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Isotropic to smectic A phase transitions in a porous matrix: a case of multiporous phase coexistence

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Abstract

The one-dimensional smectic ordering of the liquid crystal 10CB incorporated in the pores of a silica aerogel has been investigated via x-ray scattering. Although the smectic order is made short-ranged by the aerogel host and the amplitude of the associated Bragg-like peak grows continuously with decreasing temperature, part of the first-order character of the 10CB's direct isotropic–smectic phase transition is retained in the discontinuous temperature dependence of the smectic correlation length. This behaviour contrasts with that of materials where the smectic phase develops from a locally orientationally ordered nematic and can be interpreted as a nucleation-type process.

The effect of disorder and impurities on condensed matter systems is an important and challenging problem that continues to be actively investigated. The interest in disordered systems is twofold, stemming firstly from the need to understand real materials, which always contain some amount of disordered inhomogeneity, and, secondly, because disordered systems are generalizations of clean systems, often displaying rich and complex phenomena which in turn shed new light on the disorder-free states. Artificially induced disorder is, in fact, known to dramatically modify the thermodynamic equilibrium of ordered systems, including altering their symmetry and inducing or eliminating phase transitions. Because liquid crystals (LCs) possess rather weak orientational and partial translational order, which is readily affected by surface interactions, the phase behaviour of LCs is strongly influenced by incorporation into porous media of high surface-to-volume ratio, such as silica aerogels (SAs). SAs are random porous structures with high porosity and highly interconnected voids. They thus appear as ideal hosts to exert random forces on the guest fluid without subtracting volume from it.

Systematic experimental and theoretical studies of the isotropic-to-nematic (I–N) and nematic-to-smectic A (N–A) phase transitions and the resulting nematic and smectic A ordering in SA, reveal that both nematic and smectic long-range order are lost and replaced by extended

exponentially decaying correlations [1, 2]. Phase transformations take place locally, with the correlation length for the ordered phase obeying scaling laws and behaving in agreement with a generalized version of finite size scaling [3]. The dynamics of the resulting partially oriented structure is typical of glassy states [4, 5] or of systems approaching a glass phase [3].

X-ray diffraction has proven to be particularly useful as a tool for characterizing the local smectic ordering. By studying materials featuring N–A phase transformations, it has been found that the local structure factor is a sum of two terms: one of them arising from thermally activated fluctuations, the other instead from static fluctuations due to the random quenched forces induced by the confinement in the gel [3, 6]. One or the other term prevails depending on the density and strength of the quenched disorder. Upon cooling from the nematic phase, the two relevant parameters describing such local smectic ordering, i.e. correlation length ξ and susceptibility (amplitude) χ , grow in a continuous fashion starting from small values and approximately maintain the relation $\chi \sim \xi^2$, reminiscent of bulk critical behaviour. These phenomena have been theoretically understood by extending to disordered systems modern descriptions of phase transition and phase properties, such as renormalization procedures and elastic models [3]. Remarkably, the smectic ordering of LC incorporated in aerogel, potentially intractable to theory and host-dependent, appears instead generic and well describable. This is mainly a consequence of the fact that the ordering takes place at the mesoscale, small enough to display unequivocal confinement effects, but large enough to ‘renormalize away’ the LC-to-solid coupling details at the aerogel interface.

Some mesogenic materials display a direct isotropic to smectic A (I–A) phase transition. Such a transition is strongly first order, without significant pretransitional fluctuations anticipating, on the nanoscale, the approaching macroscopic transformation. This is the case of the compound 650BC (hexyl-4'-pentyloxybiphenyl-4-carboxylate), whose bulk phase diagram is isotropic—85 °C—smectic A—68 °C—smectic B—60 °C—smectic E—55 °C—crystal. When incorporated in SA, 650BC displays an intriguing behaviour, quite different from the second-order N–A transition [7]. Upon lowering the temperature, the smectic phase of 650BC appears in a discontinuous way, immediately filling the nanoscale pores of the aerogel in a collective way, leading to micron-sized nuclei, easily visible in the optical microscope. Since 650BC has been the only I–A material studied in a random porous host, and since 650BC features in its phase diagram in-plane ordered phases which suggest strong intra-layer positional correlations, we have studied the material 10CB which features only a single LC phase, the fluid smectic A which appears upon cooling in the bulk at $T = 44$ °C via an I–A phase transition, and crystallizes at $T = 54.4$ °C. Besides the simple phase diagram, 10CB was chosen also because upon increasing aliphatic chain length n within the n CB homologous series, 10CB is the first not to have a nematic phase from which the A phase continuously grows. This suggests that the 10CB I–A phase transition may be more weakly first order than that of 650BC.

X-ray scattering measurements have been performed at the National Synchrotron Light Source. The wavevector (q) resolution, determined by a germanium 111 analyser crystal, was $\delta q = \pm 0.0005 \text{ \AA}^{-1}$. The SA host materials used in the experiment have a mass density of 0.36 g cm^{-3} , a mean solid chord $\langle s \rangle \sim 50 \text{ \AA}$, a mean pore chord $\langle p \rangle \sim 180 \text{ \AA}$ and a porosity of 79% [8]. They have been filled by 10CB (Merck) in the isotropic phase under vacuum by capillary action. The aerogel samples used here have a fractal structure in a limited range of q whose value is much smaller than typical smectic wavevectors. Previous comparisons between the structure factor measured by x-ray scattering before and after filling the sample indicate that the silica structure is for the greatest part unmodified by the insertion of the LC [8]. Thus, in the analysis of the experimental results, the diffraction spectra obtained at T high in the isotropic phase have been considered as providing a temperature-independent background

which adds to the smectic Bragg-like peaks developing at lower T . Such a background, as shown in the inset of figure 1, is well described, in the range of q of interest for our study, by a power law $I(q) \sim q^{-k}$, with $k \approx 3.5$. Figure 1 presents a selection of the scattered intensity $I(q)$ measured at various temperatures. Upon decreasing the temperature, a marked feature develops around $q_0 \approx 0.1765 \text{ \AA}^{-1}$, indicating the growth of a smectic layering structure with spatial period $d = 2\pi/q_0 \approx 35.6 \text{ \AA}$. At all T , the smectic peak never develops into a crystal Bragg peak, its width being always much larger than the resolution limit. This confirms the loss of long-range smectic order in the 10CB—aerogel system. To quantitatively extract the relevant parameters of the smectic ordering, we have fitted the A data with a Lorentzian, i.e.

$$I(q, T) = I(q, \text{high } T) + \frac{I(q_0)}{1 + (q - q_0)^2 \xi^2}$$

where ξ and $I(q_0)$ are the fitting parameters. The quality of the fit is rather good, indicating that 10CB, as with the other smectic materials so far investigated, is characterized by the layering order having a single exponential decay of the layer positional correlation. Indeed, since the studied samples have no overall macroscopic symmetry, the measured spectra result from a powder average of locally ordered correlation volumes. As discussed elsewhere [8], the powder-averaged Lorentzian structure factor indicates a local Lorentzian-squared structure factor and simple exponential correlation. This behaviour is expected when the quenched disorder dominates over the thermal disorder, and in the absence of the predicted ‘anomalous elasticity’ [9], which has been found to affect the scattering spectra at low T and low aerogel density [3]. The T dependence of the fitting parameters ξ and $I(q_0)$ is shown in figure 2. While the amplitude of the fitting Lorentzians smoothly grows as the smectic peak appears by lowering the temperature, the correlation length, from the first appearance of layering order, has a value corresponding to about six layers and increases only about 20% as T decreases. Observations of the samples by optical microscopy with crossed polarizers reveal that the smectic order does not grow at the same time in all porous cavities of the aerogel, as it does in the N–A transitions. Instead it appears in insulated nuclei that grow into micron- and then millimetre-scale domains to eventually fill the whole sample within an interval of a few degrees from their first appearance. The size of these domains combined with the x-ray scattering data implies that while the phase transition takes place simultaneously in clusters of interconnected pores, the layer correlations remain short-ranged. The growth of the domains produces the increasing scattering intensity. The coexistence of the isotropic phase with micronuclei of nanoscopically ordered smectic is the same behaviour previously observed in 65OBC. This similarity, which is shown for the x-ray data in figure 3 where the T dependence of ξ and $I(q_0)$ of 10CB-SA and 65OBC-SA are compared, supports the notion that this behaviour is not specific of a particular system, but it is a consequence of the nature of the I–A phase transition.

Figure 4 summarizes the growth of smectic A layers as observed in aerogels filled by materials where the smectic A develops from different phases. In particular it depicts the T dependence of ξ and $I(q_0)$ in two very different situations: when the smectic A develops from the N phase in the 8CB LC (diamonds) and when it forms starting from a (smectic) crystalline order (SmX) in 65OBC (full dots). In bulk materials these phase transitions are very different, the N–A is a second-order transition and the XA first order. As evident from the figure, in aerogel the two transitions are qualitatively rather similar, with ξ growing from values smaller than the typical smectic pore chord (the saturated ξ in the fully developed smectic), thus indicating intra-pore growth, with $I(q_0)$ reflecting this growth. Additionally, the X phase (open dots in figure 4) develops in a very analogous way, indicating that this behaviour is not specific to fluid phases only. The difference between the behaviour shown in figure 3 and that in figure 4 is certainly intriguing and asks for an explanation.

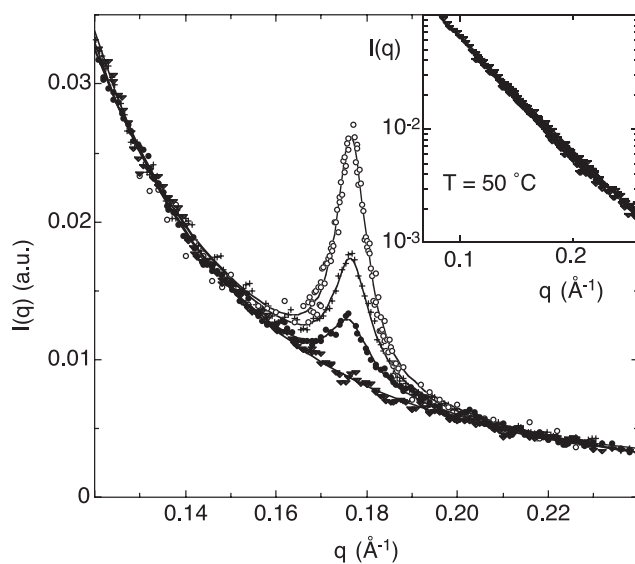


Figure 1. Scattered intensity $I(q)$ versus scattering wavevector q as measured at different temperatures: empty dots, $T = 34.0^\circ\text{C}$; crosses, $T = 45.4^\circ\text{C}$; full dots, $T = 47.2^\circ\text{C}$; triangles, $T = 50.6^\circ\text{C}$. The curves represent a best fit to a Lorentzian added to the high- T background. The data at $T = 50.6^\circ\text{C}$ are also shown in the inset on a log-log scale, together with the fitting power law $q^{-3.5}$ (mostly hidden by the data).

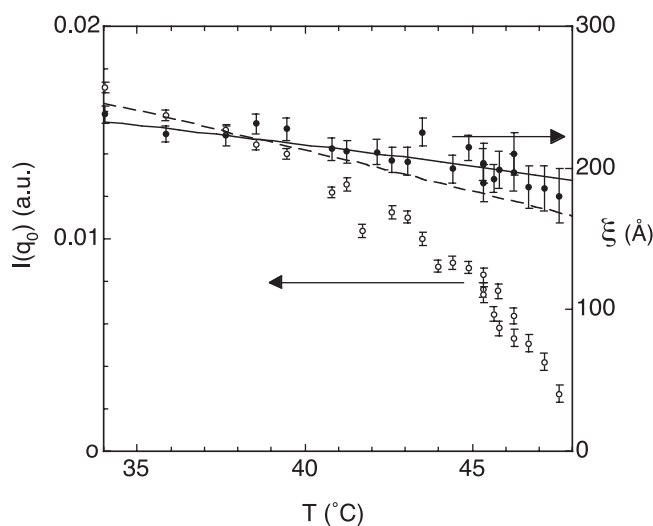


Figure 2. Amplitude $I(q_0)$ and inverse ξ width of the smectic peaks as a function of the temperature. The continuous line has been obtained as a polynomial interpolation in the ξ data, while the dashed line has been obtained as the square of the continuous line, scaled to match the low T $I(q_0)$ data.

The mass density $\psi(\mathbf{r})$ in the SmA phase, with layer normal z , is well described by $\rho(\mathbf{r}) = \langle \rho \rangle (1 + \text{Re}[\psi(\mathbf{r})e^{iq_0z}])$, where $\psi(\mathbf{r}) \equiv |\psi(\mathbf{r})|e^{iq_0u(\mathbf{r})}$ is the complex order parameter, the amplitude $|\psi(\mathbf{r})|$ describing the fractional density modulation with smectic wavevector q_0 , and the phase $q_0u(\mathbf{r})$ accounting for layer distortions. Disorder in the 1D crystal is reflected in

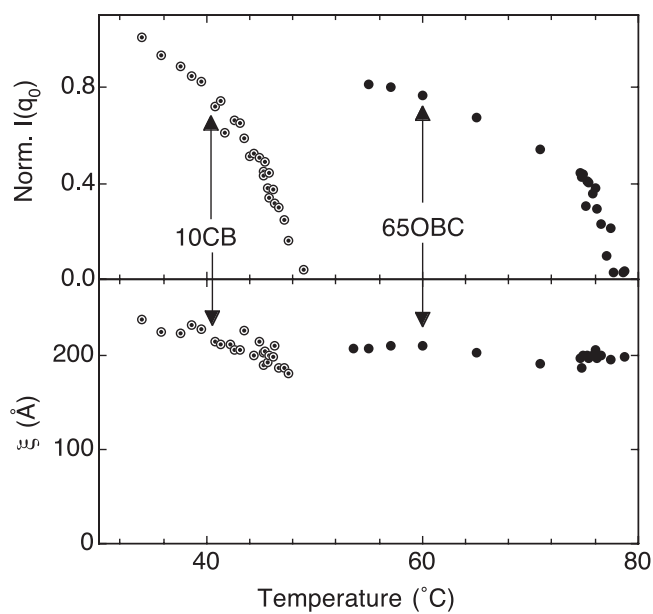


Figure 3. Comparison between the temperature dependence of amplitude and correlation length of the local smectic order measured in the two I-A materials 10CB and 65OBC.

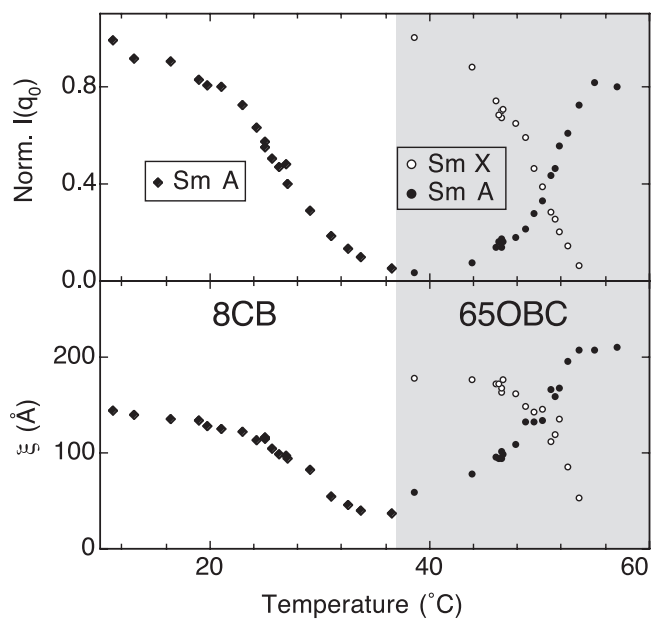


Figure 4. Comparison between the temperature dependence of amplitude and correlation length of the local smectic A order measured in the N-A materials 8CB (diamonds) and in SmXA material 65OBC (full dots). The figure also shows the parameters describing the SmX order in 65OBC.

the spatial variation of the amplitude of $\psi(r)$ and/or of its phase. As can easily be shown [8], the integrated intensity of the smectic peak resulting from the powder average over the local

order is proportional to the average squared smectic order parameter,

$$\int [I(q) - I(q, \text{high } T)] dq = \langle |\psi|^2 \rangle.$$

Thus, the intensity scattered in the smectic Bragg-like peak may grow either as the result of the growing quality of the local smectic order, or because of the increased volume fraction of the smectic phase in the I-A coexistence. On the other hand, the growth of ξ does not imply, by itself, a larger integrated intensity: the variation in the intensity scattered by each correlated domain in q_0 ($\sim \xi^6$) is compensated for by its decreased width ($\sim \xi^{-3}$) and by the reduced number of domains ($\sim \xi^{-3}$). Nevertheless, since ξ is not merely set by some intrinsic pore size of the aerogel, but rather it is set by the competition between the disordering influence of the aerogel and the smectic elasticity, and since a larger $|\psi|$ implies a larger elastic constant, the growth of ξ and of $|\psi|$ are interrelated. Specifically, in the study of the N-A phase transition of 8CB-SA it was found that $I(q_0) \propto \xi^2$ [3, 7]. To test for such dependence in 10CB-SA, we plot, in figure 2, a fitting curve for the $\xi(T)$ data (continuous line) as well as its squared value, scaled to fit the $I(q_0)$ data at the lowest measured T (dashed line). We find that the line thus produced approximates rather well the data for $T < 40^\circ\text{C}$, thus suggesting that below that temperature the whole sample has turned into local smectic. Hence, the T range over which the volume fraction of the smectic phase goes from 0 to 1 is of about 7°C .

The effects of the SA on the LC ordering can be understood as consequences of random pinning of LC molecules closest to the silica surface, which, in turn, can be accounted for by adding to the free energy terms describing positional and orientational random fields [3]. Overall, the pinning results in layer distortions (splay) and in layer compression and stretching, and possibly in random field-induced topological defects. Because of the intrinsic elasticity in spontaneously ordered structures, the smectic phase included, the free energy density for layer ordering in aerogel is increased with respect to the bulk smectic A. A simpler way to include the quenched disorder in the description of the phase transition is thus to add to a Landau-deGennes type free energy for bulk LC ($G(T)$) a term, proportional to the local random field ‘density’, which locally penalizes the smectic order. We thus propose

$$G(T) = A(T)\psi^2(\mathbf{r}) - B\psi^4(\mathbf{r}) + C\psi^6(\mathbf{r}) + L(\nabla\psi)^2 + K(\mathbf{r})\psi^2(\mathbf{r}) \quad (1)$$

where the first three terms correspond to the conventional Landau free energy yielding a first-order phase transition ($B, C > 0$). The fourth term in equation (1), also typical of bulk LC, accounts for the elastic energy associated with amplitude and/or phase variations in the smectic order. The last term includes the effects of the SA as discussed above; $K(\mathbf{r})$ locally gauges how unfavourable it is to transform from I-N. Smectic ordering is favoured when $B^2/4CA(T) > K(T)$. Moreover, since $A(T)$, at the lowest order, depends linearly on T ($A(T) \sim \alpha(T - T^*)$, T^* being the temperature of divergent susceptibility), and since at the bulk I-A transition $A(T_{I-A\text{bulk}}) = B^2/4C$, the inequality determining the most stable local phase can also be written as $\alpha(T - T_{I-A\text{bulk}}) > K(T)$.

In the absence of other constraints, equation (1) would lead to an I-A phase transformation occurring at the same time in all the pores far from the silica surfaces to gradually approach them as T decreases. This picture, in contradiction with the experimental observations, does not take into account: (a) the I-A interface thickness ξ_{I-A} and (b) the I-A surface tension γ_{I-A} . As with all first-order phase transitions, the bulk I-A phase transition takes place through nucleation of smectic domains, of minimum size $R_{\min} \sim \Delta G_{I-A}/\gamma_{I-A}$ —where ΔG_{I-A} is the (T -dependent) free energy difference between the I and A phases—and having interface thickness ξ_{I-A} —where $\xi_{I-A} = (L/A)^{1/2}$ also determines a low limit for R , $R_{\min} > \xi_{I-A}$. Both ξ_{I-A} and γ_{I-A} have difficult experimental access and thus are, so far, unknown. In our previous investigation of the behaviour of 65OBC we proposed an interpretation of the data based on

the notion that ξ_{I-A} could have been larger, or comparable, to the mean pore chord of the SA. Here we suggest that the same effects may follow, even more directly, from a non-negligible γ_{I-A} . Both interpretations appear plausible since they enable a distinction between the I-A phase transition on one hand and both the N-A and A-X transitions on the other. In the second-order N-A phase transition the interfacial thickness continuously grows upon approaching the A phase from above, its growth determining the continuous growth of A correlated volumes within the pores, while the interfacial tension vanishes at the critical point. In the crystallization process, on the other hand, the solid-liquid interfaces are typically thin and the crystal phase typically appears in nuclei much smaller than the length scales considered here.

Whatever the origin, if there is a minimum nucleus radius for the formation of the smectic phase within the isotropic fluid, the free energy of a forming nucleus is obtained by averaging over its volume. Thus the LC will not respond to the strictly local free energy but rather to a ‘smoothed’ free energy, where the spatial components having a periodicity smaller than the minimum radius are suppressed. Such a filtering process can be included in equation (1) by replacing $K(\mathbf{r})$ with $K_f(\mathbf{r}) = K(\mathbf{r}) \otimes f(\mathbf{r})$, where $f(\mathbf{r})$ is a cut-off function suppressing aerogel density fluctuations on a length scale larger than R_{min} , the radius of the smallest smectic nucleus that can be formed. The free energy then becomes:

$$G(T) = A(T)\psi^2(\mathbf{r}) - B\psi^4(\mathbf{r}) + C\psi^6(\mathbf{r}) + K_f(\mathbf{r})\psi^2(\mathbf{r}) \quad (2)$$

where the elastic term, and the implied finite interfacial thickness, is embodied in the notion of a minimum radius for nucleation. Thus, as T decreases, the filtered energy landscape for the smectic phase lowers, leading to the formation of local layering order where the (local) free energy becomes negative. At a given T , the volume fraction of the sample ϕ_{SmA} in which the LC has turned into a local smectic is:

$$\phi_{SmA}(T) = \frac{1}{V} \int_V \text{sgn}[\alpha(T - T_{I-Abulk}) - K_f(\mathbf{r})] dV \quad (3)$$

where $\text{sgn}(x) = 1(0)$ for $x > (<)0$. Equation (3) should be compared with the experimental data and in particular with the fact that:

- (i) the appearance of layer ordering in the SA takes place in an interval of about $\delta T \sim 6^\circ\text{C}$, between 42 and 48°C ;
- (ii) such an appearance is thus depressed with respect to bulk 10CB, on average by about $\Delta T \sim 9^\circ\text{C}$.

For the following we will assume, as it appears reasonable, that $K_f(\mathbf{r})$ is proportional to the silica mass density $\rho_{s,f}(\mathbf{r})$, i.e. to $\rho_s(\mathbf{r})$ filtered by a length R_{min} . The statistics of $K_f(\mathbf{r})$ is thus proportional to the statistics of $\rho_{s,f}(\mathbf{r})$. In particular $\langle K_f \rangle \propto \langle \rho_s \rangle$ and the standard deviation from the mean value $\delta K_f \propto \delta \rho_{s,f}$. Hence, from equation (3), it follows that $\Delta T \propto \langle \rho_s \rangle$, $\delta T/2 \propto \delta \rho_{s,f}$ and thus, using the experimental data, $\delta \rho_{s,f}/\langle \rho_s \rangle \sim \delta T/(2\Delta T) \sim 0.33$. Given that SA structure contains either empty sites or silica twigs, one can immediately evaluate both $\langle \rho_s \rangle = \phi_s \rho_{\text{SiO}_2}$ and $\langle \rho_s^2 \rangle = \phi_s \rho_{\text{SiO}_2}^2$, where ρ_{SiO_2} is the silica density within the solid (silica) fraction. Thus $\delta \rho_s/\langle \rho_s \rangle = (1/\phi - 1)^{1/2} \sim 1.94$. We conclude that the ‘filtering’ process produced by the existence of a minimum nucleus radius, significantly smoothes out the SA density fluctuations, since $\delta \rho_{s,f}/\delta \rho_s \sim 0.17$. To estimate the filtering length R_{min} , we assume $f(\mathbf{r})$ to be, in the q space, simply a sharp cut-off for $q > 2\pi/R_{min}$. By approximating the aerogel structure factor with $I_{SA} \propto (1 + q^2 \langle l \rangle^2)^{-2}$, where $1/\langle l \rangle = 1/\langle s \rangle + 1/\langle p \rangle$ [10, 11], and by taking into account that $\delta \rho_s^2 \propto \int I_{SA}(q) d^3q$, we obtain an explicit expression for $\delta \rho_{s,f}/\delta \rho_s$ as a function of $R_{min}/\langle l \rangle$. We finally obtain $R_{min} \sim 330 \text{ \AA}$. This length is compatible with the observation that the onset of local smectic ordering takes place simultaneously in nuclei larger

than the typical lengths characterizing the SA, and thus structures over the correlation length are basically independent of the total volume occupied by the smectic phase in the sample. This conclusion, although obtained through a slightly different, and simpler, way than in [7], is similar to that obtained in the analysis of the 65OBC-SA data.

This paper describes the isotropic-to-smectic A phase transition in a 10CB LC incorporated in the random interconnected pores of a SA. The behaviour observed matches well that of the previous observations of the I-A phase transition in 65OBC in aerogel; in both cases it is found that a short-ranged A phase and the isotropic phase coexist over a rather extended temperature interval. The domains of the coexisting phases always have sizes much larger than the typical pore size of the aerogel, and the correlation length of the smectic layering order is small and only weakly dependent on T . This behaviour appears to be unique to the I-A phase of LC incorporated in SAs, since both the second-order IN and the first-order A-crystal transitions occur within each single-pore cavity, the correlation length of the developing order smoothly growing from the molecular size. We interpret this behaviour as a consequence of either I-A interfacial thickness or the I-A interface tension, both forbidding the formation of smectic nuclei smaller than the SA pores.

Acknowledgments

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