Nematic-smectic A-reentrant nematic transitions in 80CB : 60CB mixtures
A.R. Kortan, H. Von Känel, R.J. Birgeneau, J.D. Litster

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Résumé. — Nous avons étudié par diffusion des rayons-x à haute résolution les transitions nématic-smectique A (N-SA) et nématic réentrant-smectique A (RN-SA) dans des mélanges de octyloxycyanobiphenyle (8OCB) et de hexyloxycyanobiphenyle (60CB). Sur le graphe température en fonction de y, rapport moléculaire 60CB:8OCB, la frontière smectique A-nématic est une parabole centrée autour d'une température moyenne $T_M = 38.06 \, ^\circ C$. La phase smectique existe pour $y$ inférieur à $y_0 = 0.427$. Nous avons étudié les fluctuations smectiques dans la phase nématic pour $y = 0.33 ; 0.413$ et 0.420. Nous avons fait aussi des expériences pour $y = 0.429 ; 0.440$ et 0.443 où la longueur de corrélation smectique et la susceptibilité présentent un maximum à $T_M$.

Il a été possible d'analyser quantitativement les résultats en employant une extension de la théorie de Pershan et Prost qui suppose une densité optimale. On trouve un bon accord entre les données et la théorie avec les exposants critiques $v_I = 0.76 \pm 0.03$, $v_L = 0.62 \pm 0.05$ et $\gamma = 1.49 \pm 0.07$, qui correspondent bien aux valeurs obtenues pour un smectique monocouche ayant une phase nématic de même taille. Donc, les transitions N-SA et RN-SA sont de même nature que la transition N-S_A habituelle si on tient compte de la frontière parabolique. Nos observations du facteur de structure fluide dans le plan des couches des phases N, S_A et RN montrent que la séparation moyenne des molécules et les corrélations de position ressemblent à ceux des smectiques monocouches. Dans chaque phase le facteur de structure est bien décrit par une Lorentzienne après moyenne azimutale avec une longueur de corrélation de 6.9 Å. Ces résultats vont à l'encontre des modèles expliquant le comportement réentrant par un changement de couplage moléculaire. Nous discutons le modèle de densité optimale, qui a réussi ici, et d'autres modèles de paramètre d'ordre en compétition qui sont nécessaires pour expliquer le comportement observé dans d'autres matériaux polaires.

Abstract. — We have carried out an extensive high resolution x-ray scattering study of the nematic-smectic A (N-SA) and reentrant nematic-smectic A (RN-SA) phase transition behaviour in mixtures of octyloxycyanobiphenyl (8OCB) and hexyloxycyanobiphenyl (60CB). The smectic A phase boundary is found to be parabolic in the temperature-concentration plane with a median temperature $T_M = 38.06 \, ^\circ C$ and a critical concentration $y_0 = 0.427$; here $y$ is the 60CB:8OCB molecular ratio. Detailed studies of the smectic fluctuations in the nematic phase are reported for $y = 0.33, 0.413, 0.420, 0.429, 0.440$ and 0.443. The first three concentrations exhibit N-SA and RN-SA transitions, whereas in the latter three samples with decreasing temperature the smectic correlation lengths and susceptibility exhibit maxima at $T_M$ and then decrease with a further decrease in temperature.

The data are analysed using an extension of the Pershan-Prost optimal density theory. All of the data are well-described by the phenomenological theory; the critical exponents so-obtained are $v_L = 0.76 \pm 0.03$, $v_I = 0.62 \pm 0.05$ and $\gamma = 1.49 \pm 0.07$. These agree quantitatively with values obtained in single layer materials with comparable nematic ranges; thus the N-SA and RN-SA transitions are identical in character to conventional N-SA transitions provided that one includes the crossover effects inherent in the parabolic phase boundary. Studies of the in-plane fluid structure factor in the N, S_A and RN phases show that the mean molecular spacings and positional correlations are closely similar to those in single layer materials; in each phase the structure factor is well described by a circularly-averaged Lorentzian with a correlation length of 6.9 Å. These results argue strongly against pairing models for the reentrant behaviour. We conclude with a phenomenological discussion of the optimal density model which is so successful here and models based on competing order parameters which are required to describe the varied behaviour observed in other polar materials.

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1. Introduction.

Reentrant behaviour in liquid crystals was first discovered by Cladis [1]. Successive nematic (N), smectic A (SA) and reentrant nematic (RN) phases as a function of decreasing temperature could be produced either by pressure in a single material [2] or by making appropriate mixtures of materials with and without smectic A phases [1, 3]. Since this seminal work, a large number of materials and mixtures have been discovered which exhibit reentrant phenomena [4]. These materials all possess in common the features that the constituent liquid crystal molecules have strongly polar end groups such as CN\(^-\) and that the smectic A lattice constant is incommensurate with respect to a single molecular length. In a series of beautiful experiments the Bordeaux group [4] and others [5] have shown that these polar materials exhibit unexpectedly rich behaviour with at least six distinct smectic A or C phases. The reentrant phenomenon must ultimately be understood within this broader context.

Reentrant behaviour at first seems to violate the intuitive notion that less ordered phases should exist at higher temperatures than high symmetry ones. In fact, however, reentrancy is observed in a broad range of physical systems. Examples include reentrant behaviour in magnetic superconductors [6], reentrant spin glass behaviour in mixtures of ferromagnets and antiferromagnets [7], and reentrant melting in surface monolayers exhibiting commensurate and incommensurate periods [8]. This final example is particularly germane to the liquid crystal problem. In all of these cases the return to a disordered state with decreasing temperature is caused by competing order parameters. It is likely that competing order parameters account for the N-SA-RN behaviour in the polar liquid crystal systems. However, because of our rather poor understanding of the microscopic interactions responsible for smectic ordering in the first place, it is not obvious what is the appropriate choice of order parameters. Further, predictive theory turns out to be quite difficult. Early theories [2], inspired by the bilayer \( d = a / r \) where \( r \) is the molecular length and \( 1 < a < 2 \) nature of the A phase, introduced the degree of pairing as an order parameter. This has been elaborated on by Longa and de Jeu [9]. Others have included the dipole moment \([10, 11]\) as the additional order parameter. An alternative approach, based on the concept of an optimal density for smectic ordering, has been given by Pershan and Prost [12]. Unfortunately, these theories are all primarily qualitative in character although by appropriate measurements it is possible to show that certain of them are highly implausible. We shall discuss the applicability of these theories to the octyloxybiphenyl : hexyloxybiphenyl (8OCB:6OCB) system in detail in the final section of this paper.

One of the simplest and most important questions is whether or not the critical behaviour characterizing the N-SA and RN-SA transitions is identical to that in ordinary single layer N-SA transitions. The latter is by now well characterized experimentally although there is not as yet a wholly convincing theory [13]. In order to determine the critical behaviour it is also necessary to incorporate properly the crossover effects which are attendant with the geometry of the reentrant phase boundary. The principal purpose of our study was to carry out a detailed study of the N-SA and RN-SA critical behaviour in 8OCB:6OCB mixtures with emphasis on the concentration region where the bilayer smectic state ceases to be stable.

The format of this paper is as follows. The experimental details are given in section 2. Section 3 presents an extension of the Pershan-Prost model to incorporate critical rather than mean field behaviour and to include gradient terms. The experimental results and interpretation are given in section 4. Finally, a critical discussion of current theoretical models and our conclusions are given in section 5.

A preliminary report of part of these results was given in [14].

2. Experimental.

The 6OCB and 8OCB compounds studied in this experiment were used as received from British Drug Houses. Seven different mixtures were prepared by weighing sufficient quantities that concentrations were known to better than \(10^{-3}\) molar fraction. Samples were sealed in aluminum cells of dimensions \(1.5 \times 8 \times 10\) mm with 10 mil Be windows. A calibrated thermistor embedded in the aluminum cell enabled us to measure the temperature with mK precision, while a two-stage oven controlled the sample temperature to 2 mK. Nematic to smectic transition temperatures could be identified to within 2-10 mK by a sharp increase in sample mosaicity and remained stable during the course of the experiments.

A 12 kW Rigaku source provided x-rays at the Cu-K\(\lambda\) wavelength \((\lambda = 1.54\) Å\). Incident and scattered beams were collimated by (111) reflections from perfect Si crystals. The longitudinal resolution in the scattering plane was typically 1 µm in real space; precise values for each measurement are given in table I. The spectrometer transverse in-plane resolution is essentially perfect; however, near \(T_c\) some slight broadening may arise from the sample director mosaicity that originates in the competition between wall alignment forces and the 4 kOe magnetic field used to align the sample. Nematic phase mosaicities ranged from 0.05° to 0.2°, giving as an upper limit the resolution shown in table I. When the mosaicity is less than 0.001 \(q_0\), \(q_0 = 0.206\) Å\(^{-1}\), correction for it does not alter the results of data analysis measurably; accordingly no corrections for mosaicity were made for...
Table I. — The experimentally determined values of various parameters for the seven different mixtures studied (see text).

<table>
<thead>
<tr>
<th>Sample (y)</th>
<th>Transition</th>
<th>$T_c$ (°C)</th>
<th>$q_0$ (Å$^{-1}$)</th>
<th>Longitudinal resolution (°)</th>
<th>Vertical resolution (°)</th>
<th>Mosaicity (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>N-S$_A$</td>
<td>66.920</td>
<td>0.198</td>
<td>$8.27 \times 10^{-4}$</td>
<td>0.235</td>
<td>(°)</td>
</tr>
<tr>
<td>0.330</td>
<td>N-S$_A$</td>
<td>50.915</td>
<td>0.204</td>
<td>$11.05 \times 10^{-4}$</td>
<td>0.235</td>
<td>0.001</td>
</tr>
<tr>
<td>0.413</td>
<td>N-S$_A$</td>
<td>43.190</td>
<td>0.206</td>
<td>$10.68 \times 10^{-4}$</td>
<td>0.443</td>
<td>0.004</td>
</tr>
<tr>
<td>0.413</td>
<td>RN-S$_A$</td>
<td>32.940</td>
<td>0.206</td>
<td>$10.68 \times 10^{-4}$</td>
<td>0.443</td>
<td>(°)</td>
</tr>
<tr>
<td>0.420</td>
<td>N-S$_A$</td>
<td>41.975</td>
<td>0.206</td>
<td>$12.52 \times 10^{-4}$</td>
<td>0.231</td>
<td>(°)</td>
</tr>
<tr>
<td>0.420</td>
<td>RN-S$_A$</td>
<td>34.153</td>
<td>0.206</td>
<td>$23.89 \times 10^{-4}$</td>
<td>0.231</td>
<td>0.003</td>
</tr>
<tr>
<td>0.429</td>
<td>—</td>
<td>—</td>
<td>0.206</td>
<td>$10.43 \times 10^{-4}$</td>
<td>0.231</td>
<td>—</td>
</tr>
<tr>
<td>0.440</td>
<td>—</td>
<td>—</td>
<td>0.207</td>
<td>$6.37 \times 10^{-4}$</td>
<td>0.231</td>
<td>—</td>
</tr>
<tr>
<td>0.443</td>
<td>—</td>
<td>—</td>
<td>0.207</td>
<td>$7.05 \times 10^{-4}$</td>
<td>0.231</td>
<td>—</td>
</tr>
</tbody>
</table>

(°) Units of $q_0$, half width at half maximum.
(°) Measured mosaic is less than 0.001 $q_0$.

three of the samples studied. In the other cases the mosaicity correction only affects the points closest to $T_c$. Resolution normal to the scattering plane was determined by slits and varied from $4.7 \times 10^{-2}$ Å$^{-1}$ to $9.1 \times 10^{-2}$ Å$^{-1}$ as given in table I.

Sample concentrations were expressed as the parameter $y$ which is the ratio of 60CB to 80CB molecules in the mixture; $y$ is 1.10 times the weight ratio. Smectic phases were observed in samples with $y \leq 0.420$ (see Fig. 1); however the smectic A-reentrant nematic (SA-RN) transition occurs below the solidification point and can only be observed by supercooling the latter transition. Scans with momentum transfer along, $q_y$, and transverse, $q_z$, to the director for the necessary temperatures to study the SA-RN transition typically took a week. For samples with $y = 0.000$ and 0.300 crystallization prevented studying the RN-S$_A$ transition. In samples with $y = 0.413$ and 0.420 no sign of crystallization occurred even after ten days. We also studied the S$_A$ short range order in three samples, $y \geq 0.429$, which did not have a smectic phase.

3. Phenomenological model.

As we reported in a preliminary publication [14], our results could be quantitatively described by extending the phenomenological model proposed by Pershan and Prost [12]. Before presenting our results we outline the model used to analyse them. The Pershan and Prost model was a mean field one; our modifications included changes to accommodate non-classical critical exponents and the addition of gradient terms to the free energy expansion.

The N or RN phase free energy density for S$_A$ fluctuations can be expanded in a power series in the S$_A$ order parameter $\psi$ as

$$
\Phi_s = \Phi_0 + \frac{1}{2} a (T - T^*)^2 |\Psi|^2 + \frac{1}{4} b (T - T^*)^2 |\Psi|^4 + \frac{1}{2} M_v |\nabla_\parallel \Psi|^2 + \frac{1}{2} M_T |(\nabla_\perp + iq_0 \partial_{n_\perp}) \Psi|^2 + \cdots
$$

(1)
where \( \Phi_N \) is the N phase, \( \Psi = 0 \), free energy density. In this expression \( y \) and \( \beta \) are the usual critical exponents, and transition to a smectic phase occurs at \( T = T^* \). The value of \( T^* \) is a measure of the strength of the interaction that produces \( S_A \) ordering and it will depend upon external variables such as the 8OCB concentration and the density of the fluid. The suggestion of Pershan and Prost was that there is an optimum density, \( \rho_0 \), for the smectic interaction. They also assumed a reduction in the smectic interaction proportional to \( y \). This leads to

\[
T^* = T_1 - t_1 y - c_1 (\rho/\rho_0 - 1)^2 .
\] (2)

If one assumes the density to vary with temperature as

\[
\rho(T - T_0) = \rho(T_0) [1 - \beta T (T - T_0) + \cdots]
\]

with \( \beta_T \) the thermal expansion coefficient, then

\[
T^* = T_1 - t_1 y - c_2 (T - T_0)^2
\] (3)

follows straightforwardly. In these equations \( T_1 \) would be the \( S_A \)-N transition temperature for pure 8OCB at its optimum density, which is the density that would occur at \( T_0 \). The phase boundary \( T_c(T, y) \) is found by solving the equation \( T_c = T^* \). With the definitions

\[
\Delta T = (1/c_2) [1 - 4 c^2 (T_0 - T_1 + t_1 y)]^{1/2}
\] (4a)

\[
T_M = T_0 - 1/2 c^2
\] (4b)

and

\[
y_0 = [1 + 4 c^2 (T_1 - T_0)]/4 c^2
\] (4c)

we find

\[
T_c = T_M \pm \sqrt{t_1 (y_0 - y)/c_2} = T_M \pm \frac{1}{2} \Delta T .
\] (5)

Thus the simplest coupling between \( \Psi, \rho \) and \( y \) which is qualitatively consistent with the phase diagram predicts a parabolic phase boundary; this is a consequence of the analytic dependence on \( \rho \) and \( y \) which was assumed in (2).

As we showed previously [14], the phase diagram is represented within experimental errors by equation 5, provided the OCB concentration is expressed as \( y \) rather than as the mole fraction \( x = y/(1+y) \). The fit is shown in figure 1. We found the parameters \( t_1/c_2 = 1.936 \, \text{K}^2 \), \( y_0 = 0.4267 \), and \( T_M = 311.215 \, \text{K} \); these agree well with \( t_1/c_2 = 1.929 \, \text{K}^2 \), \( y_0 = 0.4231 \), and \( T_M = 310.3 \, \text{K} \) which we obtained from the phase diagram of Guillon et al. [3]. The parameter \( T_0 \) is apparently independent of \( y \); since the density increases with \( y \), if equation 3 follows from equation 2 it must be that \( \rho_0 \) also increases with \( y \) in order to keep \( T_c \) constant.

If the pressure is changed, one would expect from equation 2 that the phase boundary should satisfy

\[
T_1 - t_1 y - T_c - c_1 (\rho/\rho_0 - 1)^2 (T_0 - T_c + (\kappa_T/\beta_T) P)^2 = 0
\] (6)

where \( \kappa_T \) is the isothermal compressibility of the mixture. The maximum pressure at which a smectic phase can exist is readily found to be

\[
P_M = \left( \beta_T/\kappa_T \right) (T_1 - t_1 y - T_0 - 1/4 c_2)
\]

thus \( P_M \) is predicted to decrease linearly with \( y \) and to go to zero at \( y = y_0 \). As a caution, we point out that Cladis et al. [2] found \( P_M \) to decrease linearly with the quantity \( 2 x(1-x) - x^2 \), and to vanish at \( x_0 = y_0/(c + y_0) \). It seems that a more complicated expression than equation 6, presumably including higher order terms, is required to represent the global pressure, temperature, and concentration phase diagram. The fact remains however that equation 5 represents the phase diagram at constant pressure very well and, as we shall show presently, provides a basis for a quantitative description of the smectic A short range order.

Since \( \Psi \) is the amplitude of the \( S_A \) mass density wave, \( \rho = \langle \rho \rangle = [1 + R_x \{ \Psi(r) e^{i\varphi(r)} \}] \), an expression for the mass density fluctuations may be straightforwardly obtained from the Fourier transform of equation 1. For \( y < y_0 \), we define \( \delta T = |T - T_c| \) so that \( T - T^* = c^2 (\delta T/\Delta T) + \Delta T^* \); then with \( t = \delta T/\Delta T \) the fluctuations may be written

\[
\langle |\delta \Psi(q)|^2 \rangle \sim \frac{kT \delta T^{-\gamma}}{1 + \xi_{\|}^2 (q-\tilde q_0)^2 + \xi_\perp^2 q_\perp^2} .
\] (7)

In equation 7 \( \xi_{\|}^2 = aM \alpha T \) and \( \xi_\perp^2 = aM \alpha r^2 \). Since the observed correlation lengths have different critical exponents, we must write \( M_{\alpha} \sim (T - T^*)^{2\nu_{\alpha} - \gamma} \) and \( M_r \sim (T - T^*)^{2\nu_r - \gamma} \). The correlation lengths are given by

\[
\xi_{\|} q_0 = c_{\|} \{ (T_c \Delta T) [t + (T_c/\Delta T)^2] \}^{-\nu_{\|}}
\] (8a)

and

\[
\xi_\perp q_0 = c_\perp \{ (T_c \Delta T) [t + (T_c/\Delta T)^2] \}^{-\nu_\perp}
\] (8b)

where \( c_{\|}, c_\perp \) are constants. Since \( \Delta T \) is the width of the \( S_A \) range, these equations predict that the bare correlation lengths should increase and the effective exponents crossover from \( \nu \) to \( \nu_r \) as \( \alpha T \to 0 \). The crossover exponent of \( \nu_r \) is a consequence of the mathematical form of equation 2 or equivalently, the fact that the phase boundary empirically is parabolic in form.

When \( y > y_0 \) there is no stable smectic phase and one finds short range order given by:

\[
\langle |\delta \Psi(q)|^2 \rangle \sim \frac{kT [T - T_M]^2 + (t_1/c_2) (y - y_0)]^{-\gamma}}{1 + \xi_{\|}^2 (q - \tilde q_0)^2 + \xi_\perp^2 q_\perp^2}
\] (9)

with

\[
\xi_{\|} q_0 = c_{\|} \{ (T - T_M)^2 + (t_1/c_2) (y - y_0) \}^{-\nu_{\|}}
\] (10a)

and

\[
\xi_\perp q_0 = c_\perp \{ (T - T_M)^2 + (t_1/c_2) (y - y_0) \}^{-\nu_\perp} .
\] (10b)

The above theory leaves out certain subtle features of the N-S\(_A\) transition. Experiments [13] have shown
that both the exponents and the bare lengths increase slightly with increasing nematic range. Thus for example in 40.8, which has a nematic range of 15 K, \( \nu_\parallel = 0.70, \nu_\perp = 0.57, \gamma = 1.31 \) and \( \xi_0 q_0 = 1.04 \) [15] whereas 40.7, with a nematic range of 26 K, has \( \nu_\parallel = 0.78, \nu_\perp = 0.65, \gamma = 1.46 \) and \( \xi_0 q_0 = 1.55 \). The exponents and lengths in 80CB [16], which has a 14 K nematic range are closely similar to those in 40.8 (see Table II); since adding 60CB decreases \( T_{N/A}/T_{NI} \) we might expect a corresponding increase in the exponents and lengths beyond those predicted by equations 10a, b.

4. Results and interpretation.

4.1 Comparison of scattering results with the model. —Experimental scans were made along \( q_\parallel \) and along \( q_\perp \) for a series of temperatures near N-S\(_A\) and RN-S\(_A\) transitions for \( y < y_0 \). We emphasize that \( T_c \) was measured rather than treated as an adjustable parameter. The data at each temperature were fit to

\[
R(q) = \frac{\sigma_0}{1 + \xi_0^2 (q_\parallel - q_0)^2 + \xi_0^2 q_\perp^2 + \xi_0^2 q_\perp^2} \cdot R(q)
\]

(11)

where \( R(q) \) was the measured spectrometer resolution function. As in many previous experiments, the \( \xi_0^2 q_\perp^2 \) form was required in order to fit the data; we shall discuss it presently. In analysing data at various temperatures \( \sigma_0 \) was assumed to vary as \( r^{-\gamma} \), \( c \) was taken to be a free parameter, and the correlation lengths were fit to equation 8 for \( y < y_0 \) and equation 10 for \( y > y_0 \). \( T_M \) was found to be independent of \( y \) and \( \Delta T \) was obtained from the phase boundary. We first allowed \( \xi_\parallel, \xi_\perp, \nu_\parallel, \) and \( \nu_\perp \) to assume their optimum values for each sample; the results for the exponents are given in Table II. Both the exponents and the amplitudes increase slightly with increasing nematic range as found in pure systems. In the final fits, the exponents for \( y \neq 0 \) were held fixed to their average values \( \nu_\parallel = 0.76 \) and \( \nu_\perp = 0.62 \). The results of these fits are shown as solid lines in figure 2. The amplitudes \( c_\parallel \) and \( c_\perp \) approximately double in going from pure 80CB to \( y = 0.42 \).

For comparison purposes, we also fit the correlation lengths with \( y < y_0 \) to simple power laws and obtained the effective exponents given in Table III. The simple power laws described the data poorly, because of the increasing curvature in the log-log plots with increasing \( y \). It is clear from figure 2 that equation 8 with a single set of exponents can describe the divergences in the correlation lengths quite well. The anisotropy in exponents, \( \nu_\parallel - \nu_\perp \simeq 0.14 \), is in agreement with other studies of the smectic A to nematic transition [13].

The correlation lengths in three mixtures with no smectic phase were fit to equation 10 and the results are given in Table II. The measured correlation lengths are shown in figure 3 along with the fit results where \( \nu_\parallel \) and \( \nu_\perp \) were held to their average values.

Table II. — The critical exponents extracted from the best fits to the equations (8a, 8b), (10a, 10b), (12a, 12b) that are derived from the phenomenological theory.

<table>
<thead>
<tr>
<th>Sample (y)</th>
<th>Transition</th>
<th>( \nu_\parallel )</th>
<th>( \nu_\perp )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>N-S(_A)</td>
<td>0.71</td>
<td>0.58</td>
<td>1.32</td>
</tr>
<tr>
<td>0.330</td>
<td>N-S(_A)</td>
<td>0.76</td>
<td>0.57</td>
<td>1.49</td>
</tr>
<tr>
<td>0.413</td>
<td>N-S(_A)</td>
<td>0.78</td>
<td>0.60</td>
<td>1.48</td>
</tr>
<tr>
<td>0.413</td>
<td>RN-S(_A)</td>
<td>0.80</td>
<td>0.70</td>
<td>1.56</td>
</tr>
<tr>
<td>0.420</td>
<td>N-S(_A)</td>
<td>0.75</td>
<td>0.58</td>
<td>1.38</td>
</tr>
<tr>
<td>0.420</td>
<td>RN-S(_A)</td>
<td>0.73</td>
<td>0.64</td>
<td>1.42</td>
</tr>
<tr>
<td>0.429</td>
<td>Single fit</td>
<td>0.79</td>
<td>0.62</td>
<td>1.43</td>
</tr>
<tr>
<td>0.440</td>
<td>Single fit</td>
<td>0.74</td>
<td>0.59</td>
<td>1.52</td>
</tr>
<tr>
<td>0.443</td>
<td>Single fit</td>
<td>0.75</td>
<td>0.67</td>
<td>1.49</td>
</tr>
<tr>
<td>Averaged values</td>
<td></td>
<td>0.76</td>
<td>0.62</td>
<td>1.49</td>
</tr>
</tbody>
</table>

Fig. 2. — Parallel and perpendicular correlation lengths measured for four different mixtures of 80CB:60CB. The dramatic increase in the lengths with increasing \( y \) is accompanied by slight increases in the slopes and the curvature. Note the similarity of the reentrant nematic-smectic A transition divergences to those of the nematic-smectic A transition. The solid lines are fits to (8a) and (8b) with \( \nu_\parallel = 0.76 \) and \( \nu_\perp = 0.62 \).
Table III. — Results of fits of N-SA correlation lengths and smectic susceptibility to single power laws.

| Sample (γ) | v_|| | v_⊥ | γ   |
|-----------|-----|-----|-----|
| 0.000     | 0.71| 0.58| 1.32|
| 0.330     | 0.81| 0.61| 1.61|
| 0.413     | 0.93| 0.70| 1.77|
| 0.420(*)  | 0.95| 0.73| 1.75|

(*) RN-S_A transition data.

The data for the intensity of the scattering were fit to these expressions following the same procedure as for the correlation lengths. That is, T_c, ΔT, and T_M were set equal to the measure values while the coefficients and exponents were varied for each sample; then the exponent was fixed at the average value given in table II and the coefficients varied. As with the correlation lengths, holding γ = 1.49 did not significantly increase \( \chi^2 \). The data and fit results are shown in figures 4 and 5.

As we mentioned previously, the \( c \xi^2 q^4 \) term in equation 11 is necessary to obtain an acceptable fit to the transverse scans, as has also been observed in all previous high resolution x-ray scattering from smectic A short range order. Previous experiments also suggested [17] the coefficient c became small as \( T \to T_c \). If c were, in fact, to vanish as a power of \( T - T_* \), then we would expect to observe the same doubling of exponents for \( y \to y_o \) that occurs in other quantities. The values of c obtained from our fits are rather uncertain but are indeed consistent with the exponent doubling. Furthermore, just as the correlation lengths for a given \( T - T_c \) become longer as \( y \to y_o \), we also found the value of c to become much smaller at fixed \( T - T_c \) as the smectic range narrowed. These trends are illustrated in figure 6.

It is evident that the simple phenomenological model gives a good description of the data. The exponents in the neighbourhood of \( y_o = 0.427 \) are \( v_\parallel = 0.76, v_\perp = 0.62 \) and \( γ = 1.49 \). These agree quite well with the values for materials with a comparable nematic range such as 40.7 where \( v_\parallel = 0.78, v_\perp = 0.65 \) and \( γ = 1.46 \). As we noted previously the values for

The susceptibility is predicted from the model to follow

\[
\sigma_0 = c_\sigma \left\{ (T_c - \Delta T) \left[ t + (T_c / \Delta T) \xi^2 \right] \right\}^{-\gamma} \quad y < y_0
\]

or

\[
\sigma_0 = c_\sigma \left\{ c_2 (T - T_M)^2 + t_1 (y - y_o) \right\}^{-\gamma} \quad y > y_0.
\]

The susceptibilities for the smectic A like fluctuations of the mixtures with \( y > y_o \) far away from \( T_M \) lengths diverge with doublet effective exponents but they saturate to finite values as \( T_M \) is approached. The solid lines are fits to equation 10, with \( v_\parallel = 0.76 \) and \( v_\perp = 0.62 \).

Fig. 3. — Parallel and perpendicular correlation lengths for the smectic A like fluctuations of the mixtures with \( y > y_o \). Far away from \( T_M \) lengths diverge with doublet effective exponents but they saturate to finite values as \( T_M \) is approached. The solid lines are fits to equation 10, with \( v_\parallel = 0.76 \) and \( v_\perp = 0.62 \).

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\]
Fig. 5. — The measured susceptibility at $q = q_0$ versus temperature for $y > y_0$. The maximum occurs at $T_M = 38.065$ in all $y > y_0$ samples. The solid lines are the results of fits to equation 12b.

80CB agree well with those in 40.8. The bare lengths increase slightly with increasing nematic range. For example $c_i(N-S_A) \approx 0.8 c_i(RN-S_A)$. This again is consistent with the behaviour seen in ordinary N-S_A transitions. It is possible that one could incorporate these subtle effects into the model, albeit at the expense of making it much more complicated. However, we prefer to leave $c_i$ and $c_2$ as adjustable parameters.

To conclude this section we can make a quantitative comparison with the heat capacity measurements of Lushington et al. [18] who studied pure 80CB and mixtures with $y = 0.15, 0.275$, and 0.407. They observed that the $y = 0.15$ and $y = 0.275$ data coincided with $y = 0$ data if scaled by 2.38 and 7.14, respectively, while the specific heat peak was too small to observe when $y = 0.407$. We may use the hypothesis of two scale factor universality [19] which assumes the free energy per correlation volume is a universal number, to estimate the appropriate scaling factors. Using our model to estimate correlation lengths we calculate scaling factors of 2.6 at $y = 0.15$ and 7.1 at $y = 0.275$, in good agreement with Lushington et al. For $y = 0.406$ the specific heat anomaly should be about 0.4% of the background and therefore not observable in the experiments. It should be noted that two scale factor universality also describes well the difference in heat capacity amplitudes for 80CB and 40.8 [15].

4.2 IN-PLANE CORRELATIONS. — In the previous section we discussed studies of the smectic A density wave, whose wave vector is parallel to the nematic director. We also studied mass density correlations perpendicular to the nematic director in order to test pairing models for the reentrant behaviour. These measurements were made on a sample with $y = 0.420$ as nematic, smectic, and reentrant nematic phases were all easily accessible.

A special sample cell with electrically insulated Be windows allowed us to align the molecules with a 800 V/mm ac field at 200 Hz. This frequency and voltage choice was found to produce the best alignment, with a mosaic spread of about one degree. To eliminate charge injection into the sample, Kapton insulation was placed between the sample and the electrodes.

An x-ray intensity monitor in the beam was used to correct for variations in the incident x-ray power. Scans were made over a wide range of in-plane momentum transfers, from 0.15 Å$^{-1}$ to 4.5 Å$^{-1}$, at various temperatures. The only feature observed was the liquid structure factor shown in figure 7 as contours of equal intensity. The peak position at 1.447 Å$^{-1}$ corresponds to an average intermolecular distance normal to the director of 5.01 Å, which is about the size of a single biphenyl group.

This matches to within 1% the average transverse spacing between the molecules in such single layer smectic materials as 40.7 and 885 [20]. Careful scans of the liquid peak were made at several temperatures both normal to and along the director. In figure 8 we
Fig. 7. — Constant intensity contours of the transverse liquid structure factor in the \((H, 0, K)\) plane. The units of \(H\) and \(K\) are \(1.447 \text{ Å}^{-1}\) and \(0.206 \text{ Å}^{-1}\) respectively.

Fig. 8. — Parallel and perpendicular scans of the in-plane peak in the nematic, smectic A and reentrant nematic phases. Correlations within the smectic layer appear liquid-like in all three mesophases and further the profiles are identical except for a subtle change in the overall intensity. The solid lines are fits to the circularly-averaged Lorentzian model of reference 20 (see text).

show these scans in the N, \(S_A\) and RN phases. The liquid structure factor is identical in all three phases except for a small change in the intensity scale factor (see Fig. 9).

In order to describe the transverse intermolecular correlations quantitatively we use a model introduced by Ocko et al. [20]. As discussed extensively in reference 20, \(S^T(q)\) may be described by a three-dimensional Lorentzian which is circularly averaged in the plane perpendicular to the director. The results of fits to this model are shown as the solid lines in figure 8; clearly the model describes the data quite well. The transverse positional correlation length so-obtained in each of the N, \(S_A\) and RN phases is \(6.9 \text{ Å}\); this is about a factor of 2 smaller than that in 4O.7 and \(~ 1.5\) less than that in 8S5.

5. Discussion and conclusions.

The most important result of these experiments is that a very simple model based on the concept of an optimal density for bilayer smectic ordering describes the phase boundary and critical behaviour for both N-\(S_A\) and RN-\(S_A\) transitions quite well. This includes the observed doubling of the exponents near the critical concentration. Further, both the exponents and the amplitudes are consistent with those found in ordinary single layer N-\(S_A\) transitions. It is not immediately obvious from a microscopic point of view why this model is so successful. There are many distinct contributions to the free energy in these bilayer materials including the usual entropy and attractive interaction terms as well as the antiferroelectric interactions between the dipoles. Although it is possible to construct many heuristic arguments as to why these might generate an optimal density we do not find any of these (including our own) very convincing; certainly such explanations are not unique. In any case, if the optimal density idea is used in isolation one cannot understand the remarkable variety of smectic phases and phase transitions observed for polar materials as a whole [4, 11]. Thus a broader explanation is required.

In the early stages attempts were made to understand the reentrant behaviour using a pairing model [2, 3, 9]. In these models it is assumed that isolated molecules favour smectic ordering and that pairs of associated molecules favour the nematic state, that is, the degree of molecular association represents the competing order parameter. The pairing fraction is assumed to increase with decreasing temperature thus generating
the reentrant behaviour. Although this model has some attractive features, it is evident that it is incompatible with our in-plane structure factor measurements. As we have emphasized in the previous section, the transverse positional correlations in these bilayer materials are indistinguishable from those in single layer materials; further the correlations do not exhibit a measurable change throughout the N, S\textsubscript{A} and RN phases. Thus any changes in the pairing order parameter would have to be extraordinarily delicate, certainly much less than those estimated, for example, by Longa and de Jeu [9].

We should also note that in certain of the models it is implicitly assumed that the smectic ordering in these reentrant systems is anomalously weak. Our results show that this is not the case. Part of the evidence which is typically cited is the absence of higher harmonics in the mass density order parameter [21]. In fact, the best evidence for a purely sinusoidal mass density wave is for single-layer rather than bilayer materials [20].

In another model [10] there is a competition between short range positional order and long range antiferroelectric order. When solved in a two dimensional approximation, this model predicts a reentrant phase diagram similar to that observed. However it proposes a mechanism quite different from that for ordinary N-S\textsubscript{A} transitions; this must be reconciled with our measurements showing that the N-S\textsubscript{A} transitions in the 80CB:60CB system are identical in character to second order transitions in single layer materials such as butoxybenzylidene octylaniline (40.8). We have also shown that in-plane molecular positional correlations only extend over 6.9 Å in all phases. It is difficult for us to believe that this would be adequate to generate antiferroelectric disorder due to frustration. Finally, the dielectric permittivity varies smoothly through the N, S\textsubscript{A}, and RN phases [22]. Presumably any significant changes in antiferroelectric long or short range order would have a more dramatic effect on the dielectric properties.

As we stated in the introduction to this paper, the multiplicity of smectic phases now observed for polar materials [4] necessitates a description based on competing period order parameters [11]. This may be discussed qualitatively as follows. Here we limit ourselves to consideration of the bilayer (\(d \approx 1.3\) Å) and monolayer (\(d \approx l\)) phases; here \(l\) is the molecular length. Following Prost and Barois [11] if the free energy is expanded in a Fourier series in the mass density \(p(q)\) then minima may occur for both \(p(2\pi/\lambda)\) where \(1 < \alpha < 2\) and \(p(2\pi/l)\). In constructing the free energy one must incorporate the van der Waals interactions, dipole-dipole interactions etc. as well as the entropy. It seems evident that the bilayer phase is favoured by entropy since the loose packing in the aliphatic tail region allows for relatively unrestricted rotation of the \(\text{C}_n\text{H}_{2n+1}\) group. Thus, if the interaction energies of the bilayer and monolayer states are comparable then with decreasing temperature the minimum in the free energy may change from \(q = 2\pi/\lambda\) to \(q = 2\pi/l\).

In a mean field description, this would precipitate a first order bilayer-monolayer transition. However, fluctuations may alter this conclusion. It is well known that S\textsubscript{A} states exhibit Landau-Peierls behaviour [21] due to divergent long wave length fluctuations so that the N-S\textsubscript{A} transition deviates maximally from the mean field limit. The essential physical idea is that in the bilayer state as the free energies \(\Phi(q = 2\pi/\lambda)\) and \(\Phi(q = 2\pi/l)\) become comparable the system will begin to exhibit local fluctuations into the monolayer phase and these fluctuations destroy the bilayer order. An approximate calculation which illustrates this effect has been given by Prost and Barois [11]. Perhaps more convincingly, this reentrant behaviour due to competing periods is well known for surface overlayers. For example, for monolayer krypton on graphite the krypton-krypton van der Waals interactions favour one period whereas the graphite substrate favours another. In the monolayer coverage region the commensurate state occurs at higher temperatures; with decreasing temperature and/or increasing density the commensurate phase melts into a reentrant liquid [8]; this liquid then freezes into the incommensurate state with further decrease in temperature. Although the physics in the two cases differs we believe that they have in common the feature of large scale fluctuations between two competing periods for systems at their lower marginal dimensionality.

The above model almost certainly applies for reentrant systems such as T8 [23] which exhibits both bilayer and monolayer phases. However, we have not been able to observe the monolayer phase in 80CB:60CB mixtures. In fact, however, it involved considerable difficulty on our part to stabilize the reentrant nematic phase for a long enough time period for us to carry out the measurements reported in this paper. Thus if a monolayer smectic phase did occur at lower temperatures it would be totally inaccessible due to crystallization. The applicability of the competing period model to 80CB:60CB thus must remain speculative. It is interesting to point out, nevertheless, that 50:50 mixtures of 80CB and 40.8 do indeed exhibit a monolayer structure [24].

Finally, neither current statistical mechanical techniques nor our microscopic understanding of liquid crystals are well enough developed to enable one to make a quantitative theoretical connection between the optimal density theory and the competing period parameter theories. This remains an important theoretical challenge in the liquid crystal field.

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