Calorimetric Study of Phase Transitions in Confined Liquid Crystals

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Using an ac calorimetry technique we measured the specific heat at the nematic-isotropic, smectic-A-nematic, and smectic-A-isotropic phase transitions, for the alkylcyanobiphenyl liquid crystal nCB series confined to the 0.2-μm-diam pores of Anopore membranes. Studies were also performed as a function of nematic director alignment within the pores. Novel effects regarding specific-heat amplitudes, transition-temperature shifts, and broadening and rounding of phase transitions are found. They are strongly dependent on the director orientation and on the order of the phase transition.

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Surface effects in thermotropic liquid crystals have been studied mostly in nematic liquid crystals primarily because they are used in display cells where surface properties play a major role in their operation [1]. Surface effects may also be probed by confining liquid crystals to submicron-size pores. Deuterium nuclear magnetic resonance (^{2}H-NMR) work [2] on 4′-pentyl-4-cyanobiphenyl (5CB) confined to the pores of Nuclepore membranes [3], in the isotropic phase, found a weakly orientationally ordered molecular layer at the pore wall governed by local molecular interactions, and a temperature-independent surface order parameter. NMR studies were extended [4] to 5CB confined to Anopore membranes [5]. The degree of nematic order at the pore wall in the isotropic phase and the surface coupling constant were determined for various treatments of the pore wall. In the nematic phase, the NMR work led to the first experimental determination of the surface elastic constant K_{24} [6].

We present the *first specific-heat measurements* on the nCB (n is the number of carbons) liquid-crystal series confined to the nearly cylindrical pores of Anopore membranes. This work, which complements aspects of the NMR work [4] and parallels specific-heat work in confined superfluid helium [7], *simultaneously probes orientational and confining effects* at the weakly first-order nematic-isotropic (NI), the second-order smectic-A-nematic (AN), and the first-order smectic-A-isotropic (AI) phase transitions. Novel and striking phenomena strongly dependent on surface treatment, the order of the phase transition, and the molecular length are found. A quantitative analysis of the heat-capacity results and complementary phase shift information are deferred to a longer version of this paper [8].

Anopore membranes, produced from an electrochemical anodizing process [9], are made from a high-purity alumina matrix with 0.2-μm-diam pores extending through its 60-μm thickness [10]. They were cut, shaped as disks, and cleaned in an ultrasonic acetone bath. After solvent evaporation, they were dipped in the liquid-crystal material and heated deep into the isotropic phase, to insure complete filling of the pores. The liquid crystal outside the pores was completely removed by pressing the disks between Whathan filtration paper. The pores were also treated with lecithin, known to produce homeotropic surface alignment [11]. Confined liquid crystals with different director orientation were studied. From NMR [4], it is known that the 5CB nematic director in the untreated membranes is aligned parallel to the pores axis (axial case); after lecithin treatment, it is constrained in a radial type of alignment at the surface.

A single 0.9-cm-diam Anopore disk, completely filled with nCB material ($m < 3$ mg), was placed on a 1-cm-diam, 0.01-cm-thick sapphire disk. A 50-Ω evanohm heater and a 10-kΩ thermistor were glued to the sapphire disk with 1266 Stycast [12]. Temperature was regulated to about 0.3 mK and changed by 3–5-mK steps. In bulk studies, less than 8 mg of nCB material was used.

An ac technique [13], successfully used to study phase transitions in liquid crystals [14–16], operating at a typical heating frequency of 0.11 Hz and induced temperature oscillations of 2 mK or less, was employed. The addendum contribution was measured and subtracted from the total heat capacity. More details will be given elsewhere [17].

The specific heat at the NI transition for confined samples of 5CB, 7CB, and 8CB is shown in Figs. 1–3. In contrast with the bulk, no divergent specific heat is apparent. Sizable changes in transition temperature, peak height suppression, and rounding are evident and are stronger for the radial alignment. A broader transition is found as n increases (longer molecules). For the axial case, the specific heat retains the bulklike sharp decrease at T_{NI}; the radial case shows a more symmetric peak, reminiscent of continuous nematic ordering. The peak is more greatly suppressed for wider nematic range. Pretransitional effects appear to depend on director orientation (see inset of Fig. 3). At the same $t = |T/T_{NI} - 1|$, near and above T_{NI}, the specific heat is higher for the radial than for the axial case, both above bulk, reflecting the residual nematic order near the pore wall that extends deeper into the isotropic phase than shown here [4].

Bulk 5CB-lecithin mixtures were studied to determine whether detachment of lecithin from the pore wall contaminates the liquid crystals, thus contributing to these effects [18]. A nearly perfect specific-heat matching

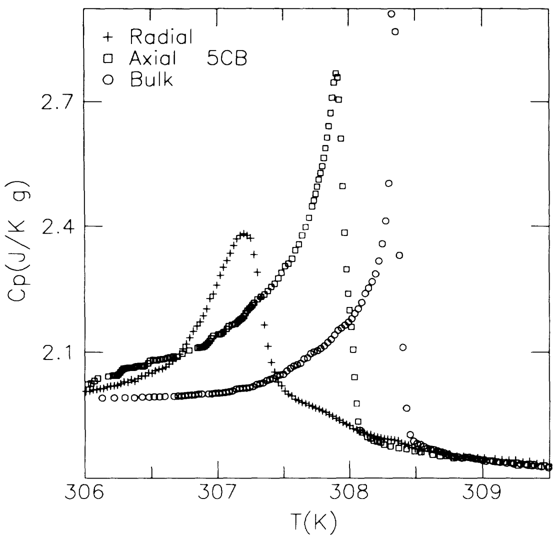

FIG. 1. Specific heat as a function of temperature at the *NI* phase transition for 5CB. The transition temperatures are 308.33, 307.89, and 307.20 K for bulk, axial, and radial alignment, respectively.

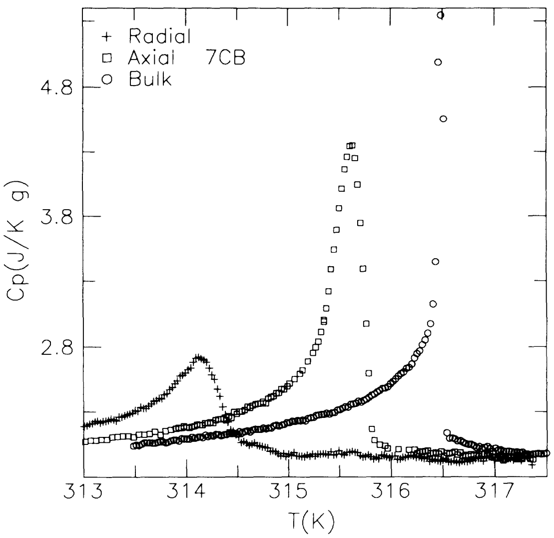

FIG. 2. Specific heat as a function of temperature at the *NI* phase transition for 7CB. The transition temperatures are 316.48, 315.61, and 314.11 K for bulk, axial, and radial alignment, respectively.

(identical pretransitional effects) on the nematic and isotropic sides was found. We calculated that a (3–5)% mixture (our estimate for the largest possible contamination in the radial case) would show a 0.01-K shift and less than 5% peak suppression. These effects are too small to be relevant on the scale of these observations.

The peak suppression might be understood by considering that, upon heating through the transition, only a fraction of the liquid-crystal material within the pores disorders (see also Ref. [19]). As a result of substrate inhomogeneities [10], pinning (weaker for the axial case) of liquid-crystal molecules at the wall surface is occurring. Increased pinning leads to a smaller peak as less material undergoes the transition. For axial 5CB, about 20% of the molecules need to be pinned, corresponding to a shell, about 100 Å thick, of nematic material. Surface-induced nematic lengths on this order have been seen in dielectric studies [20]. From NMR [4], the surface coupling constant, an order of magnitude larger for the radial than the axial case, leads to a smaller peak at T_{NI}, and a larger specific heat (residual nematic order) at the same reduced temperature above T_{NI}. Dielectric spectroscopy measurements would be useful for these systems.

Impurities and elastic strains induce a downward temperature shift, while surface-induced nematic order is expected to produce an upward shift [21]. The purity of all of our samples was determined to be better than 99.9%; our bulk transition temperatures are as high as reported in the literature. Our measured shifts, of the same order as in other confined liquid-crystal studies [19,22], are consistent with recent calculations by Lin, Palffy-Muhoray, and Lee [23]. In the radial case, the shift is mostly due to the surface aligned (nematic) material at the pore wall acting as an imposed deformation. Nematic material near the center of the pore must arrange to minimize the elastic energy in accordance with the existing distortion [22]. Expressing the free energy up to quadratic terms in the order parameter, the shift due to elastic distortions is given by $\Delta T = (\kappa/2a_{20})(2\pi/R)^2$. The Frank elastic constant is assumed to behave as $\kappa \approx \kappa_0 S^2$, with S the nematic order parameter, and a_{20} is the constant of the temperature-dependent coefficient of the quadratic term in the free energy. Using typical values for *n*CB materials we find $\Delta T \approx 1$ K, in reasonable agreement

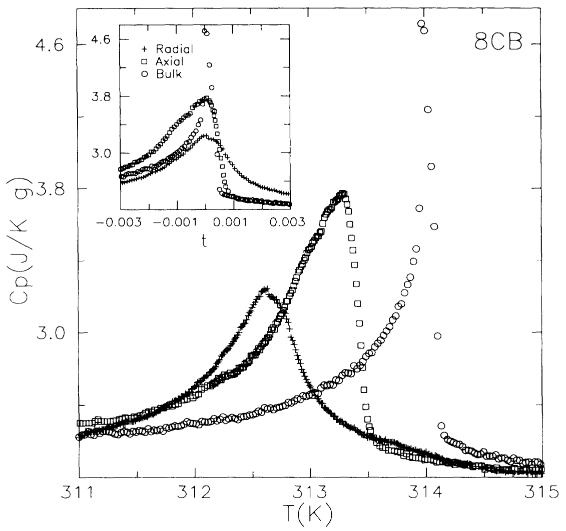

FIG. 3. Specific heat as a function of temperature at the *NI* phase transition for 8CB. The transition temperatures are 314.02, 313.27, and 312.62 K for bulk, axial, and radial alignment, respectively. Inset: Same data as a function of reduced temperature.

with our results. In the axial case, the shift, surprisingly, is related to the weaker surface coupling constant (see PIBMA treatment in Ref. [4]). The measured transition temperatures were reproducible to within 0.1 K when different batches of Anopore were used. These differences, likely due to impurities, are 7 times smaller than the smallest experimental shift. Studies as a function of pore size, with Nuclepore, would be useful.

The specific heat at the *AN* transition for 8CB, as a function of reduced temperature, is shown in Fig. 4. The peak is dramatically suppressed, nearly vanishing for the radial alignment. The peak heights are 16% and 7.5% that of bulk, for the axial and radial cases, respectively. Confinement has a much stronger effect for the *AN* than for the *NI* transition for both alignments, with a larger suppression for the radial case (5 times) than for the axial (3.5 times). As the pore size is decreased, we expect [19] that the *AN* peak will disappear while the *NI* peak will remain prominent; this will occur at a pore size dependent on director orientation.

Finite-size effects, aside from orientational effects, are important at a second-order phase transition. A rounded specific heat, as found for both alignments, is a signature of finite-size behavior [7]. The larger suppression on the radial specific-heat peak may be partly attributed to the lecithin treatment which introduces a stronger surface interaction (thicker nematic shell) effectively reducing the pore size. For example [24], for $t=(T-T_{AN})/T_{AN}=10^{-3}$, $\xi_\parallel$ is 380 Å, comparable to the pore radius.

Although a larger peak is found, T_{AN} shifts to lower temperatures for the axial than for the radial case, contrary to the T_{NI} shift. The nematic range is slightly wider for the axial case than for bulk but 1 K narrower for the radial case. If impurities (inherent to Anopore) were the main reason for the shifts, we expect the transition temperature to be always lower for the radial than the axial case due to larger elastic strains present in the radial alignment. This is contrary to what we observe at the *AN* and *AI* transitions (see below). Therefore, impurities play a secondary role here.

X-ray studies of samples confined to larger pore sizes [25] showed that smectic layers (distorted and of variable thickness and separation) form only near the pore wall as the energy cost to completely bend the nematic director near the center of the pores would be high; a radial nematic configuration is retained to lower temperatures as smectic layers are less tolerant of elastic distortions. These effects are stronger for the smaller pore size in Anopore. Axially aligned smectic layers are affected by the weak surface anchoring at diametrically opposing surfaces. With decreasing pore size, smectic layers that uniformly span the entire diameter of the pore are increasingly more difficult to form. This may explain the lower *AN* transition temperature found for the axial case. X-ray studies on Anopore are needed.

We also studied the first-order *AI* phase transition for 10CB and 12CB. For brevity, only data for 10CB are shown (Fig. 5). Unexpectedly, the bulk specific-heat

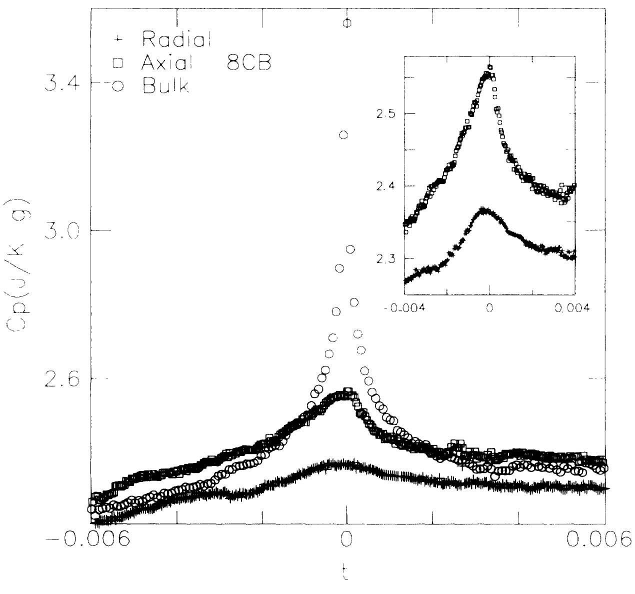

FIG. 4. Specific heat as a function of $t=|1-T/T_{AN}|$ at the *AN* phase transition for 8CB. The transition temperatures are 307.02, 306.12, and 306.38 K for bulk, axial, and radial alignment, respectively. Inset: Expanded plot for axial and radial cases.

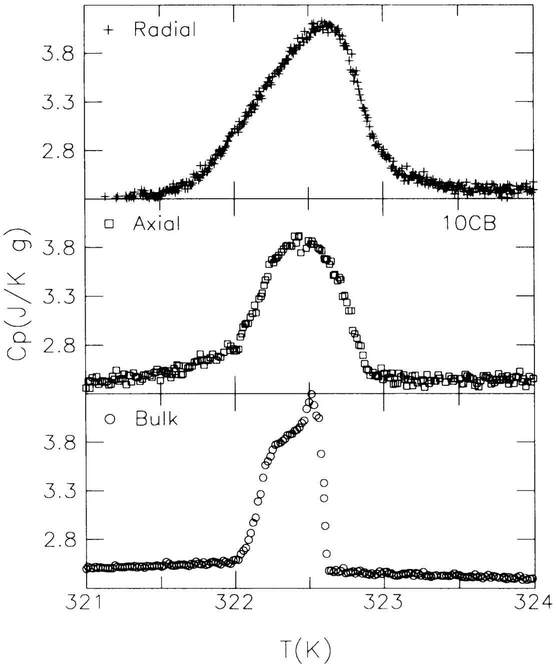

FIG. 5. Specific heat as a function of temperature at the *AI* phase transition for 10CB. The transition temperatures are 322.52, 322.47, and 322.60 K for bulk, axial, and radial alignment, respectively.

data show a sharp peak on top of a broader bump. This, only seen at the *AI* transition, may be related to the curvature of the bulk drop, and a temperature-dependent anchoring energy [26]. For instance, focal conic textures have been studied using a similar experimental configuration [27]. The data for confined samples show a smoother and broader peak than for the bulk, weakly dependent on surface treatment. Unlike the *NI* or *AN* transitions, there is no peak suppression and no temperature shift for the axial case; a small upward shift is found for the radial case. This is similar to the *AN* transition where T_{AN} was higher for radial (narrow nematic range) than for axial alignment (wider than bulk nematic range). The confined *AI* transition should be probed with other techniques.

We have presented *the first specific-heat studies* on *n*CB liquid crystals confined to Anopore membranes as a function of orientation, molecular length, and order of phase transition. Strong, and in some cases surprising, departures from bulk behavior have been observed. The first-order *AI* transition appears to be the least affected by confinement or orientation, with a transition broader than for the bulk. The *NI* transition is strongly dependent on the director orientation within the pores and the nematic range of the material; the *AN* transition is also affected by confinement and is likely to disappear with decreased pore size. To separate orientational from confining effects, studies as a function of pore size (with Nuclepore membranes) are under way.

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