Universality of Phase Diagrams near the Nematic, Smectic-*A*, Smectic-*C* Multicritical Point

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High-resolution phase diagrams of four binary liquid-crystal mixtures exhibiting nematic, smectic-*A*, smectic-*C* multicritical points are found to be universal.

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The nematic, smectic-*A*, smectic-*C* multicritical point (NAC point), first predicted theoretically by Chen and Lubensky[1] and by Chu and McMillan,[2] was realized experimentally by Johnson *et al.*,[3] and Sigaud, Hardouin, and Achard,[4] in binary liquid-crystal mixtures $\overline{7}$S5/$\overline{8}$S5 and 7ONE/8OCB, respectively. Recently $\overline{7}$S5/$\overline{8}$S5 has been carefully studied by high-resolution ac calorimetry[5] and x-ray scattering,[6] thus initiating explicit comparisons with theoretical predictions. These comparisons suggest that the above models will not account for the observed x-ray line shapes, phase diagram topology, or evolution of thermal anomalies and correlation lengths along the nematic-smectic phase boundaries. However, both models were solved only in the mean-field approximation, and so renormalization may improve the situation. On the empirical side, published phase diagrams of 7ONE/8OCB and $\overline{7}$S5/$\overline{8}$S5 differ drastically, the former being in qualitative agreement with the mean-field Lifshitz-point[7] model of Chen and Lubensky. This leads one to question whether the topology of the NAC phase diagram is universal.

The purpose of this Letter is to present high-resolution phase diagrams which show that, in spite of gross differences in global features, universality rules near the NAC point. Quantitative evidence favoring universality is presented in the form of relationships among parameters describing the NA and NC boundaries, namely, the exponent η and the amplitudes $A_{\mathrm{NC}}, A_{\mathrm{NA}}$ defined by

$$T_{\mathrm{NA}} - T_{\mathrm{NAC}} = A_{\mathrm{NA}}(X_{\mathrm{NA}} - X_{\mathrm{NAC}})^{\eta} + B(X_{\mathrm{NA}} - X_{\mathrm{NAC}}), \tag{1a}$$

$$T_{\mathrm{NC}} - T_{\mathrm{NAC}} = A_{\mathrm{NC}}(X_{\mathrm{NAC}} - X_{\mathrm{NC}})^{\eta} + B(X_{\mathrm{NAC}} - X_{\mathrm{NC}}), \tag{1b}$$

where X is the mole fraction of material exhibiting the NA transition.[8] For lack of renormalization-group treatments of the NAC multicritical point, results are compared with magnetic Lifshitz points.[7, 9] Finally, a comment is made on a recent suggestion[10] that the NAC point is a tricritical point on the smectic-*C* phase boundary.

Figures 1–4 display phase diagrams of four binary mixtures in the immediate vicinity of their NAC points. The phase transitions were observed under a Leitz polarizing microscope with a Mettler heating stage. Larger than expected scatter and systematic variations were found for the 7ONE/8OCB mixtures because of the chemical instability of 7ONE. In spite of large quantitative differences, suppressed by choice of scale factors, the phase diagrams are strikingly similar.

The reason for substantial quantitative differences among the phase diagrams is threefold. First, some materials, such as 8OCB, neither exhibit smectic-*C* phases nor would they if supercooled to much lower temperatures; thus, the very strong suppression of the AC line on increasing concentration of 8OCB. Other materials, such as $\overline{8}$S5 or 9S5, either have smectic-*C* phases or would have if mildly supercooled; thus the AC line is unsuppressed or only mildly suppressed by their addition. Second, the amplitudes of the leading singularities of the NA and NC lines [A_{NA} and A_{NC} of Eq. (1), discussed below] vary by a factor of ~4 (see Table I). Third, the nonsingular background slope on which the singularity is superimposed varies considerably and even changes sign (dashed lines in the figures).

The steepness of the NA line at the NAC point suggests a singularity of the form given in Eq. (1a) with $0 < \eta < 1$, and the weak upward curvature

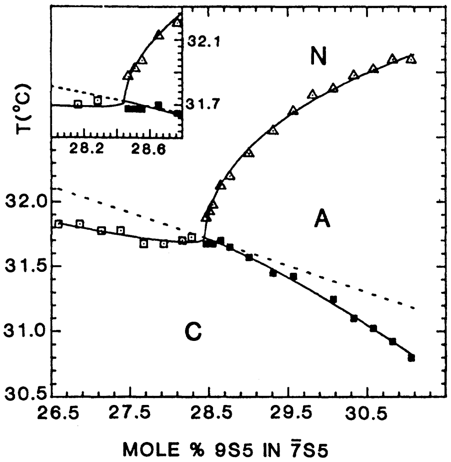

FIG. 1. Range of thermal stability of the nematic (N), smectic-*A* (A), and smectic-*C* (C) phases of 9S5 (4-*n*-pentyl-phenylthiol-4′-nonylbenzoate) in $\bar{7}$S5 (4-*n*-pentyl-phenylthiol-4′-heptyloxybenzoate) near the NAC multicritical point.

of the NC line suggests that $A_{\mathrm{NC}}<0$ and $|A_{\mathrm{NC}}| \ll A_{\mathrm{NA}}$. Results of fitting the data by Eq. (1) with and without universality constraints on η and $A_{\mathrm{NA}}/A_{\mathrm{NC}}$ are in Table I. Solid lines in the figures show that fits constrained to have universal values of η (0.573± 0.02) and $A_{\mathrm{NA}}/A_{\mathrm{NC}}$ (− 5.96± 1.3) are excellent except for the 7ONE/8OCB data which exhibit small systematic variations, probably experimental artifacts as discussed above. Goodness of fit is objectively indicated by the small increases in χ^2 that accompany application of universality constraints. Dashed lines in the figures represent the best-fit slope (B) term in

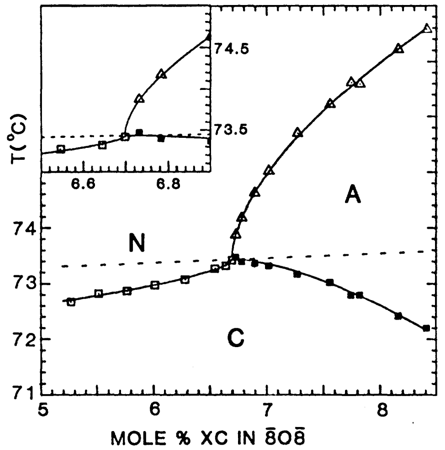

FIG. 2. Range of thermal stability of the nematic (N), smectic-*A* (A), and smectic-*C* (C) phases of XC [4-propionylphenyl-*trans*(4-*n*-pentyl)cyclohexane carboxylate] in $\bar{8}$O$\bar{8}$ (4-*n*-octyloxyphenyl-4′*n*-octyloxybenzoate).

Eq. (1) with the constraints in effect. The figures suggest that the AC line approaches the NAC point at this same slope. Solid lines through the AC data represent equations of the form of Eq. (1) with B, X_{NAC}, and T_{NAC} constrained at values derived from the NA/NC fits (with the exponent and amplitude-ratio universality constraints in effect) and with the further constraint that η_{AC} (1.52± 0.03) is universal. Again the fits are excellent. Therefore, with a simple choice of scaling axes, the NAC phase diagrams exhibit quantitative universality. Because of systematic errors in the data of Fig. 4, it is of interest to fit only the data of Figs. 1–3. The results are

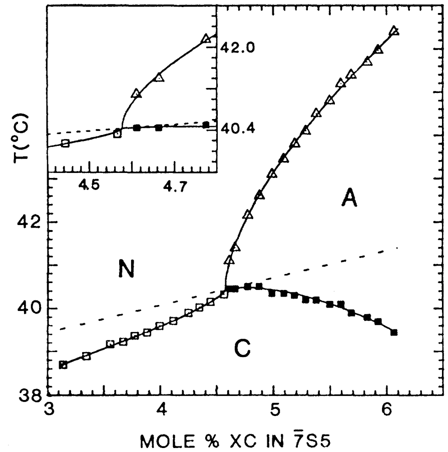

FIG. 3. Range of thermal stability of the nematic (N), smectic-*A* (A), and smectic-*C* (C) phases of XC [4-propionylphenyl-*trans*(4-*n*-pentyl)cyclohexane carboxylate] in $\bar{7}$S5 (4-*n*-pentylphenylthiol-4′-heptyloxybenzoate).

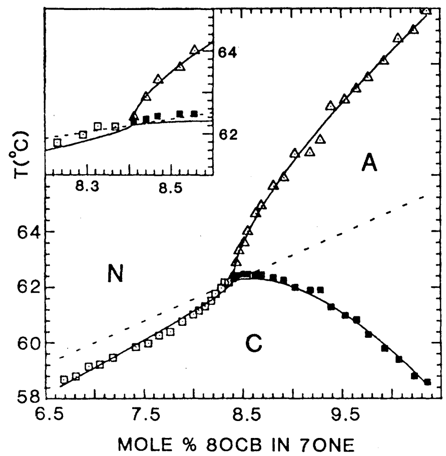

FIG. 4. Range of thermal stability of the nematic (N), smectic-*A* (A), and smectic-*C* (C) phases of 8OCB (octyloxy-cyanolbiphenyl) in 7ONE (2*p*-*n*-heptyloxybenzylidene amino fluorenone).

TABLE I. Best-fit parameters and values of χ^2 for fits of data by equations of the form of Eqs. (1). See the text for details and discussion. Numbers in parentheses exclude 7ONE/8OCB. $R \equiv A_{NA}/A_{NC}$.

<table>
<tr><th></th><th>$\overline{7}$S5/9S5</th><th>$\overline{8}$O$\overline{8}$/XC</th><th>$\overline{7}$S5/XC</th><th>7ONE/8OCB</th></tr>
<tr><td>η</td><td>0.77 ± 0.14</td><td>0.56 ± 0.03</td><td>0.55 ± 0.02</td><td>0.78 ± 0.08</td></tr>
<tr><td>R</td><td>−1.9 ± 1.0</td><td>−5.8 ± 2.0</td><td>−9.8 ± 4.0</td><td>−1.7 ± 0.4</td></tr>
<tr><td>A_{NC}</td><td>−30 ± 48</td><td>−6.7 ± 3.5</td><td>−5.0 ± 2.6</td><td>−161 ± 147</td></tr>
<tr><td>B</td><td>−78 ± 77</td><td>8.4 ± 16</td><td>83 ± 16</td><td>−160 ± 230</td></tr>
<tr><td></td><td colspan="4">$\chi^2 = 1.015$ (0.924)</td></tr>
<tr><td>η</td><td colspan="4">0.573 ± 0.02
(0.556 ± 0.02)</td></tr>
<tr><td>R</td><td colspan="4">−5.96 ± 1.3
(−7.63 ± 2.2)</td></tr>
<tr><td>A_{NC}</td><td>−2.6 ± 0.9
(−1.9 ± 0.7)</td><td>−6.9 ± 2.3
(−4.9 ± 2)</td><td>−9.4 ± 3.1
(−6.6 ± 2.6)</td><td>−10.3 ± 3.4</td></tr>
<tr><td>B</td><td>−20 ± 4.2
(−18 ± 4)</td><td>8 ± 10
(18 ± 10)</td><td>63 ± 13.6
(75 ± 13)</td><td>157 ± 16</td></tr>
<tr><td></td><td colspan="4">$\chi^2 = 1.162$ (1.00)</td></tr>
<tr><td>η_{AC}</td><td>1.76 ± 0.3
(1.71 ± 0.3)</td><td>1.4 ± 0.07
(1.41 ± 0.1)</td><td>1.47 ± 0.04
(1.48 ± 0.04)</td><td>1.6 ± 0.04</td></tr>
<tr><td></td><td colspan="4">$\chi^2 = 0.869$ (0.914)</td></tr>
<tr><td>η_{AC}</td><td colspan="4">1.52 ± 0.03
(1.46 ± 0.03)
$\chi^2 = 0.977$ (0.919)</td></tr>
</table>

shown in Table I in parentheses and are the same, within statistical uncertainties, as the results of fitting all four sets of data. Furthermore, it is found that the AC lines of Figs. 1–3 continue to be fitted well by Eq. (1) with universal exponents, and with slopes constrained to the values derived from the fully constrained NA/NC fits of the three data sets. The new value of η_{AC} (1.46 ± 0.03) is not significantly different from the old (1.52 ± 0.03).

It is relevant to ask why the $\overline{7}$S5/$\overline{8}$S5 mixtures studied earlier[5] exhibited a continuous smectic-C line which is certainly inconsistent, we believe, with these data and with the working assumptions used in the present data analysis. The answer lies in the small amplitude of the NC line divergence, A_{NC}, and the lower data density and precision of the $\overline{7}$S5/$\overline{8}$S5 experiments. A_{NA} is found to be approximately 40% that of the $\overline{7}$S5/9S5 system. Assuming a universal amplitude ratio of ~ -6 gives $A_{NC} \sim 1.1$. Thus, for $\eta = 0.57$, a point on the NC line 2% away from the NAC point would lie only 0.12 °C below the extrapolated AC line, making the kink in the smectic-C line unobservable. Furthermore the AC line of $\overline{7}$S5/$\overline{8}$S5 shows much less curvature because both materials exhibit a C phase, contrary to mixtures in the present study.

Unfortunately, there are no theoretical predictions with which to compare. Although the theory of the magnetic Lifshitz point is quite well developed, the liquid-crystal Lifshitz point is complicated by the lack of long-range order in the smectic-A and smectic-C phases,[11,12] and the fact that the NC transition is apparently driven first order by fluctuations.[1,13] Moreover, the $m = 2$ Lifshitz point is at its lower dimensionality in three dimensions[7,14] (at least for $n > 2$) which complicates both Lifshitz-point problems.

The exactly solvable $n = \infty$, $m = 1$ magnetic Lifshitz-point model gives $A_H/A_F = -2\cos(\pi d/2)$ and $\phi^{-1} = d - 2.5$ for arbitrary dimensionality d.[9] For $d = 3.075$ (!) this gives -6.02 and 0.575, respectively. Close agreement with the results of Table I ($-5.96, 0.573$) is somewhat fortuitous and certainly curious, but of unknown relevance. Perhaps the strongest support for the Lifshitz-point interpretation is that the NA and NC lines show universal singularities and these are stronger than the AC line singularities. This is consistent with the idea that the NAC point divides an order-disorder transition line (the nematic-smectic line) into two parts and the AC line divides an ordered region (the smectic region) into two parts of different symmetry. Thus the central features of a Lifshitz-point model are consistent with the data.

It has been speculated recently[10] on the basis of an analysis of x-ray and heat-capacity data near the AC line of $\overline{7}$S5/$\overline{8}$S5, that the NAC point is a tricritical point on the smectic-C line. The NC line should then lie above and curve away from the linearly extrapolated AC line, whereas instead it dips below it. Thus the speculation is not supported by the data. The fact that the nematic-smectic transition is suppressed as fluctuations become more C-like and eventually becomes first order when the fluctuations center on two rings in k space is more suggestive of the fluctuation phenomenon studied by Brazovskii[15] and applied to liquid crystals by Chen and Lubensky[1] and Swift.[13]

More phase diagram, thermodynamic, light-scattering, and x-ray experiments are needed to provide a complete and accurate empirical characterization of the NAC point; nevertheless, the accumulation of high-resolution data that now appears in the literature certainly warrants a renewed theoretical effort to improve our poor understanding of this difficult and interesting multicritical point.

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