, \tag{9}$$

where h is the height of the barrier separating the ordered and disordered states and ξ is the temperature-dependent coherence length. Close to T_K the important fluctuations involve regions of volume ξ^3 and (9) states that fluctuations leading from order to disorder or vice versa do not occur with high probability. Under these conditions the molecular-field description will be valid. If we approach the transition from above but with T close to T_K,

$$h = L(T_K - T_c^*)/16T_K, \quad \xi^2 = D/A = \xi_0^2 T_c/(T - T_c^*), \tag{10}$$

where ξ_0 is the zero-temperature coherence length and (9) becomes, for $T = T_K$,

$$\frac{L\xi_0^3}{16}\left(\frac{T_K}{T_K - T_c^*}\right)^{1/2} \gg kT_K. \tag{11}$$

Below T_K a similar result is obtained. As an example, for p-azoxy anisole $L = 0.68$ cal/gm,[10] $T_K \simeq 130$°C, and assuming that $\xi_0 = 20$ Å, we find the left-hand side of (11) is 4×10^{-13} for $T_K - T_c^* = 1$°C. This is to be compared with $kT_K = 4\times10^{-14}$. We conclude that the molecular-field description of the phase transition may well be inadequate and critical behavior may be observable close to T_K.

A more quantitative result than (11) is obtained by calculating the contributions of the cubic and quartic terms in (2) to the fluctuations. Thus the intensity of light scattering above T_K in the isotropic phase is proportional to

$$\langle|\Delta_{xy}(q)|^2\rangle = \frac{kT}{2A(q)}\left[1 - \frac{7kTC}{A(q)}f_1 + \frac{7}{6}\frac{kTB^2}{A(q)}f_2 \cdots\right], \tag{12}$$

where $A(q) = A + Dq^2$ and

$$f_1 = \frac{1}{V}\sum_{q<q_m}\frac{1}{2\pi^2 D^3}(q_m\xi - \tan^{-1}q_m\xi). \tag{13}$$

$$f_2 = \frac{1}{V}\sum_{q_1<q_m}\sum_{q_2<q_m}\frac{\delta_{q+q_1+q_2}}{A(q_1)A(q_2)} \underset{q\to0}{=} \frac{\xi}{4\pi^2D^2}\left(\tan^{-1}q_m\xi - \frac{q_m\xi}{1+q_m^2\xi^2}\right). \tag{14}$$

We can express the second and third terms in (12) for $q = 0$ more conveniently by means of (7), (8), and (10). In (13) and (14) we take $q_m\xi \simeq 1$ and replace the brackets by unity. Then

$$\frac{7kTC}{A}f_1 = \frac{7}{2\pi^2}\frac{kT_c^*}{L\xi_0^3}\left[\frac{(T_K - T_c^*)^2}{T_c^*(T - T_c^*)}\right]^{1/2}, \quad \frac{7}{6}\frac{kTB^2}{A}f_2 = \frac{63}{8\pi^2}\frac{kT_c^*}{L\xi_0^3}\left(\frac{T_K - T_c^*}{T_c^*}\right)^2\left(\frac{T_c^*}{T - T_c^*}\right)^{3/2}. \tag{15}$$

Then the light-scattering intensity may increase more rapidly than $(T - T_c^*)^{-1}$ close to T_K. Evidence for this effect has recently been obtained by Litster and Stinson[11] who have observed light scattering in the isotropic phase of p-methoxy benzylidene p-n-butylaniline. We also note that the magnetic birefringence is proportional to (12) with $q = 0$.

When a magnetic or electric field is applied to the liquid crystal, if the molecules prefer to order parallel to the field the uniaxial solution (3) is still appropriate. The initial effect of the field is to raise the transition temperature. For a strong enough field no transition at all will be observed. A more interesting situation arises if the molecules prefer to lie transverse to the field and thus α_a or

χ_a in (2) is negative. This is more equally accomplished with an electric rather than a magnetic field. In this case the phase transition can become second order and the state is a biaxial one. Assuming the electric field to be along the z axis an appropriate form for the order parameter is

$$\Delta_{xx}=-(B/C)(\tfrac{1}{2}\eta+p),\quad \Delta_{yy}=-(B/C)(\tfrac{1}{2}\eta-p),\quad \Delta_{zz}=+(B/C)\eta, \tag{16}$$

with other components zero. The parameter η describes the tendency of the molecules to lie in the xy plane and p describes the ordering which takes place in this plane. For $p>0$ the material is ordered along x and for $p<0$ it is ordered along y. Substituting in (2) the free energy (in units of B^4/C^3) is

$$F=\tfrac{3}{4}\beta\eta^2+\tfrac{1}{4}\eta^3+\tfrac{9}{16}\eta^4-\tfrac{3}{4}\gamma\eta+p^2(\beta-\eta+\tfrac{3}{2}\eta^2)+p^4, \tag{17}$$

where $\gamma=-(2/9)(C^2/B^3)\alpha_aE^2$ and is positive. The parameters p and η are determined by minimizing F which leads to the equations

$$p(\beta-\eta+\tfrac{3}{2}\eta^2)+2p^3=0, \tag{18}$$

$$\tfrac{3}{2}\beta\eta+\tfrac{3}{4}\eta^2+(9/4)\eta^3-\tfrac{3}{4}\gamma+p^2(3\eta-1)=0. \tag{19}$$

Equation (18) has solutions

$$p=0, \tag{20a}$$

$$p^2=-\tfrac{1}{2}(\beta-\eta+\tfrac{3}{2}\eta^2). \tag{20b}$$

We first determine the region of the β, γ plane in which a local minimum of the free energy with $p\neq 0$ exists. Thus substituting (20b) in (19) we obtain

$$\eta^2-\tfrac{1}{6}\eta+\tfrac{1}{6}\beta-\tfrac{1}{4}\gamma=0 \tag{21}$$

and the solution corresponding to a free-energy minimum is

$$\eta=\tfrac{1}{12}[1+(1-24\beta+36\gamma)^{1/2}]. \tag{22}$$

Substituting in (20b) we find

$$p^2=\tfrac{1}{32}[1-12\beta-6\gamma+(1-24\beta+36\gamma)^{1/2}]. \tag{23}$$

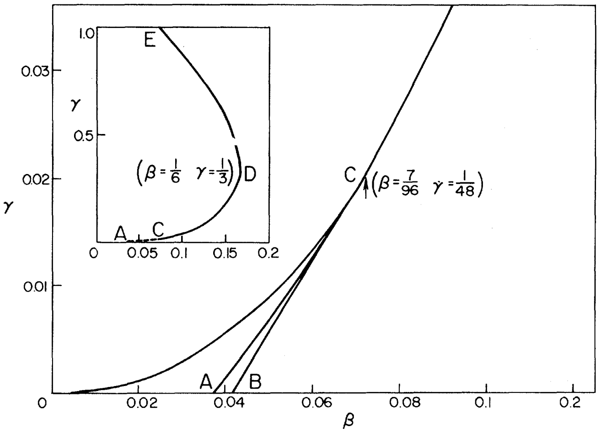

FIG. 1. Phase diagram for a nematic liquid crystal in a transverse field. $\beta=(A'C/B^2)(T-T_c{}^*)$ $\gamma=-(2/9)(C^2/B^3)\alpha_aE^2$.

The region in which p^2 is real and positive is to the left of the curve $BCDE$ in Fig. 1. The branch BC is determined by $1-24\beta+36\gamma=0$, CD by

$$\gamma=\tfrac{2}{3}-2\beta-\tfrac{2}{3}(1-6\beta)^{1/2},$$

and DE by

$$\gamma=\tfrac{2}{3}-2\beta+\tfrac{2}{3}(1-6\beta)^{1/2}.$$

We can also determine simply the region in which the disordered state $p=0$ is a local minimum of the free energy. In this case η must simultaneously satisfy (19) and (20b) with $p=0$. This leads to the curves $\gamma=\frac{2}{3}-2\beta\mp\frac{2}{3}(1-6\beta)^{1/2}$ which are OCD and DE, respectively, in Fig. 1. To the right of this region the disordered state is a local minimum of the free energy. Finally the first-order phase-transition curve AC in Fig. 1 has been determined by numerical methods. The curve CDE therefore is a second-order transition line. The point C where the first-order transition line ends is determined by $\beta=7/96$, $\gamma=1/48$. This corresponds to an electric field such that $\alpha_aE^2\approx kTn$, where n is the number density which leads to quite a large field of order of magnitude 10^5-10^6 V/cm. If it can be arranged that the molecules have a dipole moment μ perpendicular to their long axes, then the above condition becomes $\mu E\approx kT$ which can be satisfied for lower fields. Also we note from Fig. 1 that as the field is increased along AC the transition approaches more closely a second-order one.

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[1] A. Saupe and W. Maier, Z. Naturforsch. A 15, 287 (1960).

[2] P. G. de Gennes, Phys. Lett. 30 A, 454 (1969).

[3] We use a tensor notation and a summation is implied over repeated indices.

[4] C. W. Oseen, Trans. Faraday Soc. 29, 883 (1933).

[5] F. C. Frank, Discuss. Faraday Soc. 25, 1 (1958).

[6] A. Saupe, Z. Naturforsch. A 15, 810 (1960).

[7] Orsay Liquid Crystal Group, J. Chem. Phys. 51, 816 (1969).

[8] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958), Chap. XIV.

[9] V. L. Ginzburg, Fiz. Tverd. Tela 2, 2031 (1960) [Sov. Phys.-Solid State 2, 1824 (1960)].

[10] E. M. Barrall, R. S. Porter, and J. F. Johnson, J. Phys. Chem. 68, 2810 (1964).

[11] J. D. Litster and T. W. Stinson, J. Appl. Phys. 41, 969 (1960), and T. W. Stinson and J. D. Litster, Phys. Rev. Lett. 25, 503 (1970).

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

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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 $\epsilon_{\alpha\beta} = \bar{\epsilon}\delta_{\alpha\beta}$