Light-Scattering Study of a Smectic-A Phase near the Smectic-A – Nematic Transition*

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From light scattered by director modes in the smectic-A phase of cyanobenzylidene octyloxyaniline (CBOOA) and octyloxy cyanobiphenyl (8OCB) we deduce that the restoring force for phase fluctuations in the smectic order parameter vanishes as $(T_c - T)^{0.33}$ as the nematic phase is approached. In CBOOA the force maintaining the molecules normal to the layers vanishes as $(T_c - T)^{0.50}$. We conclude that de Gennes's analogy between charged superfluids and the smectic-A phase is not entirely correct.

Since McMillan[1] and Kobayashi[2] proposed their original models which suggested that the smectic-A–nematic phase transition could be second order, there has been considerable theoretical and experimental interest in the smectic-A phase of liquid crystals. A focus for these efforts has been provided by de Gennes who proposed an attractively simple model[3] which is mathematically isomorphous to the Ginsburg-Landau theory of superconductivity. Studies of the smetic-A phase have been carried out both by light scattering[4] and by the production of elastic buckling instabilities,[5,6] but the major experimental activity has been studies of pretransitional effects, analogous to fluctuation diamagnetism, in the nematic phase.[7-14] Here we present the results of a detailed series of measurements of the spectrum and intensity of light scattered by director fluctuations in the smectic-A phase of cyanobenzylidene octyloxyaniline (CBOOA) and octyloxy cyanobiphenyl (8OCB). We write this Letter to point out that a quantitative interpretation of our measurements using de Gennes's model indicates that the smectic-A–nematic transition is governed by two characteristic lengths; thus either the model lacks some essential physics or this transition is not described by the scaling-law hypothesis.

In what follows we first summarize the important predictions of de Gennes's model, and then present our measurements and interpret them in terms of the model. De Gennes proposed that the order parameter for a smectic-A phase be defined by a density wave along the z direction (perpendicular to the layers), *viz.*

$$\rho = \rho_0\{1 + \mathrm{Re}[\psi \exp(iq_0 z)]\}. \tag{1}$$

Here $a = 2\Pi/q_0$ is the smectic layer spacing, and $\psi = |\psi| \exp(iq_0 u)$ is the smectic-A order parameter; when the phase of ψ is written as $q_0 u$, u represents a displacement of the layers in the z direction. Thus defined, ψ is a two-component order parameter analogous to the order parameter of superfluids. In the smectic-A phase $\langle|\psi|\rangle = \psi_0$, the unperturbed director[15] $\vec{n}_0$ lies along z, and the mean squared director fluctuations of wave vector $\vec{q}$ ($q_y = 0$) are readily calculated to be

$$\langle n_x^2(\vec{q})\rangle \simeq kT[K_1 q_x^2 + B(q_z/q_x)^2]^{-1}, \tag{2}$$

$$\langle n_y^2(\vec{q})\rangle = kT[D + K_2 q_x^2 + K_3 q_z^2]^{-1}. \tag{3}$$

The K_i are the Frank elastic constants,[15] and $B = \psi_0^2 q_0^2/M_v$ is the restoring force for fluctuations in the phase of ψ (i.e., layer thickness) while $D = \psi_0^2 q_0^2/M_t$ is the force keeping the molecules normal to the layers. The quantities M_v and M_t (analogous to the effective mass in Ginsburg-Landau theory) are discussed by de Gennes.[3] Equation (3) is exact, while (2) is correct to order $(q_z/q_x)^2$ if $B \gg K_3 q_z^2$, which is true for $T_c - T > 10$ mK in our experiment; Brochard[16] gives an exact expression.

Equations (2) and (3) describe the two independent director modes in the smectic-A phase; the coupling of these modes to light is given by $\delta\epsilon_{zi}(q) = \epsilon_a n_i(q)$, where $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$ is the anisotropy in the optical dielectric constant parallel and perpendicular to the optic axis of the liquid crystal. Thus, for example, the field autocorrelation function for light scattered by fluctuations in $n_x(q)$ will be proportional to

$$\langle \delta\epsilon_{zx}^*(q,0)\delta\epsilon_{zx}(q,\tau)\rangle = \epsilon_a^2\langle n_x^2(q)\rangle e^{-\Gamma\tau}, \tag{4}$$

where for $q_x \gg q_z$,

$$\Gamma = [K_1 q_x^2 + B(q_z/q_x)^2]/\eta_s, \tag{5}$$

with η_s the splay viscosity; η_s is not expected to be affected by the smectic order.

Our CBOOA samples were obtained from Eastman Kodak and recrystallized from heptane; the 8OCB was used as received from British Drug

Houses Chemicals. Samples about 40 μm thick were prepared in the planar configuration (molecules parallel to the plates) between glass plates and the alignment checked with a polarizing microscope. For reasons we discuss elsewhere,[17] the planar configuration offers experimental advantages. Our samples were prepared between microscope slides treated by skew evaporation[18] of SiO and the incident laser power was 750 μW at 6328 Å.

We used the sample itself as a sensitive thermometer (through the rapid variation of B/K_1 with temperature near T_c) to determine that there was no significant heating by the laser beam. The oven used to control the sample temperature had a short-term stability of 0.5 mK and was mounted on the divided circle of a transit so that we could adjust the angle θ between $\vec{q}$ and the smectic layers with a precision of 10 arc secs.

In order to determine B/K_1, we chose the scattering geometry to select light scattered only by fluctuations in n_x and measured the intensity and decay time Γ at from five to nine values of θ over the range $-2^\circ < \theta < 2^\circ$ ($|q_z| < 0.03|q_x|$) at each temperature. From the curvature of Γ as a function of q_z we obtained B/K_1. The results for CBOOA are shown in Fig. 1 for three different samples with smectic-A–nematic transition temperatures, T_c, ranging from 82.1 to 82.9°C. Data for each sample were fitted by the expression $B/K_1 = b(1 - T/T_c)^{\varphi}$ and, as can be seen in the figure, they fall on the same curve when adjusted for the different values of T_c. Our fit gave the result $\varphi = 0.333 \pm 0.05$ with uncertainties determined by the χ^2 test. The solid line of Fig. 1 is $B/K_1 = 2.01 \times 10^{14}(1 - T/T_c)^{0.333}$ cm^{-2} and extrapolates to a penetration depth $\lambda = (K_1/B)^{1/2} = 13.5$ Å at 75°C, in good agreement with the value 14 ± 1 Å reported by Ribotta, Salin, and Durand.[4]

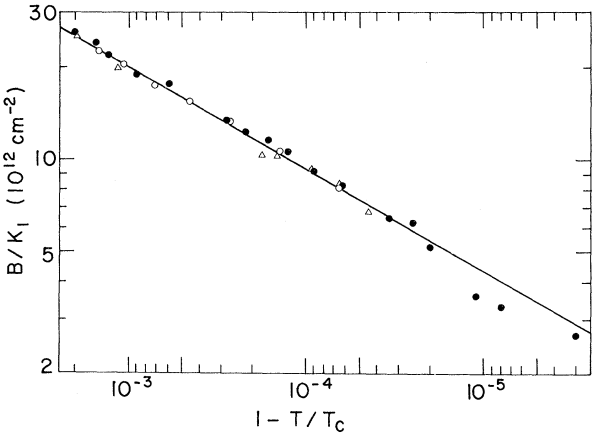

FIG. 1. Plot of B/K_1 for CBOOA. The different symbols are used for samples with different phase transition temperatures.

In 8OCB we also found B/K_1 to vanish as $(1 - T/T_c)^{0.33}$, but a first-order phase transition intervened 20 mK below the extrapolated value of T_c.

The exponent $\varphi = 0.33$ has also been obtained in CBOOA by Ribotta[5] and Clark[6] by inducing an elastic buckling instability. One may question the reliability of this method since it involves the study of a metastable state that relaxes by the nucleation of dislocations[19] and there is the possibility of a consequent renormalization of the elastic constants.[20] Thus it is important that the exponent is confirmed by our light scattering measurements. The instability produced can be one of several possible orders and it is a delicate matter to determine the correct numerical value of B/K_1 this way (Ribotta reports[5] values about five times greater than we find), but the proper temperature dependence of B/K_1 can still be obtained.[21]

Linewidth measurements in CBOOA at $q_z = 0$ gave us $K_1/\eta_s = (1.95 \pm 0.05) \times 10^{-6}$ cm^2 sec^{-1}, independent of T within experimental error for $T_c - 0.9$ K $< T < T_c + 0.5$ K. This agrees well with the value of Ribotta, Salin, and Durand[4] of $(2.0 \pm 0.2) \times 10^{-6}$ cm^2 sec^{-1}, at 75°C. Simultaneous intensity measurements showed K_1 to be temperature independent within ± 3% over the same temperature range.

We also measured D in CBOOA by changing the scattering geometry to collect only light scattered by the mode n_y with $q_x = 0$. One then observes scattered light of intensity proportional to $(D + K_3 q^2)^{-1}$ and the results of our measurements, normalized to unity at $T_c - T = 1$ K, are shown in Fig. 2. Close to T_c, the $K_3 q^2$ term is not negligible and our data also encompass the critical nonhydrodynamic region $q\xi > 1$. The data for $1 - T/T_c > 1.4 \times 10^{-3}$ are quite well described by a power law $(1 - T/T_c)^{\varphi'}$ with $\varphi' = 0.50 \pm 0.02$. We have made nematic-phase measurements[22] of $K_3 q^2$ which are fitted by a theoretical expression derived by Jahnig and Brochard[23] and which can be used to estimate the value of $K_3 q^2$ in the smectic phase. Adding this estimate to the above power law gives values of $D + K_3 q^2$ lying between the dashed lines in Fig. 2. Details will be published elsewhere, but we should remark for our experiment that nonhydrodynamic behavior of B and D is determined by the size of $q_z \xi_{\parallel}$ and $q_x \xi_{\perp}$, respectively.

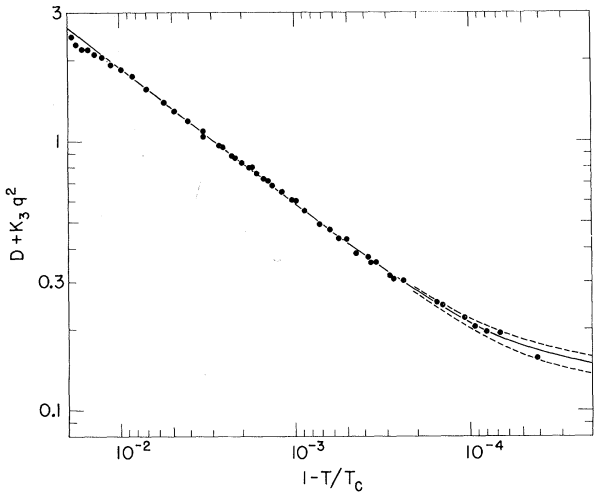

FIG. 2. A plot of $D+K_3q^2$ for CBOOA. The solid line is a $(1-T/T_c)^{0.50}$ power law with various corrections for K_3q^2 (as discussed in the text) lying between the dashed lines.

In order to indicate the significance of our central result, which is the different and unexpected values for the exponents φ and φ', we discuss the expected behavior under various circumstances. We assume q_0 to be temperature independent, as indicated by x-ray scattering measurements.[24] In a mean-field model, analogous to superconductivity, one expects M_v and M_t to be independent of temperature and thus $\varphi=\varphi'=1$. Since ψ is a two-component order parameter in three dimensions, renormalization-group calculations show that the asymptotic critical behavior should not be of mean-field type.[3] In that case, as for ordinary critical points,[25] the coefficients in the free-energy expression can be modified to give nonclassical behavior. When this is done, consistent with the scaling laws, one finds $B\sim\xi_{\parallel}^{-1}$ and $D\sim\xi_{\perp}^{-1}$. Thus nonclassical exponents φ and φ' should be the same as those for divergence of the correlation lengths in the smectic phase, and we would expect typical values (as, for example, in superfluid ^{4}He) $\varphi'=\varphi\simeq\frac{2}{3}$. However, we find exponents ($\varphi'=0.50$, $\varphi=0.33$) which are not equal either to each other or to the expected values; they also differ from correlation-length exponents estimated from pretransitional nematic-phase studies.[7-12,24] The unequal exponents are also not consistent with the scaling-law hypothesis, which is based on behavior near order-disorder phase transitions being dominated by a single divergent correlation length.

As an alternative explanation we considered the fact that ψ_0^2 appears to vary as $(1-T/T_c)^{1/3}$ over a narrow temperature range near a weakly first-order classical phase transition[26]; but our power law is obeyed over nearly three decades in reduced temperature and the data do not allow this explanation. It is also true that $\psi_0^2\sim(1-T/T_c)^{1/2}$ is the behavior expected near a tricritical point; however explanations in terms of analogies to known phase transitions all fail because the two exponents are not equal. Thus, while de Gennes's proposed form for the free energy, and the resulting analogy to charged superfluids, leads to a description of the smectic-A-phase mode structure which is qualitatively correct, it also predicts behavior near the phase transition which is in quantitative disagreement with the scaling hypothesis. Since the latter has been confirmed by a wide variety of experiments, we believe that the problem lies in the details of the proposed model. More precise x-ray studies of the smectic-A-phase would be valuable to ascertain directly if there are different divergences for the longitudinal and transverse correlation lengths. Both CBOOA and 8OCB are compounds with two molecules per smectic layer[27] and one should investigate single-layered smectics.

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Orbital Dynamics of ^{3}He-*A*

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We present a phenomenological theory, valid for $\hbar\omega \ll \Delta(T)$, which incorporates the ideas of Cross on normal-superfluid locking but uses quite different kinematics. Our results agree with his in the "overdamped" region, while we also predict a low-temperature "flapping" mode, orbital effects on the NMR, and a linear orbit-wave spectrum at $T=0$.

The dynamics of the vector $\vec{l}$ which describes the spatial orientation of the Cooper pairs in the superfluid *A* phase of ^{3}He [the Anderson-Brinkman-Morel (ABM) phase[1]] is currently the subject of much controversy.[2-4] In this Letter we present a phenomenological theory which should, we believe, be valid for all $\omega \ll \Delta(T)/\hbar$. An adequate account of the microscopic foundations for our phenomenological equations requires more space than is available here,[5] so we shall simply state them and derive some consequences, making them plausible only by intuitive arguments and, where appropriate, a comparison with the results of kinetic-equation calculations. (We shall however quote the microscopic formulas for relevant coefficients, so as to establish orders of magnitude.) We confine ourselves to the spatially uniform case except in application (4). We assume "particle-hole symmetry" (cf. Combescot[2]) except where otherwise stated; the more general case is briefly discussed in the last paragraph.

Our (intuitive) argument rests heavily on an analogy with the phenomenological spin dynamics.[6,7] However, at the outset it is necessary to recognize two important differences between the two cases (cf. Combescot[2]; a third difference, connected with the question of the spontaneous orbital angular momentum of the ABM phase,[8] plays no special role in our argument). (1) As first recognized by Cross[3] and independently by Combescot,[2] rotation of the $\vec{l}$ vector at fixed quasiparticle occupation number changes the energy of the system; we will call this the "normal locking" effect. (2) While the moment of inertia ("orbital susceptibility") of the normal component is proportional to $V^{5/3}$ (V = volume), one would expect that of the pairs to be at most[9] of order V. Thus, if a small increment of total angular momentum $\vec{L}$ is given to the system and hydrodynamic equilibrium is attained by $\vec{L}$-conserving collisions, the increment ends up carried almost exclusively by the normal component and is therefore ineffective in generating rotations of the pair order parameter. There is therefore *no* immediate analog of the hydrodynamic theory of Ref. 6 for the orbital dynamics.[10]

However, it *is* possible to adapt the ideas of