

Direct measurement of surface-induced orientational order parameter profile above the nematic – isotropic phase transition temperature

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The spatial and temperature dependence of the surface-induced orientational order parameter $S(z, T)$ was determined in the isotropic phase. An optical fiber was immersed in a thin liquid crystal layer and the retardation was measured as a function of the fiber's height above the surface, from which the *model-independent* $S(z, T)$ was deduced with resolution $\sim 1 - 2$ nm. It was found that: i) $S(z = 0) \lesssim 0.12$ close to the nematic transition temperature, ii) the susceptibility is mean-field-like, and iii) $S(z, T)$ deviates significantly from exponential spatial decay. The results are discussed in terms of a nonlocal potential.

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The subject of surface-induced orientational order at the nematic-isotropic (NI) phase transition has received extensive scrutiny — both experimental and theoretical — over many years [1–22]. Above the bulk NI transition temperature T_{NI} , an appropriately prepared surface induces nematic ordering in the otherwise isotropic bulk phase, with the orientational order decreasing as one moves away from the surface and into the bulk. The behavior of the scalar orientational order parameter $S(z) [\equiv \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle]$, where θ is the angle from the nematic director \hat{n}] depends on the nature of the interaction energy between the liquid crystal and the alignment layer(s), the physical properties and thickness of the liquid crystal layer, and the temperature T . It generally is assumed that the surface potential is localized to the interface at $z = 0$ [3, 5, 10, 11]. In this context, the uniaxial order parameter at the interface $S_0 [\equiv S(z = 0)]$ is determined by the form of the potential, which can contain both ordering and disordering components [3, 5, 9, 11]. If the surface-induced order is not sufficiently large, only partial wetting by the nematic phase occurs. On the other hand, if the interaction between the liquid crystal and the surface is sufficiently strong, $S(z)$ integrated through the cell thickness diverges logarithmically on approaching the first order phase-transition temperature [1–3, 12]; this would correspond to complete wetting by the nematic phase. Moreover, “capillary condensation” – a transition to the nematic phase in a localized boundary layer – has been predicted theoretically [4, 11] and observed experimentally [13, 17–19]. Sheng also predicted [5] a “prewetting transition” in which there is a discontinuous jump of the order parameter at the surface at a temperature $T > T_{NI}$; this has been observed by means of calorimetry in confined pores [22].

To date quantitative determinations of the order parameter profile $S(z)$ as a function of temperature have used probes with visible light wavelength resolution — this is much larger than the length scale of the surface layer — and so required specific models in conjunction with this macroscopic data in order to extract $S(z)$. The earliest and still most common approach is that of Miyano, who measured the integrated optical birefringence (approximately proportional to the integral of $S(z)$ through the cell thickness) and fitted this macroscopic data to a Landau mean-field description of the nematic order [1, 2]. As a result, deviations of the actual orientational profile from a specific model may not be readily apparent, as the data may fit many different profiles $S(z)$ and surface potentials equally well. Even improved techniques that measure local quantities, such as evanescent wave and second harmonic generation experiments [6–9], ultimately require specific models to extract

order parameter profiles on very short length scales. Recently, however, has shown that a tapered optical fiber may be immersed into a liquid crystal and, as it is moved through the liquid crystal, the resultant light output through an analyzer is well approximated by the total optical retardation from the fiber aperture through the birefringent medium to the surface [23, 24]. This allows us to obtain orientational order information in three dimensions out to $z \sim 500$ nm above the interface, with lateral resolution of ~ 125 nm and vertical resolution as small as a few nanometers. Here we apply this technique to surface-induced nematic order, whereby we immerse the fiber into a thin liquid crystal film and measure the optical retardation α between the fiber aperture and the substrate as a function of the aperture's height h and temperature $T > T_{NI}$. This allows us to extract the *model-independent* profile $S(z)$ vs. T close to the substrate. In particular, we find that $S_0 \lesssim 0.12$ and that S_0^{-1} vs. T is mean-field-like, scaling approximately as $T - T^*$, where T^* is the supercooling limit of the isotropic phase, indicating the absence of capillary condensation in our system for the temperatures studied. Moreover, we found that $d\alpha/dh$ varies slowly with h out to $h \approx 10$ nm, substantially different from the quasi-exponential decay expected for weak surface-induced order in the absence of capillary condensation [3, 5]. This behavior will be discussed in terms of nonlocal interactions at the interface.

A glass substrate was spin-coated with the polyamic acid RN-1175 (Nissan Chemical Industries, Ltd.), prebaked according to manufacturer's specifications at 100 °C for 3 min, then fully baked at 230 °C for 60 min to achieve near complete imidization. To establish the azimuthal orientation of the planar alignment, the polyimide-coated slide was rubbed with a rubbing strength $n_f = 1.5 \times 10^6$ cm⁻¹ using a cotton cloth and rubbing machine; details of the rubbing may be found in Ref. [25]. The slide then was coated with a thin film (a few μm) of the liquid crystal pentylcyanobiphenyl ("5CB", Merck) and placed into a Veeco Aurora near field scanning optical microscope (NSOM). [See Ref. [24], Fig. 1 and Supplementary Fig. 1]. The fiber was illuminated by circularly polarized light at wavelength $\lambda = 532$ nm that first passed through a light chopper. The light emerged from the fiber's output tip (diameter $d_f < 200$ nm, including cladding), which was immersed into a thin layer (a few μm) of liquid crystal. The approximately circularly polarized transmitted light (extinction ratio $\sim 1.2 : 1$) passed through the liquid crystal, the alignment layer, the glass slide, an analyzer rotated by 45° with respect to the rubbing direction, and was collected downstream by a photomultiplier tube. The output from the photomultiplier was input

to a lockin amplifier referenced to the light chopper; a 10 s time constant output filter was used. A long time constant was needed because of the very high level of noise due to the low signal strength and order parameter/director fluctuations of the liquid crystal in the small gap between the fiber aperture and substrate. The entire assembly, including the fiber, motion control, and collection optics, were housed in a box; a string of resistors was placed along the inner walls of the box and used as a heating source in conjunction with a temperature feedback system; not only was good thermal stability (< 10 mK) maintained during data collection at each temperature, but also good temperature homogeneity as well (< 5 mK cm^{-1}).

The sample was stabilized in the isotropic phase about 1.8°C above T_{NI} and the fiber was lowered so that it made contact with the substrate, corresponding to $z = 0$. In light of the long time constant filter, the intensity was recorded after a delay of approximately 50 s. The fiber then was elevated a few nanometers to height z_1 , the signal was allowed to stabilize for another 50 s, and the intensity was again recorded. This procedure was repeated about 20 times in order to construct an intensity I vs. height h profile at this temperature. The temperature then was reduced by a few tens of millikelvins and, after allowing 2 h for the temperature to stabilize, the measurement procedure was repeated to obtain I vs. h at this temperature. Data were collected at multiple temperatures down to $T_{NI} + 50$ mK; Figure 1a shows I vs. h for all temperatures relative to T_{NI} , where the position of each baseline varies from run to run. It is apparent from the data that I varies linearly with h out to ~ 10 nm, beyond which dI/dh decreases until I becomes constant for $h \gtrsim 30$ nm.

To relate the intensity data to a physical quantity, we note that the intensity at a fixed temperature is approximately proportional to the optical retardation α , although the proportionality constant $C(T)$ was found empirically to depend on T due to the thermal characteristics — including those from temperature gradients — of the fiber. To obtain $C(T)$, we placed a top slide treated for homeotropic alignment on the sample, using a spacer of nominal thickness 10 μm . The now enclosed cell was then placed into a temperature controlled oven and birefringence apparatus consisting of a modulated Pockels cell, a pair of crossed polarizers, and a detector; details are described elsewhere [26]. The beam from a He-Ne laser at wavelength $\lambda_0 = 633$ nm was focused to a spot of approximately 100 μm diameter at the sample, and the total retardation $\alpha_{tot}(T)$ through the cell was measured as a function of temperature. Because α_{tot} is proportional to the intensity difference ΔI between the

baseline and saturation value measured at each temperature, i.e., $\alpha_{tot}(T) = C(T)\Delta I(T)$, $C(T)$ was extracted and the intensity data in Figure 1a was converted to retardation α vs. h at each temperature (Fig. 1b) for wavelength λ_0 .

Let us now turn to the meaning of α vs. h . We begin by noting that $\alpha(h) = \int_0^h k_0 \Delta n(z) dz$, where k_0 is $2\pi/\lambda_0$ and $\Delta n(z)$ is the birefringence at $\lambda_0 = 633$ nm for the liquid crystal at height z . Because the birefringence $\Delta n = DS$ for small S , where the constant of proportionality $D = 0.28$ for 5CB [27, 28], $\alpha(h) = k_0 D \int_0^h S(z) dz$. That $\alpha \propto h$ for $h \lesssim 10$ nm suggests one of two scenarios: Either i) $S(z)$ varies weakly over this height range $0 < z < h$, or ii) the profile $S(z)$ varies significantly with position h of the fiber aperture but its integral always happens to be proportional to h over this range. We discount mechanism (ii) because this scenario would require the coincidence of far too many conditions, such as anchoring potentials at the substrate and fiber having the correct forms. Thus we believe that $S(z)$ decays slowly near the substrate; whence $S_0 = (d\alpha/dh)_{h=0}/k_0 D$. In order to differentiate numerically the data in Fig. 1b and avoid the noise generally associated with numerical differentiation, we regularized the differentiation by fitting a piece-wise smooth Bezier curve of third degree to five representative data points, such that the values and derivatives were matched for each section. Typical examples are shown by the solid curves in Fig. 1b. $S(z)$ for each temperature then was obtained from the derivative of the Bezier curve; the results are shown in Fig. 2. From the data in Fig. 2 we extract S_0 and plot S_0^{-1} vs. T in Fig. 2, inset. There are three important features to note. First, S_0 is relatively small for all temperatures, having a maximum value of $S_0 \approx 0.12$ at $T - T_{NI} = 0.05$ °C. These values are considerably smaller than surface order parameters predicted theoretically [4, 5] and measured experimentally [13, 17] when capillary condensation occurs. The data also indicate that no prewetting transition [5] was observed, at least for $T > T_{NI} + 0.05$ °C. Second, the behavior of S_0^{-1} vs. T in Fig. 2, inset is reminiscent of the mean field behavior for the orientational susceptibility in the isotropic phase, associated with a susceptibility exponent $\gamma = 1$ and a value to $T_{NI} - T^* \sim 1$ °C. The observed downward deviation of S_0^{-1} from linearity close to T_{NI} also is commonly observed [29] in bulk measurements, although in our case this may be due to experimental scatter. In contrast, Sheng's model [5] for capillary condensation for walls spaced < 5 nm apart predicts a highly nonlinear variation of S_0^{-1} with temperature and an extrapolation to a supercooling limit more than 4 °C below T_{NI} , which

is contrary to our results. Third, $d\alpha/dh \sim 0$ for $h > 30$ nm, indicating that $S \sim 0$ beyond this range. This length scale differs from capillary condensation, where nonzero values of S tend to be observed experimentally for substrates separated by hundreds of nanometers [13]. Overall, our results suggest that our fiber has little effect on the induced order, consistent with previous experimental work by our group and others [23, 24, 30]. Thus, empirically we can treat $(d\alpha/dh)_{h=z}/k_0D$ as $S(z)$, facilitating a measurement of the order parameter profile without requiring a specific model. This result is corroborated by our calculations [5] for $S(z, T)$ when $S_0 \lesssim 0.12$ with the boundary condition $dS/dh|_{z=0}$ at the fiber, which indicate that corrections to the profile for $S(z)$ in Fig. 2 are no greater than 10% .

Moving beyond the surface, perhaps our most important observation is that the order parameter profile falls off slowly over many nanometers before decaying more rapidly. This behavior is *not* consistent with the exponential decay characterized by a temperature-dependent nematic correlation length ξ that is expected when S_0 is small [3, 5]; a possible mechanism for the decay profile will be discuss below. Nevertheless, the increase in the aperture height h_s at which α seems to saturate with decreasing temperature [Fig. 1b] presumably is due to an increasing correlation length ξ on approaching the transition. To make this more apparent, in Fig. 3 we have plotted the quantity α/S_0 at three representative temperatures. As expected, the initial slopes are the same, but at higher temperatures α/S_0 “saturates” at a lower height h_s than it does at higher temperatures.

The initial slow spatial decay of the order parameter raises questions about the physics near the interface. Hsiung, et al used an exponential form for $S(z)$ to analyze their evanescent wave ellipsometry data, obtaining an excellent fit and information about the correlation length vs. temperature. In their case this form likely was justified, as the *homeotropic* alignment of the liquid crystal was controlled by silane molecules at the surface that provided a well localized potential. In our experiment, however, we obtain *planar* alignment by mechanically rubbing a polyimide. The rubbing process has two effects: it creates shallow grooves in the surface and it realigns the polymer backbone, which can extend to some depth into the polyimide layer. Because the grooves’ radii of curvature $R \sim 700$ nm [31] are considerably larger than the fiber diameter d_f , the grooves are unlikely to influence significantly the order parameter near the surface. On the other hand, the realignment of the backbone, which is due in part to mechanical pressure in conjunction with heating,

can extend a distance of many nanometers into the polymer film [8, 32, 33]. Given this situation, Barbero and Evangelista showed [34] how quadrupole-quadrupole interactions can act over a range of several nanometers; an inhomogeneous spatial distribution of adsorbed charges at the interface [35] also would give rise to nonlocal forces. Nonlocal interactions have been shown to affect physical quantities such as surface viscosity [36] and elasticity in free-standing smectic- C films [37] where, for example, the length scale of the nonlocal interactions extends $\xi \sim 5$ to 10 nm and results in a greatly reduced elastic constant for films thinner than ξ [37]. As the data in Fig. 2 clearly show deviations over these length scales close to the substrate from behavior predicted by a Landau-DeGennes picture with a highly localized potential, we speculate that, in addition to the limited validity of the continuum approximation at such short length scales as well as “order electricity” for which there is a spontaneous polarization $P \propto \nabla S$ [38], the nonlocality of the “surface” potential may be playing an important role. To be sure, such a scenario does not necessarily apply to all types of interfaces; as noted above, homeotropic orientation resulting from a surface agent such as a silane is likely to be highly localized. The same holds true for alignment due to a surface grating [39], although in this case it is more difficult to define the actual “interface” due to its wavy nature. Nevertheless, for planar alignment that relies on anisotropic attractive interactions, especially those in which the anisotropy extends some distance beneath the surface and into the “bulk” polymer alignment film, the extended range of interactions may result in an $S(z)$ profile within several nanometers of the interface that is very different from exponential decay.

To summarize, we have demonstrated that a variation on the technique of optical nanotomography [23, 24] facilitates a model-free determination of the surface-induced orientational profile. Moreover, the behavior of S vs. z is apparently very different from that expected from the oft assumed Landau-DeGennes model with a highly localized potential at the surface, suggesting that a nonlocal surface potential and/or other mechanisms are needed to describe the behavior of rubbed polymer alignment layers.

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- [1] K. Miyano, *Phys. Rev. Lett.* **43**, 51 (1979); *J. Chem. Phys.* **71**, 4108 (1979)
- [2] J.C. Tarczoz and K. Miyano, *J. Chem. Phys.* **73**, 1994 (1980)
- [3] D.W. Allender, G.L. Henderson, and D.L. Johnson, *Phys. Rev. A* **24**, 1086 (1981)
- [4] P. Sheng, *Phys. Rev. Lett.* **37**, 1059 (1976)
- [5] P. Sheng, *Phys. Rev. A* **26**, 1610 (1982)
- [6] W. Chen, L.J. Martinez-Miranda, H. Hsiung, and Y.R. Shen, *Phys. Rev. Lett.* **62** 1860 (1989)
- [7] H. Hsiung, Th. Rasing, and Y.R. Shen, *Phys. Rev. Lett.* **57** 3065 (1986)
- [8] M.B. Feller, W. Chen, and Y.R. Shen, *Phys. Rev. A* **43**, 6778 (1991)
- [9] T. Moses, and Y.R. Shen, *Phys. Rev. Lett.* **67**, 2033 (1991)
- [10] T.J. Sluckin and A. Poniewierski, *Fluid and Interfacial Phenomena*, ed. by C.A. Croxton, (John Wiley & Sons, NY, 1986)
- [11] T.J. Sluckin and A. Poniewierski, *Liq. Cryst.* **2**, 281 (1987)
- [12] B. Jérôme, *Rep. Prog. Phys.* **54**, 391 (1991)
- [13] H. Yokoyama, S. Kobayashi, and H. Kamei, *Mol. Cryst. Liq. Cryst.* **99**, 39 (1983); *Appl. Phys. Lett.* **61**, 4501 (1987)
- [14] G. Barbero and G. Durand, *J. Physique II* **1**, 651 (1991)
- [15] R. Barberi and G. Durand, *Phys. Rev. A* **41**, 2207 (1990)
- [16] S.-T. Wu and U. Efron, *Appl. Phys. Lett.* **48**, 624 (1986)
- [17] A. Borstnik Bracic, K. Kocevar, I. Musevic, and S. Zumer, *Phys. Rev. E* **68**, 011708 (2003)
- [18] K. Kocevar, A. Borstnik, I. Musevic, and S. Zumer, *Phys. Rev. Lett.* **86**, 5914 (2001)
- [19] K. Kocevar and I. Musevic, *Phys. Rev. E* **64**, 051711 (2001)
- [20] B. Wen, J.-H. Kim, H. Yokoyama, and C. Rosenblatt, *Phys. Rev. E* **66**, 041502 (2002)
- [21] J.-H. Kim and C. Rosenblatt, *J. Appl. Phys.* **84**, 6027 (1998)
- [22] X. Liu, D.W. Allender, and D. Finotello, *Europhys. Lett.* **59**, 848 (2002)
- [23] V. Barna, A. De Luca, and C. Rosenblatt, *Nanotechnology* **19**, 325709 (2008).
- [24] A. De Luca, V. Barna, T. Atherton, G. Carbone, M. Sousa, and C. Rosenblatt, *Nature Physics* **4**, 869 (2008).
- [25] J.-H. Lee, T.J. Atherton, D. Kang, R.G. Petschek, and C. Rosenblatt, *Phys. Rev. E* **78**, 021708 (2008)

- [26] C. Rosenblatt, F.F. Torres De Araujo, and R.B. Frenkel, *Biophys. J.* 40, 83 (1982).
- [27] P.P. Karat and N.V. Madhusudana, *Mol. Cryst. Liq. Cryst.* 36, 51 (1976)
- [28] N.V. Madhusudana and R. Pratibha, *Mol. Cryst. Liq. Cryst.* 89, 249 (1982)
- [29] T.W. Stinson, J.D. Litster, and N.A. Clark, *J. Physique*, 33, C1-69 (1972)
- [30] T. Tadokoro, T. Saiki, and H. Toriumi, *Jpn. J. Appl. Phys.* 41 (part 2A), L152 (2002); *Jpn. J. Appl. Phys.* 42 (part 2), L57 (2003).
- [31] M.P. Mahajan and C. Rosenblatt, *J. Appl. Phys.* 83, 7649 (1998)
- [32] J.-H. Kim and C. Rosenblatt, *J. Appl. Phys.* 87, 155 (2000)
- [33] S. Kuniyasu, H. Fukuro, S. Maeda, K. Nakaya, M. Nitta, N. Ozaki, and S. Kobayashi, *Jpn. J. Appl. Phys.* 27, 827 (1988)
- [34] G. Barbero and L.R. Evangelista, *Adsorption Phenomena and Anchoring Energy in Nematic Liquid Crystals*, Wiley, N.Y. 2005
- [35] G. Barbero and G. Durand, *J. Appl. Phys.* 67, 2678 (1990)
- [36] G.E. Durand and E.G. Virga, *Phys. Rev. E* 59, 4137 (1999)
- [37] C. Rosenblatt, R. Pindak, N.A. Clark, and R.B. Meyer, *Phys. Rev. Lett.* 42, 1220 (1979)
- [38] G. Barbero, I. Dozov, J.F. Palierne, and G. Durand, *Phys. Rev. Lett.* 56, 2056 (1986).
- [39] D. W. Berreman, *Phys. Rev. Lett.* 28, 1683 (1972)

FIG. 1: a) Intensity vs. aperture's height h above substrate at different temperatures $\Delta T = (T - T_{NI})$. The different baselines for each temperature are due to drifts that are very slow compared to the data acquisition time at a given temperature and to a systematic variation of the baseline with temperature due to the thermal characteristics — including those from temperature gradients — of the fiber. b) Retardation α vs. height h extracted from intensity data in (a) and normalized to the total retardation α_{tot} through entire cell at each temperature. Each set of data was regularized as discussed in text, and two examples are shown by the solid lines.

FIG. 2: The quantity $(d\alpha/dh)/k_0D$, which corresponds approximately to the nematic order parameter S , vs. height h at different temperatures. Inset: S_0^{-1} vs. $T - T_{NI}$.

FIG. 3: The quantity α/S_0 vs. height at three representative temperatures. Vertical arrows show the height h_s (± 3 nm) at which the data “saturate”.





