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Ellipsometry at the nematic-isotropic phase transition in a confined geometry

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Small, parallel, cylindrical pores in a thin polymer film were impregnated with the liquid crystal pentylcyanobiphenyl. Optical retardation measurements, performed around the bulk nematic-isotropic phase transition temperature, are reported. Relative to the bulk, a depression ΔT_{NI} of the phase transition temperature region was observed, although for the smallest diameter pores ($d=150$ Å), ΔT_{NI} was found to be larger than expected. The profile of the optical retardation vs temperature was also found to be anomalously sharp for the $d=150$ Å pores. The results are discussed in terms of current models.

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The physics of fluids in confined geometries is rich and complex. Studies of structure, phase transitions, and dynamic behavior have often been enigmatic, requiring additional and more incisive efforts to develop a comprehensive understanding of these systems. After early investigations of liquid crystals in pores [1,2], significant efforts were made on ^{4}He at the superfluid transition [3,4] and on binary liquid mixtures (BLMs) at a consolution point [5–7]. Recently, attention has refocused on liquid crystals and their phase transitions in highly restricted geometries [8–14]. Unlike in ^{4}He and BLMs, orientational symmetry is broken in liquid crystals. The feature adds an additional complexity to the problem and, in consequence, has added to our understanding of the problems of both confined fluids in general, as well as finite-size effects on liquid crystals.

During the 1970s Sheng [15,16] theoretically studied wetting at the nematic-isotropic (NI) phase transition in confined films. He showed that the transition temperature $T_{\mathrm{NI}}(t)$ increases with decreasing film thickness t and that the NI coexistence line on a temperature-thickness phase diagram terminates at a critical point. More recently, Poniewierski and Sluckin (PS) [17,18] have extended his theory by including disordering surface effects, whereby near an interface a given molecule has fewer nearest neighbors with which to interact. This tends to reduce the order and thus facilitates the possibility of a decrease in T_{NI} with decreasing film thickness. A similar approach was used in a lattice model of free-standing liquid-crystal films [19,20]. Experimentally, Kuzma and Labes [21] studied pentylcyanobiphenyl (5CB) impregnated 0.2-μm-diam cylindrical pores in polycarbonate Nuclepore membranes [22]. They found a depression of T_{NI} by ~ 1 K, attributing this behavior to a pinned disclination and the associated free energy cost of the surrounding elastic deformation. A similar depression in T_{NI} was observed by Zidansek *et al.* [14] in a porous silica aerogel. In a systematic study involving polyvinyl alcohol-treated and SiO-treated substrates, Yokoyama [23] found both an increase and a decrease in T_{NI}, as well as a critical point, depending upon the ordering or disordering nature of the substrate. His results were in good qualitative and semiquantitative agreement with the models of Refs. [16–18].

A major success in understanding the influence of confinement not only on the nematic-isotropic phase transition but the effect of confinement on molecular ordering of nematic liquid crystals was achieved in 1988 by Golemme *et al.* [24]. Nematic droplets in a polymer matrix were studied by deuterium NMR, and for droplets less than 350 Å in diameter it was shown that a small degree of orientational order ("paranematic order") still exists, even at temperatures corresponding to a bulk isotropic phase. Moreover, it was shown that the NI phase transition is replaced by a continuous evolution from paranematic to nematic order. This work represented a clear experimental confirmation of the theoretical prediction [15] that the NI coexistence curve in a restricted geometry terminates at a critical confinement size. This research [24] was complemented by a detailed theoretical analysis [25] of possible structures within a confined spherical nematic droplet and the effects of the surface interaction strength, droplet radius, and sample temperature on the stability of these structures. In addition, a series of detailed investigations soon appeared that examined the orientational order [26], elastic properties [27], and the director field [28] of confined liquid crystals by NMR techniques. Further studies on anchoring and the orientational wetting transition [29], as well as on issues involving director configurations [30], have recently been reported.

With the advent of "microconfined" systems—liquid crystals confined to regions no more than a few nematic correlation lengths in extent—new investigations have

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become possible. Iannacchione *et al.* [12] have studied 5CB by ^{2}H-NMR and calorimetry in a random porous glass network, where the average pore diameter was ~ 70 Å and the length ~ 300 Å. They found a significant depression of the temperature of the NI transition region, which is consistent with a Landau–de Gennes model having either a large disordering term or surface-induced deformations. Additionally, they found that the transition region was even more spread out than expected—the very small pore size placed the sample beyond the critical point on the temperature-thickness phase diagram—owing largely to the required averaging over a wide distribution of the coefficient of the disordering term in the Landau free energy. The continuous change of orientational order with temperature is also consistent with light scattering and calorimetry data for octylcyanobiphenyl in a silical aerogel [9]. Other work has been done on the effects of aligning agents, such as lecithin in silica aerogels [11] or aliphatic acid on alumina membranes [29], in which several effects were observed, including surface ordering in the isotropic phase, a spread of the NI transition region, and orientational transitions of the director profile. We may thus draw several general conclusions from these various studies. The orientation within the cell may be modified by surface agents or temperature. For sufficiently confined samples, the NI transition becomes rounded, independent of orientation, and significant orientational order may exist at temperatures corresponding to the bulk isotropic phase. However, the suppression (or enhancement) of the transition temperature region and its mechanism are not well established, and the role of "end effects" (i.e., significant pore curvature) is not well understood. Moreover, the polydispersity of both pore size and orientation has often made analysis of the data quite ambiguous.

The purpose of this paper is to report on temperature-dependent birefringence measurements for 5CB in parallel, cylindrical pores that run perpendicular to the plane of a polymer film. The motivation for this work was to determine the influence of pore size in a simple geometry on the nematic-isotropic phase transition and to investigate the concomitant ordering of liquid crystals using optical retardation methods. Such studies provide us with quantitative information about the behavior of liquid crystals as a function of temperature, whereas visual observations using polarizing microscope [21] provide only the average NI phase transition temperature. Conceptually, we need to distinguish between two effects that influence the physical properties and behavior of liquid crystals in pores: (i) effects due to randomness and (ii) effects due to confinement. For our case of cylindrical pores, the problem of the influence of the randomness simply does not exist owing to the structural properties of the matrices. Moreover, the geometry of the confining pores in our experiment is quite simple and permits us to exclude the influence of disorder, which arises from random porous structures in, e.g., Vycor or aerogel-like porous media. Issues involving confinement therefore dominate the problem and are discussed herein.

For parallel cylindrical pores we might expect the birefringence Δn would be approximately proportional to the scalar nematic order parameter S, where $S=\langle \frac{3}{2}\cos^2\theta-\frac{1}{2}\rangle$ and θ is the orientation of the principle molecular axis. Since the thickness of the porous films is small, they are sufficiently transparent to observe Δn with ordinary optical methods after impregnation with a liquid crystal. Three different pore sizes were examined, such that for all three pore sizes we found a rounding of the NI transition, as well as a depression of the transition region relative to that of the bulk. The observed trends, however, are not monotonic in pore diameter and raise important issues about the analysis of data in these systems.

Polyethylene terephthalate films of thickness 10 μm were prepared by the heavy-ion method [31,32] at the United Institute for Nuclear Research in Dubna, Russia. The original films were bombarded by heavy ions and the resulting tracks were leached by an alkali with subsequent washing of possible chemical impurities from the pores. We note that chemical purity was established by spectroscopic methods, which show an absence of incidental inclusions. The final pores are therefore cylindrical and approximately parallel. (Deviations from mutual parallel orientations were less than 5°.) The pore diameters were determined by means of electron microscopy and found to be $d=(150\pm30)$ Å, $d=(350\pm50)$ Å, and $d=(3000\pm300)$ Å. We note that between crossed polarizers, the film was observed to be optically birefringent, with two eigenvectors $\vec{\varepsilon}_1$ and $\vec{\varepsilon}_2$ corresponding to nondegenerate optical eigenvalues lying in the film plane (Fig. 1). Thus it is important to achieve proper alignment of the film, as described below, in the birefringence apparatus.

A film fragment of area 1 cm^2 was placed into a watch glass and immersed in 5CB at 42 °C (~ 7 °C above the bulk T_{NI}) for 72 h. The film was then removed and gently wiped with a Kimwipe cloth [33] until no additional bulk material could be detected at the surface of the film. The impregnated film fragment was then placed between two microscope slides; very little light scattering was observed by eye, as the film was nearly transparent. The

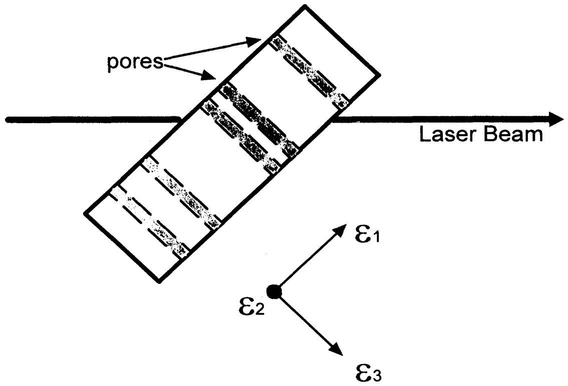

FIG. 1. Schematic representation of the experimental geometry.

glass-encased film was placed into an oven, which was temperature controlled to 50 mK. The assembly was then placed into a birefringence apparatus based upon a modulated Pockels cell, which is described in detail elsewhere [34]. Because the main symmetry axis of the sample ($\vec{\varepsilon}_3$) is perpendicular to the film, the film was rotated about its $\vec{\varepsilon}_2$ axis by an angle of 45°, where $\vec{\varepsilon}_2$ is perpendicular to the laser beam. This geometry facilitates an optical retardation measurement of the liquid crystal, as the apparatus measures the retardation between two modes: one polarized perpendicular to the pores ($\vec{\varepsilon}_2$) and the other having a component of polarization parallel to the pore axis (in the $\vec{\varepsilon}_1$-$\vec{\varepsilon}_3$ plane). Moreover, in this geometry the total retardation is a sum of the retardation due to the liquid crystal plus the inherent contribution of the film. In consequence, the film's birefringence could simply be subtracted off.

Figure 2 shows the adjusted birefringence vs temperature, with data taken on cooling from 55 °C to approximately 16 °C. The data were adjusted in two ways. At high temperatures the total retardation was found to approach a limiting value for each film, corresponding to the birefringence of the film itself. Thus the "background birefringence" at 55 °C was subtracted from all the data for each pore size. Although a remnant contribution from the liquid crystal likely exists at this temperature (well above the bulk $T_{\rm NI}$), it was apparently small and would not significantly affect the interpretation of the results. The second correction involves a linear scaling of the retardation. As the pore density differs significantly from one film to another, the absolute retardation differs as well. In consequence, we have scaled the birefringence data so that after subtracting off the background due to the film, the scaled retardation was set equal to unity at ~ 16 °C.

Several features are immediately apparent from Fig. 2. For the largest pore size $d = 3000$ Å, the crossover from isotropic to nematic appears to be discontinuous, or at least nearly so; the temperature resolution of the apparatus did not permit an unequivocal determination of the order of the transition, although the apparent jump seems to argue for a first-order transition. The theories of Sheng [15,16] and of Poniewierski and Sluckin [17,18] predict a thickness-dependent critical point which depends upon the values of the ordering and disordering parameters. Under different anchoring conditions in nearly planar cells Yokoyama [23] found that the critical thicknesses $d_{\rm cr}$ are approximately 920 and 180 Å, both considerably smaller than the diameter of our pores. Additionally, we note that there is a small pretransitional increase in the retardation above the transition, similar to the partial wetting behavior observed by Miyano and others [35,36,37]. If the surface-induced order parameter $S_{\rm surface}$ were larger than δS, where δS is the order parameter discontinuity at the bulk NI transition, one would expect a *divergence* of the retardation near $T_{\rm NI}$ [35,36]. Although the retardation is limited by the finite extent of the pores, the apparent smallness and nondivergent behavior of the retardation at the transition is likely indicative of weak (rather than strong) ordering at the surface, at least where $S_{\rm surface} < \delta S$. We can estimate $S_{\rm surface}$ by noting that for bulk 5CB at 20 °C the order parameter $S_{\rm bulk} \sim 0.65$ [38]. Moreover, just above the bulk $T_{\rm NI}$ the correlation length ξ is typically ~ 150 Å, corresponding to a volume fraction $f \sim 0.1$ of oriented liquid crystal for pores of diameter $d = 3000$ Å. Thus $S_{\rm surface} \sim [(\text{scaled retardation}) \times S_{\rm bulk}/f] \sim 0.18$. Finally, we note that the apparent transition temperature $T_{\rm NI}$ is ~ 1.5 °C below the bulk transition temperature. The depression of $T_{\rm NI}$ is qualitatively consistent with the existence of a disordering term in the free energy, wherein the Kelvin equation predicts a depression $\Delta T_{\rm NI}$ $[\equiv T_{\rm NI}(d) - T_{\rm NI}(\text{bulk})]$ $\propto d^{-1}$ [21]. The observed $\Delta T_{\rm NI}$, however, seems to be somewhat larger than might be expected theoretically with realistic material parameters [18] and may be due in part to elastic effects. Simoni *et al.* [31] inferred planar-radial anchoring conditions for a cyanobiphenyl mixture (Merck mixture E7) in these porous films, which would also give rise to an elastic depression of the transition temperature, in this case $\Delta T_{\rm NI} \propto d^{-2}$ [19]. In fact, the elastic model predicts a $\Delta T_{\rm NI}$ of approximately -0.5 °C, which is smaller than that observed. This issue will be considered again below.

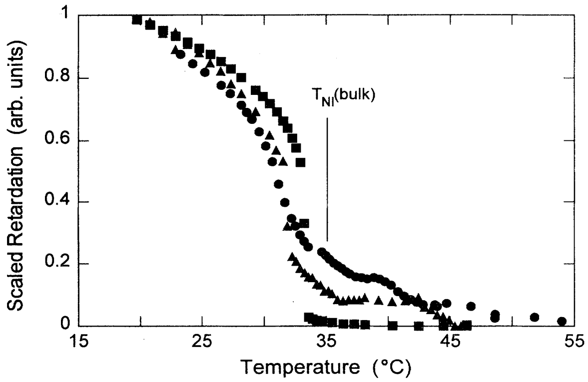

FIG. 2. Scaled retardation (see the text) vs temperature. ■ corresponds to the $d = 3000$ Å pores, ● to the $d = 350$ Å pores, and ▲ to the $d = 150$ Å pores.

The adjusted retardation for the $d = 350$ Å films is qualitatively consistent with the model of PS. As the data exhibit significant rounding, we can safely place the thickness $d < d_{\rm cr}$. The pretransitional wetting is also enhanced: Not only is the pore diameter smaller and closer in size to the (temperature-dependent) nematic correlation length, but the lateral surface region of the pores comprises a larger fraction (approximately $\propto d^2$, or about a factor of ~ 75 larger than for the $d = 3000$ Å pores) of the total pore volume. Thus, as a fraction of the order at 20 °C, the liquid crystal in the smaller 350-Å pores exhibits considerably more retardation in the high-temperature region than does the liquid crystal in the larger pores. We also note that the apparent "transition temperature"—actually, the midpoint of the rounded transition region—has been suppressed by approximately

6 °C from the bulk T_{NI}. Although the Kelvin equation is generally valid only down to d_{cr} [18], it can be satisfied if partial wetting conditions obtain. Here theory would predict ΔT_{NI} to be ~ 8 times larger than for the $d = 3000$ Å case, or approximately -10 °C. This theoretical prediction is *larger* than the experimental value of ΔT_{NI}, although the theoretical and experimental results are not too dissimilar. On the other hand, the elastic-induced depression of T_{NI} would predict a *much larger* $\Delta T_{\mathrm{NI}} \sim -40$ °C, which is clearly inconsistent with experiment. To be fair we note that neither picture perfectly models the data and, with different choices of parameters, the elastic picture can be forced to better mimic the experimental observations.

The smallest pore size $d = 150$ Å is an enigma: Not only is the apparent suppression of the transition temperature region smaller than for the $d = 350$ Å sample, but the transition is less rounded as well. These results are inconsistent with extant theory, insofar as the theories consider a specific anchoring profile. If the anchoring and resulting director profile for $d = 150$ Å pores were *not* planar radial, then both the disordering and ordering coefficients in the Landau theory would be different from the case of the larger pore sizes. This would give rise to both a different retardation vs temperature profile, as well as a different ΔT_{NI} from what would be expected in a purely planar-radial configuration. Another possible reason for the anomalous behavior associated with the $d = 150$ Å pores would involve temperature-dependent elastic constants and/or anchoring strengths. Imagine that the director configuration for all three pore sizes were the same but were *not* planar radial, as inferred by Simoni *et al.* [31]. Instead they might be, e.g., planar polar [28,30]. In this case the equilibrium director profile throughout the pore would involve at least two temperature-dependent elastic constants, as well as the anchoring strength coefficient. In consequence, as the relative values of these constants change with temperature, the director profile in the pore would change as well. Under these conditions one cannot assume that the measured retardation is proportional to S, a situation that becomes particularly egregious in smaller pores where elastic effects are especially important.

Taken as a whole, the results indicate that in smaller pores the NI transition becomes continuous and there is a depression in the transition temperature region. The variation of the retardation with temperature, which can be equated approximately with a temperature variation of the nematic order parameter, is somewhat stronger than observed by Iannocchione *et al.* [12] using NMR in random porous media. This behavior might be attributed to the likelihood in the network of Iannocchione *et al.* of more and especially a wider distribution of defects, producing a spread of transition temperatures in the random porous medium. Although somewhat equivocal, the data indicate that ΔT_{NI} in our system is primarily due to the disordering effects of the interface rather than pinned deformations. Moreover, behavior of the retardation in the smallest pores might indicate a director configuration different from the larger pores or a configuration that might be changing rapidly with temperature. Clearly this a system with extraordinarily rich physics, which will require significantly more work in order to achieve a fuller understanding of the variety of physical phenomena just being uncovered.

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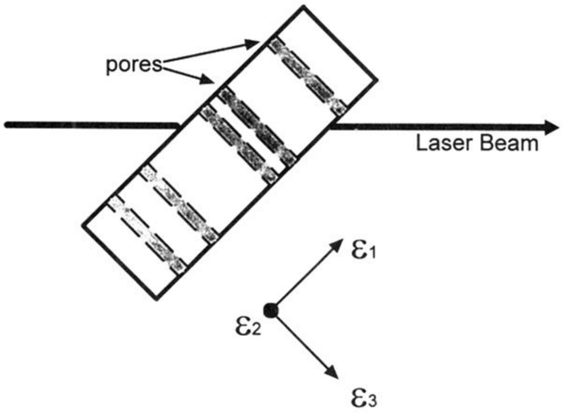

FIG. 1. Schematic representation of the experimental geometry.