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Some Recent Studies of Liquid Crystals: A Review

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The following topics are reviewed briefly: (i) The first experimental determination of the decrease in the smectic A–nematic transition temperature brought about by a twist deformation, an effect which is the analog of the influence of a magnetic field on the superconductor–normal metal transition; (ii) the similarity between the hydrodynamics of cholesteric liquid crystals and superfluid hydrodynamics, and some of its consequences, e.g., the possibility of a temperature wave attending second sound in the cholesteric phase; and (iii) the nematic–smectic A–smectic C multicritical point.

KEY WORDS: Smectic A–nematic transition; hydrodynamics of cholesterics; nematic–smectic A–smectic C multicritical point.

1. INTRODUCTION

It is now well accepted that there is a certain unity in the basic physical concepts involved in the description of apparently diverse phenomena. The aim of this review is to illustrate this with specific reference to liquid crystals,[1] choosing as examples some recent work carried out at Bangalore and elsewhere.

2. THE EFFECT OF A TWIST DEFORMATION ON THE SMECTIC A–NEMATIC TRANSITION POINT

Recognizing the analogy between the smectic A phase and the superconductor, de Gennes[2] predicted that a twist or bend distortion (both of which involve curl **n**, where **n**, the director, plays the role of the magnetic vector potential in the superconductor) should depress the smectic A–

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nematic transition point, T_{AN}, relative to the curvature-free sample. The nature of the phase diagram depends on whether the material is of type I or type II, i.e., on whether the Ginzburg–Landau parameter, λ/ξ, is less or greater than $1/\sqrt{2}$, where λ is the penetration depth for a twist or bend deformation and ξ the coherence length. However, compounds which exhibit a second-order or nearly second-order A–N transition are expected to be of type I.[3] The threshold curve is then given by[2]

$$\frac{\alpha^2}{2\beta} = \frac{1}{2} k_{ii}(\operatorname{curl} \mathbf{n})^2, \qquad i = 2 \text{ or } 3$$

where α and $\frac{1}{2}\beta$ are the usual coefficients of the second- and fourth-order terms in the Ginzburg–Landau free-energy expression, and k_{22} and k_{33} the Frank elastic constants for twist and bend, respectively.

The influence of a magnetic field on the superconductor–normal metal transition has, of course, been very well studied. Typical curves are shown in Fig. 1. Surprisingly, although it is now over 10 years since de Gennes predicted a similar type of diagram for T_{AN} versus $|\operatorname{curl} \mathbf{n}|$, there have been (until recently) only two experiments that have taken note of this effect in

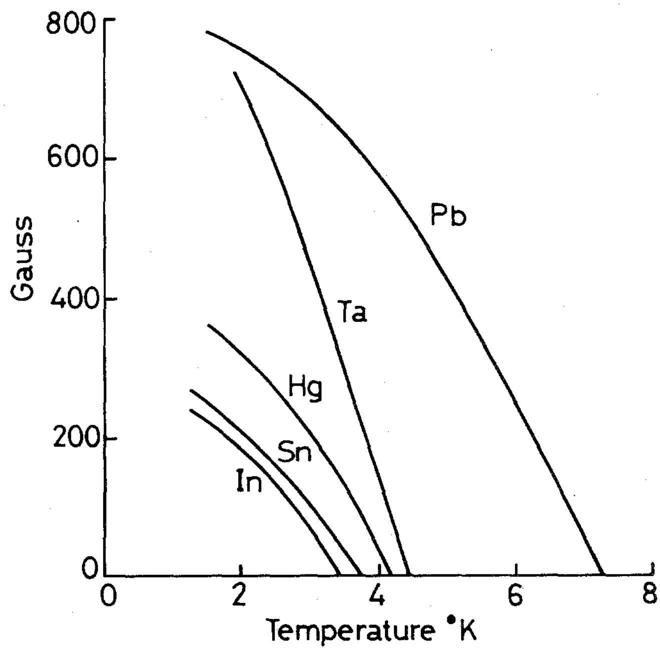

Fig. 1. Variation of the superconductor–normal metal transition temperature with the applied magnetic field (from Roberts and Miller[4]).

attempting to give a qualitative explanation of some observations. The first was by Cladis and Torza,[5] who observed a "striped" texture when a sample of CBOOA (*N*-*p*-cyanobenzylidene-*p*′-octyloxyaniline, which has a nearly second-order A-N transition) with a strong bend distortion was cooled to T_{AN}. This they interpreted as the formation of an "intermediate" state with the A and N phases coexisting. Subsequently, similar observations were reported by Hinov[6] on CBOOA with a bend induced by an electric field.

The first quantitative measurements of the dependence of T_{AN} on $|\mathrm{curl}\,\mathbf{n}|$ were made only very recently by Madhusudana and Srikanta.[7] (For details of the experimental configuration used by them, reference may be made to their original paper.) Their results for CBOOA are presented in Fig. 2, and as can be seen, T_{AN} shows the expected trend. It is remarkable that such an extremely weak type of elastic deformation can produce a detectable change in the transition temperature.

There are other aspects of this analogy. For example, there should be pretransition anomalies: the coherence length, which is a measure of the size of the smecticlike clusters in the nematic phase, and the related properties should diverge as the temperature approaches T_{AN}. This has been extensively studied using a variety of techniques. The critical exponents associated with this divergence have been the subject of much

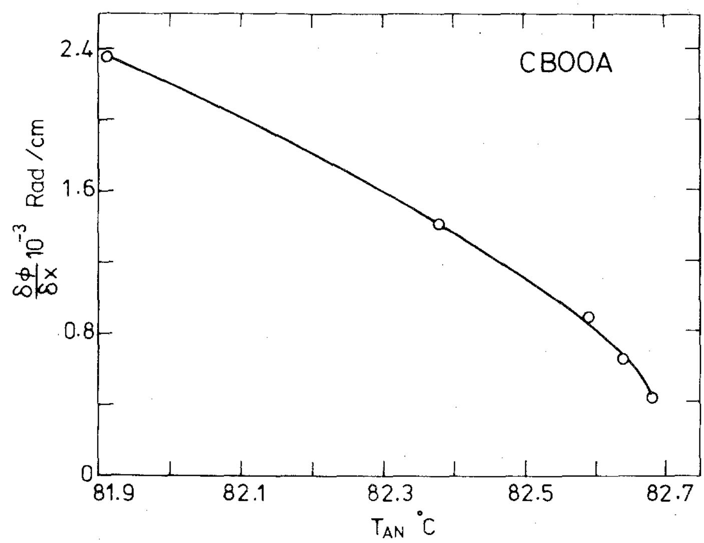

Fig. 2. Variation of the smectic A–nematic transition temperature with the twist per unit length ($\delta\varphi/\delta x$) for CBOOA (Madhusudana and Srikanta[7]).

discussion, and unfortunately the experimental values reported by the different investigators are not in agreement.[8] However, the latest position, which is based on the very precise studies by the MIT group, is that it is definitely not mean field, but closer to the ^{4}He analogy, though there are significant departures from this analogy which still remain to be understood from the theoretical point of view. (For excellent up-to-date accounts of the current situation see Lister *et al.*[9] and Lubensky.[10])

3. THERMOMECHANICAL EFFECTS IN CHOLESTERIC LIQUID CRYSTALS

Smectic A has a complex order parameter, $\psi = |\psi|\exp(i\varphi)$, where $|\psi|$ is the amplitude of the one-dimensional density wave and φ a phase factor that determines the positions of the layers.[2,11] In effect, the layer displacements are uncoupled with the density. There are two propagating acoustic modes: one is the usual longitudinal (or compressional) wave, and the other associated with oscillations in the layer spacing without appreciable density changes (i.e., oscillations in the phase of the complex order parameter) and may be compared with the phonon branch in superfluids known as *second sound*. The velocity of second sound in smectic A is determined by the elastic modulus for the compression of the layers.

For long wavelength fluctuations, for which the distortions vary smoothly and slowly over several pitches, the cholesteric may also be looked upon as a layered structure, rather like smectic A. One can then employ a "coarse-grained" approximation (de Gennes, see Ref. 1) and express the modulus for the layer compressibility (B) in terms of the Frank constant (k_{22}):

$$B = k_{22}q_0^2 \tag{3.1}$$

where $q_0 = 2\pi/P_0$, P_0 being the pitch of the undistorted cholesteric. Thus second sound may be expected to occur in cholesterics also, as was first discussed by Lubensky,[12] but there is an additional effect which has recently been investigated by Ranganath,[13] viz., that *the phase fluctuations should be accompanied by temperature fluctuations as well*, bringing the analogy with superfluids even closer.

To appreciate the origin of this effect, we go back to an observation reported by Lehmann in 1900[14] very soon after the discovery of liquid crystals. Lehmann noted that when the cholesteric material was taken between glass plates and heated from below the different droplets appeared to be rotating violently, but on closer examination he concluded that it was not the droplets themselves but the structure that was rotating. In 1968, Leslie[15,16] pointed out that the absence of a plane of symmetry in the cholesteric structure automatically implies that there can be a coupling between thermal and mechanical effects. Specifically, his equations showed that when a thermal gradient is imposed along the helical (z) axis, then the director (which is in the x–y plane) should experience a torque about z; or, conversely, a rotational motion of the director about the z axis should, in principle, generate heat flow along z. It is seen at once that this explains Lehmann's rotation phenomenon and, in fact, Leslie[15] derived an expression for the angular velocity of the director in the presence of a thermal gradient along the helical axis.

Now, a compression of the cholesteric layers (which, as we have seen, determines the second sound velocity) means a change of pitch or, equivalently, a change in the twist per unit length of the director. It follows therefore that fluctuations in the layer spacing should be accompanied by orientational fluctuations of the director about the helical axis, and this in turn, because of the thermomechanical coupling, should result in temperature fluctuations.

Suppose that the distortions are of small amplitude and that they vary slowly and smoothly over several pitches. Under these circumstances, one may ignore the director inertia and average out all the high-frequency components. Suppose also that the distortions are such that the tilt of the director away from the plane of the local layer is small. Then taking the cholesteric axis to be along the x_3 direction (z axis), Leslie's equations simplify to

$$\frac{1}{\rho}\frac{\partial \rho}{\partial t} + v_{i,i} = 0$$

$$\rho\frac{\partial v_i}{\partial t} = -P_{,i} + \delta_{i3}g + t'_{ij,j}$$

$$\frac{\partial u}{\partial t} - v_3 = -\left(\frac{1}{\lambda_1 q_0^2}\right)g - \left(\frac{\lambda_3}{\lambda_1 q_0}\right)T_{,3}$$

$$\frac{dQ}{dt} = K_{\parallel}T_{,33} + K_{\perp}(T_{,11} + T_{,22}) - \lambda_3 q_0\left(\frac{\partial u}{\partial t} - v_3\right)$$

$$g = k_{22}q_0^2 u_{,33}$$

Here, we employ the Cartesian tensor notation, repeated tensor indices being subject to the usual summation convention, the comma denoting partial differentation with respect to spatial coordinates (i.e., $v_{i,i} = \partial v_i/\partial x_i$; $T_{,33} = \partial^2 T/\partial x_3^2$ etc.); ρ is the density, v_i the velocity, P the pressure, t'_{ij} the hydrodynamic stress tensor, uq_0 the change in the local orientation of the director in its own plane, λ_1 the twist viscosity coefficient, λ_3 the thermomechanical coefficient, Q the heat supply per unit volume, and $K_{\parallel}$

and $K_\perp$ are the thermal conductivity coefficients along and perpendicular to the twist axis. We have also assumed Onsager's reciprocal relations for irreversible processes.

From these equations, it is easily shown that there are two propagating modes. One is the usual longitudinal wave, whose velocity is practically independent of the direction of propagation and is determined by the volume compressibility, and the other is the second sound, whose velocity is

$$c_2 = (B/\rho)^{1/2} \sin\theta\cos\theta \tag{3.2}$$

where B is given by Eq. (3.1) and θ is the angle between the wave vector and the z axis. Equation 3.2 was first derived by de Gennes[1] for smectic A, and by Lubensky[12] for the cholesteric, but additionally we now have temperature fluctuations associated with second sound. The ratio of the amplitude of the temperature wave to that of the phase wave is[13]

$$f = -k_{22}q_0/\lambda_3$$

For positive λ_3 the temperature wave is a propagating mode, while for negative λ_3 it is not.

Similarly, Ranganath[13] has shown that in the case of steady flow, neglecting viscous effects and permeation,

$$\partial P/\partial T = -\lambda_3 q_0$$

which is comparable to London's equation for the fountain effect in superfluids, and also that there can be an extra thermal conductivity analogous to thermal superconductivity.

However, we shall not discuss these effects in any further detail because the experimental situation is not at all clear. As far as I am aware, no one has succeeded in reproducing Lehmann's observations. We therefore felt that it might be worthwhile devising some experiments which should enable a determination of the magnitude and sign of the thermomechanical effect, if it exists. With this in view, we have recently proposed two experimental geometries.[17]

In the first geometry, the sample is taken in a capillary with the cholesteric axis along the capillary axis. The inside surface of the capillary is supposed to be treated so that the cholesteric layers are firmly anchored and prevented from moving, at least at low shear rates.[18] A temperature gradient along the capillary axis should then result in a helical motion of the director and give rise to fluid flow. The quantity of fluid flowing per second is given by

$$Q = \frac{\pi R^2}{q_0}\frac{\lambda_3}{\lambda_1} T_{,z}$$

where R is the radius of the capillary, λ_1 the usual twist viscosity coefficient and $T_{,z}$ the temperature gradient. Conversely, as shown by Prost,[19] if flow is induced by a weak pressure gradient, a temperature difference should develop across the ends of the capillary. Either of these measurements should yield λ_3 in sign and magnitude.

In the second geometry,[17] a temperature gradient is imposed at right angles to the cholesteric axis. The theory shows that the uniaxial symmetry of the structure will then be destroyed. A measurement of the birefringence for light propagating along z provides an estimate of the thermomechanical coefficients.

The experiments have yet to be conducted, but if it does turn out that the thermomechanical effect is of measurable magnitude, then the analogies with superfluid hydrodynamics will become more meaningful, and this should certainly open up interesting areas for further study.

4. THE NEMATIC–SMECTIC A–SMECTIC C MULTICRITICAL POINT

The nematic–smectic A–smectic C (NAC) point was predicted theoretically by Chen and Lubensky[20] as a possible realization of a Lifshitz point in a liquid crystalline system. The Lifshitz point itself was proposed earlier by Hornreich, Luban, and Shtrikman,[21] who had in mind, as an example, the meeting point of the para-, ferro-, and helicoidal magnetic phases in the temperature (T) versus pressure (P) or concentration (X) diagram.

The first observations of the NAC point were made by Johnson *et al.*[22] and independently by Sigaud *et al.*[23] in the T–X diagrams of binary systems. Johnson *et al.*, who studied the $\bar{7}$S5/$\bar{8}$S5 (heptyl/octyl-oxy-p'-pentylphenylthiol benzoate) mixture, also reported accurate calorimetric measurements and established the following facts: the NA transition is throughout continuous, the AC transition is also throughout continuous, whereas the NC transition is weakly first order away from the NAC point but becomes continuous very close to and at the NAC point itself. Thus the NAC point is a multicritical point at which the three phases become indistinguishable.

Safinya *et al.*[24] carried out a high-resolution study of the X-ray diffuse scattering arising from the smecticlike fluctuations in the nematic phase of the $\bar{7}$S5/$\bar{8}$S5 system. They found that close to the NC line the critical fluctuations are smectic C-like, but away from it the fluctuations become smectic A-like. However, the q dependence of the intensity of scattering in the vicinity of the NAC point did not quite agree with the Chen–Lubensky mean field model, which predicts a $q_\perp^{-4}$ variation. (According to Safinya *et al.*,[24] another model for the NAC point proposed by

Chu and McMillan[25] was found to be unsatisfactory in explaining these experimental results.)

More recently, Brisbin *et al.*[26] have investigated four other binary systems. They have found that despite differences in the global features, the topology of the phase diagrams around the NAC point itself is strikingly similar in all cases, so much so that they have suggested that the topology should be universal for this multicritical point. Their phase diagrams are reproduced in Fig. 3.

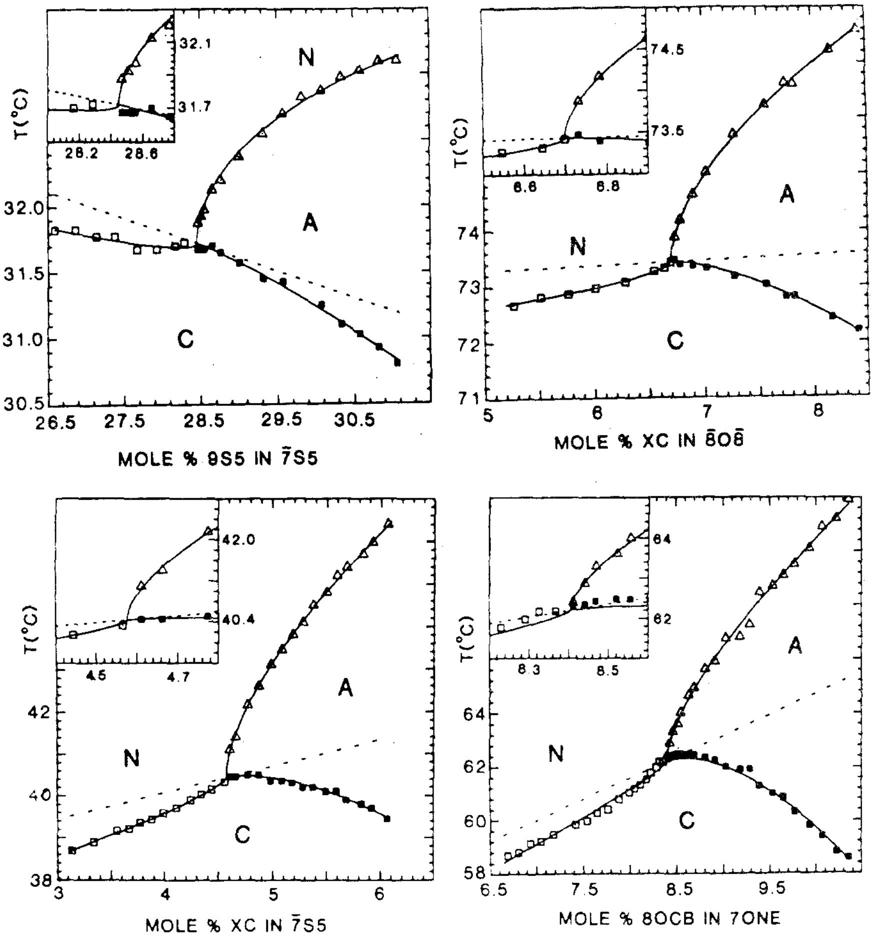

Fig. 3. T–X phase diagrams for four binary systems in the vicinity of the NAC point (Brisbin *et al.*[26]).

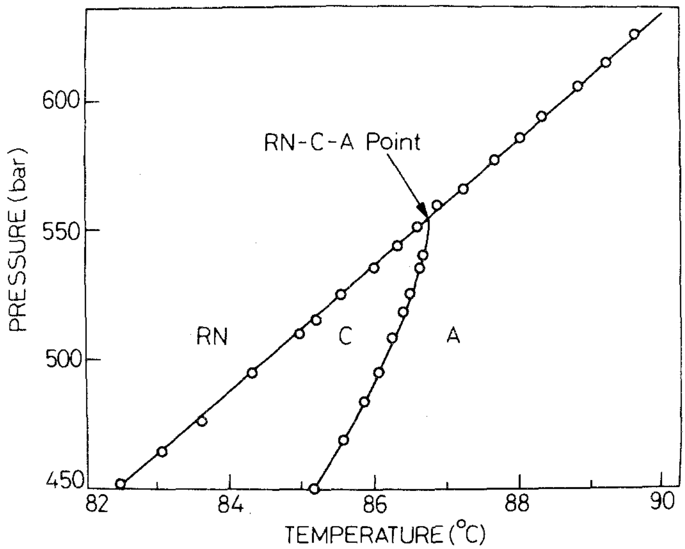

Fig. 4. *P–T* phase diagrams for DOBBCA in the vicinity of the reentrant nematic–smectic C–smectic A point (Shashidhar *et al.*[29]).

Meanwhile, we have been exploring the possibility of observing the NAC point in a pure compound. The compound "50.6" appeared to be promising in that the temperature range of the smectic A phase decreased initially with increase of pressure, but above about 4 kbar the NA and AC lines became nearly parallel (separated by just 0.4°C) and the NAC point proved to be elusive.[27] Subsequently, Shashidhar *et al.*[28] discovered a new kind of multicritical point in the compound DOBBCA [4(4-*n*-decyloxybenzoyloxy) benzylidene-4′-cyanoaniline] which, at atmospheric pressure, shows the following sequence of transitions *on cooling*:

isotropic → nematic → sm A → sm C → reentrant nematic → crystal

This compound shows a reentrant nematic–smectic C–smectic A (or RN–C–A) point.[28] In order to get a better idea of the topology Shashidhar improved the accuracy of the pressure measurements (from ±15 bar to ±0.3 bar) and redetermined the *P–T* diagram. The latest phase diagram[29] for this compound in the neighborhood of the RN–C–A point is presented in Fig. 4. Independently, Sigaud *et al.*[30] observed a similar point, which they referred to as the "inverted NAC point," in the *T–X* diagram of a binary system. Interestingly their diagram (reproduced in Fig. 5), is quite similar to that for DOBBCA; for example the RN–C and RN–A lines are

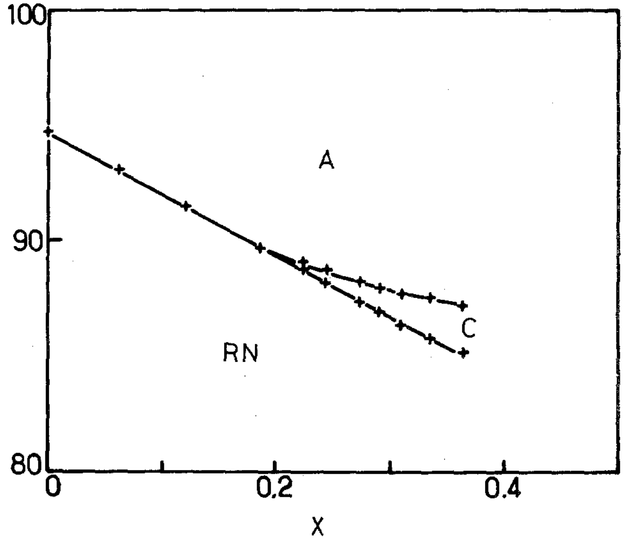

Fig. 5. T–X phase diagrams for binary system composed of DOBBCA and 4-cyano-benzylidene-4′-(4″-decyloxybenzoyloxy) aniline showing a reentrant nematic–smectic C–smectic A point (Sigaud *et al.*[30]).

collinear in both cases. However, more experiments are needed to draw definitive conclusions regarding the topology in the vicinity of this new multicritical point. Also it is of considerable importance to find a normal NAC point in a pure compound to verify that Johnson's conclusions have general validity. On the theoretical side, what is needed is perhaps a more refined form of the Chen–Lubensky model which goes beyond the mean field approximation.

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