Calorimetric study of the isotropic to nematic phase transition in an aligned liquid crystal nano-colloidal gel

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A high-resolution calorimetric study of the specific heat ($C_p$) has been carried out for the isotropic to nematic phase transition in an aligned liquid crystal (octylcyanobiphenyl - 8CB) and aerosil nano-colloid gel. A stable alignment was achieved by repeated thermal cycling of the samples in the presence of a strong uniform magnetic field, which introduces anisotropy to the quenched random disorder of the silica gel. In general, the specific heat features of the $I-N$ transition in aligned (anisotropic) gel samples are consistent with those seen in random (isotropic) gel samples, namely the observance of two $C_p$ peaks and non-monotonic transition temperature shifts with increasing silica concentration. However, larger transition temperature shifts with silica density, modification of the phase conversion process in the two-phase coexistence region, and a larger effective transition enthalpy are observed for the aligned samples. The lower-temperature aligned $C_p$ peak is larger and broader while exhibiting less dispersion than the equivalent peak for the random gel. This may be a consequence of the alignment altering the evolution from random-dilution-dominated to random-field-dominated effects. The exact origin of the larger transition temperature shifts is uncertain but the larger enthalpy suggests that the nematic state is different in the aligned system than in random gels. The general non-monotonic behaviour of the transition temperature is interpreted using dimensional analysis as a combination of an effective elastic stiffening of the liquid crystal combined with a liquid crystal and aerosil surface interaction energy.

Keywords: calorimetry; nematic; aerosil gel; quenched disorder

1. Introduction

Because of the wide range of physics involved, the study of quenched random disorder on phase structure and transitions is an important area that continues to attract extensive research activity. Here, the use of complex fluids or soft-systems in the presence of quenched random disorder has recently played a central role. In particular, progress has been made using liquid crystal (LC) as the host material and a variety of porous media or dispersed solids as the mechanism to introduce quenched random disorder (QRD).

One useful physical model is the LC+aerosil system where the QRD is created by a dispersed gel of silica aerosil particles that form a weakly linked gel and is varied by changing the density of aerosils in the dispersion. Numerous studies have previously been carried out by various groups on LC+aerosil (1) and the related LC+aerogel system (2), where aerogels are strongly linked (fused) silica gels. The most thoroughly studied LC+aerosil system is the dispersion of type-300 aerosil in octylcyanobiphenyl (8CB), denoted 8CB+sil. Detailed calorimetric (3–5), x-ray scattering (6, 7), x-ray intensity fluctuation spectroscopy (8, 9), static and dynamic light-scattering (10–12), and deuterium nuclear magnetic resonance (NMR) (13) studies on the nematic to smectic-$A$ (N–Sm$A$) and the isotropic to nematic ($I-N$) phase transitions of this system have shown that there are clear quenched random-field characteristics as well as finite-size scaling effects (1).

The effect of the aerosil gel network on the orientational order of the nematic phase is two-fold. The silica gel firstly dilutes the LC and secondly creates a preferred local orientation (14). However, when the random gel responsible for the imposing of this random-field effect is strained, i.e. the gel takes on some anisotropy, a long-range ordered anisotropic nematic state is predicted (15). This is analogous to a similar situation for smectic ordering where disorder anisotropy may lead to an ‘$XY$-Bragg glass’ phase (16, 17) as opposed to a smectic Bragg glass for isotropic disorder (18, 19). Experimental evidence supporting both predictions of anisotropic disorder has recently been found by a high-resolution x-ray study of smectic ordering in aligned 8CB+sil samples (20). The present calorimetric work is stimulated by the x-ray study but focuses on the $I-N$ transition of...
aligned 8CB+sil. The results of a high-resolution calorimetric study on the smectic ordering in aligned 8CB+sil samples will be presented in a separate paper.

In this work, the effect of anisotropy is studied by calorimetry on the weakly first-order \( I \rightarrow N \) transition by preparing orientationally aligned 8CB+sil gels, denoted as a8CB+sil, and compared to unaligned, random, 8CB+sil samples, denoted as r8CB+sil. A convenient measure of the introduced disorder in these systems is the grams of silica per cm\(^3\) of LC, denoted the conjugate silica density \( \rho_S \), which is directly related to the surface area of solids as well as the mean distance between solid surfaces \( (I, 4) \). The units of \( \rho_S \) will be dropped hereafter. In general, the specific heat \( (C_p) \) signatures of the \( I \rightarrow N \) transition in a8CB+sil are found to be consistent with previous measurements on r8CB+sil samples \( (I) \). The anisotropy only subtly affects the shape of the \( C_p(T) \) variation near the transition, where double specific heat peaks are signatures characteristic of LC+sil systems with \( \rho_S \leq 0.1 \). This double-peak feature can be understood as a cross-over from random-dilution-dominated to a random-field-dominated \( I \rightarrow N \) phase conversion \( (2I) \). Significant departures from the r8CB+sil results in a larger magnitude of the transition temperature shift and in the evolution of the effective transition enthalpy as a function of \( \rho_S \) for the a8CB+sil system. The counter-intuitive result of a lower \( T_{IN} \) for a8CB+sil despite having longer-range nematic order may be the result of larger nematic domains encompassing more disorder sites. The larger effective transition enthalpy and qualitatively different \( \rho_S \) dependence suggests that the nematic state for the aligned system is different than that in the random system.

An empirical modelling of the effective double-peak specific heat in the \( I \rightarrow N \) coexistence region has been developed in order to extract the \( \rho_S \) dependence of the low- and high-temperature peaks. This analysis indicates that the low-temperature, random-field-dominated peak is essentially constant over the range of \( \rho_S \) studied while the high-temperature, random-dilution-dominated peak decays rapidly with increasing aerosil density, disappearing at \( \rho_S \approx 0.13 \). Finally, a dimensional analysis of the general non-monotonic transition temperature shift has been performed. The analysis yields a consistent scaling for a variety of disordering porous media and may indicate that the interplay of surface interaction energy and effective elasticity of the host fluid within an ordered domain is modified systematically by the colloidal dispersions.

Section 2 describes the preparation of the 8CB and aerosil dispersion samples in the random and aligned states as well as the ac-calorimetry technique employed. Section 3 presents an overview of the calorimetric results. These results are discussed in Section 4, with emphasis on the \( C_p \) doubling near the \( I \rightarrow N \) transition and the non-monotonic transition temperatures shifts as a function of \( \rho_S \). The conclusions are summarized in Section 5.

2. Sample preparation and calorimetry

Nano-colloidal mixtures of the LC+sil samples were prepared using the solvent-dispersion method \( (4) \). The LC octylcyanobiphenyl (8CB, obtained from Frinton Laboratories Inc. and having a molar mass of 291.44 g mol\(^{-1}\)) and the hydrophilic type-300 aerosil (sil, obtained from DeGussa, Inc. having 7-nm diameter particles and 300 m\(^2\) g\(^{-1}\) specific area) were prepared after thoroughly degassing at high temperature and under vacuum for at least 2 h. After dispersing measured amounts of 8CB and sil in high-purity (low-water) acetone, the solvent was allowed to evaporate slowly over several hours. The final mixture was then degassed at \( \sim 320 \text{ K} \) for 2–3 h to ensure complete removal of the acetone. Six different 8CB+sil batches were made with densities in the range \( \rho_S = 0.030–0.150 \). The resulting 8CB+sil has a dispersed aerosil gel structure that is fractal in character over a range of length scales \( (4, 9) \) and is termed here a random sample.

The aligned 8CB+sil, a8CB+sil, samples were achieved by thermally cycling a given mixture in a sealed calorimeter cell \( \sim 100 \text{ times} \) through the \( I \rightarrow N \) phase transition in the presence of a 2 T magnetic field. For \( \rho_S \gg 0.1 \), no significant alignment could be imposed. Two control random 8CB+sil, r8CB+sil, samples at \( \rho_S = 0.050 \) and 0.130 were also made from the same batch of 8CB and they experienced the exact same thermal history except with no aligning magnetic field present. In the presence of a magnetic field, the nematic director of 8CB tends to align parallel to the field, and this tendency competes with the quenched random disorder of the gel. Due to the elasticity of the LC and the compliance of the gel, this competition leads to restructuring of the gel to accommodate the magnetic anisotropy. As a result, the quenched disorder becomes no longer random but on average orients nematic domains along the direction of the applied field. After removal of the field and subsequent temperature cycling, the aligned structure of the gels continues to promote macroscopic long-range order of the nematic, with a narrow distribution of director orientations as evidenced by x-ray studies on nearly identically prepared samples \( (20, 22) \). The x-ray studies also found that the aerosil gel scattering was nearly independent of the alignment procedure, indicating that the alignment is
maintained by a rearrangement of the aerosil gel on very long length scales and the gel remains random locally (22). It may be expected then that the large length scales of nematic (director) ordering would be affected by the alignment, which is the focus of this work.

High-resolution ac-calorimetry was performed using a home-built calorimeter whose basic characteristics have been described elsewhere (23). The technique consists of applying heating power to the cell as \( P_{ac} \) and detecting the resulting temperature oscillations having an amplitude \( T_{ac} \) and a relative phase shift of \( \varphi = \Phi + \pi / 2 \), where \( \Phi \) is the absolute phase shift between \( T_{ac}(\omega) \) and the input power. The specific heat at a heating frequency \( \omega \) is given by

\[
C_p = \frac{C_{\text{filled}} - C_{\text{empty}}}{m_{\text{sample}}} = \frac{P_{ac} \cos \varphi/\omega |T_{ac}| - C_{\text{empty}}}{m_{\text{sample}}},
\]

and

\[
C_{\text{filled}}' = \frac{P_{ac}}{\omega |T_{ac}|} \sin \varphi - \frac{1}{\omega R}.
\]

where \( C_{\text{filled}}' \) and \( C_{\text{filled}}'' \) are the real and imaginary components of the heat capacity, \( C_{\text{empty}} \) is the heat capacity of the cell and silica, \( m_{\text{sample}} \) is the mass in grams of the LC (the total mass of the 8CB+sil sample was \( \sim 15 \) mg, which yielded \( m_{\text{sample}} \) values in the range \( 10-15 \) mg), and \( R \) is the thermal resistance between the cell and the bath (typically \( 200 \) K W\(^{-1}\)). Equations (1) and (2) require a small correction to account for the finite internal thermal resistance compared to \( R \), and this was applied to all samples studied here (24). Measurements were conducted at various frequencies in order to ensure the applicability of Equations (1) and (2) by checking that \( C_{\text{filled}}' \approx 0 \) through the effective \( N \)-Sm\( A \) transition at \( T^* \) and that \( C_p \) was independent of \( \omega \). All data presented here were taken at \( \omega = 0.1473 \) s\(^{-1}\) at a scanning rate of less than \( \pm 200 \) mK h\(^{-1}\), which yielded essentially static \( C_p \) results. All 8CB+sil samples experienced the same thermal history after mounting; 6 h in the isotropic phase to ensure equilibrium, then a slow cool deep into the smectic phase before beginning the first detailed scan upon heating.

Extraction of the enthalpy behaviour involves integrating the excess specific heat \( \Delta C_p = C_p - C_{BG} - \delta C_{NA} \), where \( C_{BG} \) is a linear background describing the specific heat temperature dependence far above \( (+6 \) K) and below \( (-13 \) K) \( T_{IN} \) and \( \delta C_{NA} \) is the \( N \)-Sm\( A \) excess specific heat contribution. Note that the high-temperature limit of the two-phase \( I-N \) coexistence range, easily identified in \( C_p' \) is taken as \( T_{IN} \). Direct integration of \( \Delta C_p \) yields \( \delta H_{IN}^* \), which contains only a portion of the transition latent heat (4). Replacing the \( \Delta C_p \) behaviour in the \( I-N \) coexistence region with a linear extrapolation between the boundary points as in (4) and then integrating yields the fluctuation dominated ‘wing’ enthalpy \( \delta H_{IN}^* \). The difference \( H = \delta H_{IN}^* - \delta H_{IN} \) is the effective phase conversion enthalpy observed by ac-calorimetry. In this study, the 19 K range of integration, temperature scan rates, heating frequency and sample thermal history were all the same for all samples in order to facilitate comparisons. However, due to uncertainties in background subtractions, the absolute accuracy in \( \delta H_{IN}^* \) is about 10%.

3. Results

An expanded view of the excess specific heats for the aligned and random 8CB+sil samples along with pure bulk 8CB from \(-12 \) K below to \(+5 \) K above the \( I-N \) transition are shown in Figure 1. Here, we take as the transition temperature the high-temperature point where \( C_p'' \neq 0 \), i.e. the high-temperature limit of the \( I-N \) coexistence. The excellent overlap of \( \Delta C_p \) in the isotropic and smectic-\( A \) phases is consistent with previous measurements on the (random) 8CB+sil...
system indicating that the anisotropy imposed by the alignment does not affect the short-range orientational fluctuations and that these remain bulk-like independent of the aerol sil structure. However, large differences are seen in the nematic temperature range where there is clearly an excess of enthalpy. This excess generally decreases with increasing $r_S$ and approaches the bulk curve.

Figure 2 provides an overlay of $\Delta C_p$ for the six $a8CB$+sil samples studied near and about the $I-N$ coexistence region. As with the random sil system, a double-peak feature is clearly seen and this is currently understood to be marking the crossover from random-dilution-dominated to random-field-dominated disorder (21). In addition, a dramatic suppression of the dilution-dominated sharper, high-temperature $\Delta C_p$ is also seen in the aligned samples for $\rho_S \geq 0.100$, marking the boundary between the soft and stiff gel regime (4).

To highlight the effect of alignment, two samples from the same mixture batch at low and high $\rho_S$ were also studied without any field alignment (random) but experiencing identical experimental conditions. Comparisons between the random and aligned samples are shown in Figure 3 for the $\rho_S=0.050$ and Figure 4 for the $\rho_S=0.130$ samples. For the low density sample, alignment appears to broaden and enhance both $\Delta C_p$ transition peaks but the width of coexistence is unchanged. Also, the imaginary part indicates that the lower-temperature, random-field-dominated peak is less dispersive. For the higher density sample, the excess specific heat is somewhat broadened but is essentially unchanged by the alignment as is the coexistence range. As with the low-density comparison, the dispersive nature of the low-temperature $\Delta C_p$ peak is suppressed by the alignment.

In both cases, the imaginary enthalpy (integrated area under $C_p^*$) is smaller for the aligned as compared to the random samples. The real effective enthalpy $\delta H_{IN}$ over a wide temperature range is larger for the $a8CB$+sil samples, due primarily to the excess heat capacity seen throughout the nematic temperature range. See Figure 5. This is in contrast to that seen in the previous $8CB$+sil results where the heat capacity wings far away from $T_{IN}$ overlapped each other and that of bulk $8CB$. For the two $r8CB$+sil samples studied here, the wings yield an $\rho_S$-independent enthalpic contribution $\delta H_{IN}^{r8CB}=5.5$ J g$^{-1}$, consistent with previous measurements on unaligned $8CB$+sil samples (4). Also seen in Figure 5, the evolution of $\delta H_{IN}^{a8CB}$ for the $a8CB$+sil system appears to join that for the $r8CB$+sil system for $\rho_S=0.150$. 

![Figure 2](image-url)  
**Figure 2.** Overview of the excess specific heat over the two-phase $I-N$ coexistence region of the $I-N$ phase transition for the $a8CB$+sil samples. The inset denotes the symbols for the $\rho_S$ values of the six samples. Note that the transition temperature $T_{IN}$ is taken as the high-temperature limit of the coexistence region.

![Figure 3](image-url)  
**Figure 3.** Comparison of the real excess specific heat, $\Delta C_p$, and imaginary (dispersive) specific heat, $C_p^*$, for the aligned and unaligned random $\rho_S=0.050$ $8CB$+sil sample as a function of temperature near $T_{IN}$. Note the broadening and enhancement of the low-temperature $\Delta C_p$ peak along with a suppression of its dispersive nature for the aligned compared to the random sample.
While the excess specific heat is slightly altered by alignment, a more dramatic effect is seen in the behaviour of the transition temperatures. Qualitatively, the transition shifts to lower temperature as $r_S$ increases in a similar manner as for the random samples. However, for all aligned samples, the magnitude of the shift with respect to the pure bulk value $\Delta T_{IN} = T_{IN}^{bulk} - T_{IN}(r_S)$ is approximately 0.5 K larger; see Figure 6. A comparison of the width of the nematic temperature range $\Delta T_{nem} = T_{IN} - T_{NA}$, shown in Figure 7 for the aligned and random samples, reveals that $\Delta T_{nem}$ for aligned samples is approximately 0.2 K less than for bulk 8CB while $\Delta T_{nem}$ for unaligned samples is essentially independent of $r_S$ in the range of values studied here. Finally, the isotropic plus nematic coexistence range $\delta T_{I+N}$, determined by the temperature width of $C_p^\prime$, for the aligned samples is essentially identical to that for random samples as seen in Figure 8.

It is important to note that sample degradation due to the repeated thermal cycling during sample preparation can be ruled out as the cause of the larger transition shifts for the aligned compared to the random sample.
random 8CB+sil samples. The LC 8CB is known to be a stable compound when properly degassed and hermetically isolated as done in these calorimetric cells. Also, the coexistence width $d_{TI+N}$, which should be sensitive to the quality of the LC, appears to be unaffected by the sample preparation when compared to previous, more gently treated, measurements. See Figure 8. More convincingly, the control random samples measured in this study were subjected to identical thermal histories as were the aligned samples but nevertheless display smaller transition temperature shifts that are essentially identical to those measured for r8CB+sil samples in previous studies (4).

If the alignment is imprinted on the aerosil gel only on long length scales (22) and the local aerosil gel distribution remains unchanged, then the larger transition temperature shifts for the aligned samples may be the result of the larger nematic domains encompassing more aerosil gel (disorder). Additionally, the rearrangement of the aerosil gel for the aligned samples may also result in a stiffer gel as compared to the equivalent random, unaligned, gel and contribute to a larger $\Delta T_{IN}$. Table 1 summarizes the transition temperatures, nematic temperature range, width of the two-phase coexistence and the effective enthalpy for the $I-N$ transition in six aligned and two random 8CB+sil samples studied.

Table 1. Summary of the calorimetric results on the isotropic to nematic phase transition for the six aligned and two unaligned 8CB+sil samples. The units for conjugate aerosil density $\rho_S$ are grams of aerosil per cm$^3$ 8CB; the transition temperature $T_{IN}$, nematic range $\Delta T_{Nem}$ and coexistence width $d_{TI+N}$ are in Kelvin; the effective ac-enthalpy $\delta H'_{IN}$ and the contribution of the high-temperature peak $h_1$ and low-temperature peak $h_2$ effective enthalpies are in Joules per gram 8CB (see the text for details). For all parameters, the uncertainties are ± $2$ in the last digit except for $\delta H'_{IN}$, which is ±0.07, and the effective enthalpies $h_1$ and $h_2$, where it is ±10%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_S$</th>
<th>$T_{IN}$</th>
<th>$\Delta T_{Nem}$</th>
<th>$d_{TI+N}$</th>
<th>$\delta H'_{IN}$</th>
<th>$h_1$</th>
<th>$h_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aligned</td>
<td>0.030</td>
<td>312.226</td>
<td>6.941</td>
<td>0.19</td>
<td>6.88</td>
<td>0.62</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>0.050</td>
<td>312.555</td>
<td>6.929</td>
<td>0.22</td>
<td>6.92</td>
<td>0.39</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>0.070</td>
<td>312.721</td>
<td>6.870</td>
<td>0.26</td>
<td>6.78</td>
<td>0.24</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>313.044</td>
<td>6.903</td>
<td>0.24</td>
<td>6.79</td>
<td>0.09</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>0.130</td>
<td>313.064</td>
<td>6.904</td>
<td>0.28</td>
<td>6.54</td>
<td>0.01</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>0.150</td>
<td>313.009</td>
<td>6.909</td>
<td>0.30</td>
<td>6.33</td>
<td>0.03</td>
<td>0.79</td>
</tr>
<tr>
<td>Unaligned</td>
<td>0.050</td>
<td>313.184</td>
<td>7.038</td>
<td>0.21</td>
<td>6.45</td>
<td>0.34</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>0.130</td>
<td>313.410</td>
<td>7.116</td>
<td>0.30</td>
<td>6.36</td>
<td>0.12</td>
<td>0.90</td>
</tr>
</tbody>
</table>
Fits made to the other samples were of similar quality. region and that a constant baseline value was subtracted.

Inated, and the lower-temperature, random-field tions between the high-temperature, dilution domi-

effects for aligned samples. Modification to the distribution of dilution and field effects for aligned samples with \( r = 0.8 \) coexistence region of the \( T_{IN} \) transition and random-field effects. In addition, the

partitioning the enthalpy between the random-dilu-

simplest means of partitioning the enthalpy between the random-field and dilution to random field crossover (21), may be
density should be isolated by this analysis as a proxy and thus the effect of both alignment and aerosil density should be isolated by this analysis as a proxy for a more detailed experimental measurement of the true total transition enthalpy.

An example of such a double-Gaussian modelling of the \( \Delta C_p \) data through the \( T_{IN} \) coexistence region is shown in Figure 9. Similar quality fits were obtained for all aligned and random samples studied. From these fit results, the area for each contribution (each truncated at the high-temperature limit of the coexistence range) \( H_1 \) and \( H_2 \), respectively, can be extracted. However, as seen in Figure 9 and similarly for all such fits, this approach clearly is inadequate to quantitatively model the peak farther than about 0.2 K from \( T_{IN} \) and so the total integration would not yield the correct \( H \) as obtained experimentally. By assuming that the ratio of each term’s area, \( R = H_1/H_2 \) is close to being correct and taking the measured \( H \), a reasonable estimate of each peak’s area may be calculated by \( h_1 = RH/(1+R) \) and \( h_2 = H/(1+R) \) for the high- and low-temperature peaks, respectively (with \( h_1 + h_2 = H \)). The uncertainties in \( h_1 \) and \( h_2 \), which are \( \sim 10\% \), are due to the quality of the fit while the uncertainty in \( H \) is typically \( \pm 0.05 J g^{-1} \). These results are listed in Table 1 for all of the samples studied. Comparison of the \( h_1 \) and \( h_2 \) contributions for the random and aligned samples with \( \rho_S = 0.050 \) indicates that, despite the obvious broadening seen in Figure 3 for the aligned sample, the relative contributions of dilution and field effects remain unchanged. However, for the sample with \( \rho_S = 0.130 \), there is a significant increase in the random-dilution contribution to the transition enthalpy for the aligned sample.

Plots of the \( \rho_S \) dependence of the peak areas \( h_1 \) and \( h_2 \) are shown in Figure 10. The low-temperature, random-field-dominated, effective enthalpy \( h_2 \) is effectively constant through this low range of aerosil densities, while the high-temperature, random-dilu-

dominated, effective enthalpy \( h_1 \) decreases rapidly with \( \rho_S \), mirroring the decrease of the total effective enthalpy \( H \), until it essentially vanishes at \( \rho_S \sim 0.13 \). Although this can be inferred from the behaviour shown in Figure 2, this analysis makes it clear that the decrease in the \( I-N \) transition enthalpy occurs in two stages. In the low-density range (\( \rho_S \lesssim 0.1 \)), the random-dilution-dominated peak decays, while the random-field-dominated peak is nearly \( \rho_S \) independent. Given the results of the wider \( \rho_S \) range studies of (4) and (26), the remaining random-field-dominated peak should begin to decrease for larger \( \rho_S \) and eventually disappear at \( \rho_S = 0.8 \). Such a scenario, coupled with the temperature-dependent total disorder strength of the random dilution to random field crossover (21), may be

\[ \begin{align*}
\Delta C_p &= C_{p,\text{base}} + (0.100 \cdot \text{Fit}) \\
&= \sum_{i=1}^{n} (h_i \cdot \text{Gaussian fit})
\end{align*} \]
important in explaining the non-monotonic transition temperature decrease with \( \rho_S \).

4.2. Dimensional analysis: \( \Delta T_{IN} \)

A striking effect of the aerosil gel on the \( I-N \) transition is the non-monotonic shift in the transition temperature, \( \Delta T_{IN} \), as shown in Figure 6. The first-order transition temperature typically shifts as a function of impurities, such as solvents, and it has been extensively studied (31–33). However, the aerosil gel here imposes quenched random disorder leading to additional interactions other than dilution that dominates in LC and solvent mixtures.

Various mechanisms have been explored to account for the observed transition temperature shift behaviour in LC+sil such as finite-size nucleation (due to the first-order character of the \( I-N \) transition), elastic strain, random pinning (see (4, 34) for a discussion of these three), and more recently an extended ‘single-pore’ model to account for surface anchoring (35). However, all current models yield smoothly varying functions of confining length or disorder (silica) density and the non-monotonic behaviour remains unexplained. Recently, it has been shown that the \( I-N \) transition in the presence of quenched random disorder proceeds via a two-step process on cooling, first random-dilution and then random-field, and this successfully accounts for the doubling of the \( I-N \) transition features (21). Further, it was speculated that this might also account for the behaviour of \( \Delta T_{IN} \) for these systems via the required temperature-dependent disorder strength (see also (27)) but this idea remains unexplored.

Other experimental observations on the LC+sil system as a function of \( \rho_S \), such as the evolution of the critical behaviour of the \( N-SmA \) (4, 20, 28) and \( \Delta C_p \) peak shape of the SmA–SmC (30) transitions, rheological studies (36) and dynamic x-ray scattering studies (8, 9), strongly suggest that the colloidal dispersion of the aerosil gel alters the effective elastic (and perhaps other material) properties of the host LC fluid.

To explore the idea that the LC material parameters may become \( \rho_S \)-dependent, a dimensional analysis may be performed on \( \Delta T_c \) based on four important quantities: the effective elastic constant of the composite, \( K \) in (J m\(^{-1}\)), the effective surface interaction energy density, \( W \) in (J m\(^{-2}\)), the conjugate aerosil density, \( \rho_S \) in (kg m\(^{-3}\)) and the transition entropy change, \( \Delta S_c \) in (J K\(^{-1}\) kg\(^{-1}\)), yielding

\[
|\Delta T_c| \sim \frac{W^2}{K\rho_S \Delta S_c} \sim \frac{W^2 T_c}{K\rho_S \Delta H_c}, \tag{3}
\]

where the entropy change at \( T_c \) is related to the enthalpy change (latent heat) by \( \Delta H_c = T_c \Delta S_c \). Note that if the bulk value of \( K \) as well as the anchoring energy density \( W \) were assumed constant, Equation (3) would also not yield the observed non-monotonic behaviour of \( \Delta T_c \). However, if \( K \) and \( W \) were aerosil dependent, then this analysis could be used to shed light on the \( \rho_S \)-dependence of the effective material parameters of the composite system. A \( \rho_S \)-dependent \( K \) is clear given that aerosils are used as thickeners and a \( \rho_S \)-dependent \( W \) is reasonable given the flexibility of the aerosil gels (9). However, for other systems such as LCs embedded in rigid aerogel or controlled porous glasses, it is more natural to consider \( W \) as a constant. Equation (3) may be rearranged to group together the experimentally accessible quantities to give

\[
\frac{|\Delta T_c|}{T_c} \Delta H_c \rho_S \sim \frac{W^2}{K}, \tag{4}
\]

which has units of (J m\(^{-3}\)) and can be termed the LC+QRD energy density. Accurate ac-calorimetric data are available for the LC 8CB in controlled porous glass (35), aerogel (37), random aerosol gel
Figure 11. Comparison of the derived LC+QRD energy density $W^2/K$ as a function of $\rho_s$ for the 8CB+QRD (8CB+aerogel (37), 8CB+CPG (35), random 8CB+sil (4) with two points from this work and the aligned 8CB+sil (this work)). See the inset for symbol labels. Both solid lines indicate a power law with an exponent of $n=1.5$. See the text for details.

(4) and the aligned aerosil gel of this work. However, each data set, although taken under similar ac-calorimetric experimental conditions, is missing a significant portion of the latent heat. Thus, the effective transitional enthalpy available from these studies are used only as a proxy for the true value of $\Delta H_{IN}$.

With Equation (4), the $\rho_s$ dependence of the combination $W^2/K$ is found and plotted in Figure 11. Given the uncertainties (primarily in estimating $\Delta H_{IN}$ from $\delta H_{IN}$), the data collapse for such a range of 8CB+QRD systems is interesting and somewhat surprising. The overall behaviour of the LC+QRD energy density is reasonably describable by a simple power law, $W^2/K \sim \rho_s^n$, where the exponent for the low-density ($\rho_s<0.1$) aerosil system and the high-density ($\rho_s>0.1$) aerosil along with the aerogel systems is $n=1.5$ (see the solid lines in Figure 11). Since the low-density aerosil gel is extremely soft as compared to the aerogel (or controlled porous glass or high-density aerosil), the dimensional analysis suggests that the non-monotonic behaviour of $T_{IN}(\rho_s)$ may reflect a change in the effective stiffness and/or anchoring of the LC to the QRD surfaces occurring over a very narrow range at or just above $\rho_s \sim 0.10$, where $W^2/K$ shifts between the two solid parallel lines in Figure 11.

Given the overall behaviour of the LC+QRD energy density, the functional dependence of $W$ and $K$ separately may be inferred for soft-systems such as low-density aerosil gels. Using the observed power law and the condition that as $\rho_s \to 0$, $W \to 0$ (no surfaces present) and $K \to K_0$ (the bare bulk LC value), this suggests $W \sim \rho_s^n$ and $K \sim K_0 + c \rho_s^n$. Noting that the exponents $n$, $w$ and $k$ must be positive, a relationship among them depends on the magnitude of $K_0$ relative to the diverging part. If $K_0$ is negligibly small, then the exponents must satisfy $2w-k=n>0$. Otherwise, the general relation $2w-k<n<2w$ applies. Overall, this result is intuitively reasonable as the random nature of the solid surfaces causes them to trap more disorder energy as the solid density increases. However, an increasing $K$ with increasing $\rho_s$, i.e. $c>0$, assumes that the composite effectively stiffens the host LC by the pinning defects and domain walls. This analysis also allows for the possibility that $K$ decreases with increasing $\rho_s$, i.e. $c<0$ with a large $K_0$ and this would represent an elastic softening of the LC due to the imposed disorder.

For rigid quenched random disorder where $W$ is likely to be constant dependent only on surface interactions, the above analysis would not hold. For such systems, these results would only shed insight into the overall behaviour of $W^2/K$.

5. Conclusions

This work presents a high-resolution calorimetric study of the effect of sil alignment on the isotropic to nematic phase transition of the quenched disordered 8CB+aerogel system. As expected, the overall specific heat signature of the $I-N$ transition in this system is weakly affected by the alignment, reflecting the scalar nature of the energy fluctuations. The results are largely consistent with results on unaligned (random gel) samples, again revealing as the most significant features the doubling of the $I-N$ transition and a non-monotonic decrease in the transition temperature with aerosil density. Thus, the imposition of long-range orientational order does not significantly change the transition characteristics. However, differences do emerge in the magnitude of the transition temperature shift, with the shift being unexpectedly larger for the aligned disorder, and there being small changes in the $C_p$ peak shapes in the coexistence range and significant excess enthalpy throughout the nematic temperature range. How the sil alignment causes these effects is not entirely clear but it may be related to the aligned samples having larger nematic domains and so being forced to encompass more aerosil surface (disorder). In addition, there is the possibility that the aligned aerosil gel may be stiffer than the random gel and so impose
greater disorder. The latter observation strongly indicates that the nematic state in the aligned samples differs significantly from that in the random samples.

An empirical analysis of the specific heat peak shapes using a two-Gaussian model yields a reasonably accurate partitioning of the effective enthalpy between the dilution-dominated and field-dominated peaks. While not containing any theoretical insights into the disorder, the decent fits indicate the normal distribution of the isotropic to nematic phase conversion under the influence of random-dilution and random-field effects with relatively little coupling. In addition, the aerosil density dependence indicates that the random-field-dominated peak $h_2$ is nearly constant from the percolation threshold ($p_S=0.015$) to $p_S=0.15$, while the random-dilution-dominated peak $h_1$ decays rapidly. This analysis combined with the results of (4) and (26) indicates that the decrease in the $I-N$ transition enthalpy $H$ determined from $C_p(qc)$ data (and presumably the total latent heat as well) occurs in two stages. As $p_S$ increases, there is a rapid decrease in the random-dilution-dominated contribution, which disappears at $p_S=0.13$, and this is followed by an eventual decrease in the random-field-dominated contribution when the aerosil density is increased above 0.15.

A dimensional analysis of the transition temperature shifts as a function of aerosil density resulted in a relationship that involves an effective elastic constant as well as a surface interaction energy. This analysis further suggests that both these quantities behave as power laws with aerosil density. In addition, the same analysis applied to a variety of 8CB systems with quenched random disorder, such as unaligned (random) aerosil gels, aerogel gels and controlled-porous glasses, reveals a general behaviour and indicates that the resulting exponents are topology independent. High-resolution latent heat measurements through the double-peak feature would greatly aid the peak partition analysis as well as better refine the LC+QRD energy density estimate. Finally, since the origin of the imprinted alignment is undoubtedly a rearrangement of the aerosil gel structure, it would be extremely useful to have a detailed structural study, such as small-angle x-ray scattering, of the aerosil gel under varying degrees of alignment.

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