# Phase Behavior of the Liquid Crystal 8CB in a Silica Aerogel

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Light scattering and precision calorimetry show that the nematic ordering of octylcyanobiphenyl (8CB) filling the connected network of pores of a silica aerogel does not occur via the first-order phase transition characteristic of the bulk. Rather, ordering is continuous with an orientational correlation length never increasing beyond the aerogel pore size. The heat-capacity anomaly of the second-order nematic–smectic-$A$ phase transition seen in the bulk is absent or greatly broadened in the aerogel.

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There is currently a great deal of interest in finite-size effects in the phase behavior of isotropic fluids incorporated into connected pore networks in solid media. For example, the normal fluid-superfluid transition of helium 4 [1] and the phase separation of the two-component lutidene-water mixture [2] are modified by intercalation into silica aerogel and Vycor, respectively. Single-component liquid crystals (LCs) exhibit a variety of experimentally accessible phase transitions, involving orientational, and one-, two-, and three-dimensional translational ordering, some of which have been extensively studied in the bulk. The orientational and layer ordering are strongly influenced by surface interactions and exhibit long-range correlations near transitions, conditions that can be expected to produce novel finite-size effects. Aerogels are particularly attractive as hosts because the liquid crystal occupies a continuously connected network of pores comprising a substantial fraction of the total sample volume. In this Letter we report the results of light scattering and calorimetry study of the principal LC ordering events of the single compound octylcyanobiphenyl (8CB) confined in a silica aerogel. For bulk 8CB there is a weakly first-order isotropic-nematic and a second-order nematic-smectic-$A$ phase transition. We find that these bulk phase transitions are significantly altered in the connected porous network of the aerogel.

The phases and phase transitions of bulk 8CB have been extensively investigated, the material exhibiting isotropic ($I$), nematic ($N$), smectic-$A$ ($A$), and crystal ($X$) [3-5] phases as follows:

$$I(T_{IN}=40.5\,^\circ\mathrm{C})N(T_{NA}=33.7\,^\circ\mathrm{C})A(T_{AX}=21.5\,^\circ\mathrm{C})X\,.$$

The aerogel used here, which was made by base-catalyzed hydrolysis and condensation of tetramethoxysilane [6], has a mass density of $\rho=0.36$ g/cm$^3$. Debye-Anderson-Brumberger [7] and Porod [8] analyses of small angle x-ray scattering data [9] show a mean solid chord length of $\sim 45$ Å and pore size (void chord length) of $\xi_p \sim 175$ Å, respectively, void volume fraction of $\phi=0.79$, solid phase density of $\rho_s=1.75$ g/cm$^3$, and void surface to volume ratio $R_{SV}=0.024$ Å$^{-1}$. The 8CB-aerogel samples were prepared under vacuum using capillary action in the nematic phase to fill 0.5- and 1-mm-thick slabs of aerogel, obtaining in this way a very slow filling that leaves the silica aerogel structure intact. The faces of the sample used in the optical measurements were optically cemented to flat glass surfaces with a UV cure adhesive to minimize the formation of superficial bulk liquid-crystal layers.

The most visibly striking feature of our samples is the temperature dependence of their optical transparency, with the visible light transmission of a 1-mm-thick slab decreasing from $\sim 1$ at 40 °C to $10^{-13}$ at 25 °C and $10^{-18}$ at 5 °C. We have measured the turbidity $\tau = l^{-1}$, where $l$ is the transport mean free path [10] for the scattering of 5145 Å light in the range $6\,^\circ\mathrm{C} < T < 41\,^\circ\mathrm{C}$, finding a smooth monotonic increase of $\tau$ with decreasing $T$ shown in Fig. 1(a). For $35.5\,^\circ\mathrm{C} < T < 41\,^\circ\mathrm{C}$, the transmitted beam intensity could be measured directly in the 0.5- or in the 1-mm-thick sample. For $T < 35.5\,^\circ\mathrm{C}$, $l$ is sufficiently short that the intensity of multiply scattered light exiting the sample in the forward direction became large compared to that of the exiting direct beam, and $l$ had to be determined by fitting the intensity profile of the exiting multiply scattered light with the solution of the diffusion equation for light propagation in turbid media [10], derived for a Gaussian illumination profile and exponential extinction.

No noticeable optical hysteresis is present when the rate of heating and cooling is less than 0.03 °C/min. The 8CB-aerogel system in the isotropic phase is optically clear and remains so upon cooling down to 1° below the bulk $I$-$N$ phase transition temperature $T_{IN}$, i.e., the bulk nematic turbidity ($l \cong 620$ $\mu$m) does not appear at $T_{IN}$.

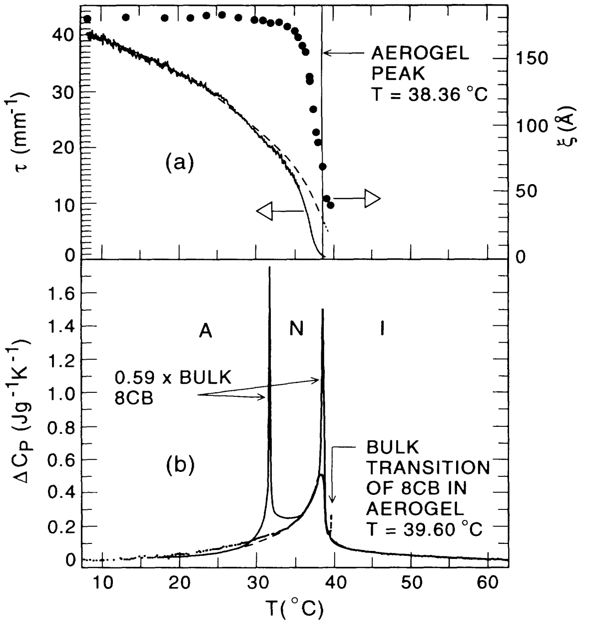

FIG. 1. (a) Temperature dependence of the turbidity, $\tau = l^{-1}$, of 8CB in the silica aerogel (——) and of the correlation length $\xi$ for nematic order (●) obtained from $\tau$ and Eq. (1). The dashed line shows the temperature dependence of $\Delta\varepsilon^2(T)$, scaled vertically to match $\tau$ at low temperature, indicating that the increase of $\tau$ for $T < 30\,°\mathrm{C}$ is due to the increase of $\Delta\varepsilon$. The dotted line is an extrapolation of $\Delta\varepsilon^2$ above $T_{IN}$. The vertical solid line is at 38.36 °C, the temperature of the peak in $\Delta C_P(T)$. (b) Temperature dependence of $\Delta C_P(T)$, the specific heat of 8CB in the silica aerogel (●) and in the bulk (——), both measured with mK resolution. The 8CB background specific heat, linear between 8 and 68 °C, has been subtracted. The small sharp peak at $T = 39.60\,°\mathrm{C}$ indicates the bulk transition of the 8CB in the aerogel, this peak coming from a small amount of 8CB in cracks, large pores, or on the surface. The bulk $\Delta C_P(T)$ has been scaled by a factor of 0.59 and shifted down in temperature to best match the 8CB-aerogel data away from the peak. The *NI* peak in the aerogel $\Delta C_P(T)$ is continuous, indicating that *NI* ordering occurs without a thermodynamic singularity. The bulk *NA* heat-capacity anomaly is greatly broadened in the aerogel, possibly appearing in the range $15\,°\mathrm{C} < T < 32\,°\mathrm{C}$ as the excess above the *IN* wing, indicated by the solid and dashed lines.

However, a small abrupt jump in turbidity ($\sim 1\%$) at $T = 39.6\,°\mathrm{C}$ is found, apparently a result of residual 8CB in cracks or large pores in the aerogel or on its surface. As $T$ is lowered, the sample becomes strongly light scattering, turning white like chalk, with $l$ decreasing to $\sim 25\ \mu\mathrm{m}$ at 6 °C. Note that the values of $l$ obtained in transmission ($T > 35.5\,°\mathrm{C}$) connect smoothly with those obtained in the diffusive regime ($T < 35.5\,°\mathrm{C}$). The turbidity shows no evident feature connected with the *N*-*A* or *A*-*X* transitions.

We have measured $C_P(T)$, the specific heat of the 8CB-aerogel sample, in the range $7\,°\mathrm{C} < T < 68\,°\mathrm{C}$, using ac calorimetry with mK resolution in $T$ [11], and show $\Delta C_P(T)$, the excess heat capacity per gram of 8CB associated with liquid-crystal ordering in Fig. 1(b) on the same temperature scale as the $\tau(T)$ data. $\Delta C_P(T)$ is obtained from $C_P(T)$ by first subtracting the specific heat of the empty aerogel (measured separately), and then subtracting an 8CB background contribution, which is linear between 8 and 68 °C, comparable to that of bulk 8CB. $\Delta C_P(T)$ shows a rounded, hysteresis-free peak at $T_p = 38.36\,°\mathrm{C}$, shifted down 1.24 °C from the minor resolution limited (mK wide) peak at $T = 39.60\,°\mathrm{C}$, coming from a small amount of residual bulk 8CB in cracks or large pores, or on the surfaces of the sample.

In order to compare the aerogel heat capacity with that of the bulk we also plot in Fig. 1(b) the bulk 8CB $\Delta C_P(T)$ data measured with comparable resolution in $T$ [5], shifted in temperature to overlap the aerogel peak, and rescaled down by a factor of 0.59, chosen to optimize the match to $\Delta C_P(T)$. For temperatures near the *IN* transition and above, the scaled and shifted $\Delta C_P$ bulk data match the aerogel $\Delta C_P(T)$ very well, indicating that the *I*-*N* pretransitional behavior is similar in the aerogel to that of the bulk behavior and that the aerogel $\Delta C_P$ peak is due solely to orientational ordering. This latter point was verified by x-ray diffraction, which shows that smectic ordering does not begin to appear until $T < 32\,°\mathrm{C}$ [12]. The scaling required indicates that only 59% of the 8CB is participating in the ordering, possibly a result of pinning of the other 41% at the 8CB-aerogel interface, as discussed below. Note that the peak in $\Delta C_P$ overlaps the temperature interval $35\,°\mathrm{C} < T < 39\,°\mathrm{C}$ where $\tau(T)$ changes rapidly.

Comparison of the bulk and aerogel $\Delta C_P(T)$ shows that in the aerogel 8CB exhibits no divergent heat-capacity singularity or latent-heat anomaly and thus that the bulk first-order *I*-*N* phase transition is replaced by a continuous nematic ordering. Also, the calorimetric data make it clear that incorporating 8CB into the aerogel has a much stronger effect on the *N*-*A* transition, the aerogel $\Delta C_P(T)$ exhibiting no sharp *N*-*A* transition peak like that observed in bulk 8CB. Figure 1(b) shows that there is a small smeared $\Delta C_P(T)$ excess over the scaled bulk *I*-*N* contribution, which may be associated with the local smectic ordering, which x-ray scattering shows appears over the broad temperature range 15–32 °C [12]. Outside of this range and away from the peak ($T < 38\,°\mathrm{C}$), $\Delta C_P(T)$ matches the scaled bulk values well, indicating a local saturation of nematic order comparable to that of the bulk in 59% of the 8CB. The nature of the smectic ordering of 8CB in the aerogel will be discussed in detail in a separate publication [12]. Crystallization of 8CB occurs at 21 °C in the bulk but is suppressed to below 0 °C in the aerogel.

The minor sharp features at $T = 39.6\,°\mathrm{C}$ noted above in the turbidity and $\Delta C_P(T)$ indicate the presence of a small amount of remnant bulk 8CB in the aerogel-8CB composite, either in large pores, in cracks, or on the surface. A similar bulk heat-capacity feature is found in the $^4$Heaerogel experiments [1]. The apparent $N$-$I$ transition temperature of this 8CB, $T=39.6\,^\circ\mathrm{C}$, is slightly below the observed bulk transition temperature of our 8CB sample, $T=40.2\,^\circ\mathrm{C}$. The fact that there is only a single sharp feature suggests that the lowering of this bulk temperature relative to that of the starting material is an impurity effect [13], rather than a size effect, since for the latter the shift would depend on the crack or surface film geometry, which is not controlled. During temperature cycling the difference in thermal expansivity between the aerogel and 8CB causes an exchange of 8CB between the pores and these bulk regions. Thus the secondary sharp feature should be a good indicator that $T=39.6\,^\circ\mathrm{C}$ is the bulk $T_{IN}$ for the 8CB in the aerogel.

A notable feature of the 8CB-aerogel system is that the optical mean free path $l$ decreases to values *far smaller* than those obtained with empty aerogel ($l \cong 4.5$ mm), with aerogel filled with isotropic 8CB ($l > 30$ mm), or with aligned bulk $N$ or $SA$ phase ($l > 0.5$ mm). The large difference in $l$ between the empty and nematic 8CB-filled aerogel indicates that the strong scattering is coming from refractive index fluctuations due *only* to spatial variation of the liquid-crystal director orientation, and not due to the index mismatch of the liquid crystal and aerogel. Thus, to interpret the $l$ vs $T$ behavior we can model the refractive index fluctuations of the 8CB-aerogel system as coming from nematic director reorientation fluctuations, i.e., as a nematic having a local director and optical anisotropy $\Delta\varepsilon$ within domains of characteristic size $\xi$, which are randomly oriented with a Debye orientational pair correlation function along a chord [7] $g(x) \sim \exp[-x/\xi]$. Following Puglielli and Ford [14], we find [15]

$$\tau = l^{-1} = \phi[2\xi^3 k^4 (\Delta\varepsilon/\langle\varepsilon\rangle)^2]/5[1+4\xi^2 k^2]\,. \qquad (1)$$

To extract $\xi(T)$ from $\tau(T)$ we used bulk nematic measurements of $\Delta\varepsilon(T)$ for the $n$CB family [5] for $T_{IN}-T < 20\,^\circ\mathrm{C}$ and extrapolated $\Delta\varepsilon$ to lower temperatures using the Maier-Saupe mean-field theory [16]. The resulting $\Delta\varepsilon(T)$ was then shifted in temperature to place the transition at the peak in $\Delta C_P$. The resulting temperature dependence of $\Delta\varepsilon^2(T)$ is shown plotted in Fig. 1(a) along with $\tau(T)$, using a vertical scale for $\Delta\varepsilon$ that superimposes $\Delta\varepsilon^2$ and $\tau$ at low temperatures. For $T < 30\,^\circ\mathrm{C}$, $\tau$ and $\Delta\varepsilon^2$ have essentially the same $T$ dependence, so in this regime we attribute the temperature variation of $\tau$ to $\Delta\varepsilon$.

Figure 1 shows $\xi(T)$ as obtained from $\tau(T)$ and Eq. (1) assuming for the ratio $\Delta\varepsilon^2/\langle\varepsilon\rangle^2$ the $T$-shifted bulk values, linearly extrapolated 1 °C into the pretransition region (dotted line). Upon decreasing the temperature from the isotropic phase, $\xi$ grows from about 30 Å (the noise limited minimum measurable $\xi$) to $\xi_{\max} \cong 180$ Å for $T < 25\,^\circ\mathrm{C}$. We thus find good quantitative agreement between the mean domain size from $\tau(T)$ and $\xi_p \sim 175$ Å, the mean pore size of the aerogel, indicating that the microscopic structure of the nematic is indeed a multidomain structure induced by the silica-8CB surface interaction, with orientational correlations limited to dimensions comparable to the aerogel pore size. The agreement also indicates that the pore size of the aerogel is not modified by the filling procedure.

We now consider the enthalpy change accompanying the nematic ordering in the aerogel, $\delta H_{\mathrm{ag}} = \int \Delta C_P(T)\,dT$, calculated numerically from the data of Fig. 1(b). We find $\delta H_{\mathrm{ag}} = 4.0 \pm 0.3$ J/g for $8\,^\circ\mathrm{C} < T < 68\,^\circ\mathrm{C}$, which can be divided into an $I$-$N$ contribution $\delta H_{IN\mathrm{ag}} = 3.6$ J/g and an $N$-$A$ contribution $\delta H_{NA\mathrm{ag}} = 0.4 \pm 0.15$ J/g estimated to be the excess over the scaled $I$-$N$ background for $15\,^\circ\mathrm{C} < T < 32\,^\circ\mathrm{C}$. These values may be compared to the corresponding bulk enthalpy of $\Delta H_b = 8.4$ J/g, composed of the $IN$ latent heat $\Delta H_{INb} = 2.1$ J/g, the $IN$ $C_P$ anomaly $\delta H_{INb} = 5.5$ J/g, and the $NA$ $C_P$ anomaly $\delta H_{NAb} = 0.8$ J/g [5]. Scaling these bulk values by 0.59 yields a net $IN$ enthalpy change of $0.59[\Delta H_{INb} + \delta H_{INb}] = 4.5$ J/g to compare with the aerogel value of $\delta H_{IN\mathrm{ag}} = 3.6$ J/g and an $NA$ enthalpy change of $0.59[\delta H_{NAb}] = 0.47$ J/g to compare with $\Delta H_{NA\mathrm{ag}} = 0.4 \pm 0.15$ J/g. Interpreted in this way it appears that the disorder imposed by the aerogel raises the enthalpy of the nematic order by $0.9 \pm 0.3$ J/g and of the smectic order by $0.07 \pm 0.15$ J/g. The downward temperature shift $\Delta T$ for establishment of substantial local nematic order must be a consequence of a nematic free energy in the aerogel which is excess by an amount $\Delta G = (\Delta T/T)[\Delta H_{INb} + \delta H_{INb}]$ over the bulk nematic. It is natural to consider that $\Delta G = \Delta U_{\mathrm{el}}$, where $\Delta U_{\mathrm{el}}$ is the elastic internal energy associated with director reorientation on the pore size length scale. This excess elastic energy can be estimated by considering a mean elastic constant $K \sim 3 \times 10^{-7}$ dyn [17], yielding $\Delta U_{\mathrm{el}} \cong 12K/\xi_{\max}^2 \simeq 0.04$ J/g, and $\Delta T \sim 0.6\,^\circ\mathrm{C}$, comparable to the 1.2 °C shift observed. $\Delta U$ may also arise from an 8CB-solid interfacial energy which increases with nematic order, which will be the case if the aerogel surfaces are disordering. Surface disordering is not only consistent with the fact that we do not observe increased nematic ordering above $T_{IN}$, but is also known to depress $T_{IN}$ in ultrathin 5CB samples confined between $\mathrm{SiO}_x$-coated plates which induce local disorder [18]. In the aerogel the large $R_{A/V} = 0.024$ Å$^{-1}$ means that $\sim 50\%$ of the 8CB volume is within a molecular length (20 Å) of a surface, so that it is possible that the pore walls act effectively as impurities: $I$-$N$ transition temperature shifts comparable to that found in the aerogel ($\Delta T \sim 1\,^\circ\mathrm{C}$) are observed in typical thermotropic liquid crystals when only $\sim 1$ vol% of a molecular dopant is present [13].

Because of the pore connectedness the random field Ising model (RFIM) with an asymmetric distribution of random fields [19] may describe some features of nematic ordering in the aerogel. Our finding that the ground state is multidomain and achieved without an ordering singularity suggests an RFIM in the regime where the field exceeds the threshold for pinning at zero temperature (region $m=2p-1$ in Ref. [19]). Such a ground state has in general no true phase transition to the high-temperature disordered state, as we observe. The $\Delta C_P(T)$ and $\xi(T)$ data show that as $T$ is lowered deviation of $\Delta C_P(T)$ from the bulk divergence begins at $\xi \sim 70$ Å, i.e., where $\xi$ has grown to become comparable to the mean pore radius, as is found for finite-size effects on second-order transitions [20].

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