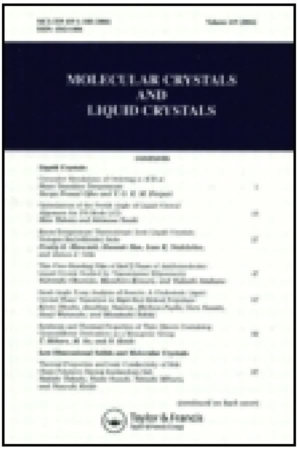

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Nematic Structures in Randomly Interconnected Porous Hosts

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Nematic Structures in Randomly Interconnected Porous Hosts

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Deuteron NMR measurements were performed on the octyl-cyanobiphenyl (8CB) liquid crystal confined to the randomly interconnected and large cavities of cellulose acetate Millipore filters and to the small pores of silica aerogel. These studies were performed as a function of sample orientation in the field, and by changing the confining size. In almost all cases, 8CB was confined to sizes smaller than the micron size magnetic coherence length, thus the observed line-shapes reflect the director pattern, $\hat{n}(\vec{r})$, and the orientational order, Q, as dictated by the porous host. The isotropic nature of aerogel yields DNMR spectral patterns consistent with powder-lineshapes. These patterns indicate a randomized $\hat{n}(\vec{r})$, characterized by a single Q. No angular dependence is found and nematic domains of finite dimension most likely exceeding the confining size are formed. In contrast, the Millipore anisotropy and larger confining sizes yield DNMR patterns dependent on the sample orientation in the field and show a competition between surface-induced and field induced molecular alignment.

Keywords: Liquid crystals; nematic director structures; porous media; surface-induced order; NMR

INTRODUCTION

The investigation of physical systems constrained to porous, randomly interconnected hosts has been prominently appearing in the scientific literature for over half a century. Yet, fundamental questions of how the phase structure or phase transitions are modified in such confining environments have not been fully answered. In particular, complex fluids confined to randomly interconnected networks are unique systems that permit addressing many challenging questions. An example is research at the confined superfluid transition that for many years was devoted to finite size effect studies [1], have recently focused on the manner that quenched random disorder modifies the critical properties of the transition [2]. Another interesting example arises from results for a binary liquid mixture confined to a random porous media. The experimental evidence suggests that a "random-field" model could describe the modifications occurring at phase transitions [3-5].

Mostly beginning in early 90's, liquid crystals started to play a prominent role among physical systems being investigated under confinement. Several investigations have dealt with effects that are introduced on liquid crystals by morphologically different confining hosts. Such systems have been probed using a wide variety of experimental techniques [6-10] since the interest in this field is continuously growing particularly because of the attractiveness that liquid crystals possess from both fundamental and applied points of view. The latter is of importance since constrained liquid crystals exhibit optical properties that can be suppressed by the application of an external field. Fundamentally, they are relevant as they form unique thermodynamic systems where a variety of different phase transitions under controlled quenched random disorder, can be studied. For instance, in confined liquid crystals, it is possible to investigate configurational or phase transition, surface wetting and elastic properties, under controlled conditions. The richness of these experimental systems has attracted extensive theoretical efforts [11-14].

With regards to thermodynamic properties, calorimetric studies [9,10] found that the first order phase transition that occurs in a parent bulk liquid crystal material (like the nematic to isotropic or N-I transition), under certain confinement conditions, can be replaced by a smooth evolution to a glassy state. Such a glassy state is characterized by a correlation length that does not exceed the pore size. In addition, the smectic-A to nematic phase transition, SmA-N, which in bulk belongs to the 3D-XY universality class, can be drastically altered under some type of confinement with the specific heat critical exponent α becomes size dependent [9,10].

Confined liquid crystals are therefore subjected to the influence of the host surfaces. Depending on the confining host geometry and confining sizes, different type of liquid crystal structures can be sustained. In the particular case of a well-defined cylindrical geometry like that found in Anopore or Nuclepore membranes, different nematic director configurations can be formed. Configurational transitions occur as driven by either changing the surface-liquid crystal interaction, or by changing the confining size [6].

The current investigation is devoted to a systematic study of the orientational order of octylcyanobiphenyl (8CB) liquid crystal confined to a series of different density silica aerogel samples, and to different sizes Millipore membranes. The density of the aerogel was varied from 0.068 to 0.6 g/cm^3 while the Millipore sizes changed form micron to submicron sizes. The confined 8CB orientational order was probed with Deuterium Nuclear Magnetic Resonance (DNMR) spectroscopy. Below, we focus on how the quenched disorder and isotropic (or anisotropic) properties introduced by the confining host influence the liquid crystal director structures that are formed.

POROUS HOSTS

The base-catalyzed silica aerogel consists of a random network of silica backbones in an openly connected void space. The silica aerogel used was prepared from the base-catalyzed polymerization of tetramethylorthosilicate in methanol. This process yields an isotropic network structure with strut dimensions on the order of 10 nm, and inter-network voids of average dimension between 12 and 91 nm. The void sizes depend on the concentration of the precursor solution and on the degree of collapse during the drying. The wet gels are all supercritically dried except for the highest density (0.6 g/cm^3) that was partially air dried (or xerogelled) prior to the final supercritical extraction.

Commercially available Millipore are thin polymeric membranes existing with several cavity sizes. Different cavity sizes result from changes in the composition of the solvents used to dissolve the original cellulose acetate/nitrate polymer. We believe that they possess anisotropic properties that change with varying size and are thus reminiscent of the type of random network obtained in liquid crystal-polymer mixtures. The manufacturer quoted Millipore sizes studied varied from 25 nm up to 8 μm.

LIQUID CRYSTAL PROPERTIES; SAMPLES PREPARATION

For this study, we used the octylcyanobiphenyl liquid crystal 8CB deuterated [23] at the first (alpha) position along the alkyl chain from the biphenyl group. Bulk 8CB, of molar mass 291.44 g/mol and molecular length l_B~ 2 nm [24], undergoes the following phase transitions: the weakly first-order N-I orientational ordering transition at approximately $T_{NI} \cong 40.8\ ^{o}C$, and the second-order SmA-N (a 1D translational ordering transition) approximately 7 °C below T_{NI}. Bulk 8CB crystallizes via a strongly first order transition at approximately 20 °C; under confinement, the transition to the crystalline phase is often substantially shifted to lower temperatures.

The filled aerogel samples were prepared in vacuum by heating the LC and aerogel just above room temperature but below the LC isotropic phase. This decreases the LC viscosity while filling and degassing both materials. The aerogel, in contact with the liquid crystal, was thus filled by capillary action. This slow (~ days long) process fully fills the voids (as determined by comparing the amount of 8CB absorbed to the available open volume) while preserving to the best extent possible the aerogel structure intact [9]. Once the aerogel filling process was completed, the outer surfaces of the aerogel samples were lightly dried with filter paper to minimize excess liquid crystal bulk material. Finally, the samples were inserted (packed) and epoxy-sealed within a glass tube, 3 mm in diameter and 2.5 cm long.

The Millipore samples were prepared by cutting the membranes to strips 3 mm wide and 25 mm long and dipped in the liquid crystal material. After removal and cleaning of the outer surfaces, they were stacked above one another within the NMR tube and initially placed in the magnet with the strips normal parallel to the magnetic field.

EXPERIMENTAL TECHNIQUE

Nuclear magnetic resonance (NMR) is a highly powerful and sensitive tool for liquid crystal research as it directly probes the orientational order Q, director configurations $\hat{n}(\vec{r})$, and molecular dynamics. Deuterium NMR, or DNMR, has been extensively and successfully applied to bulk and confined liquid crystal studies [22, 26-29].

The DNMR spectrometer consists of a 4.7 Tesla (30.8 MHz for deuterium) superconducting magnet fitted with a homemade probe tuned to deuterium, and commercially available electronics. The probe head is inserted in an oven housed in the magnet bore, through which a mixture of ethylene glycol and water circulates from an external temperature controlled bath. The probe head is provided with a calibrated 100 Ω platinum thermometer that is read after each DNMR pulse sequence and averaged over the thousands of scans accumulated in the process. The temperature stability over the entire DNMR spectra acquisition time is better than 0.050 °C with a resolution of ± 0.005 °C.

DNMR measurements used a quadrupole-echo pulse sequence (90°_x- τ - 90°_y- τ acquisition) with full phase cycling: $\tau \cong 100$ μs, $90^\circ \cong 3$ μs, a 1024 to 2048 point acquisition, and a last delay of 300 ms (to prevent T_1 saturation). This sequence was accumulated for as many as 50,000 scans over a 4-5 hours period. The final spectrum is obtained by a complex Fourier transform of the single zero-filled free induction decay (FID) with no line broadening.

The NMR spectrum from a domain of molecules with uniform director, in particular, a nematic liquid crystal compound deuterated at a specific site, consists of two sharp absorption lines separated in frequency by [26,30]:

$$\delta\nu = \frac{1}{2}\delta\nu_0 Q\left(3\cos^2\theta_B - 1\right) \qquad (1)$$

with $\delta\nu_0$ the maximum frequency splitting observable in a fully aligned bulk nematic sample, Q is the scalar order parameter, and θ_B is the angle between the nematic director $\hat{n}$ and the static magnetic field $\vec{B}_0$. For bulk, $\theta_B = 0^\circ$ due to the magnetic field-induced uniform alignment of $\hat{n}$. For sufficiently confined liquid crystals, the splitting has a positional dependence, $\delta\nu = \delta\nu(\vec{r})$, through a director structure $\theta_B = \theta_B(\vec{r})$ as well as through a scalar order parameter structure $Q(\vec{r})$. Eq. (1) becomes:

$$\delta\nu(\vec{r}) = \frac{1}{2}\delta\nu_0 Q(\vec{r})\left(3\cos^2\theta_B(\vec{r}) - 1\right) \qquad (2)$$

It should be emphasized that the director structure is solely dictated by the porous host and unaffected by the external magnetic field if the confining length L (the aerogel void size or the Millipore cavity size) is smaller than the magnetic coherence length ξ_M [26,27]:

$$\xi_M = \sqrt{\frac{\mu_0 K}{B_0^2 \Delta\chi}} \approx 1\mu m \qquad (3)$$

In Eq. (3) K is the average Frank elastic constant (single elastic constant approximation) and $\Delta\chi$ a measure of the anisotropy of the magnetic susceptibility. For all aerogel samples, ξ_M is much larger than L and the director structure is solely determined by the host. For Millipore, the cavity size changes from much larger, to comparable, to smaller than ξ_M.

The previous description does not take into account the possibility of the existence of defects, small regions of approximately 100 Å in diameter where $Q \approx 0$, nor the effects of motional diffusional averaging. In fact, it is well established that DNMR spectra are sensitive to the type of orientational ordering (as seen above) and to motional narrowing. Discussed by Zidansek et al. [22], in aerogel, motional narrowing is mostly due to the translationally induced rotation of liquid crystal molecules [31]. Whether motional averaging is significant to the extent of influencing the NMR pattern depends on the length scale L (for instance comparable to the mean void size length), over which $\hat{n}(\vec{r})$ and $Q(\vec{r})$ exhibit substantial variation. This length scale is to be compared against x_0 which is estimated from $x_0 \approx (D/Q_B\delta\nu_0)^{1/2}$. Here, x_0 effectively measures the average distance that a molecule migrates over the time scale of the NMR measurement, while D is the average translational diffusion constant. The DNMR spectra are thus fully time-averaged but are only spatial-averaged over a distance x_0.

Depending on the type of confining conditions, translational diffusion might be inhibited, particularly for a thin liquid crystal layer in contact with a solid substrate. However, for local averaging over a single void, the diffusion constant can be taken to be that of the bulk liquid crystal, or specifically for nematic 8CB, $D \cong 10^{-11}$ m^2/s and

$Q_B\delta\nu_0 \cong 40$ kHz. We find that in the nematic phase $x_0 \approx 15$ nm, while in the isotropic phase, x_0 is an order of magnitude larger or ≈ 150 nm [27-31]. Thus, if $Q(\vec{r})$ is approximately constant over the confining void size, the DNMR spectra will reflect the real static director structure. If $Q(\vec{r})$ varies substantially, as in the case of defects spaced closer than x_0, the DNMR spectra will include considerable motional narrowing of all features, directly reflecting the decrease in orientational order. In short, director field distortions are expected to extend over a length-scale determined by the confining size, here, the aerogel mean void length L. Motional averaging is more likely negligible in samples for which $x_0 >> L$ is satisfied.

RESULTS AND DISCUSSION

How confinement substantially affects the liquid crystal physical behavior or the type of structural configuration displayed by the liquid crystal molecules within the host strongly depends on the morphology and typical length scales of the host media, and on the anchoring energy and elastic distortions characterizing the host surface interactions with the liquid crystal. A relevant parameter that we have identified and that helps quantifying the confinement effects is the nematic correlation length ξ_N. At T_{NI}, the non-diverging ξ_N for 8CB grows to approximately 15 nm [32], which is of the same order than the diffusion length x_0 previously calculated.

In this study, DNMR spectral patterns for 8CB confined to eight aerogel samples, of different silica density such that the confining size is decreased from 91 nm, or 6 times larger than ξ_N, to 12 nm, which is slightly less than ξ_N. Thus, the director structure is determined by the solid host; however motional averaging does play a role. For all 8CB+aerogel samples studied, the spectra are temperature dependent and independent of sample orientation with respect to the NMR field; the latter proves the isotropic nature of the host aerogel structure.

The DNMR lineshape patterns for silica aerogel samples are shown in Fig. 1. From the patterns shown, a nematic phase is clearly formed in the aerogel host. It is characterized by a single Q and an isotropic distribution of $\hat{n}$. DNMR spectra for aerogel samples of density $\rho < 0.493$ g/cm^3 are well resolved Pake powder patterns with two low intensity shoulders separated in frequency twice as much as the two high intensity $\pi/2$ singularities. The frequency separation between the $\pi/2$ singularities (or equivalently that between the shoulders) is temperature dependent. A spectra powder pattern is retained for all samples down to temperature as low as T = 20.56 °C.

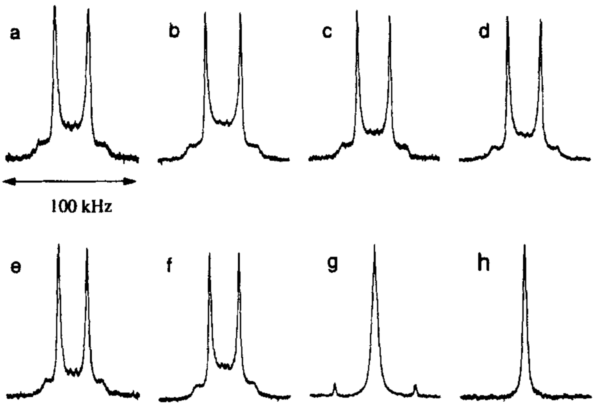

FIGURE 1. DNMR spectra for 8CB in aerogel at 30 °C. The silica densities are 0.068, 0.115, 0.124, 0.172, 0.265, 0.330, 0.493, and 0.600 g/cm^3 for a, b, c, d, e, f, g, and h, respectively.

The DNMR spectra are independent of sample orientation with respect to the static NMR field, they are of the Pake powder-type, and their shape is independent of temperature. Then, the nematic phase contains domains with an isotropic distribution of the director $\hat{n}(\vec{r})$, and a single spatially homogeneous value of Q. Due to the aerogel isotropic structure, it is expected that all orientations of $\hat{n}(\vec{r})$ occur with equal probability. This is also suggestive that a void size distribution does not play a significant role, but only that the voids are highly interconnected. The average size of the nematic domains cannot be determined from these lineshapes; any size distribution with an isotropic director alignment $\hat{n}(\vec{r})$ would lead to similar powder patterns. The Pake patterns do imply that the nematic domains are large compared to the diffusion length so that few molecules diffuse from one domain to another during the FID. Recent quasi-elastic light scattering results [33] showed that there are nematic correlations that take place over length scales approaching ~ 100 average void sizes. This collective behavior extending over several confining sizes is also common to other confined systems. Order correlated to length scales that greatly exceed the confining size has been found at the helium superfluid transition in both Vycor and aerogel [2].

The DNMR patterns for the 0.493 and 0.6 g/cm^3 aerogel samples show a (seemingly) drastically distinct behavior when compared to the less dense aerogel samples as their spectra is isotropic-like, or, a single, central, absorption peak. At lower temperatures, while the *FWHM* for the 0.6 sample monotonically increases, in 0.493 aerogel, a small splitting superimposed on the broad central peak appears actually appears. In addition, in 0.493 aerogel, a small outer doublet is evident in Fig. 1. It arises from remnant bulk material on the outer aerogel surface and are not related to confinement effect.

The behavior in 0.493 aerogel can be understood as follows. For this density, the mean void size is $L \approx 14$ nm, comparable to the translational diffusion length, $x_0 \approx 15$ nm. Thus, translational diffusion motion is fast enough causing considerable narrowing (translationally induced rotation mechanism [31]) in the resulting spectra. In general, the absorption spectra is affected if [34]:

$$\varepsilon \equiv \frac{\Delta \nu L^2}{6D} \leq 10 \tag{5}$$

Using typical values, we find for this sample that $\varepsilon \leq 1$. Consequently, the DNMR spectrum is strongly affected by motional narrowing that produces the single broad peak. Lowering the temperature slows the molecular diffusion such that a splitting, and eventually a powder pattern is resolved.

The DNMR spectra for the 0.6 g/cm^3 aerogel, average mean void length $L = 12$ nm, is a single absorption peak at all temperatures. The *FWHM* of this peak, 450 Hz (3 to 4 times broader than bulk's) at a temperature 10 °C above its T_{NI}, monotonically increases to approximately 10 kHz at 20 °C below T_{NI}. This behavior is reminiscent of that of cyanobiphenyls confined to the 7 nm Vycor glass pores [17]. Then, for confining sizes less than the nematic correlation length, the N-I phase transition is replaced by a continuous evolution of orientational order in the pores. Such glassy-like orientational order, evidenced by the broad absorption spectra, is for the most part locally determined.

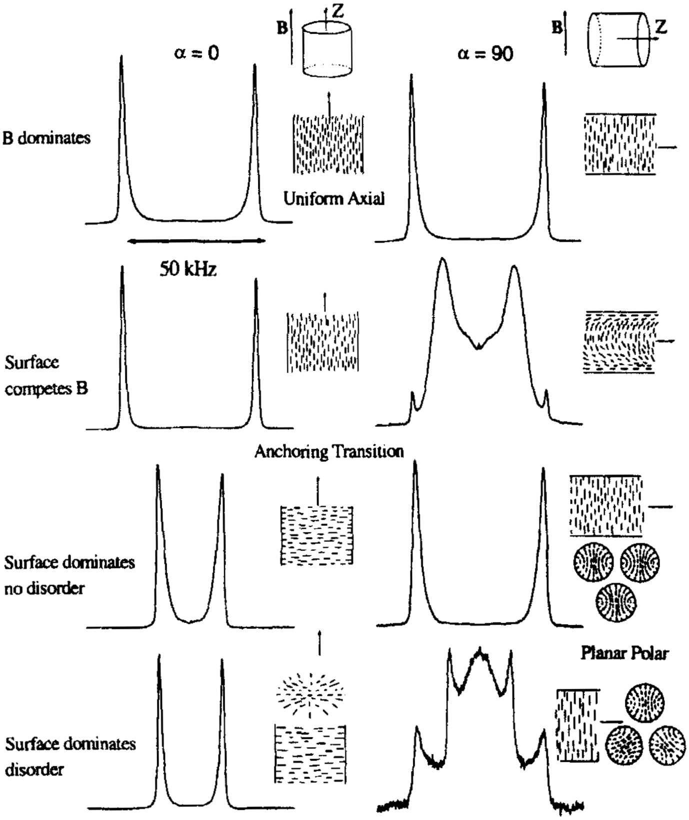

FIGURE 2. DNMR spectra in the smectic phase of 8CB in Millipore at two orientations with respect to the magnetic field. The molecular configurations sketched assume cylindrical pores of diameter comparable to the cavity size. In descending order, the Millipore sizes are 8, 0.45, 0.22, and 0.025 μm.

In the interconnected but larger Millipore cavities, the 8CB confined DNMR patterns are considerably different from those in aerogel. As seen in the left panels of Figure 2, with the Millipore strips normal parallel to the magnetic field, the DNMR pattern is nematic-like: a pair of absorption peaks signaling the onset of orientational order. Compared to bulk, for large cavity samples, the magnitude of the quadrupolar splitting is only marginally reduced. This is expected because in large cavities the magnetic field orients the liquid crystal molecules whose alignment is somewhat affected by the presence of weak surface-induced disorder. In stark contrast, in the smaller cavities, the quadrupolar frequency splitting drastically decreases to ½ that of the large cavity samples.

This can be understood as follows. When the average voids are larger than ξ_M, there is weak surface anchoring and LC molecules are reoriented and aligned by the magnetic field. With decreasing size, the molecular alignment is surface-dominated; liquid crystal molecules are mostly perpendicular to the field.

A more complete scenario emerges from studies at different sample angles with respect to the magnetic field. Also shown in Fig. 2 are results for four Millipore samples with the strips normal parallel (α = 90°) to the field. When most cavities are larger than ξ_M, regardless of orientation, the field aligns the liquid crystal; spectra at $\alpha = 0°$ and 90° are identical, as evident in the upper panels of Fig. 2. When the confining size is much smaller than ξ_M, surface-induced alignment dominates and there is an angular dependence as in the bottom four panels. If the alignment-inducing surfaces were of a isotropic nature, a Pake powder pattern, as that in aerogel, would be expected at all sample orientations. Thus, it seems that in Millipore its changing anisotropy plays a predominant role in determining the liquid crystal structure.

The nematic configurations in Millipore can be understood by if the random surfaces constrain the molecules to 2D planes such that for $\alpha = 0°$, all molecules are perpendicular to the field. Upon rotation, for the 25M sample, disorder introduced by the random surfaces is frozen-in and the liquid crystal molecules do not follow the field; the spectral pattern consists of four absorption peaks. With increasing cavity size, the surface influence weakens, disorder is no longer frozen-in but LC molecules are still constrained to 2D planes. After a 90° rotation, most LC molecules are effectively parallel to the field and are oriented by it; a bulk-like splitting doublet is obtained. Finally, for the 450M sample of average cavity size effectively equal to ξ_M, the planar alignment is lost; the random surfaces and the field compete to align the LC. At $\alpha = 0°$ they both promote the same type of orientation; they strongly compete for a preferred alignment at any other sample orientation. With decreasing size, a director configurational transition occurs which is driven by the changing anisotropy of the host. Resorting to an analogy with a cylindrical geometry, this is equivalent to a transition from a uniform axial to a planar polar configuration. These configurations are also sketched in Fig. 2.

CONCLUSIONS

We have presented DNMR results for 8CB confined to silica aerogel and Millipore membranes. In aerogel, the orientational order is characterized by powder-type DNMR spectral patterns for all densities but the highest. This indicates the presence of nematic domains randomly oriented, disordered by the isotropic structure of the random host. These domains are characterized by a single value of orientational order Q, although there may be some small variations, especially near the silica surface. In addition, this suggests a critical density for a defect free nematic ordering, $\rho < \rho_C \approx 0.5\,\text{g/cm}^3$. For $\rho > \rho_C$, equivalently, for confining sizes less than the nematic correlation length, the scenario is like that in Vycor glass, where a single absorption peak whose width continuously increases with decreasing temperature is found, indicating a continuous evolution of orientational order.

Retaining the randomness and interconnection but in less restrictive confining sizes, namely in Millipore, well-defined liquid crystal configuration are found. This is typified by a planar alignment and a director configuration transition driven by the host changing anisotropy as the confining size is reduced.

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