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Smectic liquid crystals in anisotropic colloidal silica gels

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Abstract

We report x-ray scattering studies of the smectic liquid crystal octylcyanobiphenol (8CB) confined by strained colloidal silica gels. The gels, comprised of aerosil particles, possess an anisotropic structure that stabilizes long-range nematic order in the liquid crystal while introducing random field effects that disrupt the smectic transition. The short-range smectic correlations that form within this environment are inconsistent with the presence of a topologically ordered state predicted for 3D random field XY systems and are quantitatively like the correlations of smectics confined by isotropic gels. Detailed analysis reveals that the quenched disorder suppresses the anisotropic scaling of the smectic correlation lengths observed in the pure liquid crystal. These results and additional measurements of the smectic-A to smectic-C transition in 4-n-pentylphenylthiol-4′-n-octyloxybenzoate ($\bar{8}$S5) indicate that the observed smectic behaviour is dictated by random fields coupling directly to the smectic order while fields coupling to the nematic director play a subordinate role.

1. Introduction

Liquid crystals confined by silica gels have served as useful models for exploring the consequences of quenched disorder on phase transitions [1–14]. In particular, the study in such materials of the nematic (N) to smectic-A (SmA) transition, which breaks a three dimensional (3D) XY symmetry, has provided insight into the effects of a random environment on transitions that break a continuous symmetry. A recent focus of these studies has been smectic liquid crystals confined by aerosil gels, which are hydrogen-bonded gels formed from nanometre-scale silica colloids [7–14]. X-ray scattering experiments on liquid crystal–aerosil composites have revealed that the quenched randomness introduced by interactions between the liquid crystal and the silica network prevents development of the quasi-long-range order characteristic of pure smectics and replaces the thermodynamically sharp transition with a nonsingular growth of smectic correlations [11–14]. Detailed analysis of these x-ray scattering results demonstrates quantitatively that the presence of the gel introduces random field effects to the

smectic. Specifically, the smectic correlation function is observed to contain two components, one corresponding to thermal fluctuations and one matching that expected for static fluctuations due to random fields [12]. The amplitudes and correlation lengths characterizing these contributions indicate that the disorder strength varies approximately linearly with aerosil density. The consequent ability to tune conveniently the disorder by changing density thus makes smectics confined by colloidal aerosil gels a valuable experimental realization of a random field system.

In this paper, we present an experimental study that exploits the mechanical properties of colloidal aerosil gels to investigate the effect of *anisotropic* disorder on the N–SmA transition. We create this novel random environment by confining smectic liquid crystals within strained aerosil gels. The main motivations for this work are twofold. First, through comparisons between the behaviours in isotropic and anisotropic gels, we seek to understand the precise nature of the disorder introduced by the porous structures; and second, inspired by recent theoretical ideas, we search for topologically ordered states predicted for the 3D random field XY model at low temperature. In section 2 below we outline current theoretical understanding. Section 3 details the procedure for creating the anisotropic gels and the x-ray scattering methods we use to characterize the gels and smectic behaviour. Section 4 provides a description of the strained gels and an analysis of the smectic correlations. Finally, we summarize our conclusions in section 5.

2. Theoretical background

At the simplest theoretical level the effects of confinement on liquid crystals is understood in terms of random fields that perturb the ordered states [15, 16]. In a detailed study of smectics in gels, Radzihovsky and Toner [16] treat the effect of the gel in terms of random fields and demonstrate that arbitrarily weak fields destroy the N–SmA transition. In addition to this prediction, they also postulate that the smectic exhibits enhanced anomalous elasticity and introduce the possibility that a 'smectic Bragg glass' phase appears at low temperature. This topologically ordered state is distinct from the nematic by the absence of unbound dislocation loops. Experimentally, evidence for the smectic Bragg glass in liquid crystals confined by silica gels has been contradictory. While x-ray scattering results on smectics in aerogels—rigid, chemically bonded porous silica—have been interpreted to suggest the presence of a smectic Bragg glass phase [6], smectics confined by aerosil gels possess properties inconsistent with the smectic Bragg glass [12–14]. These contradictory conclusions are surprising because aerosil gels permit access to weaker quenched disorder than do aerogels and the predictions for the smectic Bragg glass are made in the regime of weak disorder. (Weaker disorder is accessible with the aerosil gels for two reasons: the ability to assemble the colloidal gels directly within the liquid crystal allows structures with higher porosity, and compliance of the hydrogen-bonded colloidal networks leads to partial annealing of the aerosil disorder, as evidenced by the larger correlations lengths for smectics within aerosil gels than for those within aerogels of the same density.)

Indeed, given the strong evidence from simulation and theory for the existence of a topologically ordered state with algebraic decay of correlations in the 3D random field XY model at low temperature [17–19], one might expect that smectic liquid crystals confined by aerosil gels, which both possess the correct symmetry and show clear random field behaviour, would be strong candidates for realizing such a state. However, comparisons between smectics confined by gels and the 3D random field XY model could be complicated both by the soft elasticity of the smectic phase and by the nature of the random fields introduced by the gel. Specifically, Radzihovsky and Toner identify two random fields affecting the smectic in a

porous medium, a random positional field that couples directly to the smectic density wave and a random tilt field that couples to the nematic order. These distinguishing features make the smectic Bragg glass phase, which is predicted to have short range correlations, qualitatively different from the topologically ordered state of the 3D random field XY model, whose correlations are predicted to decay algebraically. At the same time, these features also prevent a conclusive prediction for the stability of the smectic Bragg glass phase in isotropic gels [16]. Additional theoretical studies, however, firmly predict that a family of Bragg glass phases will become stable in smectics with anisotropic disorder [20, 21]. The parameter in the theory quantifying the anisotropy is the uniaxial strain applied to an originally isotropic medium, such as aerogel. For example, a tensile strain creates a soft axis along which the nematic director prefers to orient, assuming parallel nematogen-surface alignment. For quenched disorder with a soft axis, the role of tilt fields is altered and nematic fluctuations are suppressed at large length scales. In this case theory predicts that the smectic falls into the universality class of the 3D random field XY model, and a low temperature XY Bragg glass with algebraic correlations becomes stable. (A compressive strain, on the other hand, introduces a hard axis, which changes the universality of the system and leads to a novel '$m = 1$ Bragg glass' [20, 21].)

3. Experimental procedures

3.1. Preparation of anisotropic gels

In order to investigate the roles played by random positional fields and random tilt fields and to search for signatures of an XY Bragg glass phase, we have conducted experiments on the smectic liquid crystal octylcyanobiphenol (8CB) confined by strained aerosil gels that possess a soft axis for nematic order. The strained aerosil gels were formed from isotropic gels in 8CB, which were prepared following established procedures [7]. The 8CB, purchased from Frinton Laboratories, had a quoted purity of 99.4% and was used without further purification. Pure 8CB undergoes an isotropic to nematic transition at 313.98 K and a nematic to smectic-A transition at 306.97 K. The aerosil (type 300), obtained from DeGussa Corporation, consists of 7 nm diameter SiO_2 spheres that are strongly hydrophilic due to a high density of surface hydroxyl groups. To create isotropic gels, appropriate quantities of degassed 8CB and dried aerosil powder were mixed with high purity acetone, and the colloidal suspensions were sonicated for several hours to achieve a uniform dispersion. The suspensions were then heated to 315 K to evaporate the acetone slowly. During this process the silica colloids aggregated via hydrogen bonding into a cross-linked gel. After no signs of the acetone remained, the samples were placed under vacuum at 10 mTorr for several hours at 320 K to remove any trace amounts of solvent or absorbed water. The resulting composites were visibly uniform; thixotropic solids that maintain a finite yield stress at temperatures well above the isotropic transition of 8CB. Detailed discussions of the fractal gel structures formed by this procedure have been reported elsewhere [7, 13].

The modification of these isotropic gels into anisotropic structures involved training the 8CB + aerosil composites by cycling through the isotropic to nematic transition in the presence of a large magnetic field [8, 22, 23]. Because of the magnetic anisotropy of nematic 8CB, the nematic director has a strong preference to orient parallel to the field. Due to the anisotropic elasticity of the nematic and the mechanical coupling between the liquid crystal and the colloidal network, this preference translates into stress on the gel with each cooling into the nematic phase that causes restructuring of the gel to accommodate the nematic alignment. We found that such repeated cycling between the isotropic and nematic phases was much more effective in restructuring the gel than simply holding the samples in the nematic phase in field.

As we demonstrate below, the resulting strained gels impose a distinct directional preference on the nematic director, stabilizing long-range nematic order in the system long after the field is removed. Since the strained silica networks also impose random positional constraints on the smectic ordering, they thus represent models of anisotropic quenched disorder with a soft axis. A series of samples with aerosil densities [7] ranging from $\rho_S = 0.027$ g SiO_2/cm^3 8CB to 0.15 were prepared in this manner. To restructure the gels, each sample was cycled between 318 and 308 K in a 2 T magnetic field at least 100 times with a cooling rate through the isotropic to nematic transition of approximately 1 K min^{-1}. Such repeated cycling was necessary to create gels with substantial macroscopic anisotropy. During this process the samples were held in 1.5 mm thick aluminium containers with kapton windows appropriate for x-ray scattering. The magnetic field, and hence the soft axis of the gels, was aligned parallel to the windows to facilitate subsequent transmission x-ray diffraction measurements of the smectic order.

3.2. X-ray scattering

Two sets of x-ray diffraction studies were conducted on the 8CB–strained aerosil gel composites. The first set, a small angle x-ray study at the 8-ID-I beam line of the Advanced Photon Source, focused on the structure of the anisotropic gels and the nature of the nematic order induced by the gels. These experiments, performed with 7.65 keV radiation used a CCD area detector to cover a wavevector range $0.003\ \text{Å}^{-1} < q < 0.5\ \text{Å}^{-1}$. The second set of x-ray measurements was a high wavevector resolution study of the smectic correlations performed at the X22A beam line of the National Synchrotron Light Source. These experiments employed 10 keV radiation and a six-circle spectrometer with a point detector and silicon analyser crystal after the sample to achieve high resolution. In both sets of experiments, the aluminum cells containing the samples were held in a copper heating block whose temperature was controlled with a precision of ± 0.001 K.

4. Results and discussion

4.1. Gel structure and nematic alignment

Figure 1(a) shows a CCD image of the x-ray scattering intensity from 8CB confined by a strained aerosil gel of density $\rho_S = 0.035$ at $T = 300.1$ K. The measurement was performed several months after removal of the external field used to train the gel and subsequent repeated heating of the sample into the isotropic phase in zero field. The smectic scattering displays pronounced azimuthal anisotropy, as evidenced by the two lobes of scattering intensity located near $0.2\ \text{Å}^{-1}$ corresponding to diffraction from the smectic layers. This anisotropy indicates that the smectic 8CB possesses a narrow distribution of layer normal orientations, indicating long-range nematic order and demonstrating the gel's ability to stabilize macroscopic nematic alignment along a soft axis. (The scattering volume was approximately 1 mm^3.) The quality of this nematic alignment can be evaluated from the width of the smectic peak as a function of azimuthal angle, ϕ, as shown plotted in figure 1(b). The Gaussian widths of these 'rocking curves', displayed in the inset of figure 1(b), increase with ρ_S. This increase reflects the decreasing mechanical compliance of the gels with increasing aerosil density. Above $\rho_S \approx 0.11$ g cm^{-3}, the procedure to train the gels is completely ineffectual, consistent with the presence of a rigidity transition near this density for aerosil gels in 8CB [13]. As mentioned above, the quality of the nematic alignment in the strained gels displays negligible change in response to temperature excursions into the isotropic phase, demonstrating that the anisotropic gel structure is stable to thermal fluctuations and sufficiently robust to align the nematic director repeatedly.

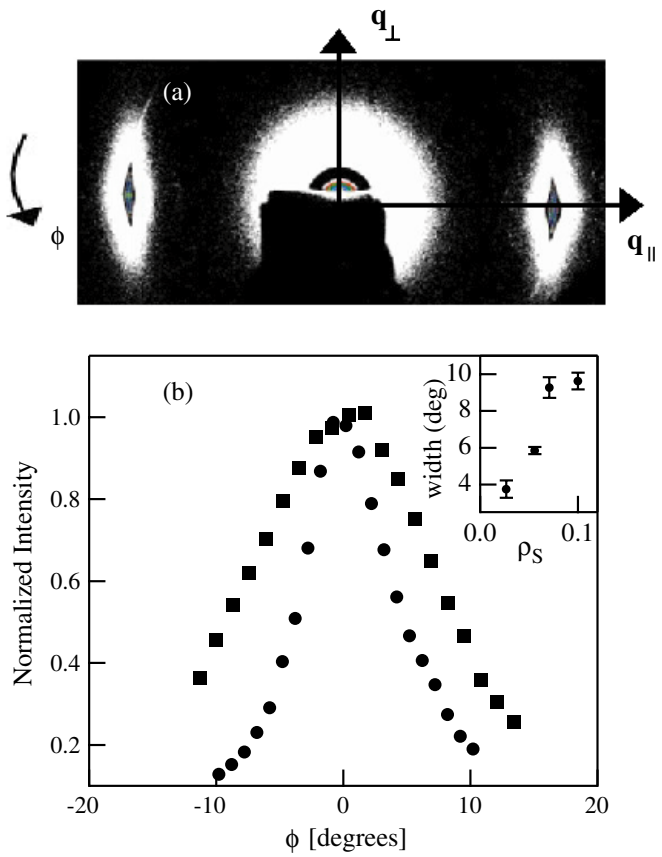

Figure 1. (a) X-ray image of the scattering intensity from smectic 8CB confined by a strained aerosil gel with $\rho_S = 0.035$ g cm^{-3} at 300.1 K. The two lobes of scattering, located near $q_\parallel \approx \pm 0.2$ Å^{-1}, correspond to Bragg reflection from smectic layers with short range correlations. The anisotropy in the scattering intensity along the azimuthal angle, ϕ, demonstrates the long-range nematic order induced by the gel structure. (b) Normalized scattering intensity of the smectic peak at fixed wavevector magnitude as a function of ϕ for $\rho_S = 0.027$ g cm^{-3} (circles) and $\rho_S = 0.100$ g cm^{-3} (squares) at 300.1 K. The Gaussian width of this azimuthal dependence, shown as a function of ρ_S in the inset, is a measure of the quality of the long-range nematic order.

(This figure is in colour only in the electronic version)

Figure 2 displays the scattering intensities as a function of wavevector both parallel, $q_\parallel$, and perpendicular, $q_\perp$, to the alignment direction. At wavevectors well below the smectic peak (below $q \approx 0.1$ Å^{-1}), the scattering is dominated by the aerosil gel structure. In this wavevector region and extending to the lowest values accessed in the measurement, $q \approx 0.003$ Å^{-1}, the scattering intensity possesses essentially identical lineshapes along the direction of the soft axis and perpendicular to it. This result indicates that the restructuring of the gel responsible for its ability to stabilize macroscopic nematic order occurs at length scales larger than ∼2000 Å and that the local structure at smaller scales remains isotropic. While this result appears surprising, we note that the nematic correlation length for liquid crystals under confinement by isotropic aerosil gels exceeds 1 μm for $\rho_S < 0.1$ [10]. Thus, structural anisotropy stabilizing long range nematic order in the strained gels might occur only at these length scales.

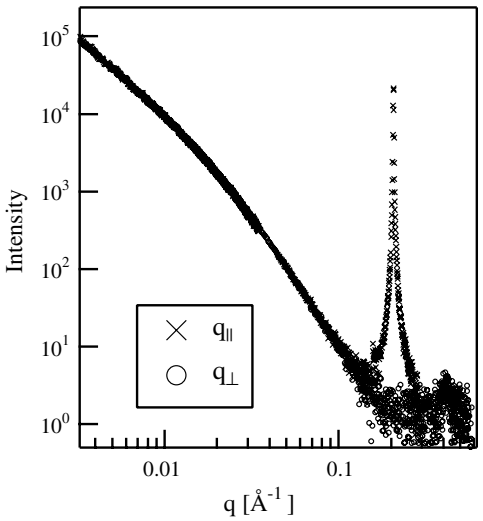

Figure 2. Scattering intensity for 8CB confined by a strained aerosil gel with $\rho_S = 0.035$ g cm^{-3} at 300.1 K along wavevectors parallel the nematic director, $q_\parallel$, and perpendicular to it, $q_\perp$. The peak located near $q_\parallel = 0.2$ corresponds to Bragg reflection from the smectic layers. The isotropic signal at small q corresponds to scattering from the gel structure.

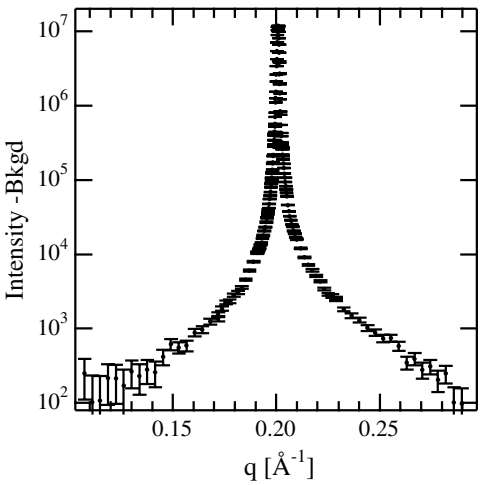

Figure 3. Smectic Bragg peak for 8CB confined by a strained aerosil gel with $\rho_S = 0.027$ g cm^{-3} at 296.1 K as a function of wavevector parallel to the gel's easy axis, $q_\parallel$. A background contribution due to scattering from the gel, determined from the intensity measured along wavevectors perpendicular to the easy axis, $q_\perp$, has been subtracted.

4.2. Smectic lineshapes

The shape of the peak near $q_\parallel = 0.2$ Å^{-1} provides a direct measure of the correlation function characterizing the smectic order in the presence of the anisotropic quenched disorder. To analyse this shape in detail, the peak must be isolated from the background scattering due to the gel. Two methods were employed to identify this background. The first used the scattering along $q_\perp$ at low temperature, as shown in figure 2, with the disadvantage that possible differences in the background along $q_\parallel$ and $q_\perp$ above $q_\parallel \approx 0.1$ Å^{-1} are unaccounted. The second method used the scattering intensity measured above the isotropic to nematic transition temperature, with the disadvantage that this scattering includes a small but undetermined contribution from the liquid structure of isotropic 8CB. Despite these uncertainties, the two methods lead to essentially identical smectic peaks after subtraction, and the results of analysis described below are insensitive to the choice of background. Figure 3 displays an example of the smectic peak after background subtraction. A noteworthy feature of the observed peak is the large dynamic range, as much as a factor of 10^5, over which the scattering intensity is determined. This range far exceeds that of previous x-ray measurements of 8CB in isotropic aerosil gels or aerogel for which the maximum ratio of peak intensity to background was typically less than 10^2 due to the relatively weak, powder nature of the smectic scattering in these systems. Thus, the azimuthal focusing of the scattering in the aligned aerosil gels enables much more rigorous evaluation of the smectic lineshape.

As illustrated in figure 4(a), the width of the smectic peak along $q_\parallel$ remains broad with respect to the instrumental resolution even for the smallest ρ_S over the full range of measurement temperatures, extending more than 10 K below the N–SmA transition temperature in pure 8CB. Several features of the observed lineshape are incompatible with the presence of an XY Bragg glass phase. Like the pure smectic-A phase, the topologically ordered XY Bragg glass phase

is characterized by algebraic spatial correlations that correspond in reciprocal space to a power-law singularity in the smectic peak [20, 21]. Unlike the pure smectic, however, the disorder-driven algebraic order in the XY Bragg glass is predicted to have both an isotropic and temperature independent shape below the transition [20, 21]. In contrast, the measured peak for 8CB in strained aerosil gels displays pronounced temperature dependence extending to low temperature, as shown in figure 4(b). Also, the shape of the peak indicates short range order rather than quasi-long-range order.

To characterize this short range order, we employ a two component lineshape that successfully describes the smectic correlations observed under confinement by isotropic aerosil gels [11, 12, 14]. Specifically, we model the smectic lineshape with the expression

$$S(\mathbf{q}) = \frac{\sigma_1}{1 + (q_\parallel - q_0)^2\xi_\parallel^2 + q_\perp^2\xi_\perp^2 + cq_\perp^4\xi_\perp^4} + \frac{a_2(\xi_\parallel\xi_\perp^2)}{(1 + (q_\parallel - q_0)^2\xi_\parallel^2 + q_\perp^2\xi_\perp^2 + cq_\perp^4\xi_\perp^4)^2}. \quad (1)$$

The first term in $S(\mathbf{q})$, an anisotropic Lorentzian with quartic corrections, matches the form for the structure factor of pure nematic 8CB and describes the critical thermal fluctuations on approaching the N–SmA transition. The second term, which is proportional to this thermal term squared, characterizes the static fluctuations due to random fields [24–26]. Figure 5 shows the results of fits to equation (1) at three temperatures for 8CB confined by a strained gel with $\rho_S = 0.027$. As part of the fitting procedure, equation (1) is integrated numerically over the distribution of layer normal orientations, as determined by low temperature rocking curves like those shown in figure 1(b), and convolved with the instrumental resolution. In previous work with isotropic gels, the perpendicular correlation length, $\xi_\perp$, and amplitude of the quartic term, c, were treated as functions of the parallel correlation length, $\xi_\parallel$, with $\xi_\perp(\xi_\parallel)$ and $c(\xi_\parallel)$ set by their relations in pure 8CB [11, 12, 14, 27]. Successfully modelling the smectic lineshape for the strained gels requires relaxing the constraint on $\xi_\perp$. In the present analysis $\xi_\parallel$ and $\xi_\perp$ are treated as independent parameters, while the amplitude of the quartic term, c, is treated as a function of $\xi_\perp$, with $c(\xi_\perp)$ set the behaviour in pure 8CB [28].

As figure 5 illustrates, equation (1) provides an excellent description of the smectic lineshape for 8CB in strained aerosil gels, demonstrating that the same analysis applies both to smectics with isotropic quenched disorder and to smectics with disorder that introduces an easy axis. We note that the need to relax the constraint on $\xi_\perp$ to model successfully the lineshape in the present analysis might not reflect any significant difference between the smectic correlations in the isotropic and anisotropic systems, but rather is likely an indication of the more rigorous analysis of the lineshapes afforded by the azimuthal focusing in the strained gels. As figure 5(c) illustrates, the differences between maintaining the correlation length ratios of pure 8CB and making $\xi_\perp$ a free parameter become important only in the far tails of the peak, which are not resolved in the results for isotropic gels. Thus, we believe that the forms of the smectic correlations in the presence of isotropic and anisotropic disorder are likely identical despite the vastly different random tilt field distributions that the smectic encounters in each system.

4.3. Correlation lengths and susceptibilities

The strong similarity between the effects on the N–SmA transition from isotropic random fields and random fields that introduce a soft axis is further evident in the temperature dependence of the parameters that characterize the short-range smectic correlations. Figure 6(a) shows the temperature dependence of the correlation length along the direction parallel to the layer normal, $\xi_\parallel$, extracted from the fits to equation (1) for 8CB confined by strained aerosil gels with densities $\rho_S = 0.027$ and 0.100. Consistent with the behaviour observed for 8CB confined

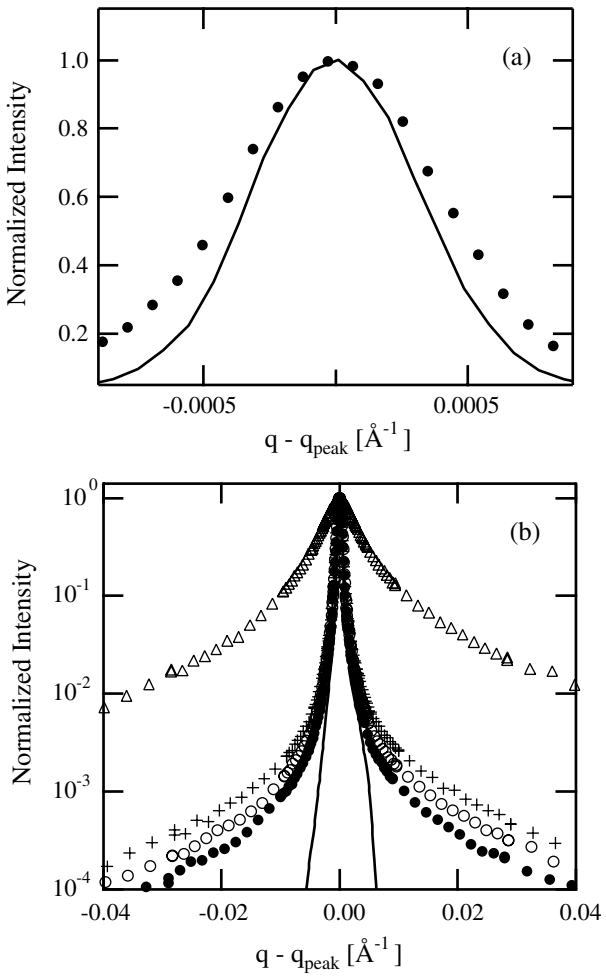

Figure 4. Comparison of the smectic Bragg peak measured for 8CB confined by a strained aerosil gel with the experimental resolution (solid curve), as determined from the direct x-ray beam profile. The density of the gel is $\rho_S = 0.027$ g cm^{-3}. All peak heights have been normalized to 1. (a) Even at the lowest experimental temperatures (296.1 K shown here) the width of the peak is broader than the resolution, indicating that the smectic correlations remain short-ranged to low temperatures due to the disorder imposed by the gels. (b) The shape of the peak evolves over the full experimental temperature range; shown in the figure are results for 296.1 K (solid circles), 302.1 K (open circles), 304.6 K (crosses), 306.4 K (triangles).

by isotropic aerosil gels [12], $\xi_\parallel$ increases rapidly on cooling through a pseudocritical region and saturates to a roughly constant value at low temperature. The low temperature values of the correlation length are $\xi_\parallel^{LT} = 6400 \pm 600$ Å for $\rho_S = 0.027$ and $\xi_\parallel^{LT} = 3150 \pm 500$ Å for $\rho_S = 0.100$. These values match closely those reported previously for 8CB in isotropic aerosil gels. Specifically, for 8CB in isotropic aerosil gels, $\xi_\parallel^{LT}(\rho_S^{iso} = 0.025) = 8200 \pm 3000$ Å and $\xi_\parallel^{LT}(\rho_S^{iso} = 0.105) = 3300 \pm 600$ Å [12]. The results for the thermal susceptibility, σ_1, for 8CB confined by strained aerosil gels similarly increase rapidly on cooling through the pseudocritical region and saturate at low temperature, as shown in figure 6(b), again matching the behaviour observed previously for 8CB confined by isotropic aerosil gels [12]. We note

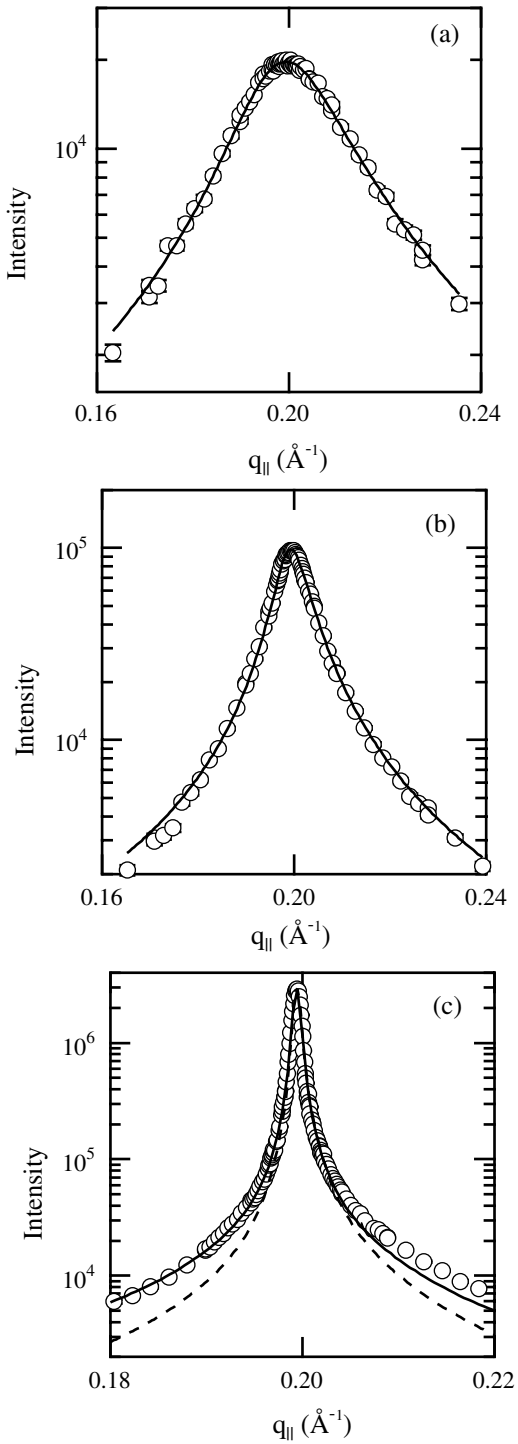

Figure 5. X-ray scattering intensity of the smectic peak with background subtracted for 8CB confined by a strained aerosil gel with $\rho_S = 0.027$ g cm^{-3} at (a) 308.9 K, (b) 306.5 K, and (c) 305.7 K. The solid curves are the results of fits to equation (1). The dashed curve in (c) is a fit to equation (1) with $\xi_\perp(\xi_\|)$ set by its relation in pure 8CB.

that both $\xi_\parallel$ and σ_1 display a small peak in the pseudocritical region which was not observed for the case of the isotropic aerosil. However, we believe that such features likely also occur for isotropic gels but that the fitting strategy used in that work, which assumed $\sigma_1(T)$ was constant at low temperature, suppressed them. For the second term in equation (1), the random-field-induced disconnected susceptibility, the parameter a_2 is proportional to the integrated intensity. For 8CB confined by isotropic aerosil gels this intensity was observed to grow on cooling like an order parameter squared [12]. As figure 6(c) illustrates, the temperature dependence of a_2 for 8CB confined by strained gels shows the same trend.

Thus, the smectic correlations of 8CB under confinement by isotropic gels and by strained gels not only obey an identical functional form but also have essentially the same temperature dependence. This observed similarity lends significant support to the validity of equation (1) in describing the behaviour of smectics confined by silica gels. Specifically, when proper account is taken in the analysis for the vastly differing distributions of the smectic layer orientations, identical pictures for the behaviour emerges, a result that is likely not coincidental. Furthermore, this strong similarity indicates that the random tilt fields generated by interactions between the liquid crystal and the gel, which clearly have different properties at long length scales in the two cases, are less important than the random positional fields in determining the smectic behaviour, in contrast with theoretical expectations [16].

As mentioned above, the superior signal to background for measurements of the smectic peak of 8CB confined by strained gels requires us to treat the correlation lengths parallel to the layer normal, $\xi_\parallel$, and perpendicular to it, $\xi_\perp$, as independent parameters. In pure 8CB, these correlation lengths display anisotropic scaling in the critical region [28]:

$$\xi_\parallel \sim (T - T_{\mathrm{NA}})^{-\nu_\parallel}, \qquad \nu_\parallel = 0.70 \tag{2}$$

$$\xi_\perp \sim (T - T_{\mathrm{NA}})^{-\nu_\perp}, \qquad \nu_\perp = 0.49 \tag{3}$$

The relation, $\xi_\perp \sim \xi_\parallel^{0.70}$, for pure 8CB was assumed also to hold in previous analysis of 8CB confined by isotropic aerosil gels. Such anisotropic scaling, characterized by $\nu_\parallel > \nu_\perp$, is a general feature of the N–SmA transition. Despite considerable theoretical efforts, no consensus has emerged for an explanation of this behaviour. Figure 7 shows the results for $\xi_\perp$ as a function of $\xi_\parallel$ for 8CB confined by strained gels with $\rho_{\mathrm{S}} = 0.027$ and 0.100. Also depicted in the figure is the relation for pure 8CB [28]. As the figure demonstrates, the anisotropy in the scaling that is observed in the pure material is greatly reduced by the presence of the quenched disorder. Results of best fits to the correlation lengths, shown as solid lines in the figure, give $\xi_\perp \sim \xi_\parallel^{0.94\pm0.01}$ for $\rho_{\mathrm{S}} = 0.027$ and $\xi_\perp \sim \xi_\parallel^{0.96\pm0.01}$ for $\rho_{\mathrm{S}} = 0.100$. Thus, consistent with theoretical predictions [16, 26], the correlation lengths display nearly isotropic scaling in the presence of random fields.

4.4. Smectic-C transition under anisotropic confinement

As mentioned above, the smectic correlations under confinement by strained gels and their similarity to those observed in isotropic gels indicate that random tilt fields are unimportant in determining the observed smectic behaviour. This conclusion is supported by additional measurements tracking the SmA to smectic-C (SmC) transition in 4-*n*-pentylphenylthiol-4′-*n*-octyloxybenzoate ($\bar{8}$S5) confined by strained aerosil gels. The SmA–SmC transition is characterized by a tilting of the nematic director from its orientation normal to the smectic layers. For the transition to proceed in the presence of random tilt fields and random positional fields, the free energy associated with at least one of these fields must increase. That is, either the director or the layer normal must reorient. In a comprehensive x-ray study of the SmA–SmC transition in $\bar{8}$S5 confined by isotropic aerosil gels, Clegg and co-workers [27] have found that the temperature dependence of the tilt angle, which serves as the order parameter for the transition, is

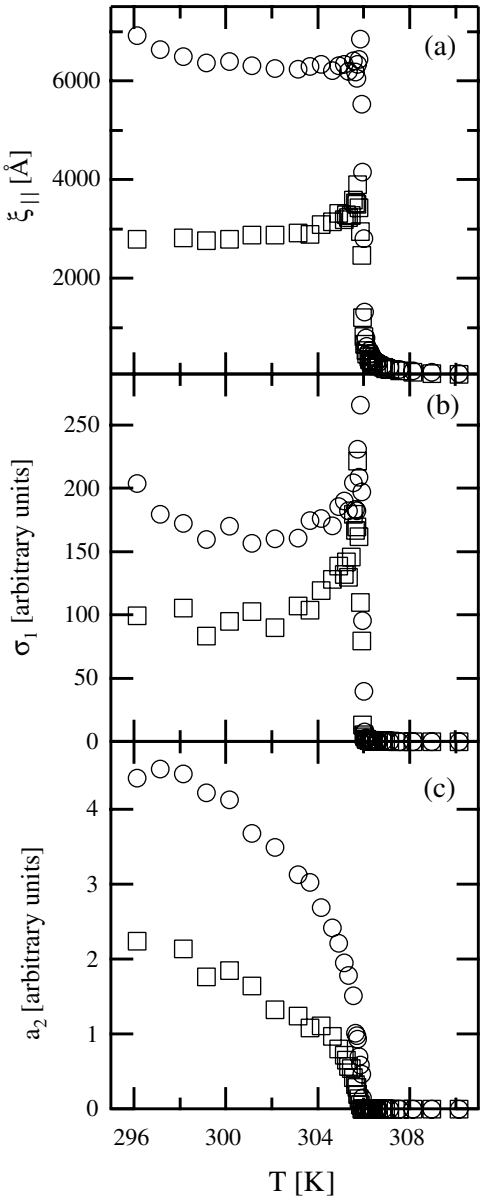

Figure 6. Parameters from the results of fits to equation (1) characterizing the smectic correlation functions for 8CB confined by strained aerosil gels with $\rho_S = 0.027$ g cm^{-3} (circles) and $\rho_S = 0.100$ g cm^{-3} (squares) as a function of temperature. The three parameters—(a) the smectic correlation length along the direction parallel to the nematic director, $\xi_\parallel$; (b) the amplitude of thermal fluctuations, σ_1, and (c) the integrated area of the static fluctuation term, a_2—display temperature dependences very similar to those observed for isotropic aerosil gels [12].

unaffected by the random confinement. From this observation they infer that the smectic layer orientation and not the molecular orientation becomes fixed by the quenched disorder. Our observations of $\bar{8}$S5 confined by strained gels demonstrate the accuracy of this conclusion.

Figure 8 shows the results of rocking curve measurements through the smectic peak in $\bar{8}$S5 confined by a strained aerosil gel with $\rho_S = 0.070$ at 329.2 K, above the SmA–SmC

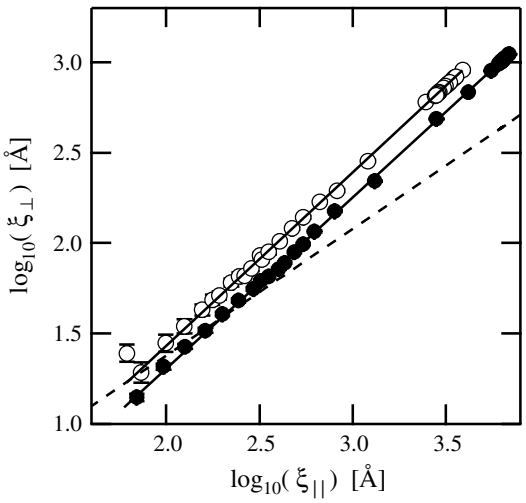

Figure 7. The smectic correlation length along the direction perpendicular to the layer normal, $\xi_\perp$, as a function of the correlation length parallel to the layer normal, $\xi_\parallel$, for 8CB confined by strained aerosil gels with $\rho_S = 0.027$ g cm^{-3} (solid circles) and $\rho_S = 0.100$ g cm^{-3} (open circles). The dashed line shows the behaviour for pure 8CB [26]. The solid lines are the results of fits to the form $\xi_\perp \sim \xi_\parallel^x$ with $x = 0.94 \pm 0.01$ for $\rho_S = 0.027$ and $x = 0.96 \pm 0.01$ for $\rho_S = 0.100$, demonstrating that the anisotropic scaling observed in the pure liquid crystal is suppressed by the quenched disorder. The displayed results are for the full experimental temperature range (296.1–311.1 K).

transition, and at 315.2 K, approximately 8 K below the transition. The peak at 329.2 K demonstrates that, as expected for the SmA phase, the smectic layer normal has a narrow distribution of orientations due the easy axis for the nematic ordering. On cooling to 315.2 K, the smectic peak wavevector, q_0, increases by an amount that corresponds to a tilt of the director by approximately 18° from the layer normal [29]. If the director orientation is fixed in space, as it is for example in studies of pure $\bar{8}$S5 aligned with an external magnetic field [29], then the rocking curve at 315.2 K should bifurcate into two peaks separated by twice this angle as the distribution of layer normal orientations changes to accommodate the tilt. By contrast, figure 8 shows only a small change in the rocking curve between 329.2 K and 315.2 K. (This change is reversible, indicating that it results from some minor redistribution of layer normal orientations and not from any restructuring of the gel.) The arrows in the figure mark the positions one would expect to find peaks if the director orientation were fixed by tilt fields. The relative insensitivity of the layer normal orientation distribution to the SmA–SmC transition demonstrates that essentially all of the smectic-C tilt is accommodated by reorientation of the director. Thus, although the random tilt fields generated by the strained gels are sufficient to create a reproducible soft axis for the nematic director, they cannot compete with the random positional fields in dictating smectic behaviour. A detailed account of SmA–SmC transition in strained aerosil gels will be published elsewhere [30].

5. Conclusions

In conclusion, colloidal aerosil gels have proved to be excellent experimental models for imposing quenched disorder on liquid crystals. In particular, as the results presented here illustrate, the mechanical compliance of the colloidal gels provides a unique method to tune controllably the nature of the disorder. By changing the distribution of tilt fields that couple to the nematic director, we have demonstrated the primary importance of random positional fields

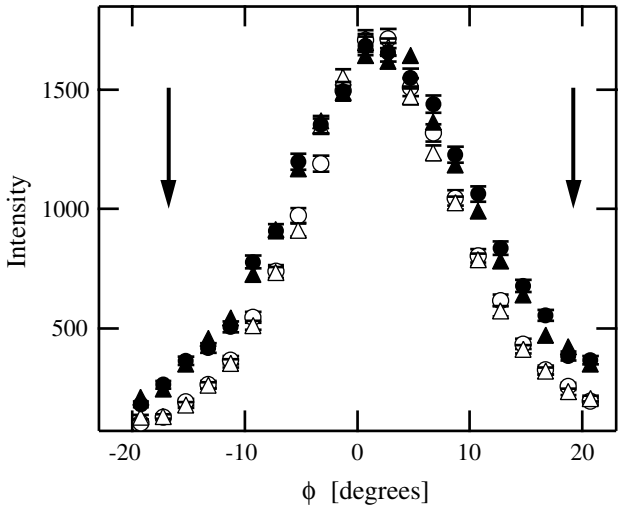

Figure 8. X-ray scattering intensity as a function of azimuthal angle, ϕ, through the smectic peak for $\bar{8}$S5 confined by a strained aerosil gel with $\rho_S = 0.070$ g cm^{-3} in the SmA phase at 329.2 (open symbols) and 8 K below the SmA–SmC transition at 315.2 K (solid symbols). The circles and triangles correspond to cooling through the transition for the first and second time, respectively, showing that the small change in the peak width is reversible. If the nematic director were pinned by the gel so that the smectic layer normal reoriented to accommodate the angle between director and layer normal in the SmC phase, then the peak at 315.2 K would bifurcate to two peaks at the positions of the arrows.

coupling directly to the smectic order parameter in dictating the smectic behaviour. While the resulting smectic with anisotropic disorder appears to be the best experimental candidate to date for realizing an XY Bragg glass state, no signatures of this phase are apparent in the smectic correlations. Thus, the outstanding question remains whether this topologically ordered state, which has been observed in simulation and predicted theoretically for the 3D random field XY model [18, 19], can be realized experimentally with a smectic in the presence of random fields.

Consistent with earlier studies on smectics confined by isotropic aerosil gels, liquid crystals confined by strained gels display a clear pseudocritical region in which smectic correlation lengths and thermal susceptibility grow rapidly before saturating. While this saturation is a signature that quenched disorder destroys the N–SmA transition, details of this pseudocritical behaviour may offer insights into the nature of this transition in pure liquid crystals. In pure systems, the critical behaviour at the N–SmA transition is strongly influenced by coupling of the smectic order to the nematic order parameter and fluctuations in the nematic director. While the consequences of these couplings, specifically a driving of the critical exponents away from 3D XY toward tricritical values and the anisotropic scaling of the correlation lengths, are well documented [31], a comprehensive theoretical understanding of these effects remains elusive. As documented previously [12, 13], the pseudocritical behaviour of smectics confined by aerosil gels is characterized by critical exponents for the order parameter and specific heat that systematically move toward 3D XY values with increasing disorder. In addition, as the current results demonstrate, confinement by aerosil gels strongly suppresses anisotropic scaling. Taken as a whole, these findings provide a clear picture in which quenched disorder drives the N–SmA critical behaviour toward that of the conventional 3D XY model, a potentially important clue for unravelling the persistent puzzles underlying the nature of the N–SmA transition. Further theoretical and experimental work that detail this influence of disorder and its significance would be highly valuable.

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