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Critical Behavior at the Smectic-A to Nematic Transition of Confined Liquid Crystal Mixtures

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High resolution calorimetry studies at the smectic-A to nematic phase transition confined to the random interconnected voids of Millipore filters were performed. Measurements took place with pure 9CB and (9 + 10)CB mixtures, for bulk and in 0.05 μm void size Millipore samples. This work focuses on the competition between the confinement which affects the bulk-like critical behavior by weakening the coupling between the nematic and smectic order parameters, and the increased coupling that results from the addition of a smectic liquid crystal component.

Keywords: Critical behavior; confinement; smectic nematic transition

1. INTRODUCTION

Probing thermodynamic properties near tricritical and triple points constantly attracts theorists and experimentalists because of the richness of physics phenomena involved. In liquid crystal materials, the alkylcyanobiphenyl *n*CB series (*n* the number of carbons in the alkyl chain) is a popular choice for phase transitions research as its phase diagram has both tricritical and triple points when *n* is between 9 and 10. For $n = 5, 6, 7$, the liquid crystal exhibits a nematic to isotropic (NI) transition which is either 1st order or weakly 1st order; when $n = 8, 9$, both the 2nd order smectic-A to nematic (AN), and the NI transitions are present. When *n* is increased to 10,

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the nematic phase which exists in 8CB and 9CB with width 7.1 K and 1.9 K respectively, shrinks to zero. Thus, with $n = 10, 11, 12$, a 1st order smectic-A to isotropic (AI) transition is present. In addition, with nCB liquid crystals, mixtures are easily prepared and it is possible to study changes in the order of the phase transition, from a 2nd order AN for 9CB to a 1st order AN for (9 + 10)CB mixtures.

The smectic-A to nematic transition is presumed to belong to the 3D–XY universality class characterized by a heat capacity exponent $\alpha = -0.007$ [1]. In reality, the critical behavior is dominated by the strength of the coupling between the orientational (nematic) order parameter and that of the one-dimensional translationally ordered layered structure of the smectic-A phase. For liquid crystal materials of narrow nematic range, the coupling between the order parameters is very strong with the critical behavior being tricritical, or, $\alpha = 0.5$, as is the case for 9CB. By increasing the nematic range and thus decreasing the order parameters coupling, the heat capacity exponent α is driven towards zero, approaching the expected 3D-XY behavior. For intermediate nematic ranges, measurements often find an effective exponent that ranges between the two universality classes [1–4]. Two liquid crystal series, the nCB and $\bar{n}$S5 are two such examples [1].

Also of great interest is the study of phase transitions in confined geometries. By confining liquid crystals to submicron size porous materials it is possible to study the confinement influence on the layered smectic formation [5] and on the orientational order [6], and, on the critical behavior at phase transitions [4,7]. The latter effects have been difficult to ascertain at the smectic-A to nematic phase transition as in most substrates the formation of smectic layers is considerably inhibited and specific heat peaks at the AN transition are too suppressed to allow a fully reliable determination of critical exponents [7]. To this date, such a determination has only been possible under Millipore filters confinement, where, at a liquid crystal dependent critical size, the effective heat capacity exponent is driven towards zero [8] by effectively weakening the coupling between nematic and smectic order parameters. As shown below, by increasing the smectic component in the confined system (doping 9CB with 10CB) and consequently strengthening the order parameter's coupling, the bulk-like tricritical behavior is recovered.

2. EXPERIMENTAL ASPECTS

Millipore filters are made from pure biologically inert mixtures of cellulose acetate and cellulose nitrate. For the work presented here, we used filters

with voids 0.05 μm nominal size; however, from SEM photography studies, we have determined the actual void size to be roughly six times larger. The porosity for this size Millipore exceeds 60%.

Heat capacity measurements were performed using an ac calorimetry technique operating at a voltage frequency of 60 mHz [9]; the frequency is chosen after performing frequency scans to determine a frequency independent heat capacity. The samples consisted of a squared Millipore sample, 6 mm to the side, 110 μm thick. The samples typically contained less than 5 mg of liquid crystal materials.

3. RESULTS

Heat capacity measurements for bulk 9CB and confined to the 0.05 μm Millipore voids are shown in Figure 1, where we plot the excess AN specific heat (ΔC_P) after substraction of the low temperature wing of the higher temperature NI transition. For bulk, the transition temperatures are $T_{AN} = 321.1$ K and $T_{NI} = 323.08$ K, yielding a nematic range of 1.87 K. In the confined case, both transitions are shifted to low temperature by 230 mK, thus, the nematic range remains the same. The transition shifts are not consistent with finite size effect, and are most likely determined by elastic constraints dictated by the tortuous geometry [4,7]. The transition enthalpy, calculated from the integral of ΔC_p over a 2.2 K total temperature range centered at the individual AN transition yields 1.26 ± 0.09 and 1.2 ± 0.05 J/g for bulk and confined 9CB respectively. The most noticeable, yet expected, difference between the two sets of data is the 50% peak suppression in the confined case as compared to bulk. Given the equal areas, the peak suppression indicates that changes in the divergent nature of the transition are taking place.

The effect of confinement is emphasized by exploring the AN critical behavior. The excess specific heat data is fitted to a power law in reduced temperature that includes a correction-to-scaling term [1,10]:

$$\Delta C_P = B_C + Lt + (A_\pm/\alpha)|t|^{-\alpha}(1 + D_\pm|t|^{1/2}), \quad t = (T/T_{AN} - 1) \qquad (1)$$

where the $\pm$ subscripts represent data above (+) and below (−) T_{AN}, which are simultaneously fitted. The constant and linear terms are included to account for any remnant regular background. Data fitting includes over 500 data points and standard range shrinking procedures.

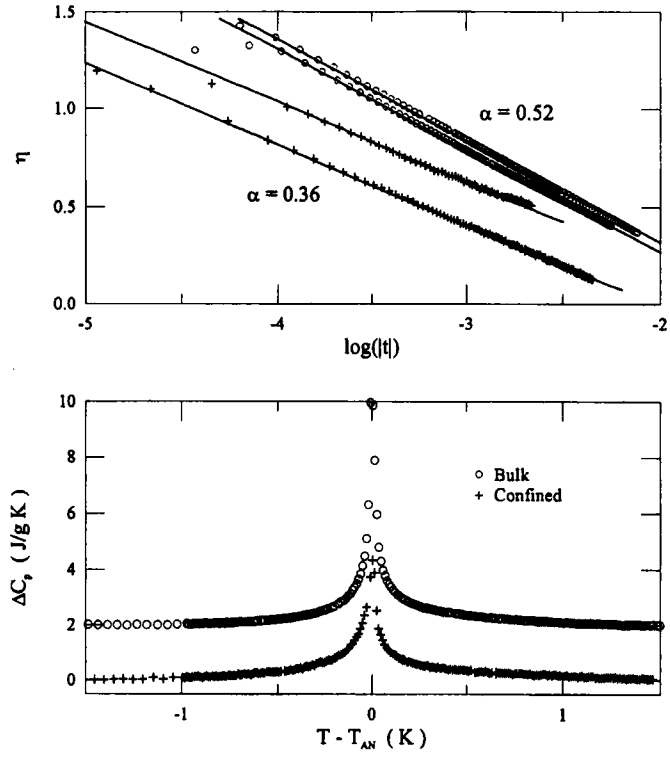

FIGURE 1 Bottom: Excess AN specific heat for bulk (o) and Millipore confined (+) 9CB. The bulk data is shifted up for clarity. Top: Fits according to Eq. (1) shown by the solid lines. Upper branches are data for $T < T_{AN}$. η is defined as Log $(|(\Delta C_P - B_C - Lt)/(1 + D_{\pm}|t|^{1/2})|)$.

Fits to Eq. (1) for bulk 9CB find $\alpha = 0.52 \pm 0.02$ with an amplitude ratio $A_-/A_+ = 1.32 \pm 0.05$. This agrees with expectations that a tricritical exponent should be found [3]. Under the 0.05 μm Millipore confinement, an effective heat capacity exponent is found, with α decreasing to 0.36 ± 0.02 while the amplitude ratio increases to 1.53 ± 0.05. The differences between the bulk and confined critical behavior are evident from the top of Figure 1. There, the critical exponent is represented by the slope while the separation between the upper ($T < T_{AN}$) and lower ($T > T_{AN}$) branches is related to the amplitudes ratio ($-\text{Log}\{A_-/A_+\}$). Since the nematic range is unchanged by the Millipore confinement, the effects on the critical behavior can be attributed to a substrate-induced weakening of the coupling between order parameters and a suppression of fluctuations to wavelengths comparable to the void size. This has been shown in a systematic study for 8CB and 9CB confined to Millipore filters with voids sizes ranging from 0.8 to 0.025 μm,

where the heat capacity exponent is eventually driven to zero at a liquid crystal dependent void size.

A bulk-like critical behavior can be recovered if the order parameters coupling is strengthened. This can be achieved by decreasing the nematic range of the liquid crystal through the addition of pure smectic liquid crystal. Here, this is accomplished by doping 9CB with small amounts of 10CB, which is beyond the triple point and thus lacks a nematic phase.

Accordingly, specific heat measurements were performed for a bulk mixture of 11.4 % of 10CB in 9CB, and also confined to the 0.05 μm Millipore voids. The AN transition excess specific heat for the mixture is shown in Figure 2. As expected because of the increase in the smectic component, the bulk mixture T_{AN} increases to 321.57 K while its T_{NI} decreases to 322.87 K, consistent with literature results [3]. Compared to pure 9CB, the nematic

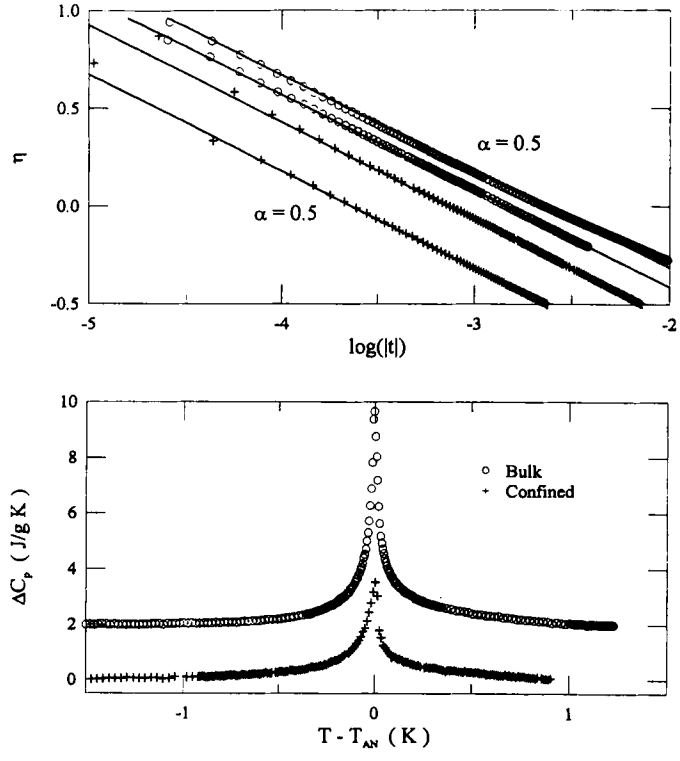

FIGURE 2 Bottom: Excess AN specific heat for bulk and Millipore confined mixture of 11.4 % 10CB in 9CB. The bulk data is shifted up for clarity. Top: Fits according to Eq. (1) are shown by the solid lines. Legends are as in Figure 1.

range is effectively reduced by $\sim 30\,\%$, to 1.3 K, while the transition enthalpy now calculated over a narrower temperature range ($T_{AN} \pm 0.8$ K) is 1.32 ± 0.09 J/g. As before, under confinement, both transition temperatures are shifted down by nearly the same amount, 0.68 K i.e., this particular substrate does not change the nematic range. The confined transition enthalpy decreases to 0.9 ± 0.09 J/g. Noting that the narrower nematic range renders the substraction of the NI transition more difficult, but in light of the critical fits discussed below, the decrease in transition enthalpy may reflect that the confined peak is simply a truncated bulk peak, thus, the loss in area.

The mixture data is also fitted to Eq. (1). The critical behavior of the bulk mixture is identical to that of the pure case, with $\alpha = 0.05 \pm 0.01$ and $A_-/A_+ = 1.44 \pm 0.02$, i.e., as expected in the neighborhood of the tricritical point. In the confined situation, where in the pure 9CB case an effective exponent was found ($\alpha = 0.36$), for the mixture, the tricritical behavior is recovered: $\alpha = 0.5 \pm 0.01$, but with a large amplitude ratio of 2.51 ± 0.17. The latter results are nevertheless consistent with other mixture studies [11]. Evidently, the narrower nematic range which strengthens the coupling between nematic and smectic order parameters overcomes the weakening induced by the confinement. The addition of 10CB introduces a non-zero latent heat [3] which increases the fluctuations and makes the substrate-induced decoupling less significant. Therefore, to affect the critical exponent for this particular mixture, void sizes probably even smaller than 0.025 μm would be required.

4. CONCLUSIONS

We have shown that the critical behavior at the smectic-A to nematic phase transition is affected by confinement introduced by the random interconnected voids of Millipore filters. By weakening the coupling between order parameters and suppressing fluctuations, for 9CB, the critical exponent is driven from tricritical ($\alpha = 0.5$) to an effective one ($\alpha = 0.36$). With increased confinement, α can be driven to zero, i.e., approaches the 3D-XY value [8]. This effect is overcome by increasing the smectic component of the liquid crystal material; with the addition of 10CB to 9CB, the tricritical exponent value is recovered.

Complementary specific heat studies would be useful to better quantify the effect. The present mixture should be studied in smaller void sizes. For a fixed void size of 0.05 μm, mixtures studies as a function of 10CB concentration, particularly with amounts less than 5% would be illuminating. Similar

studies with liquid crystal homologous series of wider nematic ranges would be important as the change in critical exponent should be observed with less restrictive confining sizes.

Acknowledgements

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