

Structure in a Confined Smectic Liquid Crystal with Competing Surface and Sample Elasticities

Stefan H. J. Idziak,¹ Ilya Koltover,¹ Jacob N. Israelachvili,² and Cyrus R. Safinya¹

¹Materials Department, Materials Research Laboratory, Physics Department,
and Biochemistry and Molecular Biology Program, University of California, Santa Barbara, California 93106

²Department of Chemical Engineering, Materials Department,
and Materials Research Laboratory, University of California, Santa Barbara, California 93106

(Received 20 July 1995)

We report on studies using the x-ray surface forces apparatus (XSFA) to compare the structure of a liquid crystal confined between hard surfaces and, for the first time, between soft surfaces that can deform due to the stresses imposed by the confined fluid. We find that the alignment of smectic domains in confined films depends critically on both the shape and compliance of the confining walls or surfaces: “Soft surfaces” exhibit a critical gap thickness of $3.4 \mu\text{m}$ for the liquid crystal studied at which maximum alignment occurs, while “hard surfaces” do not exhibit gap-dependent alignment.

PACS numbers: 61.30.Eb, 82.70.Kj

The interplay between the intrinsic length scales of a system, such as the domain size, particle size, or molecular dimension, and the length scale due to confinement is of fundamental scientific importance. Simple and complex fluids undergo significant changes in their structural and rheological behavior as they are progressively confined between narrowing walls [1,2]. The understanding of these new fluid properties is of both intrinsic and practical interest ranging from thin film lubrication to catalysis and separations. The effects of confinement on molecular structure and dynamics have been studied theoretically with molecular dynamics simulations [3,4,5] and experimentally by probing porous media having different pore sizes using techniques such as spectroscopy [1], calorimetry [6], neutron scattering [7], and the surface forces apparatus (SFA) technique [8,9,10]. The SFA is the only technique that allows *in situ* control of gap separations spanning a wide range from microns to angstroms. The SFA has been used to study direct forces, frictional forces, and rheological properties of confined fluids at the molecular level [11]. Recently, the merging of the SFA with the powerful, noninvasive technique of x-ray diffraction to create the x-ray surface forces apparatus (XSFA) [12] has yielded a formidable new tool for studying confinement phenomena in the mesoscopic regime of length scales; the XSFA is capable of imaging the structure of confined complex fluids nondestructively and on length scales from nanometers to microns.

Traditionally, the surfaces used in SFA experiments as well as in past work with the XSFA [12,13,14] have been mica sheets, rigidly attached to hard silica-glass disks. We have developed two new types of surface mountings, shown in Fig. 1, which allow the effects of surface geometry and flexibility (i.e., the elastic deformations of the surfaces) to be explored. For the purposes of this paper, “surface” refers to the actual surface in contact with the fluid, as well as its underlying support. To create a “soft” surface [Fig. 1(b)] a hole in an aluminum

cylindrical disk is covered with a thin $3 \mu\text{m}$ sheet of mica. This thin sheet is somewhat flexible, and significant distortion of two approaching surfaces can be observed when a fluid sample is squeezed between them into gaps less than $1 \mu\text{m}$. To create a “hard” surface [Fig. 1(c)] the hole is first covered with a sheet of quartz glass, which is then covered with a thin mica sheet. These hard surfaces, while not as stiff as the conventional silica disks used in SFA experiments, are quite rigid and do not deform appreciably when compressing the sample.

In this Letter, we will discuss the behavior of the liquid crystal 8CB, confined between two hard or two soft surfaces. When confined between two soft surfaces, the smectic phase exhibits a critical gap for alignment (orientational coarsening) which is not seen in the case of hard surface confinement.

The experiments were conducted at the Stanford Synchrotron Radiation Laboratory beamline 6-2 using the 54 pole wiggler; 8 keV x-rays were used for all measurements. The beam was collimated using a $150 \mu\text{m}$ pin-

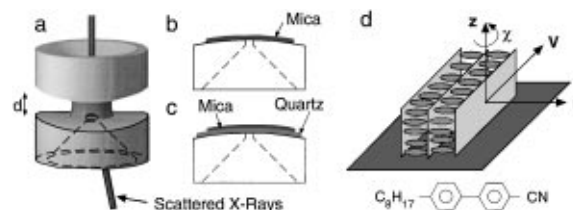


FIG. 1. (a) Surface geometry in an XSFA experiment showing the x rays scattered by a sample confined between two cylindrical surfaces (disk mounts) with radius of curvature 20 mm. (b) “Soft surfaces” consisting of a thin mica sheet ($\sim 3\text{--}5 \mu\text{m}$ thick) glued to the disk surface only around the central hole. (c) “Hard surfaces” are constructed by first gluing a thin sheet of quartz glass over the hole, followed by the mica sheet. The molecular structure of 8CB (4-cyano-4'-octylbiphenyl) is shown in (d). This system forms a smectic liquid crystalline phase at room temperature as shown schematically and described in the text.

hole and was then passed through the sample and scattered into a 180 mm diameter two-dimensional imaging plate detector. The instrument was aligned to produce an in-plane resolution of 0.002 \AA^{-1} while the resolution in the azimuthal (χ) direction was 0.3° . Images were exposed for 20 min for soft surfaces and for 10^6 monitor counts (~ 10 min) for hard surfaces. This detector allows the mosaic and orientation of the sample to be determined quickly, enabling multiple gaps to be reasonably studied.

The mica sheets used in these experiments were silvered on their back surfaces before being installed into the XSFA. This allowed the gap between the surfaces to be determined by passing yellow sodium light through the sample and observing the sharpened Newton's rings on the other side, using a microscope. The mica sheets are oriented such that the crystallographic axes of both surfaces are rotated 90° with respect to each other. The gap was measured at the point of contact of the two crossed cylinders; there is still sample in the beam due to the curvature of the surfaces and the finite size of the x-ray beam. During experiments, the surfaces were accessed simultaneously by x rays and optical light by means of aluminized Mylar mirrors. The two surfaces can be sheared using a piezoelectric bimorph device applying shear at constant velocity.

The role of the surface stiffness can best be described by comparing the surface elasticity with the sample "elasticity." In the case of the hard silica disks used in most SFA experiments, the elasticity of the fluid sample is always much smaller than that of the confining surfaces so that surface deformations can be ignored. However, as the confining gap decreases, the viscous and elastic forces of the confined liquid crystal generally increase [15,16,17]. If these forces increase to the point where they approach or exceed the stiffness of the surfaces, the latter will deform and the nature of the confinement will be fundamentally different. With hard surfaces, the fluid is forced to conform with the shapes of the surfaces at all times; with soft surfaces, the surfaces deform to accommodate the stresses and structure of the confined fluid.

In this work, we report results of x-ray diffraction studies on confinement-induced alignment effects in the common smectic liquid crystal 8CB [Fig. 1(d)] whose structure under bulk flow has been previously characterized [18,19,20] and is thus ideal for this study. The three possible orthogonal orientations of a layered smectic phase on a surface are described in Fig. 1(d). The *a* orientation is shown in Fig. 1(d) where the layer normal \hat{n} is parallel to the surfaces but orthogonal to the shear velocity direction (\mathbf{v}). In the *b* orientation, the layer normal and shear velocity point in the same direction. Note that this arrangement is intrinsically unfavorable as the shear will deform the layered structure. Finally, in the *c* orientation, the layer normal lies perpendicular to the two surfaces, along the *z* direction. Under static conditions, 8CB is known to lie in the parallel or "planar" orientation

on a mica surface [21], and so we do not expect to observe the perpendicular ("homeotropic" or *c*) orientation.

For all the samples which have been studied, while the mica crystallographic axis has been randomly set with respect to the surface cylindrical axis, we observe that the liquid crystal orientational peaks occur roughly over the same angular χ range. The mechanical loading process, which unavoidably involves flow, initially selects the observed average layer direction.

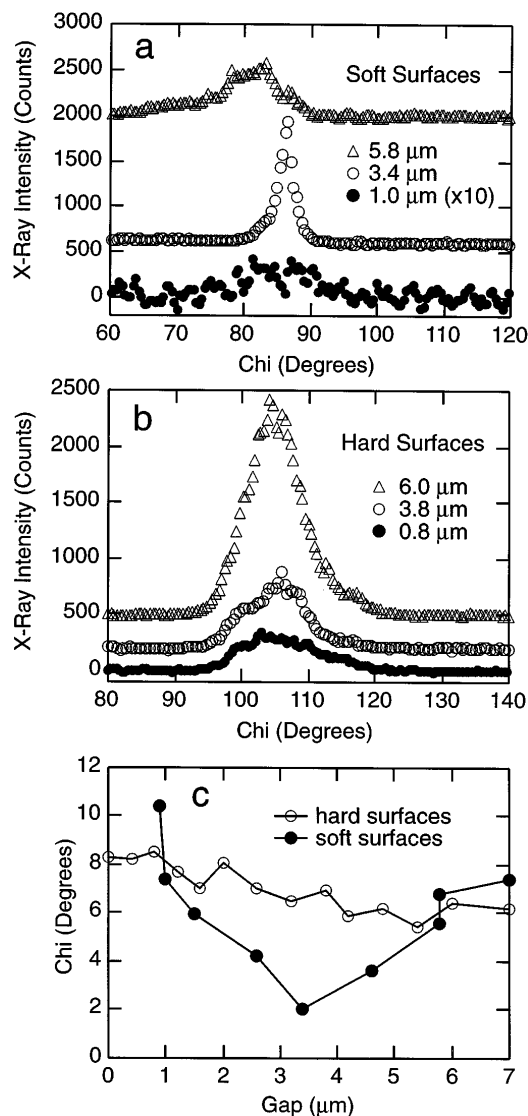


FIG. 2. (a) X-ray orientation scan showing the alignment of smectic layers between two soft surfaces for three different gaps clearly shows the significant alignment occurring at a critical gap of $3.4 \mu\text{m}$. (b) Orientation scans for a sample confined between two hard surfaces. Note that the degree of orientation does not change significantly with gap. (c) Plot of the peak width versus gap for 8CB confined between soft surfaces (closed circles) and for hard surfaces (open circles). Because these two measurements are done with different lineups, the integrated intensities of the different peaks for different runs cannot be compared. Within a single experiment, the integrated peak intensities do scale with the gap.

X-ray diffraction scans for 8CB confined between two SOFT surfaces are shown in Fig. 2(a). The top curve shows an orientational scan at a gap of $D = 5.8 \mu\text{m}$, yielding a mosaic angle of 6.8° . When the surfaces are brought closer to $D = 3.4 \mu\text{m}$, the mosaic sharpens substantially to 2.0° . This is indicative of an extremely well-oriented system and suggests that an “orientational coarsening” (to well-oriented domains within the sample) had occurred between 5.8 and $3.4 \mu\text{m}$. Surprisingly, when the gap is further decreased to $1.0 \mu\text{m}$, the orientational ordering decreases as the mosaic angle increases to 7.4° , effectively destroying the previous order. In contrast, for 8CB confined between two hard surfaces [Fig. 2(b)], the mosaic is essentially constant over the same range of gap widths. The mosaics for the hard and soft surfaces are compared in Fig. 2(c), which clearly demonstrates that the orientational coarsening seen between the soft surfaces is absent between the hard surfaces. These scans were derived from two-dimensional images by measuring the intensity as a function of angle on a circle of radius corresponding to the layer spacing 8CB (31.73 \AA). The scans have been offset by 0, 600, and 2000 counts, respectively, in Fig. 2(a) and by 0, 200, and 500 counts in Fig. 2(b). The direction of orientation depends on the alignment of the XSFA and the actual position of the point of contact of the two surfaces; for a given experiment, the orientation direction did not change.

If a liquid crystal sample is confined between two arbitrarily shaped surfaces, the alignment at small gaps would be determined both by the surface geometry and the “epitaxial” ordering imposed by the two surface lattices. In general, since neither the shape nor the two lattices are perfectly aligned, imperfect ordering of molecules or domains would result as shown in Fig. 3(a). If the gap is increased, the grain boundary energy arising from the different domains present would be expected to linearly increase with the gap size. This is because as a domain, which is in contact with both surfaces at small gaps, grows, the area in contact with the surfaces does not change, yet the rest of the area does increase to accommodate the growing domain volume. This increase in surface energy as a function of increasing gap would provide a driving force for domain coarsening. In the case of soft surfaces, the initially curved surfaces deform and flatten on approach. The pliant surfaces now allow the defects to migrate and anneal out when the gap is increased. This would account for the domain coarsening observed between the soft, deformable surfaces as the gap thickness increases to $\sim 3 \mu\text{m}$ [Fig. 3(b)]. In the case of hard surfaces that do not distort during their approach, domain defects, such as splay distortions, are pinned and cannot easily align, mutually orient, fuse, or anneal as the sample is squeezed, resulting in a roughly constant mosaic size and distribution with changing gap thickness.

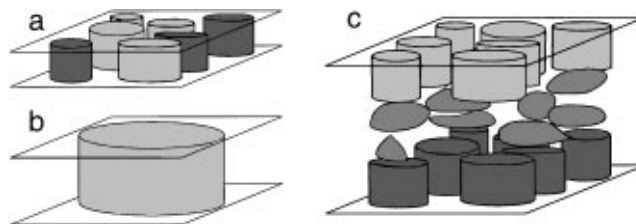


FIG. 3. The orientational coarsening seen in soft surface confinement is shown schematically where many small domains at small gap (a) merge into a large, singly oriented domain at medium gap (b). This effect can be very clearly seen for the soft surface case while no similar effect is seen for the hard surfaces. At very large gaps (c), the surfaces align the nearby sample while the center of the sample remains in a bulk powder form. Lightly shaded domains are aligned by the top surface, while dark domains are aligned by the bottom surface in this schematic.

The phenomenon can also be understood by considering the effects of decreasing the gap. At large gaps, the sample would be a randomly oriented bulk powder. The soft surfaces can deform. This enables them to (i) retain the larger, intrinsically singly oriented grains in the gap, and (ii) reorient the confined domains along a common axis [Fig. 3(b)]. However, as the thickness was further reduced, a decreased alignment was observed [Fig. 2(c)]. Observation of the surfaces with Newton’s rings revealed that highly localized surface distortions, resulting from the competition between surface elasticity and the increasing elasticity of the confined fluid, become enhanced in gaps less than $1 \mu\text{m}$, forcing the singly oriented domains to fracture into many smaller grains to conform to the preferred surface alignment imposed by the surface geometry.

This domain orientational ordering is a dramatic example of new structural and rheological behavior arising in confined geometries when the effective elasticity of the confined fluid material competes with the elasticity of the confining surfaces. This effect is in addition to, but quite different from, the ordering produced in thin films by favorable surface-fluid intermolecular, such as epitaxial, interactions.

Strikingly different behavior was observed under shear flow. The results show that similar shear-induced alignment occurs in both soft and hard surfaces (shown for soft surfaces only in Fig. 4). The shear has been applied along the $\chi = 0^\circ$ direction. Figure 4(a) shows a typical two-dimensional x-ray diffractogram where the smectic peaks can be seen for a 4000 \AA thick sample at rest (no shear), with a mosaic of 9.5° . When a 500 s^{-1} shear is applied, the sample orients in the pure a orientation [cf. Fig. 1(d)] with a mosaic of 3.2° [Fig. 4(b)], demonstrating the strong shear-induced ordering and alignment. One-dimensional orientational scans derived from these images are shown in Fig. 4(c), quantitatively illustrating the effect of shear-induced alignment. Our best case shear alignment is shown in Fig. 4(d) where a mosaic angle of

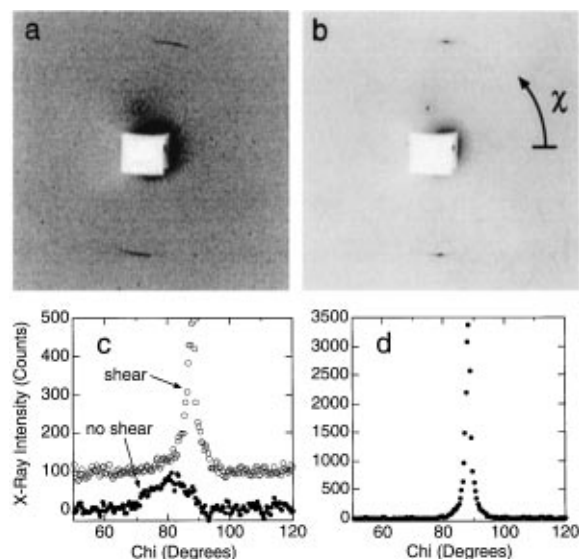


FIG. 4. Alignment of 8CB between two shearing surfaces separated by a gap of 4000 \AA is clearly demonstrated in the two images shown in (a) with zero shear and in (b) where the shear has been increased to 500 s^{-1} . The shear has been applied along the $\chi = 0^\circ$ direction. Linear orientational scans corresponding to these two-dimensional images are shown in (c) for no shear (closed circles) and for applied shear (open circles). The plot in (d) demonstrates the best alignment we have obtained with this technique, producing a mosaic of only 1.3° .

1.3° was obtained. These results indicate that the nonequilibrium flow-induced forces dominate over the surface forces on the liquid crystal orientation at these shear rates.

We have demonstrated that the domain orientational structure of a layered smectic-A liquid crystal depends critically on the mechanical properties, such as the flexibility, of the confining surfaces or walls. The removal of the hard wall constraint allows for a competition between surface and sample elasticities (or stresses), resulting in new structural behavior in the confined fluid. Although soft confinement alone can enhance the alignment of molecules or domains within a sample, the application of shear produces additional alignment effects that will also compete with and often dominate over the effects of “static” confinement. Our findings show that the stresses and microstructures produced on surfaces and in confined fluids depend not only on the geometry of the confining surfaces but also on their mechanical properties.

These findings therefore suggest that to reduce high stresses, frictional losses, and surface damage of, for example, machine components, a consideration of surface shape alone is not sufficient for optimum performance—the mechanical properties of the underlying substrate material may be just as crucial for obtaining desirable

properties, and its consideration adds another variable in design strategies.

We thank Robijn Bruinsma and Robert Hill for helpful assistance. This work was supported by the ONR Grant No. N00014-93-1-0269. The Stanford Synchrotron Radiation Laboratory is supported by the U.S. DOE. The Materials Research Laboratory at Santa Barbara is supported by Grant No. NSF-DMR-9123048.

- [1] J. M. Drake, J. Klafter, and P. Levitz, *Science* **251**, 1574 (1991).
- [2] J. M. Drake and J. Klafter, *Phys. Today* **43**, No. 5, 46 (1990).
- [3] M. Schoen, D. J. Diestler, and J. H. Cushman, *J. Chem. Phys.* **87**, 5464 (1987).
- [4] C. L. Rhykerd, Jr., M. Schoen, D. J. Diestler, J. H. Cushman, *Nature (London)* **330**, 461 (1987).
- [5] P. A. Thompson, G. S. Grest, and M. O. Robbins, *Phys. Rev. Lett.* **68**, 3448 (1992).
- [6] T. Bellini, N. A. Clark, C. D. Muzny, L. Wei, C. W. Garland, D. W. Schaefer, B. J. Oliver, *Phys. Rev. Lett.* **69**, 788 (1992).
- [7] M. Y. Lin, S. K. Sinha, J. M. Drake, X.-I. Wu, P. Thiagarajan, H. B. Stanley, *Phys. Rev. Lett.* **72**, 2207 (1994).
- [8] J. N. Israelachvili, A. M. Homola, and P. M. McGuiggan, *Science* **240**, 189 (1988).
- [9] J. Klein, D. Perahia, and S. Warburg, *Nature (London)* **352**, 143 (1991).
- [10] J. van Alsten and S. Granick, *Phys. Rev. Lett.* **61**, 2570 (1988).
- [11] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, New York, 1991).
- [12] S. H. J. Idziak, C. R. Safinya, R. S. Hill, K. E. Kraiser, M. Ruths, H. E. Warriner, S. Steinberg, K. S. Liang, J. N. Israelachvili, *Science* **264**, 1915 (1994).
- [13] S. H. J. Idziak, C. R. Safinya, E. B. Sirota, R. F. Bruinsma, K. S. Liang, J. N. Israelachvili, in *Structure and Flow in Surfactant Solutions*, edited by C. A. Herb and R. K. Prud'homme (American Chemical Society, Washington, 1994), Vol. 578, pp. 288.
- [14] S. H. J. Idziak, J. Koltover, K. S. Liang, J. N. Israelachvili, C. R. Safinya, *Int. J. Thermophys.* **16**, 299 (1995).
- [15] J. L. Ericksen, *Arch. Ration. Mech. Anal.* **4**, 231 (1960).
- [16] F. M. Leslie, *Q. J. Mech. Appl. Math.* **19**, 357 (1966).
- [17] O. Parodi, *J. Phys. (Paris)* **31**, 581 (1970).
- [18] C. R. Safinya, E. B. Sirolo, R. Plano, R. F. Bruinsma, *J. Phys. Condens. Matter* **2**, SA365 (1990).
- [19] C. R. Safinya, E. B. Sirota, and R. Plano, *Phys. Rev. Lett.* **66**, 1986 (1991).
- [20] C. R. Safinya, E. B. Sirota, R. F. Bruinsma, C. Jeppesen, R. J. Plano, L. J. Wenzel, *Science* **261**, 588 (1993).
- [21] P. Pieranski and B. Jerome, *Phys. Rev. A* **40**, 317 (1989).