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 nano-colloidal dispersions of aerosils in the liquid crystal 4-n-pentylphenylthiol-4'-n-octyloxybenzoate (85S) 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 \( \alpha \approx 0.013 \) 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 introduced quenched random disorder while the peak height and enthalpy can be well described by considering a cut-off length scale to the quasi-critical 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 non-polar 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 \( \rho_{\text{S}}^{1.8} \) 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.

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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 onto 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. This model is applicable to a terrific range of phenomena: This 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 focussed 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 \(^{3}\text{He} \) and \(^{4}\text{He}-^{3}\text{He} \) mixtures in a variety of porous media \([1,2]\) as well as doped magnetic systems \([3] \) but many questions remain due to the quantum nature of the former and the glass-like behavior of the latter \([4]\).

In the random-field approach, the effect of the disorder is mapped onto a local field, \( \vec{h}(\vec{r}) \), 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 \( \langle \vec{h} \rangle_{\vec{r}} = 0 \) while \( \langle \vec{h} \cdot \vec{h} \rangle_{\vec{r}} \neq 0 \). Because the nature of the imposed disorder is modelled 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. A particularly fruitful physical system to explore QRD effects in general and the random-field model in particular, have been nano-colloidal 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 3D-XY universality class \([6]\). In general, high-resolution x-ray \([7,8,9,10]\) and calorimetry \([8,11,12,13,14,15]\) studies on the N-SmA+sil transition have found that the (quasi-) long-range ordered smectic phase is destroyed for all densities of aerosil.

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However, below a silica density of about 0.1 grams of SiO$_2$ per cm$^3$ of LC (the so-called conjugate density, $\rho_S$ [1]), whose units will be dropped hereafter), a pseudo-transition displaying quasi-critical 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 pseudo-transition $T^*$) and a random-field structure factor (dominate below $T^*$) given by the bulk thermal form squared, the so-called “lorentzian+lorentzian squared” form [3]. 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 [7] and 8OCB [8] in aerosils or begins to decrease upon further cooling towards the SmC phase for 8S5+sil system [10]. This broadening observed for 8S5+sil [10] and anisotropic (field aligned) 8S5+sil 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, quasi-critical, power-law divergences for the heat capacity for $\rho_S < 0.1$, while all phase transitions appear to be elastically smeared for larger $\rho_S$ [11]. The evolution of an effective critical 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 quasi-critical transition for low aerosil density revealed the importance of both random-field and finite-size-like effects [3, 12]. The dimensionality of the system also played a role and was consistent with the expected dimensional rise, $d_{eff} = d + 2$, for a system with random-field disorder [13, 14]. 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 $\rho_S = 0.1$ [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 [3, 10]. The smectic-A to smectic-C (SmA-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 [3]. 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 [24, 21]. For weaker aerosil gel induced disorder, the Landau mean-field heat capacity signature was found to be unaffected by hydrophobic aerosils [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 $\rho_S$ [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 (SmC*), the effect of even the aerosil induced disorder generally suppresses and smears the transition [5]

The present work focuses on the effect of quenched random disorder induced by a nano-colloidal dispersion of hydrophilic type-300 aerosil forming a mass-fractal gel within the liquid crystal 4-n-pentylphenylthiol-4’-n-octyloxybenzoate (88S5) that closely follows the previously reported x-ray studies [10]. High-resolution calorimetry has been carried out on these 8S5+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 $\alpha \lesssim 0$. 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 decreases 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 quasi-critical behavior for this system with QRD is consistent with our understanding of the influence of the gel on the underlying nematic order. Since in the bulk material the nematic susceptibility is low before SmA order begins to form, the gel has little scope to reduce this quantity.

The second is a mean-field Landau tricritical smectic-A to smectic-C phase transition. The SmA-SmC remains mean-field for all aerosil concentrations studied with an continuous evolution from the bulk’s tricritical to a simple mean-field step heat capacity behavior analogous to that seen for the pure SmA-SmC* transition in binary LC mixtures [22]. In particular, the SmA-SmA heat capacity maximum at the transition scales as $\rho_S^{-0.5}$. The stable mean-field character of the SmA-SmA 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 SmA-SmA 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 [11] describes the preparation of the 8S5+sil dispersions as well as the ac-calorimetry technique employed. Section [11] presents the results of the calorimetric study, while Section [11] discusses the significance of the evolution of an XY transition as well as a crossover
The liquid crystal $s85$, synthesized at Kent State University, was used after degassing in the isotropic phase for two hours. The best literature reported transition temperature values in the bulk for this liquid-crystal molecule ($M_w = 412.64 \text{ g mol}^{-1}$) are $T_{IN}^o \approx 359.6 \text{ K}$ for the weakly first-order isotropic to nematic ($I-N$) transition, $T_{NA}^o \approx 336.58 \text{ K}$ for the XY-like continuous nematic to smectic-$A$ ($N$-$SmA$) transition, and $T_{AC}^o \approx 329.35 \text{ K}$ for the monotropic Landau tricritical smectic-$A$ to smectic-$C$ ($SmA$-$SmC$) transition [23]. At lower temperatures on cooling, a monotropic smectic-$C$ to crystal-$B$ ($SmC$-$CrB$) transition occurs at $T_{CrA}^c \sim 304 \text{ K}$. The strongly first-order Crystal-$SmA$ ($Cr$-$SmA$) transition occurs reproducibly on heating at $T_{CrA}^o \sim 332 \text{ K}$. The measured transitions temperatures for our bulk material occur at $T_{NA}^o \approx 336.64 \text{ K}$, $T_{AC}^o \approx 328.96 \text{ K}$, and $T_{CrA}^o \sim 331.0 \text{ K}$, which are in reasonable agreement with the literature bulk values. However, $s85$ 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 Fig. 1 and 2 as well as Table II. 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 aerosil disorder should be preserved.

The nano-colloidal mixture of hydrophilic type-300 aerosil in $s85$ 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 $300 \text{ m}^2 \text{ g}^{-1}$ [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 $s85$+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 home-built calorimeters at WPI. The sample cell consisted of a silver crimped-sealed envelope $\sim 10 \text{ mm}$ in diameter. The specific surface area of type-300 aerosil is $320 \text{ m}^2 \text{ g}^{-1}$ and the specific surface area of type-300 aerosil is $320 \text{ m}^2 \text{ g}^{-1}$.
TABLE I: Summary of the calorimetric results for \(\bar{8}S5+\)sil samples. Shown are the conjugate silica density \((\rho S\) in grams of aerosil per cm\(^2\) of \(8S5\)), the mean-void length \(l_v = 2/\alpha p_S\) (where \(\alpha = 300\) m\(^2\) g\(^{-1}\)) is the specific surface area of this aerosil) within the gel in \(\AA\), the \(N\)-Sm\(A\) (\(T_{NA}\)) and the Sm\(A\)-Sm\(C\) (\(T_{AC}\)) pseudo-phase 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 \((\delta H_{NA}\) in J g\(^{-1}\)) and specific heat maximum \(\delta C_p\) values for the \(N\)-Sm\(A\) pseudo-phase transition. The final column tabulates the specific heat in J K\(^{-1}\) g\(^{-1}\) of the Sm\(A\)-Sm\(C\) phase transition \(\delta C_{AC}\) averaged between heating and cooling scans and taken as the value of the excess specific heat \(-6\) K below \(T_{AC}\).

| \(\rho S\) | \(l_v\) | \(T_{NA}\) | \(T_{AC}\) | \(\Delta T_A\) | \(\delta H_{NA}\) | \(\delta C_{AC}\) |
|---|---|---|---|---|---|---|
| 0 | \(\infty\) | 336.626 | 329.099 | 7.517 | 2.136 | 0.726 |
| 0.025 | 2636 | 336.073 | 328.836 | 7.237 | 1.985 | 0.541 |
| 0.041 | 1636 | 336.524 | 329.136 | 7.388 | 1.897 | 0.530 |
| 0.051 | 1303 | 336.315 | 329.124 | 7.191 | 1.780 | 0.377 |
| 0.078 | 859 | 336.519 | 329.527 | 6.992 | 1.834 | 0.487 |
| 0.105 | 636 | 336.676 | 329.210 | 7.466 | 1.952 | 0.444 |
| 0.161 | 414 | 336.573 | 329.456 | 7.117 | 1.573 | 0.302 |
| 0.220 | 303 | 336.865 | 329.915 | 6.950 | 1.561 | 0.284 |
| 0.347 | 192 | 336.505 | 329.621 | 6.884 | 1.404 | 0.231 |

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-M\(\Omega\) carbon-flake thermistor, a constant current was placed across the heater to maintain the cell temperature well above \(T_{1N}\). 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 \(P_{ac}e^{j\omega t}\) 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 \(C^* \equiv P_{ac}/\omega |T_{ac}|\) is given by

\[
C_p = \frac{[C^\prime_{filled} \, C^\prime_{empty}]}{m_{sample}} = \frac{C^* \cos \varphi - C^\prime_{empty}}{m_{sample}},
\]

\[
C^\prime_{filled} = C^* \sin \varphi - \frac{1}{\omega R_e},
\]

where \(C^\prime_{filled}\) and \(C^\prime_{empty}\) are the real and imaginary components of the heat capacity, \(C^\prime_{empty}\) 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 \(8S5+\)sil sample was \(\sim 20\) mg, which yielded \(m_{sample}\) values in the range of \(13 - 20\) mg), and \(R_e\) is the external thermal resistance linking the cell and the bath (here, \(\sim 200\) K W\(^{-1}\)). Equations \(\ref{eq:1}\) and \(\ref{eq:2}\) require a small correction to account for the finite internal thermal resistance compared to \(R_e\), 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. \(\ref{eq:1}\) and \(\ref{eq:2}\). For all results presented here, \(C^\prime_{filled} \approx 0\) through the \(N\)-Sm\(A\) and Sm\(A\)-Sm\(C\) transitions, which is expected for continuous phase transitions, and that \(C_p\) 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 \(\pm 100\) mK h\(^{-1}\), which yielded static \(C_p\) results. This equilibrium behavior relates only to the pseudo-critical smectic fluctuations that are the focus of this work. The glass-like behavior, that has been observed in rheological studies in this frequency range \(32\), is a characteristic of these systems away from the pseudo-transition.\(^7\)

The bulk \(8S5\) and all \(8S5+\)sil samples experienced the same thermal history after mounting; six hours in the isotropic phase to ensure homogeneous gelation, then a slow cool into the smectic phase at \(\sim 320\) K before beginning the first detailed heating scan to \(\sim 345\) K followed immediately by a detailed cooling scan over the same range. Tests on bulk \(8S5\) 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 \(\bar{8}S5\) is shown in Fig. \(\ref{Fig.1}\). Clearly visible are the XY-like \(N\)-Sm\(A\) phase transition at 336.71 K and a Landau mean-field Sm\(A\)-Sm\(C\) at 328.82 K. These are in good agreement with Schantz and Johnson \(22\). The excess specific heat due to the \(N\)-Sm\(A\) 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 \(C_p(\text{background})\) is shown as the dashed line in Fig. \(\ref{Fig.1}\) and represents the \(C_p\) variation of the low-temperature wing of the \(I-N\) transition. This expression
The result for all samples studied are shown in Fig. 3. Also apparent is the systematic reduction of the step magnitude with increasing $\rho_S$ as listed in Table II. 

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 $T_{NA}(\rho_S)$ and $T_{AC}(\rho_S)$ reported here is in contrast to that found in the recent x-ray study that found large non-monotonic transition temperature shifts with $\rho_S$ [14]. 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. The 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 [23] in terms of the reduced temperature $t = \frac{|T - T^*|}{T^*}$ given by

$$\Delta C_p(NA) = A^\# t^{-\alpha}(1 + D^\# t^{\Delta_1}) + B_c,$$

where the critical behavior as a function of reduced temperature $t$ is characterized by an exponent $\alpha^*$, amplitudes $A^\#$ above and below the transition, a critical background term $B_c$, and corrections-to-scaling terms having an amplitude $D^\#$ and exponent $\Delta_1 \approx 0.5$. 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 represented by some $\delta C_p(NA)$ values not describable by the power-law given in Eq. (6). These fit results for the sets of heating and cooling scans of bulk 8S5 and 8S5+sil samples are presented in Tables III and IV respectively. In addition to fits with the effective critical exponent $\alpha_{eff}$ as a free parameter, fits were also performed with $\alpha_{eff}$ fixed to the 3D-XY value of $\alpha_{XY} = 0.013$. The bulk effect of the aerosils is the strong decrease in the heat capacity maximum at the transition, $h_m = \Delta C_p^{max}(NA)$, and in the transition enthalpy $\delta H_{NA}$ with increasing $\rho_S$. In addition, the value of $T_{NA}(\rho_S)$ also displays very little sensitivity to the aerosils even when the aging of the 8S5 is taken into account, in stark contrast to the non-monotonic downward shifts found for nearly all other LC+sil systems [14]. See Table I.

The result for all samples studied are shown in Fig. 2 over a $\pm 3.5$ 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 $\pm 5$ K about $T_{NA}$ were used for all samples. The specific heat contribution of the SmA-SmC transition is obtained from $\Delta C_p$ by subtracting the low-temperature heat capacity wing of the $N$-SmA transition (see Fig. I):

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

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 8S5+sil as a function of $\rho_S$ 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 $\rho_S = 0.347$ with no abrupt truncation marking a transition from soft to stiff gel behavior seen in 8CB+sil [14] and 8OCB+sil [23] systems. The $\Delta C_p(NA)$ wings on both sides of the transition decrease with increasing $\rho_S$ 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 8S5+sil system, the most striking

**FIG. 3:** Excess specific heat $\delta C_p$ of the SmA-SmC phase transition from $+2.5$ K above to $-4.5$ K below $T_{AC}$ for bulk 8S5 and 8S5+sil samples. Inset lists the $\rho_S$ for each data set shown.
The fit results are of good quality for both heating and cooling and yield a very small negative $\alpha_{eff}$ that is not significantly different from fixing $\alpha_{eff}$ to $\alpha_{XY} = -0.013$ as indicated by $\chi^2$. 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. However, it should be noted that the critical exponents for the parallel correlation length ($\nu_{||}$) and for the smeared susceptibility ($\gamma$) do not have XY values and that the $N$-SmA transition for bulk SS5 exists in a complex crossover regime.

As $\rho_S$ increases for the SS5+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 $\pm5$ 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 $\alpha_{eff}$ of the $N$-SmA transition remains unchanged in the SS5+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. It is apparent from the fits that the increasing temperature gap ($\pm t_{min}$) 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 that the critical amplitudes above and below the transition, $A^\pm$ 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 reference by using the correlation length power-law to equate the cut-off length scale (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

$$\xi_{||} = \xi_{||} d^{-\nu_{||}}. \tag{7}$$

Since Eq. 7 is defined only for $T > T^*$, 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

$$\delta T^*/T^* \approx 2t_{m}^+ = 2 \left( \frac{\xi_M}{\xi_{||0}} \right)^{-1/\nu_{||}} = 2 \left( \frac{\xi_{||0}}{2n a \rho_S} \right)^{1/\nu_{||}} \tag{8}$$

where the cut-off length scale is written in terms of $n$, the number of mean-void lengths $l_o$. 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

$$h_m = A^+ \left( \frac{\xi_M}{\xi_{||o}} \right)^{\alpha/\nu_{||}} \left( 1 + D^+ \frac{\xi_M}{\xi_{||o}} \right) \left( -\Delta_0/\nu_{||} \right) + B_c. \tag{9}$$

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 $T^*$.

The scaling analysis for the $N$-SmA transition of SS5+sil samples using the bulk $N$-SmA SS5 critical parameters. Two choices for the cut-off length scale are shown. The first choice for the cutoff correlation length $\xi_M$ uses the mean distance between silica surfaces (mean void size) $l_o = 2 / a \rho_S$, where $a$ is the specific surface area. The second choice allows $\xi_M$ to vary as some multiple of $l_o$, i.e. $\xi_M = n l_o$. The results for $h_m$ of the SS5+sil samples are in very good agreement using $\xi_M = 3 l_o$, which more closely matches the measured saturated smectic correlation length. However, $\delta T^*/T^*$ appears sharper and $\delta H_{NA}$ smaller for $\rho_S > 0.1$ than predicted by this analysis.

### B. The Landau mean-field SmA-SmA scaling analysis

The excess specific heat due to the SmA-SmA phase transition is shown in Fig. 3 for bulk SS5 and SS5+sil samples over a temperature range down to $T_{AC} - 4.5$ K. The bulk SmA-SmA transition is well described by an extended Landau theory given by

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

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 transition $\delta C_p$ for bulk SS5 and SS5+sil samples over the temperatures $T < T_{AC}$ are tabulated in Table IV. These results are the average of heating and cooling scans. 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 this is 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 7O.4 in hydrophobic aerosil. 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 $A \propto \rho_S^{0.5}$.
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 $A^{\pm}$ are given in J K$^{-1}$ g$^{-1}$. The parameters $D^{\pm}$ are dimensionless. All scans were fit from $t_{max} = 10^{-5}$ to $\pm t_{min}$. All parameters were free to vary in the fit except when the exponent was fixed to $\alpha_{2V} = -0.013$ (denoted by the square brackets).

| $\Delta$ | $T_C$ | $\alpha_{eff}$ | $B_C$ | $A^+$ | $A^-$ | $D^+$ | $D^-$ | $t_{min} \times 10^{-5}$ | $\chi^2$ |
|---------|-------|----------------|-------|-------|-------|-------|-------|-------------------------|---------|
| 0       | 335.220 | -7$\times 10^{-5}$ | 1023.600 | -1023.760 | -1023.630 | 0.0002 | 0.0022 | 1.80/-12.3 | 1.266 |
| 0.025   | 334.712 | -1$\times 10^{-4}$ | 536.893 | -536.971 | -536.845 | 0.0007 | 0.0045 | 3.50/-29.9 | 1.073 |
| 0.041   | 335.111 | -1$\times 10^{-4}$ | 383.615 | -383.643 | -383.536 | 0.0016 | 0.0060 | 2.56/-14.2 | 1.287 |
| 0.051   | 334.938 | -2$\times 10^{-4}$ | 154.089 | -154.083 | -154.025 | 0.0045 | 0.0086 | 11.4/-49.2 | 1.134 |
| 0.078   | 335.123 | -1$\times 10^{-4}$ | 376.628 | -376.688 | -376.614 | 0.0010 | 0.0036 | 3.08/-14.9 | 1.163 |
| 0.105   | 335.297 | -1$\times 10^{-4}$ | 259.368 | -259.269 | -259.171 | 0.0049 | 0.0095 | 3.63/-19.3 | 1.076 |
| 0.161   | 335.162 | -7$\times 10^{-4}$ | 18.744 | -18.680 | -18.580 | 0.0655 | 0.0615 | 5.67/-42.3 | 1.036 |
| 0.220   | 335.498 | -4$\times 10^{-4}$ | 10.314 | -10.099 | -10.048 | 0.1651 | 0.1875 | 3.59/-57.5 | 1.004 |
| 0.347   | 335.145 | -6$\times 10^{-4}$ | 6.892 | -6.724 | -6.703 | 0.1839 | 0.1400 | 27/-85.1 | 1.056 |
| 0.354   | 335.144 | -0.013 | 0.573 | -0.414 | -0.391 | 3.646 | 2.4651 | 1.056 |         |

IV. DISCUSSION

Results have been presented from a series of high-resolution ac-calorimetric experiments on 8S5+sil dispersions through the N-SmA and SmA-SmC phase transitions as a function of aerosil density. In bulk 8S5, the N-SmA is a nearly clean XY-like transition with an $\alpha \lesssim 0$ while the SmA-SmC transition is mean-field with a Landau tricritical character. Our bulk measurements are fully consistent with these behaviors. The introduction of QRD in the 8S5+sil system allows for the isolation of random-field, finite-size-like, and elastic strain effects at...
TABLE IV: Summary of the results of fitting Eq. (10) to the excess specific heat \( \delta C_p \) 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 \( \sim -7 \) 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.

| \( \rho_S \) | \( T_C \) | \( T_m \) | \( A \) | \( \chi^2 \) |
|----------|--------|--------|-----|--------|
| 0        | 328.957| 329.26 ± 0.04 | 0.108 ± 0.001 | 1.187 |
| 0.025    | 328.706| 330.32 ± 0.38 | 0.075 ± 0.002 | 1.208 |
| 0.041    | 329.090| 330.61 ± 0.36 | 0.056 ± 0.002 | 1.328 |
| 0.051    | 329.010| 332.23 ± 0.31 | 0.049 ± 0.003 | 1.323 |
| 0.078    | 329.495| 330.49 ± 0.25 | 0.051 ± 0.002 | 1.258 |
| 0.105    | 329.250| 331.08 ± 0.40 | 0.050 ± 0.010 | 2.317 |
| 0.161    | 329.390| 329.97 ± 0.44 | 0.025 ± 0.002 | 1.160 |
| 0.220    | 329.860| 331.41 ± 0.19 | 0.023 ± 0.003 | 1.206 |
| 0.347    | 329.414| 330.37 ± 0.47 | 0.016 ± 0.002 | 1.211 |

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 quasi-critical behavior is preserved and that the exponent \( \alpha_{eff} \) remains slightly negative and constant for all \( \rho_S \) studied. See Fig. 4. 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 \( \delta T^*/T^* \) 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 \( \xi_M(8S5+sil) = 3l_o \) but this does not completely describe the behavior of \( \delta H_{NA} \) nor \( \delta T^*/T^* \), especially for \( \rho_S > 0.1 \). Interestingly, when this scaling analysis is applied to the 8CB+sil and 8OCB+sil systems, equally good modelling of \( h_m \) is obtained for \( \xi_M(8CB+sil) = l_o \) and \( \xi_M(8OCB+sil) = 1.5l_o \). It is surprising that such excellent agreement is obtained over the whole range of \( \rho_S \) explored for these three LCs 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 cut-off length-scale). Also, the smectic correlation lengths measured for these systems are much larger than this cutoff length scale. This makes the geometric interpretation of the cut-off 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 70A+sil and 8S5 in aerogel as well as the SmA-SmC* transition of CE8+sil. The heat capacity associated with the SmA-SmC transition in 8S5+sil presented in this work exhibit a systematic evolution from a Landau tricritical peak to a simple mean-field step with very little smearing observed for \( T > T_{AC} \), and then only at the highest \( \rho_S \). Good quality fits were made using an extended Landau form that found the upper stability temperature increasing with \( \rho_S \) 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 \( A \propto \rho_S^{-0.5} \), see Fig. 5. It is clear that this transition, while evolving in a systematic fashion, remains mean-field over the entire range of \( \rho_S \) 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 on 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 non-polar molecules and the long nematic range) nor 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 \( \xi_M > l_o \) 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 cou-
The decrease in the nematic susceptibility with increasing aerosil density has already been discussed previously [1, 14, 17, 33] in terms of the stiffening of the LC+sil systems. A consequence of the stiffening of the LC would be similar to the engineered stiffening of polymer composite materials. 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 effective microscopic elastic stiffening of the LC is that the mean-void length $l_0$ is used as the cut-off length scale (solid lines) or $3l_0$ (dashed lines).

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 $\psi$. The mean-field phase transition behavior and the decreasing size of the step in the heat capacity is 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 SS5, the nematic and smectic phases are almost fully decoupled in the bulk while there remains significant coupling in the 8CB and SOC6 LCs. It is the latter two LCs that exhibit the strong non-monotonic transition temperature shifts downward with $\rho_{S}$ and so may be reflecting QRD effects at the I-N transition [15]. 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 aerosol study [3]. 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.

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 step-like 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

**FIG. 4:** Scaling analysis of the $N$-SmA transition in SS5+sil (solid circles) on log-log scales. Top Panel: Transition enthalpy $\delta H_{NA}$. Middle Panel: Excess specific heat maximum $h_m = \Delta C_{NA}$. Bottom Panel: Transition rounding in reduced temperature $\delta t_{\min} = |t_{\min}^{+} - |t_{\min}^{-}|$. The bulk scaling predictions are given by Eqs. 9 and 10 where the mean-void length $I_o$ is used as the cut-off length scale (solid lines) or $3I_o$ (dashed lines).

**FIG. 5:** Scaling plot of $A$ ($\delta C_p$ at $T = T_{AC}$), obtained from fitting the excess specific heat of the SmA-SmC phase transition to Eq. (10), against $\rho_{S}$. The solid line has a slope of $-0.5$ while the dashed line a slope of $-0.56$. 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 $\rho_{S}$ 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 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 step-like 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 $\psi$. The mean-field phase transition behavior and the decreasing size of the step in the heat capacity is 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 SS5, the nematic and smectic phases are almost fully decoupled in the bulk while there remains significant coupling in the 8CB and SOC6 LCs. It is the latter two LCs that exhibit the strong non-monotonic transition temperature shifts downward with $\rho_{S}$ and so may be reflecting QRD effects at the I-N transition [15]. 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 aerosol study [3]. 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 SS5+sil. In the x-ray work, it is clear that the temperature dependence of the tilt angle of the SmC phase is insensitive to $\rho_{S}$, strongly suggesting that the order-parameter $\psi$ for the SmC phase remains unchanged from bulk for all SS5+sil samples.
However, if the system remains mean-field, then the relationship $C_p \propto \partial \psi / \partial T$ should hold. In this case, the dramatic variation of $\delta C_p(AC)$ with $\rho_S$ suggests that the Sm$C$ order-parameter should be strongly $\rho_S$ 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 $\approx 1$ K) suggest 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. [17]).

Clearly, there is an important need for theoretical efforts at understanding quenched random disorder on the Sm$A$-Sm$C$ transition. The beginnings of such a theory, although for the anisotropic aerogel disordered Sm$A$-Sm$C$ transition [9], 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 cut-off length scale that seems to play an important role for the $N$-Sm$A$ as well as the observed scaling of the $\Delta C_p(AC)$ peak with $\rho_S$. Additional x-ray and calorimetric experimental work with anisotropically aligned Sm$A$-Sm$C$ as well as Sm$A$-Sm$C^*$ in aerosil gel systems are also needed and would provide important data as to the role the polar nature of the LC and the local aerosil-LC interaction.

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