Random-field effects on the nematic–smectic-A phase transition due to silica aerosil particles

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A high-resolution calorimetric study has been made on the smectic-A to nematic phase transition in liquid crystals perturbed by the dispersion of 70-Å-diam silica spheres (aerosils). The specific heat peak of this transition decreases in amplitude and shifts to lower temperatures with increasing silica density. However, it remains sharp in comparison to the effects of aerogel confinement at the same silica densities. The bulk transition in octylcyanobiphenyl (8CB) exhibits a crossover critical exponent $\alpha=0.30$, whereas on addition of aerosils the specific heat peak takes on an increasingly asymmetric appearance reminiscent of three-dimensional (3D) $XY$ criticality. Power-law fits reveal an effective $\alpha$ continuously decreasing from 0.30 to $-0.03$ with increasing silica density. No changes in the critical behavior are found when the bulk liquid crystal already possesses a small negative $\alpha$, i.e., 3D $XY$ criticality, as shown in octylphenylthiol-pentylxylenebenzoate. Apparently, the silica-dopant-induced random field drives the critical behavior towards 3D $XY$ universality in 8CB by changing the nature of the coupling between the nematic and smectic order parameters. The nematic to isotropic transition in 8CB plus aerosils has also been observed; it exhibits a bimodal character that deviates from observations in aerogel systems. [S1063-651X(97)09503-2]

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I. INTRODUCTION

Unlike idealized concepts of molecular interactions and finite-size effects, the presence of randomness greatly complicates the understanding of phase behavior. This is as true for liquid crystals as it is for any other physical system. Recently, the study of the effects of random disorder, via confinement to a gel-like porous media, on liquid crystal phase transitions has attracted considerable interest in trying to understand the role randomness plays [1]. These efforts closely parallel experimental and theoretical work on random-field effects on magnetic spin systems.

In the past, liquid crystal studies have concentrated on the effects of confinement to randomly interconnected porous media as a means of inducing randomness. The smectic A to nematic (Sm-A–N) phase transition has been an attractive candidate for such studies due to its close analogy to the superconductor-to-normal phase transition [2] as well as its easy accessibility. Ideally, the Sm-A–N transition belongs to the three-dimensional (3D) $XY$ universality class [3] although possessing only quasilong range order due to a Landau-Peierls instability. X-ray [4], light-scattering [5], and calorimetric studies [6] on the Sm-A–N transition of octylcyanobiphenyl (8CB) confined to an aerogel, a randomly interconnected silica network, found this transition diminished in magnitude, broadened, and shifted to lower temperatures as a function of decreasing mean pore size $L$ (increasing density $\rho$, defined as the mass of silica per unit total volume). In fact, for an aerogel with $L\sim120$ Å ($\rho=0.60$ g cm$^{-3}$), the $C_p$ feature of the Sm-A–N transition had completely disappeared [6]. Parallel studies employing sintered porous glasses found a similarly diminished Sm-A–N transition for $L\sim1000$ Å comparable to that in an aerogel having similar $L$, while no Sm-A–N transition was observed for $L\sim100$ Å glasses [7]. The later result was also confirmed using Vycor glass (a commercially available sintered porous glass having $L\sim70$ Å), where in fact no liquid crystal transitions of any kind were found [8].

In these studies which spanned $70<L<1000$ Å, the Sm-A–N transition was severely modified and efforts have been made to understand the destruction of all phase transitions which takes place at or below $L<1000$ Å. The theoretical work can be categorized into two general classes; the single-pore (SP) [7–9] and random-field Ising (RFI) [10,11] models. The RFI models were developed for magnetic spin systems in order to understand the role impurities and defects play on magnetic phase transitions. They typically consist of a magnetic spin Hamiltonian (such as for an Ising system) and add a nearest-neighbor interaction term which is randomly distributed throughout the system [10,11]. A closely related approach is the random-bond model [12] which has bonds between spins created randomly in space. This particular variant has been used to model gelation and polymerization in soft-state systems. The common features within this class are that the basic physics is contained in properly describing the form and distribution of the random interactions.

In contrast, the SP models arose mainly in the study of binary fluid mixtures [9] and liquid crystals [7,8] confined to sintered porous glasses. Here, the primary assumption is that each pore is essentially isolated from neighboring pores to the extent that changes in one do not affect the other. The
problem is to describe the behavior within a single pore; either phase wetting or ordering connected to some property of the pore such as shape, size, surface interaction, etc., then average over the entire sample using some distribution in the pore property. The distribution and averaging is where randomness enters. It should be noted that although both the SP and RFI models produce smaller specific heat peaks and rounded transitions that are shifted to lower temperatures, the similarities are only qualitative. Indeed, similar behavior has also been observed experimentally in uniform cylindrical confinements [13], where randomness is obviously lacking.

In this work, we follow the spirit of previous magnetic studies by using a “dopant” to impose a random-field disorder onto a liquid crystal exhibiting a Sm-A–N transition. Two liquid crystals were used which possess different structures and different bulk Sm-A–N criticality. 8CB, in which there is a strong nematic-smectic coupling due to a relatively small nematic temperature range, exhibits a crossover between XY and tricritical behavior with \( C_P \) characterized by an effective critical exponent \( \alpha = 0.30 \) [3]. Octylphenylthiophenol-pentyloxybenzoate (8S5), which has a much wider nematic range and thus weaker nematic-smectic coupling, has \( \alpha = -0.022 \) [14] or very close to the 3D XY value of \( -0.007 \). The dopants used were aerosils [15], 70 Å diam silica spheres having either hydrophilic or hydrophobic surfaces. High-resolution ac calorimetry was performed on mixtures of these liquid crystals and aerosils as a function of silica density. For liquid crystal plus aerosil mixtures with \( \rho = 0.09 \) g cm\(^{-3}\), the excess \( C_P \) associated with the Sm-A–N transition, \( \Delta C_P\text{(Sm-A–N)} \), exhibits a sharp peak which decreases in amplitude and shifts to lower temperatures with increasing \( \rho \). This is in dramatic contrast to studies of 8CB in silica aerogels of comparable density, which revealed a rounded \( C_P \) “bump” [6]. More interesting, as \( \rho \) increases, the \( C_P \) peak for 8CB becomes increasingly asymmetric, reminiscent of the shape of \( \Delta C_P\text{(Sm-A–N)} \) corresponding to 3D XY critical behavior. No essential change in the shape of \( \Delta C_P\text{(Sm-A–N)} \) is observed for 8S5, which already exhibits 3D XY behavior in the bulk. Critical fit analyses for 8CB samples show that with increasing \( \rho \) there is a decreasing value for \( \alpha \), which appears to level off at the 3D XY value. No significant change in \( \alpha \) from the bulk value was found for an 8S5 plus aerosil sample.

It appears that for a sufficient density of disordering dopant, the Sm-A–N transition in 8CB approaches 3D XY universality. Presumably, since the nematic temperature range remains essentially constant, the effect of the dopent is to effectively decouple the nematic and smectic order parameters. Evidence for a disorder-driven crossover of the Sm-A–N critical behavior was found in studies employing Milipore membranes; however, this confining media, although obviously random, was not well characterized [16].

Section II provides a description of the samples and experimental procedures. Section III contains the results and discussion, beginning with a brief account of the effects of an aerosil dopent on the nematic to isotropic (N-I) phase transition then followed by the Sm-A–N results and critical fit analyses. Section IV summarizes the most important and striking results and discusses their implications on other studies involving characterizing the smectic ordering by scattering experiments.

II. EXPERIMENTAL PROCEDURES

The two liquid crystals (LCs) used in this work, 8CB and 8S5, have been well characterized in the bulk [3,6,14,17] and have the structural formulas

\[
\begin{align*}
\text{C}_8\text{H}_{17} & \quad \text{C} \quad \text{CN} \\
\text{C}_8\text{H}_{17} & \quad \text{COS} \quad \text{C}_3\text{H}_{11}
\end{align*}
\]

(8CB) (8S5)

Our sample of bulk 8CB exhibited a first-order crystal (K) to smectic-A (K–Sm-A) transition at 293 K, a second-order Sm-A–N transition at 307.01 K, and a weakly first-order N–I transition at 314.01 K. Bulk 8S5 possesses a first-order K to smectic-C (K–Sm-C) transition at 331.50 K, a monotropic second-order Sm-C–Sm-A transition at 329.34 K, a second-order Sm-A–N transition at 336.58 K, and a weakly first-order N-I transition at 359.59 K [17]. This work concentrates mainly on the Sm-A–N transition. The aerosil was used as obtained from Degussa Corp. [15] without further processing. Two types of aerosils, hydrophilic (type 300) or hydrophobic (type R812), were employed. These are 70 Å diameter silica spheres having either –OH groups (hydrophilic) or –CH\(_3\) groups (hydrophobic) covering the surface. The hydrophilic aerosil (referred to hereafter as philic sil) has a quoted surface area of 300 m\(^2\) g\(^{-1}\) while the hydrophobic aerosil (phobic sil) has a surface area of 260 m\(^2\) g\(^{-1}\) with both aerosils having a fairly narrow particle size distribution (full width at half maximum of distribution \( \sim 75 \) Å) [15].

The LC plus aerosil mixture samples were prepared by heating the desired LC into its isotropic phase and adding the desired amount of aerosil. The mixture was then mechanically mixed with a magnetic stir bar for several hours under vacuum while maintaining the LC in its isotropic phase. The mixture was then held under vacuum at this temperature for several more hours before sealing it into the silver cell used in our calorimeters. This method appears to work well in dispersing the aerosil for silica densities less than 0.2 g cm\(^{-3}\), above which the mixture becomes too viscous to mix thoroughly by purely mechanical means.

The ac calorimetric technique is an extremely sensitive method of measuring heat capacity peaks at phase transitions
and our implementation has been described in detail elsewhere [18]. Basically, it consists of applying an oscillating heat input to a sample and detecting the temperature response, \( T(t) = \Delta T_{ac} \exp(i\omega t + \phi) \). The amplitude of the temperature oscillation, \( \Delta T_{ac} \) is inversely proportional to the heat capacity \( C \) while the phase shift \( \phi \) provides useful qualitative information regarding the presence of two coexisting phases at a first-order transition (if it occurs). The specific heat capacity of the LC is simply the total heat capacity of the LC minus \( C_c \) of the empty cell and aerosil divided by the LC mass \( (C_{v}) \). Typically, it consists of applying an oscillating heat input to a sample and detecting the temperature response, indicating that both these features are associated with transitions involving two-phase coexistence. The transition temperature shifts for these features as well as the integrated enthalpies \( \delta H_{NI} \) (defined by \( \delta H = \int \Delta C_p dT \), where \( \Delta C_p \) is the excess \( C_p \) associated with a given transition) are given in Table I. Owing to the closeness of the two \( N-I \) features, it was impossible to separate them into individual spike and shoulder \( \delta H \) contributions.

Caution is warranted in regards to the \( \delta H_{NI} \) values, as they may be distorted by two-phase coexistence effects. It should be noted that the \( \delta H_{NI} \) value for bulk 8CB given in Table I is only the pretransitional enthalpy associated with the \( C_p \) wings and does not include a latent heat \( \Delta H \) of 2.10 J g\(^{-1}\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \rho ) (g cm(^{-3}))</th>
<th>( \Delta T_{NI}^{Sp} ) (K)</th>
<th>( \Delta T_{NI}^{Sm} ) (K)</th>
<th>( \Delta T_{AN} ) (K)</th>
<th>( \Delta T_{nem} ) (K)</th>
<th>( \delta H_{NI} ) (J g(^{-1}))</th>
<th>( \delta H_{AN} ) (J g(^{-1}))</th>
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<tr>
<td>pure</td>
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<td>5.58</td>
<td>0.809</td>
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<td>-0.687</td>
<td>-0.612</td>
<td>7.06</td>
<td>3.44</td>
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<td>-0.800</td>
<td>-0.807</td>
<td>7.09</td>
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</tr>
<tr>
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<td>0.155</td>
<td>-1.332</td>
<td>-1.393</td>
<td>7.06</td>
<td>4.60</td>
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</table>

**TABLE I.** Transition temperature shifts with respect to pure 8CB of the two \( C_p(N-I) \) features and the \( C_p(Sm-A-N') \) peak for 8CB plus aerosil mixtures with silica density \( \rho \). \( \Delta T_{NI}^{Sp} \) is the shift from bulk of the sharp spike feature, while \( \Delta T_{NI}^{Sm} \) is the shift from bulk of the lower temperature shoulder feature. \( \Delta T_{nem} \) is the nematic range. The enthalpy \( \delta H \) is the integrated excess \( C_p \).

**III. RESULTS AND DISCUSSION**

**A. \( N-I \) transition**

The \( N-I \) transition is a weakly first-order transition involving the establishment of orientational order within a fluid. In a bulk liquid crystal, it possesses a moderately small latent heat and substantial pretransitional heat capacity wings. The introduction of the aerosil particles greatly modifies this transition with some similarities to the effect of aerogel confinement [6]. Plots of \( C_p \) over a wide temperature range encompassing the \( N-I \) and Sm-A-N transitions of pure 8CB and three aerosil mixtures with 8CB are shown in Fig. 1. The \( N-I \) transition shifts to lower temperatures with increasing silica density \( \rho \) in a manner similar to that observed for the shifts caused by aerogel confinement [6]. However, the \( T_{NI} \) shifts observed here are larger than those observed for comparable \( \rho \) values in aerogel systems. The shift in \( T_{NI} \) appears to be independent of the aerosil surface character, at least for the lower silica concentrations.

With the addition of relatively small amounts of aerosil \( (\rho = 0.051 \text{ g cm}^{-3}) \), the \( \Delta C_p(N-I) \) peak grows larger in amplitude than that for the bulk and develops a bimodal appearance: a large and sharp spike followed at lower temperatures by a rounded shoulder. The difference in temperature between these two features is roughly constant at \( \sim 0.08 \text{ K} \). That is, both features shift to lower temperatures with increasing aerosil density with the sharp spike gradually losing intensity for \( \rho > 0.051 \text{ g cm}^{-3} \). The phase shift exhibits two peaks: one associated with the sharp spike and the other associated with the \( C_p \) shoulder, indicating that both these features are associated with transitions involving two-phase coexistence. The transition temperature shifts for these features as well as the integrated enthalpies \( \delta H_{NI} \) (defined by \( \delta H = \int \Delta C_p dT \), where \( \Delta C_p \) is the excess \( C_p \) associated with a given transition) are given in Table I. Owing to the closeness of the two \( N-I \) features, it was impossible to separate them into individual spike and shoulder \( \delta H \) contributions. Caution is warranted in regards to the \( \delta H_{NI} \) values, as they may be distorted by two-phase coexistence effects. It should be noted that the \( \delta H_{NI} \) value for bulk 8CB given in Table I is only the pretransitional enthalpy associated with the \( C_p \) wings and does not include a latent heat \( \Delta H \) of 2.10 J g\(^{-1}\).
FIG. 2. Overlay of excess specific heats for the Sm-A–N transition, $\Delta C_p(\text{Sm-A–N})$, after background subtraction, for bulk 8CB (solid line), 0.051 g cm$^{-3}$ (○), 0.084 g cm$^{-3}$ (●), and 0.106 g cm$^{-3}$ (□) 8CB plus philic-sil mixtures.

associated with the first-order region where two phases coexist.

Since the spike and shoulder shift together, it is unlikely that the spike represents a bulk feature as was assigned for a spike seen for 8CB in aerogels. In that case, the spike was located at the temperature of the bulk transition, was independent of aerogel density, and could be removed by careful drying of the outer aerogel surface. In the aerosil case, this spike seems to reflect a first-order $N$-$I$ transition in a fairly homogeneous region relatively far from the silica surface. The $C_p$ shoulder would then correspond to a broad freezing of local orientational order caused by an aerosil imposed random field as seen in aerogel [6] and sintered porous glass [7,8]. Studies of the melting of ice impregnated with philic aerosol found a thin layer of water on the aerosil surface as far as 20 K below the bulk freezing temperature and this layer gradually increased in thickness with increasing temperature [19]. This could account for $\delta H_{N\rightarrow I}(\text{sil}) < \delta H_{N\rightarrow I}(\text{bulk})$ seen in this study since a disordered LC layer may be present at the aerosil surface, robbing the $N$-$I$ transition of some of its enthalpy.

B. Sm-A–N transition

The effects of aerosil dopant on the Sm-A–N transition differ markedly from those on the $N$-$I$ transition as well as those observed in other confined media. No bimodal behavior is observed and the $C_p$ peak remains very sharp and relatively large while still shifting to lower temperatures with increasing aerosil concentration. This is in contrast to observations in other confined systems such as aerogels and anopores, where the Sm-A–N transition $C_p$ becomes rounded and broadened [6,7,13]. The most surprising feature in this work, as shown in Fig. 2, is the emergence of an asymmetric shape for the $C_p(\text{Sm-A–N})$ peak as $\rho$ increases. This shape is reminiscent of the $C_p$ behavior observed at Sm-A–N transitions exhibiting $XY$ behavior, which will be discussed further in Sec. III C.

The shifts of $T_c$ for the Sm-A–N transition relative to bulk, $\Delta T_{AN} = T_{c}(\text{sil}) - T_{c}(\text{bulk})$, and the enthalpies $\delta H_{AN}$ are given in Table I for 8CB. Figure 3 shows the behavior of $\Delta T_{AN}$ as well as the enthalpies scaled by the bulk value ($\delta H$/$\delta H_b$) for 8CB and 8S5 aerosil mixtures along with results for 8CB and 8S5 in aerogels [6,20] as a function of silica density. The Sm-A–N transition temperature shifts all appear to fall close to a single curve for 8CB and 8S5 in both phobic- and philic-sil mixtures as well as in aerogels. The shifting of the Sm-A–N transition to lower temperatures does not appear to be related to finite size, surface disorder, or elastic distortion induced temperature scale renormalization effects, as was discussed in the aerogel study [6] and in Vycor studies which employed a SP model [8]. Although a quenched RFI model [10] predicts $\Delta T_c$ of the same order as the experimental $\Delta T_c$, the predicted shift is more strongly dependent on random field strength, proportional to silica density, than is observed in these systems. The values of $\delta H$/$\delta H_b$ also appear to lie along a similar single curve with no significant differences between the various systems in view of the somewhat greater scatter in these data. The reduction of the Sm-A–N enthalpy is related to the presence on the silica surface of a layer of liquid crystals incapable of forming a smectic phase. The liquid crystal molecules in this layer are orientationally frozen into a low-ordered state, and
the change to a smectic would be subject to prohibitive elastic deformations.

The scatter in the enthalpy and $\Delta T_{AN}$ data for the aerosol samples is likely due to the dispersion of aerosol particles, which is heavily dependent on the homogeneity of the LC plus aerosol mixture. Our method of mechanical mixing in the isotropic phase may not be completely adequate. Preliminary experiments in which the LC and aerosol are dissolved in a solvent such as acetone that is then removed by evaporation appear to improve the homogeneity of the resulting LC plus aerosol mixture.

C. Sm-$A-N$ fitting results

Because of the surprisingly sharp nature of the Sm-$A-N$ transition in the LC plus aerosol systems, a critical power-law fitting analysis could be carried out. The usual procedure begins by subtracting from the $C_p$ data a background curve corresponding to the low temperature wing of the N-I transition expected in the absence of a Sm-A phase: $\Delta C_p = C_p - C_p(\text{background})$. This procedure was used for pure 8CB and all the 8CB plus aerosol mixtures, and such background curves are represented in the vicinity of the Sm-$A-N$ transition by the dashed lines in Fig. 1. This procedure could not be carried out for pure 8S5 and 8S5 plus aerosol mixtures due to the lack of detailed $C_p$ data in the N-I region. Hence, the data were analyzed with the following power-law expressions including corrections-to-scaling terms [3],

$$\Delta C_p = B_c + A^- |t|^{-\alpha} (1 + D^- |t|^{0.5})$$

for 8CB samples, \( (a) \)

$$C_p = \Delta C_p + B_c + E_t = B + E_t + A^- |t|^{-\alpha} (1 + D^- |t|^{0.5})$$

for 8S5 samples, \( (b) \)

where $t = (T - T_c)/T_c$ is the reduced temperature. The background $C_p$ was represented by a linear term ($B_c + E_t$) and $B = B_c + B_c$ for fits to the 8S5 data. Nonlinear least-squares fits were performed with a maximum reduced temperature $|t|_{\text{max}} = 10^{-2}$, and ranging shrinking techniques, varying $|t|_{\text{max}}$ down to $3 \times 10^{-3}$, were employed to test the stability of the resulting parameters. Obviously rounded data close to $T_c$ were excluded, and the minimum usable reduced temperatures ($|t|_{\text{min}}$) are given in Table II.

Table II summarizes the values for the adjustable parameters in Eq. (1) used to fit all the $C_p$ data of 8CB and 8S5 pure and aerosol mixture samples. Results for pure ($\rho = 0$) 8CB and 8S5 conform well with published values of $\alpha(8CB) = 0.30$ and $\alpha(8S5) = -0.022$ as well as the reported amplitude ratios $A^-/A^+$ [13,14]. With the addition of disordering aerosol dopent, $\alpha(8CB)$ decreases smoothly from 0.30 to $-0.04$ for $0 < \rho < 0.09$ g cm$^{-3}$, as shown in Fig. 4, while the amplitude ratio $A^-/A^+$ remains close to 1. This trend is independent of the type of aerosol.

For 8CB aerosol mixtures with $\rho > 0.09$ g cm$^{-3}$, the $C_p$ data exhibit considerable rounding near the peak maximum. This is indicated in Table II by the larger $|t|_{\text{min}}$ values that must be used for fitting and the poorer $\chi^2_r$ values. Shown in

| Sample | $\rho$ (g cm$^{-3}$) | $\alpha_{\text{eff}}$ | $T_c$ (K) | $B_c$ (J K$^{-1}$ g$^{-1}$) | $10^2$ | $A^-$ (J K$^{-1}$ g$^{-1}$) | $A^+$ (J K$^{-1}$ g$^{-1}$) | $D^-$ | $D^+$ | $\chi^2_r$ | $10^4 |t|_{\text{min}}$ |
|--------|-----------------|-----------------|----------|-----------------|--------|-----------------|-----------------|--------|--------|--------|-----------------|
| 8CB pure | 0 | 0.30 ± 0.02 | 307.102 ± 0.001 | -0.421 | [0] | 0.0793 | 0.0756 | 3.740 | 5.171 | 1.01 | 0.30 |
| phobic sil | 0.016 | 0.24 | 306.469 ± 0.001 | -0.776 | [0] | 0.216 | 0.221 | 4.507 | 4.031 | 1.05 | 0.35 |
|philic sil | 0.084 | -0.04 | 306.248 ± 0.003 | -0.544 | [0] | 0.181 | 0.169 | 2.221 | 3.164 | 1.19 | 0.41 |
| 8S5 pure | 0 | [-0.007] | 336.578 ± 0.002 | 3.77 | -14.001 | -14.155 | 0.168 | 0.135 | 1.01 | 0.20 |
|philic sil | 0.084 | -0.019 | 335.672 ± 0.003 | 4.347 | 1.42 | -1.951 | -2.053 | 0.315 | 0.003 | 51 | 1.31 | 0.56 |

| Sample | $\rho$ (g cm$^{-3}$) | $\alpha_{\text{eff}}$ | $T_c$ (K) | $B_c$ (J K$^{-1}$ g$^{-1}$) | $10^2$ | $A^-$ (J K$^{-1}$ g$^{-1}$) | $A^+$ (J K$^{-1}$ g$^{-1}$) | $D^-$ | $D^+$ | $\chi^2_r$ | $10^4 |t|_{\text{min}}$ |
|--------|-----------------|-----------------|----------|-----------------|--------|-----------------|-----------------|--------|--------|--------|-----------------|
| 8CB pure | 0 | 0.30 ± 0.02 | 307.102 ± 0.001 | -0.421 | [0] | 0.0793 | 0.0756 | 3.740 | 5.171 | 1.01 | 0.30 |
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|philic sil | 0.084 | -0.019 | 335.672 ± 0.003 | 4.347 | 1.42 | -1.951 | -2.053 | 0.315 | 0.003 | 51 | 1.31 | 0.56 |
The transition temperature and the large difference in values between bulk $8\bar{S}_5$ and the $8\bar{S}_5$ plus aerosil sample. Also, those for $8CB$. In particular, the structure of fragile voids containing bulk $8\bar{S}_5$ that freezing of $8\bar{S}_5$ in aerogel samples will damage the shaded region in Fig. 4.

The fits for mixtures with $\rho > 0.09$ g cm$^{-3}$ seem to be artificial values that do not appear to follow the systematic trend for $\rho = 0.084$ g cm$^{-3}$. Aerosil mixtures with $\rho > 0.09$ g cm$^{-3}$ can best be described as having $\Delta C_p (Sm-A-N)$ nonsingular features like those observed in aerogel and anopore samples [6,13]. This change in character from singular $\Delta C_p$ behavior at low $\rho$ values is indicated by the shaded region in Fig. 4.

Although only one aerosil density (0.084 g cm$^{-3}$) was studied for 8S5, the results are dramatically different from those for 8CB. In particular, $\alpha$ (8S5) for the aerosil sample is essentially the same as the bulk value. Such a result is consistent with the Harris criterion that disorder will not produce a perturbation in the critical fluctuations if $\alpha_{\text{bulk}} < 0$ [21]. There is one concern about this 8S5 result. It has been shown that freezing of 8S5 in aerogel samples will damage the structure of fragile (low density) aerogels, creating large voids containing bulk 8S5 [20]. It is possible that the freezing of 8S5 at room temperature during filling of the cell could cause segregation of the aerosil particles, leaving large regions that were essentially pure bulk 8S5. The principle argument against the 8S5 phlic-sil sample merely exhibiting bulk transitions is the large ($\sim 0.906$ K) shift in the Sm-$A-N$ transition temperature and the large difference in $\delta H_{AN}$ values between bulk 8S5 and the 8S5 plus aerosil sample. Also, the $N-I$ transition and Sm-$C$-$Sm-A$ transitions shift in temperature differently (−1.59 K and −2.79 K, respectively), further evidence that the observed behavior of 8S5 is influenced by the aerosil dopant.

**IV. CONCLUSION**

We have undertaken a detailed calorimetric study as a function of aerosil dopant of the Sm-$A-N$ transition for two liquid crystals having different structures and critical behaviors in the bulk. Interesting effects were observed at both the $N-I$ and the Sm-$A-N$ transitions. The $N-I$ transition shifts to lower temperatures with increasing $\rho$ and takes on a bimodal appearance. We suggest that the spike feature may be related to a first-order transition for LC in gaps between aerosil particles while the shoulder may reflect a broad, glasslike ordering of LC close to the aerosil surface. As $\rho$ increases, the aerosil surface area increases and the volume of the gap regions decreases, thus leading to the dominance of the shoulder feature for the $N-I$ transition when $\rho$ is large.

The most striking result is the appearance of a sharp, singular $C_p$ peak at the Sm-$A-N$ transition that decreases in amplitude and shifts to lower temperature with increasing $\rho$. Although $\Delta T_{AN}$ and $\delta H/\delta H_B$ for the aerosil studies matches well the trend observed in aerogels, $\Delta C_p (Sm-A-N)$ remains sharp and takes on an increasingly asymmetric appearance in contrast to the $C_p$ bump found in aerogels [6]. A power-law fitting yielded effective critical exponents $\alpha_{\text{eff}} (8CB)$ that decrease smoothly from the bulk crossover value and appear to level off at the $3D$ $XY$ value without any parallel change in the nematic temperature range. A similar study with 8S5,
which already possesses 3D $XY$ behavior at the Sm-$A \rightarrow N$ transition in the bulk, showed no change in the singular nature of $C_P$ (Sm-$A \rightarrow N$) in aerogels. It is thus tempting to conclude that the aerosil induced random field causes a crossover of the critical behavior of the Sm-$A \rightarrow N$ transition towards 3D $XY$. This crossover was previously observed in bulk LC systems by varying the nematic temperature range and thus weakening the coupling between the smectic and nematic order parameters. In this study, we observe the crossover of the Sm-$A \rightarrow N$ transition to 3D $XY$ as well as the emergence at higher silica densities of nonsingular behavior like that observed in aerogels.

Future studies of phase transitions in LC plus aerosil systems would be extremely interesting. Most importantly, the crossover observed here in the $C_P$ critical nature of the Sm-$A \rightarrow N$ transition should be investigated for other singular quantities such as the smectic correlation length by scattering experiments, and such experiments are currently under way. Also, the nature of the aerosil distribution in LC should be explored since the phillic sils form weak hydrogen-bonded networks that may be sensitive to the mixing method employed.

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