Calorimetric study of the nematic to smectic-$A$ and smectic-$A$ to smectic-$C$ phase transitions in liquid-crystal-aerosil dispersions

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A high-resolution calorimetric study has been carried out on nanocolloidal dispersions of aerosils in the liquid crystal 4-$n$-pentylphenylthiol-4’-$n$-octyloxybenzoate (8S5) as a function of aerosil concentration and temperature spanning the smectic-$C$ to nematic phases. Over this temperature range, this liquid crystal possesses two continuous $XY$ phase transitions: a fluctuation-dominated nematic to smectic-$A$ transition with $\alpha = \alpha_{XY} = -0.013$ and a mean-field smectic-$A$ to smectic-$C$ transition. The effective critical character of the $N$-$SmA$ transition remains unchanged over the entire range of the introduced quenched random disorder while the peak height and enthalpy can be well described by considering a cutoff length scale to the quasicritical fluctuations. The robust nature of the $N$-$SmA$ transition in this system contrasts with cyanobiphenyl-aerosil systems and may be due to the mesogens being nonpolar and having a long nematic range. The character of the $SmA$-$SmC$ transition changes gradually with increasing disorder but remains mean field like. The heat capacity maximum at the $SmA$-$SmC$ transition scales as $p_s^{2.5}$ with an apparent evolution from tricritical to a simple mean-field step behavior. These results may be generally understood as a stiffening of the liquid crystal (both the nematic elasticity as well as the smectic layer compression modulus $B$) with silica density.

DOI: 10.1103/PhysRevE.72.051716  PACS number(s): 64.70Md, 61.30Eb, 65.40Ba

I. INTRODUCTION

The study of quenched random disorder effects addresses many fundamental issues of current interest in statistical mechanics. Recent experimental advances have shed considerable light on the random-field-theoretic approach, believed to be underlying the physics of quenched random disorder (QRD). In particular, these efforts have led to the systematic study of the random-field model for transitions that break a continuous symmetry [1]. This model is applicable to a terrifc range of phenomena: These include unique assemblies of colloids, complex fluids, charge density waves, spin glasses, and doped semiconductors, to name a few. The experimental efforts to date have focused on idealized physical systems in order to isolate the essential features of quenched random disorder. Considerable research has been carried out on the superfluid transition of $^3$He and $^4$He-$^3$He mixtures in a variety of porous media [2,3] as well as doped magnetic systems [4] but many questions remain due to the quantum nature of the former and the glasslike behavior of the latter [1].

In the random-field approach, the effect of the disorder is mapped onto a local field $\bar{h}(\vec{r})$ directly coupled to the order parameter. This local field varies randomly through the system on length scales smaller than the length scales of the ordered phase such that $\langle \bar{h} \rangle = 0$ while $\langle \bar{h} \cdot \bar{h} \rangle \neq 0$. Because the nature of the imposed disorder is modeled as a dilute (or weak) random field, the effect of QRD may be understood statistically. By studying in detail good realizations of particular universality classes, the results can be applied more generally to a wide variety of physical systems. Particularly fruitful physical system to explore QRD effects in general and the random-field model in particular has been nanocolloidal dispersions of an aerosil gel in a liquid-crystal (LC) host (LC+sil) [1,5].

The most well-studied LC+sil phase transition has been the continuous nematic to smectic-$A$ ($N$-$SmA$) phase transition. This transition involves the breaking of a continuous symmetry and belongs, though not simply, to the three-dimensional (3D) $XY$ universality class [6]. In general, high-resolution x-ray [7–10] and calorimetry [5,11–15] studies of the $N$-$SmA$+sil transition have found that the (quasi-)long-range-ordered smectic phase is destroyed for all densities of aerosil. However, below a silica density of about 0.1 g of SiO$_2$ per cm$^3$ of LC (the so-called conjugate density $p_s$ [1], whose units will be dropped hereafter), a pseudotransition displaying quasicritical behavior at $T = T^*$ persists. The scattering from the short-range smectic order is well described by both a bulk thermal structure factor (dominate above the
pseudotransition $T^*$) and a random-field structure factor (dominate below $T^*$) given by the bulk thermal form squared, the so-called "Lorentzian+Lorentzian-squared" form \cite{7,8}. Although the smectic correlation length is finite, it is large (spanning many mean-void lengths of the silica gel) and exhibits a power-law divergence on cooling to $T^*$ at which it saturates for 8CB \cite{7} and 8OCB \cite{9} in aerosols or begins to decrease upon further cooling towards the SmC phase for $\bar{S}S$+sil system \cite{10}. This broadening observed for $\bar{S}S$ +sil \cite{10} and anisotropic (field aligned) $\bar{S}S$+sil \cite{16} samples could be due to a distribution of SmC tilt angles and result in a lower average order parameter squared. The calorimetry studies found sharp, quasicritical, power-law divergences for the heat capacity for the heat capacity exponent $\alpha_{eff}$ with aerosil density is consistent with a gradual drop in the nematic susceptibility with increasing gel density for all $N$-SmA transitions studied to date.

A detailed scaling analysis of the $N$-SmA transition combining x-ray and calorimetry results through the quasicritical transition for low aerosil density revealed the importance of both random-field and finite-size-like effects \cite{8,17}. The dimensionality of the system also played a role and was consistent with the expected dimensional rise, $d_{ff}=d+2$, for a system with random-field disorder \cite{18,19}. This work also found in general that the effective random-field strength (or variance) scales as $\rho_S$ over the entire range of silica densities studied thus far, although there are indications of different scalings above and below $\rho_S=0.1$ \cite{17}. The experimental and theoretical results to date support the view that a random-field--XY (RF-XY) system has no new critical point.

Recently, tilted smectic phases have become the focus of studies on quenched random disorder effects \cite{10,5}. The smectic-A to smectic-C ($\text{SmA}$-$\text{SmC}$) phase transition involves the breaking of a continuous symmetry and is described by two parameters, the tilt and azimuthal angles. This transition belongs to the 3D $XY$ universality class but is mean field in character due to the relatively long bare correlation length of the SmC. The strong coupling between tilt and smectic layer compression for the SmC phase appears to place the SmA-SmC transition always close to a (Landau) mean-field tricritical point \cite{6}. A consequence of the tilt angle’s sensitivity to the layer elasticity is that this transition is much more strongly disordered by perturbations that distort the smectic layers, as in the strong disorder of aerogels, than the $N$-SmA \cite{20,21}. For weaker aerosol-gel-induced disorder, the Landau mean-field heat-capacity signature was found to be unaffected by hydrophobic aerosils \cite{12} while a recent high-resolution x-ray scattering study on a different LC in a hydrophilic aerosil found little change in the tilt-angle temperature dependence with $\rho_S$ \cite{10}. This robustness to weak disorder may be a consequence of the mean-field character of the transition, placing it effectively at its upper critical dimension. However, when the transition from the SmA phase goes to the chiral analog of the SmC phase ($\text{SmC}^*$), the effect of even the aerosil-induced disorder generally suppresses and smears the transition \cite{5}.

The present work focuses on the effect of quenched random disorder induced by a nanocolloidal dispersion of hydrophilic type-300 aerosil forming a mass-fractal gel within the liquid crystal 4-$n$-pentylphenylthiol-4’-n-octyloxybenzoate ($\bar{S}S$) that closely follows the previously reported x-ray studies \cite{10}. High-resolution calorimetry has been carried out on these $\bar{S}S$+sil dispersions as a function of aerosil concentration and temperature spanning the smectic-C to nematic phases. This liquid crystal possesses two continuous $XY$ phase transitions of interest. The first is a fluctuation-dominated nematic to smectic-A characterized by a heat capacity exponent $\alpha=0$. The critical character of the $N$-SmA transition remains unchanged with the introduction of the quenched random disorder while its enthalpy and heat-capacity maximum decrease in a manner consistent with a finite-size-like scaling without any obvious crossover from soft to stiff gel seen on other LC+sil systems. The stability of the heat capacity quasicritical behavior for this system with QRD may be a consequence of this transition being effectively, due to the long-range interactions, at its upper critical dimension. The observed crossover from tricritical to a simple mean-field step heat-capacity behavior analogous to that seen for the pure $\text{SmA}$-$\text{SmC}^*$ transition in binary LC mixtures \cite{22}. In particular, the $\text{SmA}$-$\text{SmC}$ heat capacity maximum at the transition scales as $\rho_S^{0.5}$. The stable mean-field character of the $\text{SmA}$-$\text{SmC}$ with QRD may be a consequence of this transition being effectively, due to the long-range interactions, at its upper critical dimension. The observed crossover from tricritical to a simple mean-field step behavior for the $\text{SmA}$-$\text{SmC}$ and the continuous diminishing of the $N$-SmA heat capacity peaks may be understood as a continuous stiffening of the liquid-crystal elasticity for the nematic and smectic structure with increasing silica density. However, many theoretical challenges are evident.

Section II describes the preparation of the $\bar{S}S$+sil dispersions as well as the ac-calorimetry technique employed. Section III presents the results of the calorimetric study, while Sec. IV discusses the significance of the evolution of an $XY$ transition as well as a crossover from Landau tricritical to mean-field continuous transition with increasing quenched disorder. Directions for future study will also be discussed.

II. SAMPLES AND CALORIMETRY

The liquid crystal $\bar{S}S$, synthesized at Kent State University, was used after degassing in the isotropic phase for 2 h. The best literature-reported transition temperature values in the bulk for this liquid-crystal molecule ($M_w=412.64$ g mol$^{-1}$) are $T_N^0=359.6$ K for the weakly first-order isotropic to nematic ($I$-$N$) transition, $T_A^0=336.58$ K for the $XY$-like continuous nematic to smectic-A ($N$-SmA) transition, and $T_{AC}^0=329.35$ K for the monotropic Landau tricritical smectic-A to smectic-C ($\text{SmA}$-$\text{SmC}$) transition \cite{23}. At lower temperatures on cooling, a monotropic
smectic-C to crystal-B (SmC-CrB) transition occurs at $T_{CrB}^0 \approx 304$ K. The strongly first-order Crystal-SmA (Cr-SmA) transition occurs reproducibly on heating at $T_{CrA}^0 \approx 332$ K. The measured transitions temperatures for our bulk material occur at $T_{SmA}^0 \approx 336.64$ K, $T_{SmC}^0 \approx 328.96$ K, and $T_{CrA}^0 \approx 331.0$ K, which are in reasonable agreement with the literature bulk values. However, SS5 is known to age with its transition temperatures continuously shift downward with time, especially when heated into the isotropic phase [23,24]. Fortunately, the N-SmA and SmA-SmC transitions remain relatively sharp, well defined, and consistent in shape during the sample aging; see Figs. 1 and 2 as well as Table I. Although the aging of this LC is unavoidable, the samples studied in this work all experienced the same preparation method and thermal history; thus, the relative evolution of these transitions with aerosol disorder should be preserved.

The nanocolloidal mixture of hydrophilic type-300 aerosil in SS5 was prepared following the solvent dispersion procedure outlined in Refs. [9,10]. The hydrophilic nature of the aerosils allows the silica particles to weakly hydrogen bond to each other and form a gel in an organic solvent. The specific surface area of type-300 aerosil is 300 m$^2$ g$^{-1}$ [25], and each aerosil sphere is roughly 7 nm in diameter. However, the basic free-floating aerosil unit consists of a few of these spheres fused together during the manufacturing process [14]. Each SS5+sil sample was created by mixing appropriate quantities of liquid crystal and aerosil together, then dissolving the resulting mixture in spectroscopic-grade (low-water-content) acetone. The resulting solution was then dispersed using an ultrasonic bath for about an hour. As the acetone evaporates from the mixture, a fractal-like gel forms through diffusion-limited aggregation. Crystallization of the LC host can severely disrupt the gel structure, and so care was taken to prevent any formation of the solid phase of the liquid crystal during the experiments.

High-resolution ac calorimetry was performed using two homebuilt calorimeters at WPI. The sample cell consisted of a silver crimped-sealed envelope $\sim 10$ mm long, $\sim 5$ mm wide, and $\sim 0.5$ mm thick (closely matching the dimensions of the heater). After the sample was introduced into a cell having an attached 120-$\Omega$ strain-gauge heater and 1-$\Omega$ carbon-flake thermistor, a constant current was placed across the heater to maintain the cell temperature well above $T_{IN}$. The filled cell was then placed in an ultrasonic bath to remix the sample. After remixing, the cell was mounted in the calorimeter, the details of which have been described elsewhere [26]. In the ac mode power is input to the cell as $P_{ac}e^{i\omega t}$, resulting in temperature oscillations with 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 $\omega$ using $C' = P_{ac}/\omega|T_{ac}|$ is given by

$$C_p = \frac{[C_f - C_{empty}]}{m_{sample}} = C' \cos \varphi - C_{empty},$$

$$C_{filled}^r = C' \sin \varphi - \frac{1}{\omega R_c},$$

where $C_f^r$ and $C_{filled}^r$ are the real and imaginary components of the heat capacity, $C_{empty}$ is the heat capacity of the cell and silica, $m_{sample}$ is the mass in grams of the liquid crystal (the total mass of the SS5+sil sample was $\sim 20$ mg,

![Fig. 1](image1.png)  
**Fig. 1.** The specific heat of bulk SS5 on cooling spanning the nematic, smectic-A, and smectic-C phases. The dashed line represents the linear $C_p$ (background) used to extract the excess $C_p$ associated with the $N$-SmA transition, $\Delta C_p(NA)$. The solid line represents the low-temperature wing of the $N$-SmA transition and is used to extract the excess $C_p$ associated with the SmA-SmC transition, $\Delta C_p(AC)$. 

![Fig. 2](image2.png)  
**Fig. 2.** Excess specific heat $\Delta C_p$ of the $N$-SmA transition $\pm 3.5$ K about $T_{NA}$ for bulk SS5 and SS5+sil samples. The inset lists the $\rho_S$ for each data set shown. The temperature range shown corresponds approximately to $\pm 10^{-2}$ width in reduced temperature.
TABLE I. Summary of the calorimetric results for S5+sil samples. Shown are the conjugate silica density (ρ5 in grams of aerosil per cm² of S5), the mean-void length $l_0=2/\alpha\rho_5$ (where $\alpha=300$ m² g⁻¹ is the specific surface area of this aerosil) within the gel in Å, the N-SmA (TNA) and the SmA-SmC (TAC) pseudophase transition temperatures, and the smectic-A temperature range $(\Delta T_{A}=T_{NA}-T_{AC})$ all in kelvins and averaged between heating and cooling scans. These are followed by similarly averaged enthalpy $h_m=\Delta h_{p_{\text{max}}}$ in J K⁻¹ g⁻¹ values for the N-SmA pseudophase transition. The final column tabulates the specific heat step in J K⁻¹ g⁻¹ of the SmA-SmC phase transition $\Delta c_{p_{\text{step}}}$ averaged between heating and cooling scans and taken as the value of the excess specific heat −6 K below $T_{AC}$.

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<th>$T_{AC}$</th>
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which yielded $m_{\text{sample}}$ values in the range of 13–20 mg, and $R_\sigma$ is the external thermal resistance linking the cell and the bath (here, ~200 kW⁻¹). Equations (1) and (2) require a small correction to account for the finite internal thermal resistance compared to $R_\sigma$, and this was applied to all samples studied here [27]. Measurements were conducted at various frequencies from 1 to 500 mHz in order to ensure the applicability of Eqs. (1) and (2). For all results presented here, $C_{p_{\text{filled}}}^\rho=0$ through the N-SmA and SmA-SmC transitions, which is expected for continuous phase transitions, and $C_p$ was independent of $\omega$. All data presented here were taken at a heating frequency of $\omega=0.1473$ s⁻¹ (or 23.4 mHz) and a scanning rate of less than ±100 mK h⁻¹, which yielded static $C_p$ results. This equilibrium behavior relates only to the pseudocritical smectic fluctuations that are the focus of this work. The glasslike behavior, which has been observed in rheological studies in this frequency range [35], is a characteristic of these systems away from the pseudotransition.

The bulk S5 and all S5+sil samples experienced the same thermal history after mounting, 6 h in the isotropic phase to ensure homogeneous gelation, then a slow cool into the smectic phase at ~320 K before beginning the first detailed heating scan to ~345 K followed immediately by a detailed cooling scan over the same range. Tests on bulk S5 with various thermal histories in the isotropic phase reveal an aging of the material. There are progressive shifts of the transition temperatures downward with increased time at high temperature. However, other than an increase in the rounding of the $C_p$ peaks and the downward shift of the transition with time, the critical character remains essentially unchanged.

## III. RESULTS

The specific heat on cooling for a bulk sample of S5 is shown in Fig. 1. Clearly visible are the XY-like N-SmA phase transition at 336.71 K and a Landau mean-field SmA-SmC at 328.82 K. These are in good agreement with Schantz and Johnson [23]. The excess specific heat due to the N-SmA transition $\Delta C_p(NA)$ for the bulk and LC+sil samples is obtained by subtracting from the specific heat $C_p$ a linear background:

$$\Delta C_p = C_p - C_p \text{ (background)},$$

where $C_p$ (background) is shown as the dashed line in Fig. 1 and represents the $C_p$ variation of the low-temperature wing of the I-N transition. This expression is a valid representation of $\Delta C_p(NA)$ for all $T > T_{AC}$ and the resulting $\Delta C_p(NA)$ for all samples studied are shown in Fig. 2 over a ±3.5 K temperature range about $T_{NA}$. The fluctuation dominated N-SmA transition enthalpy is defined as

$$\delta h_{NA} = \int \Delta C_p(NA)dT,$$

where consistent limits of the integration of ±5 K about $T_{NA}$ were used for all samples. The specific heat contribution of the SmA-SmC transition is obtained from $\Delta C_p(NA)$ by subtracting the low-temperature heat capacity wing of the N-SmA transition (see Fig. 1):

$$\Delta C_p(AC) = \Delta C_p - \Delta C_p^{\text{wing}}(NA).$$

The result for all samples studied are shown in Fig. 3 over a range +2 K above to −4.5 K below $T_{AC}$. The relevant thermal characteristics for both phase transitions of S5+sil is as a function of $\rho_5$ are given in Table I.

As seen in Fig. 2, the N-SmA $C_p$ peak remains sharp for all aerosil densities up to the maximum studied of $\rho_5 = 0.347$ with no abrupt truncation marking a transition from soft to stiff gel behavior seen in 8CB+sil [14] and 8OCB+sil [28] systems. The $\Delta C_p(NA)$ wings on both sides of the transition decrease with increasing $\rho_5$ in contrast with that
found for the 8CB and 8OCB in aerosils, which found significant reduction of the high-temperature $\Delta C_p(NA)$ wing [14]. Qualitatively, the $\Delta C_p(NA)$ peak shape remains remarkably stable with increasing $\rho_S$. For the $\tilde{S}5+$sil system, the most striking effect of the aerosils is the strong decrease in the heat capacity maximum at the transition, $h_m = \Delta C_p^{\text{max}}(NA)$, and in the transition enthalpy $\delta H_{\text{NA}}$ with increasing $\rho_S$. In addition, the value of $T_{\text{NA}}(\rho_S)$ also displays very little sensitivity to the aerosils even when the aging of the $\tilde{S}5$ is taken into account, in stark contrast to the nonmonotonic downward shifts found for nearly all other LC + sils systems [14]. See Table I.

The effect of increasing aerosil concentration on the SmA-SmC transition heat capacity appears entirely at and below the transition $T_{AC}$. The $\delta C_p(AC)$ peak smoothly evolves with increasing $\rho_S$ from the bulk tricritical behavior to a simple heat capacity step as shown in Fig. 3. Also apparent is the systematic reduction of the step magnitude with increasing $\rho_S$ as listed in Table I. While there is some rounding of $\delta C_p(AC)$ in the immediate vicinity of $T_{AC}$, there does not appear any strong effect of the aerosil on the high-temperature $\delta C_p$ tail. As with the $N$-SmA transition, even when aging of the bulk material is taken into account, $T_{AC}(\rho_S)$ is not shifted downward with increasing aerosil content but appears to shift slightly upward. The stability of both $T_{\text{NA}}(\rho_S)$ and $T_{AC}(\rho_S)$ reported here is in contrast to that found in the recent x-ray study that found large nonmonotonic transition temperature shifts with $\rho_S$ [10]. However, the thermal history experienced by these calorimetry samples was far less severe than that experienced by the x-ray samples which were held at high temperatures while the solvent evaporated prior to the measurements. Thus, the results presented here should reflect a consistent measure of the transition temperature shift with $\rho_S$ for this system.

A. $XY$-like $N$-SmA scaling analysis

The shape of these experimental $\Delta C_p(NA)$ data as a function of aerosil content is characterized by a power-law form [29] in terms of the reduced temperature $t=T-T^*$ given by

$$\Delta C_p(NA) = A^\pm t^{-\alpha}(1+D^\pm t^\lambda) + B_c,$$

where the critical behavior as a function of reduced temperature $t$ is characterized by an exponent $\alpha$, amplitudes $A^\pm$ above and below the transition, a critical background term $B_c$, and corrections-to-scaling terms having an amplitude $D^\pm$ and exponent $\lambda=0.5$. An increasing temperature gap of excluded data about the $\Delta C_p(NA)$ peak with increasing $\rho_S$ was required to perform the nonlinear least-squares fitting. These excluded data were identified by strong deviations in the residuals near $T^*$ and represent rounded $\Delta C_p(NA)$ values not describable by the power law given in Eq. (6). These fit results for the sets of heating and cooling scans of bulk $\tilde{S}5$ and $\tilde{S}5+$sil samples are presented in Tables II and III, respectively. In addition to fits with the effective critical exponent $\alpha_{\text{eff}}$ as a free parameter, fits were also performed with $\alpha_{\text{eff}}$ fixed to the 3D $XY$ value of $\alpha_{XY}=-0.013$. The bulk $\tilde{S}5$ fit results are of good quality for both heating and cooling and yield a very small negative $\alpha_{\text{eff}}$ that is not significantly different from fixing $\alpha_{\text{eff}}$ to $\alpha_{XY}=-0.013$ as indicated by $\chi_r^2$ [30]. This indicates that the specific heat of the $N$-SmA transition for the bulk LC behaves essentially as a clean $XY$ transition consistent with the literature [23,31]. However, it should be noted that the critical exponents for the parallel correlation length ($\nu_p$) and for the smectic susceptibility ($\gamma$) do not have $XY$ values [29] and that the $N$-SmA transition for bulk $\tilde{S}5$ exists in a complex crossover regime.

As $\rho_S$ increases for the $\tilde{S}5+$sil samples, the fits for both heating and cooling are all of good quality even up to the highest density studied. In general, the adjustable parameters have approximately a 10% uncertainty in magnitude for the bulk and the two lowest-density aerosil samples, except for $T_c$ which has an uncertainty of approximately ±5 mK for all fits. This uncertainty grows for the higher-density samples because an increasing temperature gap about the $\Delta C_p$ peak of data is excluded from the fits due to rounding. These fits show that the critical character described by the exponent $\alpha_{\text{eff}}$ of the $N$-SmA transition remains unchanged in the $\tilde{S}5$ + sil samples for all $\rho_S$ even above the $\rho_S=0.1$ where previous studies of other LC+sil samples found no critical behavior [1,14]. It is apparent from the fits that the increasing temperature gap ($\pm f_{\text{sm}}$) is dominated by rounding on the low-temperature side of the $\delta C_p(NA)$ peak. This increasing temperature gap for the fits has the effect of causing the increase in the magnitudes of the correction-to-scaling coefficients $D^\pm$ although they remain well behaved. Fixing the ratio $D^+/D^- = 1$ or setting $D^+ = D^- = 0$ resulted in significantly poorer fits for all samples. It is also evident is that the critical
TABLE II. Heating scan summary of the results of fitting Eq. (6) to the excess specific-heat peak \( \Delta C_p \) of the N-SmA phase transition on 8S5+sil samples. The transition temperature \( T_C \) is given in kelvins, while the parameters \( B_C \) and \( A^* \) are given in J K\(^{-1}\) g\(^{-1}\). The parameters \( D^\pm \) are dimensionless. All scans were fit from \( t_{\text{min}} = 10^{-2} \) to \( \pm t_{\text{min}} \). All parameters were free to vary in the fit except when the exponent was fixed to \( \alpha_{XY} = -0.013 \) (denoted by the square brackets).

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<th>( \rho_S )</th>
<th>( T_C )</th>
<th>( \alpha_{\text{eff}} )</th>
<th>( B_C )</th>
<th>( A^* )</th>
<th>( A^- )</th>
<th>( D^+ )</th>
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<td>0.051</td>
<td>334.938</td>
<td>(-2 \times 10^{-4})</td>
<td>154.089</td>
<td>-154.083</td>
<td>-154.025</td>
<td>0.0045</td>
<td>0.0086</td>
<td>+11.4/−49.2</td>
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<td>(-1 \times 10^{-4})</td>
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<td>-376.688</td>
<td>-376.614</td>
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<td>0.161</td>
<td>335.162</td>
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<td>18.744</td>
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<td>+5.67/−42.3</td>
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<tr>
<td>0.220</td>
<td>335.498</td>
<td>(-4 \times 10^{-4})</td>
<td>10.314</td>
<td>-10.099</td>
<td>-10.048</td>
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<td>0.347</td>
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<td>(-6 \times 10^{-4})</td>
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<td>-6.703</td>
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<td>+0.27/−85.1</td>
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</tr>
<tr>
<td>0.347</td>
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<td>(-0.013)</td>
<td>0.573</td>
<td>-0.414</td>
<td>-0.391</td>
<td>3.0646</td>
<td>2.4651</td>
<td>1.056</td>
<td></td>
</tr>
</tbody>
</table>

amplitudes above and below the transition, \( A^+ \), systematically decrease with increasing \( \rho_S \) although the ratio \( A^+/A^- \) remains unchanged.

The scaling analysis for the N-SmA transition in LC + aerosil systems follows that of Ref. [17] by using the correlation length power law to equate the cutoff length scale

TABLE III. Cooling scan summary of the results of fitting Eq. (6) to the excess specific-heat peak \( \Delta C_p \) of the N-SmA phase transition on 8S5+sil samples. The labels are the same as those used in Table II as well as the uncertainties of the adjustable fit parameters.

<table>
<thead>
<tr>
<th>( \rho_S )</th>
<th>( T_C )</th>
<th>( \alpha_{\text{eff}} )</th>
<th>( B_C )</th>
<th>( A^* )</th>
<th>( A^- )</th>
<th>( D^+ )</th>
<th>( D^- )</th>
<th>( t_{\text{min}} \times 10^{-5} )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
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<td>0</td>
<td>335.198</td>
<td>(-7 \times 10^{-5})</td>
<td>1047.600</td>
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<td>-1047.670</td>
<td>-0.0001</td>
<td>0.0019</td>
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<td>0.025</td>
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<td>(-1 \times 10^{-4})</td>
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</tr>
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<td>0.041</td>
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<td>(-3 \times 10^{-4})</td>
<td>141.506</td>
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<td>-141.395</td>
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<td>-216.619</td>
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</tr>
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<td>+5.65/−74.2</td>
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</tr>
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<td>-0.088</td>
<td>11.6406</td>
<td>14.1668</td>
<td>1.129</td>
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</table>
(maximum correlation length) $\xi_M$ to a minimum reduced temperature. This is closely related to a finite-size effect; however, there are no true pores and the LC-filled voids are highly interconnected. The correlation length is given by

$$\xi_l = \xi_0 g^{-n_l}.$$ (7)

Since Eq. (7) is defined only for $T > T_c$, the finite-scale-induced rounding of the transition is estimated in terms of the minimum reduced temperature on the high-temperature side of the transition $T_m^*$ by the form

$$\delta T / T^* = 2 T_m^* = 2 \left( \frac{\xi_M}{\xi_0} \right)^{-1/n_l} \rho_S^{1/n_l},$$ (8)

where the cutoff length scale is written in terms of $n$, the number of mean-void lengths $l_0$. The heat capacity maximum at the transition $h_m$ is given by substituting $T_m^*$ into Eq. (3) and is also explicitly defined for the $T > T^*$. The explicit form for $h_m$ is

$$h_m = A^* \left( \frac{\xi_M}{\xi_0} \right)^{a/l_m} \left( 1 + D^* \left( \frac{\xi_M}{\xi_0} \right)^{-3l_m} \right) + B_c.$$ (9)

Finally, the transition enthalpy $\delta H_{NA}$ resulting from this scaling analysis is determined by using $T_m^*$ to truncate the integration of Eq. (3) both above and below the transition $T^*$.

Plotted in Fig. 4 are the scaling trends for the N-SmA transition of $\tilde{S}S5$+sil samples using the bulk N-SmA $\tilde{S}S5$ critical parameters. Two choices for the cutoff length scale are shown. The first choice for the cutoff correlation length $\xi_M$ uses the mean distance between silica surfaces (mean void size), $l_0 = 2/\rho_S$, where $a$ is the specific surface area [1]. The second choice allows $\xi_M$ to vary as some multiple of $l_0$—i.e., $\xi_M = n l_0$. The results for $h_m$ of the $\tilde{S}S5$+sil samples are in very good agreement using $\xi_M = 3 l_0$, which more closely matches the measured saturated smectic correlation length [10]. However, $\delta T / T^*$ appears sharper and $\delta H_{NA}$ smaller for $\rho_S > 0.1$ than predicted by this analysis.

**B. Landau mean-field SmA-SmC scaling analysis**

The excess specific heat due to the SmA-SmA transition is shown in Fig. 3 for bulk $\tilde{S}S5$ and $\tilde{S}S5$+sil samples over a temperature range down to $T_{AC} - 4.5 \text{ K.}$ The bulk SmA-SmA transition is well described by an extended Landau theory [23,32] given by

$$\delta C_p (AC) = \begin{cases} 0 & \text{for } T > T_c, \\ A \left( \frac{T_m - T_c}{T_c} \right)^{0.5} & \text{for } T < T_c, \end{cases}$$ (10)

where $A$ is the $\delta C_p (AC)$ maximum at the transition $T_c$, and $T_m$ is the upper stability limit of the SmC phase. Results from fitting Eq. (10) to the excess specific heat of the SmA-SmA phase transition $\delta C_p$ for bulk $\tilde{S}S5$ and $\tilde{S}S5$+sil samples over the temperatures $T < T_{AC}$ are tabulated in Table IV. These results are the average of heating and cooling scan fits. The stability limit of the SmC phase appears to shift upwards from the bulk value by approximately 1.6 K with increasing $\rho_S$. Although intriguing and indicating a stabilization of the SmC phase with increased $\rho_S$, given the aging of this particular LC, it is not clear how robust is this result. The fit coefficient $A$ of Eq. (10) appears to smoothly decrease with increasing $\rho_S$. This is consistent with the behavior of the SmA-SmA transition of $T_{O.4}$ in hydrophobic aerosil [13]. The parameter $A$ is also a measure of the tricritical nature of the SmA-SmA transition. A log-log plot shown in Fig. 5 of $A$ versus $\rho_S$ reveals a power-law scaling given by $A \propto \rho_S^{-0.5}$.

**IV. DISCUSSION**

Results have been presented from a series of high-resolution ac-calorimetric experiments on $\tilde{S}S5$+sil dispersions through the N-SmA and SmA-SmA phase transitions as a function of aerosil density. In bulk $\tilde{S}S5$, the $N$-SmA is a nearly clean $XY$-like transition with $\alpha = 0$ while the SmA-SmA transition is mean field with a Landau tricritical character. Our bulk measurements are fully consistent with these behaviors. The introduction of QRD in the $\tilde{S}S5$+sil system allows for the isolation of random-field, finite-size-like, and
TABLE IV. Summary of the results of fitting Eq. (10) to the excess specific-heat peak $\Delta C_p$ of the SmA-SmC phase transition for $8S5+$sil samples. The fit results have been averaged between heating and cooling scans and were done from $-7$ K below $T_{AC}$ to a point slightly below the rounded $\Delta C_p$ peak. The transition temperature $T_C$ and the SmC stability limit $T_m$ are given in kelvins while the coefficient $A$ is given in $J K^{-1} g^{-1}$. No uncertainty is quoted for $T_C$ as it was fixed to this final value for the last fit iteration.

<table>
<thead>
<tr>
<th>$\rho_S$</th>
<th>$T_C$</th>
<th>$T_m$</th>
<th>$A$</th>
<th>$\chi^2_f$</th>
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</thead>
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<td>330.32±0.38</td>
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<td>329.090</td>
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<td>0.056±0.002</td>
<td>1.328</td>
</tr>
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<td>0.049±0.003</td>
<td>1.323</td>
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<td>0.078</td>
<td>329.495</td>
<td>334.49±0.25</td>
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<td>1.258</td>
</tr>
<tr>
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<td>331.08±0.40</td>
<td>0.050±0.010</td>
<td>2.317</td>
</tr>
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<tr>
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<td>329.414</td>
<td>330.37±0.47</td>
<td>0.016±0.002</td>
<td>1.211</td>
</tr>
</tbody>
</table>

elastic strain effects at a pure $XY$ and mean-field transition.

The $N$-SmA transition transition temperature does not exhibit a sensitivity to the aerosil (and in fact increases slightly) in stark contrast to that seen in nearly all other LC+sil studies. Although the $\Delta C_p(NA)$ decreases uniformly in size with increasing $\rho_S$, it remains sharp and is well characterized over the whole range of aerosil concentration. The power-law fits reveal that quasicritical behavior is preserved and that the exponent $a_{eff}$ remains slightly negative and constant for all $\rho_S$ studied. See Fig. 6. The systematic decrease of the coefficients $A^+$ but nearly constant ratio $A^+/A^-$ is a reflection of the uniform decrease in the size of $\Delta C_p(NA)$ (as well as $\delta H_{NA}$). This analysis is consistent with the view that the aerosil gel effectively increases the nematic range. That is, the nematic susceptibility decreases with increasing $\rho_S$ and this is reflected in a substantial change in the pseudo-critical properties for cyanobiphenyl-aerosil systems. For $8S5+$sil where the bulk material already has a long nematic range, little change is observed.

Because of the good-quality power-law fits available in this study, a detailed scaling analysis was performed and compared to the heat-capacity maximum $h_m=\Delta C_p^{max}(NA)$, transition enthalpy $\delta H_{NA}$, and transition temperature rounding $T^*/T^*$ of the $N$-SmA phase transition. This analysis uses the bulk parameters and an adjustable cutoff length scale $\xi_M$ and found excellent agreement for $h_m$ using $\xi_M(8S5+sil)=3\xi_0$ but this does not completely describe the behavior of $\delta H_{NA}$ nor $T^*/T^*$, especially for $\rho_S>0.1$. Interestingly, when this scaling analysis is applied to the 8CB+sil and 8OCB+sil systems, equally good modeling of $h_m$ is obtained for $\xi_M(8CB+sil)=5\xi_0$ and $\xi_M(8OCB+sil)=5\xi_0$. It is surprising that such excellent agreement is obtained over the whole range of $\rho_S$ explored for these three LC’s despite the apparent violation of the classic expectation of finite-size scaling (that is, the truncation of the bulk $\Delta C_p$ behavior at the cutoff length scale). Also, the smectic correlation lengths measured for these systems are much larger than this cutoff length scale [33]. This makes the geometric interpretation of the cutoff length puzzling but ultimately connected to the strength of the disorder.

For the mean-field SmA-SmC phase transition, the transition temperature also exhibits very weak sensitivity to the presence of aerosil (even increasing slightly rather than decreasing). This is also in stark contrast to that seen for the SmA-SmC transition in 7O.4+sil and 8S5 in aerogel [27] as well as the SmA-SmC transition of CE8+sil. The heat ca-
capacity associated with the SmA-SmC transition in $\text{8S5+sil}$ presented in this work exhibits a systematic evolution from a Landau tricritical peak to a simple mean-field step with very little smearing observed for $T>T_{KC}$, and then only at the highest $p_S$. Good-quality fits were made using an extended Landau form that found the upper stability temperature increasing with $p_S$, consistent with the shift of the observed transition. In addition, the coefficient $A$, representing the heat-capacity maximum at the SmA-SmC transition, exhibits a scaling with the aerosil conjugate density as $A \propto p_S^{-0.5}$; see Fig. 5. It is clear that this transition, while evolving in a systematic fashion, remains mean field over the entire range of $p_S$ studied. This may be a reflection of the SmA-SmC transition behaving as if it were at its upper critical dimension moderating the effect of the QRD produced by the aerosil gel.

In this study of $\text{8S5+sil}$, it appears that the random-field QRD of the aerosil gel plays a relatively weak role at the $N$-SmA transition (due to the nonpolar molecules and the long nematic range) and also at the SmA-SmC transition (due to either its proximity to its upper critical dimension or that the QRD does not couple linearly to the SmC order parameter and so does not provide a random-field interaction). It is clear that a special length scale is present with $\xi_M > l_0$ but it does not appear to play a leading role for the SmA-SmC transition. How, then, does one understand the evolution of this transition with increasing QRD of aerosil and in light of the other LC+sil and LC+aerogel results? One possibility is that the aerosil gel, due to its flexibility, is closer to thermodynamic equilibrium with the host LC and so causes the LC+sil to behave as a stiffer LC as well as provide QRD. The aerosil gel has been shown to exhibit dynamics coupled to the host liquid crystal [34], and recent work has followed its quenching as aerosil density increases [35,36]. This increase in the effective microscopic elastic stiffness of the LC would be similar to the engineered stiffening of polymer composite materials. A consequence of the stiffening of the nematic phase in LC+sil systems has already been discussed previously [1,14,17,33] in terms of the decrease in the nematic susceptibility with increasing $p_S$ to explain the crossover from tricritical to XY behavior for the $N$-SmA transition. The present view is to extend this concept to the general stiffening of the LC within the $\text{LC+sil}$. In the case of the SmA-SmC transition the quenched disorder is also changing the character of the transition. With increasing aerosil density, the peak at the transition is being suppressed in favor of a steplike behavior. This indicates that the transition is being driven away from tricriticality toward mean-field character alone. The proximity to tricriticality is controlled by the layer compression elastic constant $B$ in the modified fourth-order free-energy coefficient $b = b_0 - 2\lambda^2/B$, where $b_0$ is the original value of this coefficient and $\lambda$ is the strength of the coupling between the tilt angle and the layer compression [6]. The mean-field phase transition behavior and the decreasing size of the step in the heat capacity are indicative of a hardening of the layer compression elastic constant $B$.

This effect would serve to explain the evolution of the SmA-SmC transition from Landau tricritical to step in terms of a stiffening of the smectic layer compression modulus $B$ and account for the general stability of the transition temperatures. Note that for $\text{8S5}$, the nematic and smectic phases are almost fully decoupled in the bulk while there remains significant coupling in the $\text{8CB}$ and $\text{8OCB}$ LC’s. It is the latter two LC’s that exhibit the strong nonmonotonic transition temperature shifts downward with $p_S$ and so may be reflecting QRD effects at the $I-N$ transition [37]. It would be expected that twisted (or chiral) phases would be more disordered and smeared due to this general LC stiffening as seen in a recent SmA-SmC + in aerosil study [5]. Also, if the silica gel is too rigid, then this LC stiffening effect is supplanted by the strong quenched disorder as seen in LC in aerogel and in high-density aerosil gel.

Finally, there seems to be an apparent inconsistency between the experimental results of the x-ray study [10] and this calorimetry study on $\text{8S5+sil}$. In the x-ray work, it is clear that the temperature dependence of the tilt angle of the SmC phase is insensitive to $p_S$, strongly suggesting that the order-parameter $\psi$ for the SmC phase remains unchanged from bulk for all $\text{8S5+sil}$ samples. However, if the system remains mean field, then the relationship $C_T \propto \partial \phi^2/\partial T$ should hold. In this case, the dramatic variation of $\delta C_p$ with $p_S$ suggests that the SmC order-parameter should be strongly $p_S$ dependent. Comparison of the $\delta C_p$ data in Fig. 3 (one data point every 0.1 K) and the tilt angle data in Fig. 6 in Ref. [10] (one data point every ≈1 K) suggests that the situation is more ambiguous. A suppression of the tricritical character may be consistent with the more sparse x-ray data (see note [21] in Ref. [10]).

Clearly, there is an important need for theoretical efforts at understanding quenched random disorder on the SmA-SmC transition. The beginnings of such a theory, although for the anisotropic aerogel-disordered SmA-SmC transition [38], are emerging but much is left to be done. A coherent framework must account for the apparent connection with elasticity of both the host material and the disorder-inducing gel. It must also provide for an interpretation of the cutoff length scale that seems to play an important role for the $N$-SmA as well as the observed scaling of the $\Delta C_p(AC)$ peak with $p_S$. Additional x-ray and calorimetric experimental work with anisotropically aligned SmA-SmC as well as SmA-SmC + in aerosil gel systems is also needed and would provide important data as to the role the polar nature of the LC and the local aerosil-LC interaction.

**ACKNOWLEDGMENTS**

The authors wish to thank N. A. Clark, C. W. Garland, R. Leheny, and T. Bellini for many helpful and useful discussions. P.S.C. and R.J.B. wish to thank the Natural Science and Engineering Research Council of Canada while staying in Toronto. The funding in Edinburgh was provided by the EPSRC (Grant No. GR/S10377/01). The work at WPI was supported by the NSF under NSF-CAREER Award No. DMR-0092786.
[25] Degussa Corp., Silica Division, 65 Challenger Road, Ridgefield Park, NJ 07660. Technical data is given in the Degussa booklet AEROSILS.
[30] The reduced chi-squared parameter 
\[ \chi^2 = \frac{1}{\nu} \sum_{i} \frac{(y_i - f(x_i))^2}{\sigma_i^2}, \]
where \(\nu = N - n\) is the degrees of freedom fitting \(N\) data with \(n\) parameters in a model \(f(x_i)\), is the mean-squared deviations normalized to measurement errors \(\sigma_i\) in \(y_i\).