ELSEVIER

Physica B 221 (1996) 289–295

PHYSICA B

Structure under confinement in a smectic-A and lyotropic surfactant hexagonal phase

Stefan H.J. Idziak[a,*], Ilya Koltover[a], Patrick Davidson[a,1], Marina Ruths[c], Youli Li[b], Jacob N. Israelachvili[c], Cyrus R. Safinya[a]

[a] *Materials Department, Materials Research Laboratory, Physics Department, and Biochemistry and Molecular Biology Program, University of California, Santa Barbara, CA 93106, USA*

[b] *Materials Research Laboratory, University of California, Santa Barbara, CA 93106, USA*

[c] *Department of Chemical Engineering, Materials Research Laboratory, Materials Department, University of California, Santa Barbara, CA 93106, USA*

Abstract

Simple and complex fluids undergo significant changes in their structural and rheological behaviour as they are progressively confined between narrowing walls. The understanding of these new fluid properties is of fundamental interest in applications ranging from thin film lubrication in micromachines to catalysis. The X-Ray surface forces apparatus (XSFA) is capable of non-destructive imaging of the structure of confined complex fluid systems, on length scales ranging from nanometers to several tens of microns. In this article, recent work is presented on studies of confined complex fluids with the XSFA. Confinement can significantly align the liquid crystalline smectic phase. The degree of orientation depends critically on the compliance of the confining surface: "soft surfaces" exhibit a critical gap for alignment of 3.4 μm, while "hard surfaces" do not exhibit gap dependent alignment. Shear-induced orientation has been shown to dominate over confinement induced alignment with the systems studied. In the final part of the paper, we discuss an important new development where it is demonstrated that the XSFA may be used as an alignment tool for lyotropic liquid crystals.

1. Introduction

The competition between an intrinsic length scale in a system, and a length due to confinement is of fundamental scientific interest. The effect of confinement on molecular organization and dynamics has been studied with molecular dynamics simulations [1–3], which indicate that increasing confinement may change the density and positional order, in addition to the molecular orientational order. This occurs especially as the confining gap approaches this inherent length scale in the problem, such as a colloid size, or the radius of gyration of a polymer, or ultimately, the size of a single molecule. Confined systems have been probed using porous media with a large distribution of pore sizes with techniques such as spectroscopy [4], calorimetry [5], and neutron scattering [6]. In addition, recent neutron diffraction studies on block copolymer systems confined in a fixed geometry have been performed [7]. The surface forces apparatus (SFA) [8–10], however, is the only technique that allows for such studies with controllable separations spanning a wide range from > 10000 Å down to a few

* Corresponding author.

[1] Permanent address: Laboratoire de Physique des Solides, associé au CNRS, Bat. 510, Université Paris Sud, 91405 Orsay cedex, France.

SSDI 0921-4526(95)00939-6

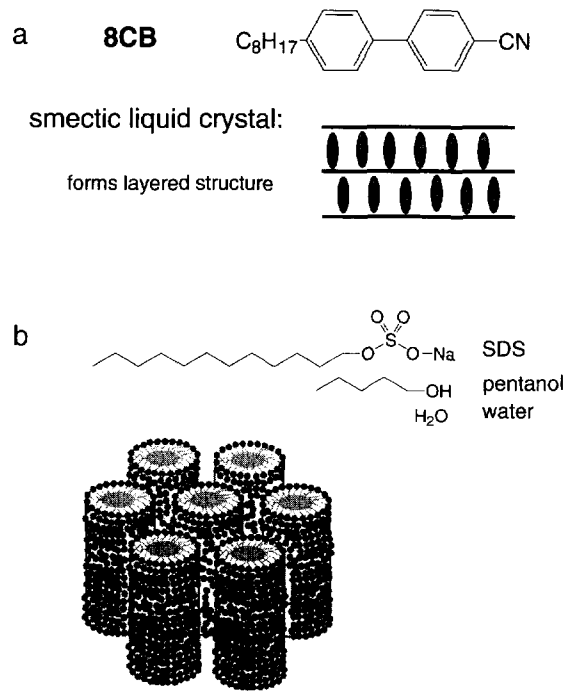

Fig. 1. The two systems studied in this work are the smectic liquid crystals 8CB (4-cyano-4′-octylbiphenyl) which forms a layered smectic phase at room temperature, and a lyotropic liquid crystalline mixture of sodium dodecyl sulfate (SDS), water and pentanol which forms an hexagonal phase at room temperature.

angstroms. The SFA has been used to study direct forces, frictional forces, and rheological properties at the true molecular level [11]. Recently, the merging of the SFA with the powerful, non-invasive technique of X-ray diffraction to create the X-ray surface forces apparatus (XSFA) [12–16] has yielded a formidable new tool for the study of confinement in the mesoscopic regime.

The invention of the XSFA has enabled complex fluids confined between two surfaces of well characterized physico-chemical origin with precisely controllable separations to be probed with X-rays, which enables the structure to be directly measured. Such a probe clearly permits investigations of a number of important physical phenomena. First, by controlling the nature of the confining surfaces, it would be possible to separate the effects induced by surface-specific interactions [11] from effects purely due to confinement. Second, by allowing the confining surfaces to be moved with respect to each other, one could study the effects of shear on the structure of a confined fluid [13–15]. Conceivably, by moving the surfaces fast enough and by decreasing the separation between the surfaces to a few angstroms one could achieve extremely high shear rates.

Bulk shear flow experiments have been performed on the smectic liquid crystal 8CB and the lyotropic SDS-pentanol-dodecane-water system (Fig. 1) as well as other systems [17–19]. These complex fluid studies were carried out between concentric cylinders transparent to X-rays, in a specially designed X-ray couette shear cell [20], as shown in Fig. 2(A). In the experiments, the outer cylinder was rotating with the inner cylinder held fixed. This geometry results in a linear velocity profile with a constant shear rate $\dot{\gamma} = v/D$, where the gap size D varied between 250 and 2000 μm. The a, b, c layer orientations, originally introduced by Miesowicz [21], refer to cases with the layer normal $\hat{n}$ pointing respectively along the $\hat{z}$ direction, the velocity (v), and the velocity gradient (∇v) directions (see Fig. 2(B)).

At low shear rates in the smectic phase of 8CB, heterogeneously mixed SmA domains with layer orientations between that of a and c were observed [17–19]. At high shear rates, a pure orientation regime was observed where the layers orient perpendicular to the shearing plates (a orientation of Fig. 2(B)). The SmA data

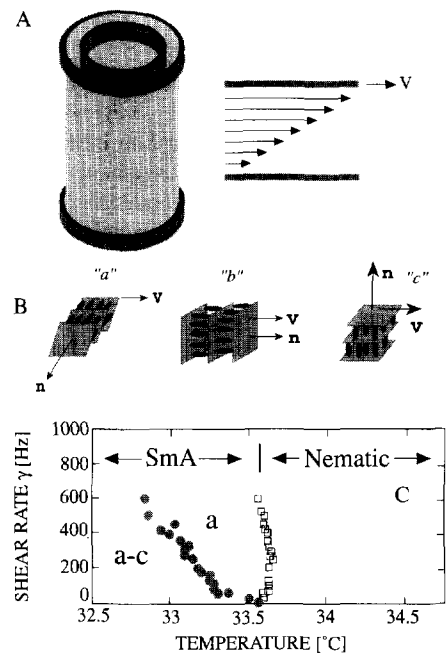

Fig. 2. Bulk shear flow experiments conducted in an X-Ray couette shear cell shown in (A) with a velocity profile between the two cylinders as shown. The three orthogonal orientations of a layered system between two sliding surfaces are shown in (B). (C): shear rate-temperature phase diagram of 8CB under flow showing the absence of the b orientation [19].

showing the (shear rate–temperature) phase diagram in the SmA phase in the vicinity of the transition temperature $T_{NA} = 33.58°C$ are summarized in Fig. 2C. A larger shear rate is required to remain in the pure *a* layer orientation state as the temperature is lowered below T_{NA} into the SmA phase.

In this work, we review results of X-ray diffraction studies on confinement-induced alignment effects in the common smectic liquid crystal 8CB (Fig. 1(A)) which is also a well-characterized model boundary lubricant and is thus ideal for this study. These results will be contrasted with the bulk flow experiments described above. We also describe new work on the highly ordered hexagonal samples (see Fig. 1(b)) of sodium dodecyl sulfate (SDS), pentanol and water. This lyotropic liquid crystal phase has been extensively studied in the bulk, both under static [22, 23] and flow [19] conditions.

2. Experimental

The XSFA is based on the conventional SFA (Mk III) [124]. This apparatus allows the gap between two atomically smooth surfaces to be adjusted from a few angstroms to several microns with angstrom resolution. A schematic of the XSFA is shown in Fig. 3. In this device, X-ray and optical access have been permitted through the use of thin mylar windows which also allow the sample environment to be controlled. The gap between the two surfaces is adjusted through the use of a micrometer-differential spring mechanism as shown in the schematic. The piezoelectric bimorph device used for applying shear can also be seen.

The surfaces typically used in the SFA are made of solid glass cylindrical lenses that have been covered with atomically smooth cleaved mica. The curvature of each surface allows a single point of contact to be created between the two surfaces. The surfaces in the XSFA were modified to allow direct X-ray access to the confined sample. Two different types of surfaces were developed for these experiments, which we refer to as a hard surface and a soft surface.

These two new types of surfaces, shown in Fig. 4, allow the effect of flexibility and surface geometry to be explored. For the purpose of this paper, surface refers to the actual surface in contact with the liquid crystal, as well as its underlying support. The soft surface is shown in Fig. 4(b). Here, a hole in an aluminum cylindrical disk is covered with a thin 3 μm sheet of back-silvered mica. This thin sheet is somewhat flexible and significant distortion of the surfaces can be observed when the sample is squeezed into gaps less than 1 μm. An alternative surface is shown in Fig. 4(c). Here a thin sheet of quartz covers the hole; the quartz is in turn covered with mica.

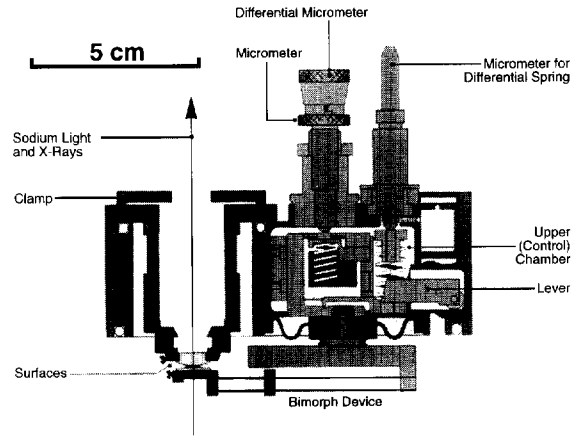

Fig. 3. Schematic of the X-Ray Surface Forces Apparatus without the lower sealed chamber. The two micrometers used for varying the gap can be seen at the top of the device, while the piezoelectric bimorph shearing device is on the bottom. Figure adapted from Ref. [24].

These surfaces, while not as stiff as the conventional silica disks used in SFA measurements, are quite rigid and do not appreciably deform while compressing the sample. These hard surfaces do have the disadvantage that there is now more material in the beam path that will contribute to overall background scattering.

The mica sheets were silvered on their back surfaces before being installed into the XSFA. This allowed the gap between the surfaces to be determined by shining yellow sodium light through the sample and observing the transmitted Newton's right pattern on the other side. During experiments, the sample was examined simultaneously by X-rays and optical light by means of aluminized mylar mirrors.

The 8CB (4-cyano-4'-octylbiphenyl) experiments were conducted in open air. The lyotropic studies were performed in a sealed environment. Sodium dodecyl sulfate was purchased from Sigma. The lyotropic sample studied has composition: SDS 36.1 wt%, pentanol 7.78 wt%, and water 56.12 wt%. Samples were loaded by carefully placing a drop between the two surfaces after the XSFA had been installed and aligned. 8CB was studied with both hard and soft surfaces; the lyotropic liquid crystal was studied with hard surfaces only.

The X-ray diffraction experiments were conducted at the multipole wiggler beamlines 6-2 and 10-2 at the Stanford Synchrotron Radiation Laboratory (SSRL). A Si(111) monochromator was used to select an 8 keV X-ray beam focused on the sample position. This beam was further defined by slits and a 125 μm pinhole located a few inches from the sample as shown in Fig. 5. The

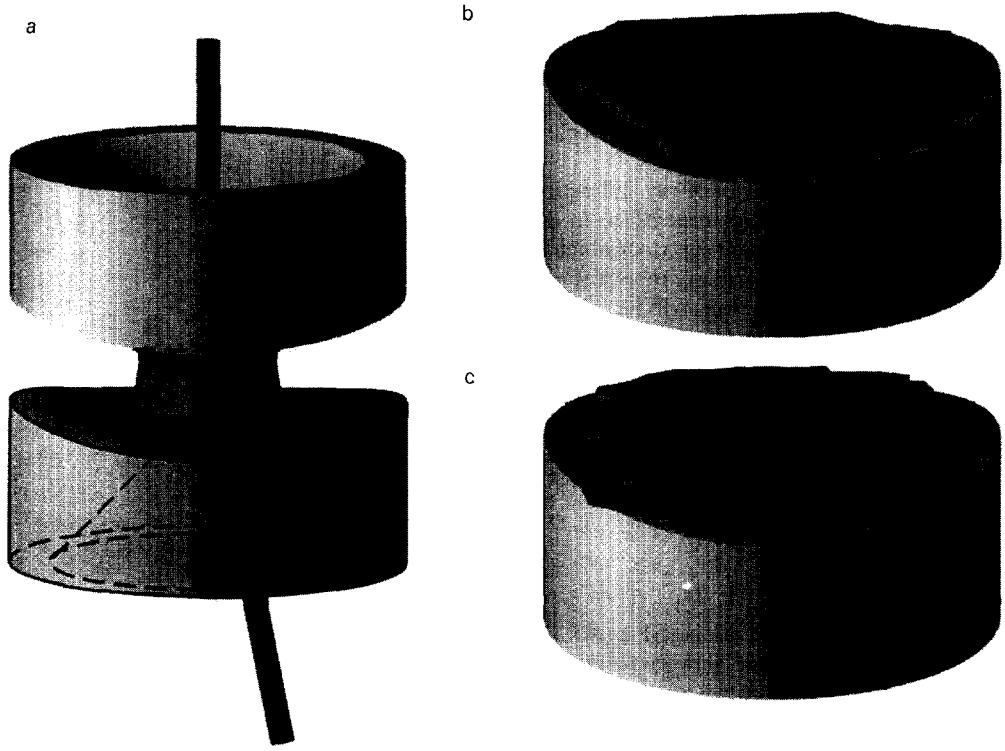

Fig. 4. (a) Surface geometry in an XSFA experiment showing the X-rays scattered by a sample confined between two cylindrical surfaces (disk mounts). (b) "Soft surfaces" consisting of a thin mica sheet (~ 3–5 μm thick) glued to the disk surface only around the central hole. (c) "Hard surfaces" are constructed by first gluing a thin sheet of quartz glass over the hole, followed by the mica sheet.

instrument was aligned to produce an inplane resolution of 0.002 $Å^{-1}$ while the azimuthal resolution was 0.3°. Diffraction patterns were then recorded with a 180 mm diameter MAR image plate two-dimensional detector. This allowed multiple gaps to be explored in a reasonable time.

3. Discussion

In this section, we will first discuss the results based on 8CB confined between shearing surfaces. This will be followed by a discussion of the unusual behaviour seen between hard confining surfaces and soft, flexible surfaces. We will end with a discussion of the lyotropic hexagonal phase of the SDS system.

There are two possible orthogonal orientations of a layered smectic phase on a surface. Under static conditions, 8CB is known to lie in the parallel or "planar" orientation on a mica surface (a–c plane) [25] and so we do not expect to observe the perpendicular ("homeotropic" or "b") orientation. A two dimensional X-ray diffraction scan for 8CB confined between two soft surfaces is shown in Fig. 5. This scan also illustrates the large degree of alignment that arises simply from confining the smectic liquid crystal. Fig. 6 shows linear X-ray diffraction patterns demonstrating the alignment and orientation of smectic 8CB between two soft mica surfaces at two different gaps in the case of no shear and applied shear. These scans also clearly show the significant alignment that occurs purely as a result of confinement. Confinement can orient the sample either by allowing orientational epitaxial ordering to occur or by imposing a finite size constraint on the sample. In the case of either the 6000 Å or 2.9 μm gaps, the application of moderate shear is enough to reorient the sample into the pure a orientation (see Fig. 6 bottom), as seen in the case of bulk flow. At these gaps, confinement alone can orient a sample, but the effects of confinement are insufficient to overcome bulk flow alignment.

The effects of surface rigidity on smectic alignment has been previously reported [16] and will be summarized here. Both hard and soft surfaces will induce smectic alignment under confinement. In the case of soft surfaces, at a gap of 6 μm, the sample mosaic will typically be 6°. When the surfaces are brought closer together, to 3.4 μm,

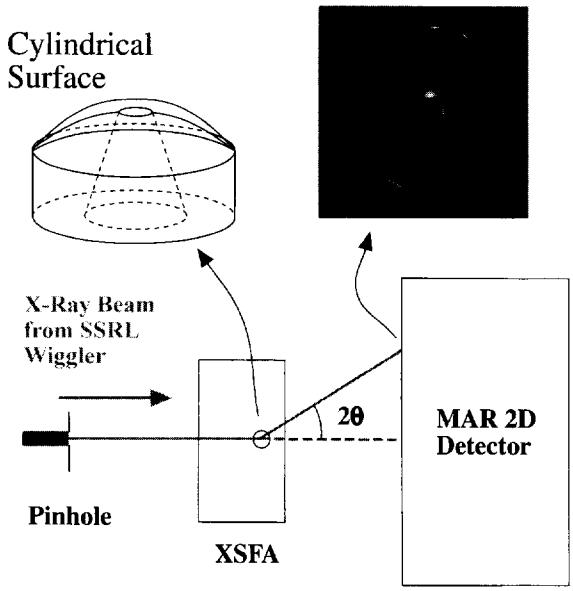

Fig. 5. Schematic of the XSFA experimental setup. X-rays from Stanford Synchrotron Radiation Laboratory wiggler beamline 6-2 impinge on a 125 μm pinhole to produce a high resolution setup. The X-rays then scatter off the sample confined between cylindrical surfaces into an MAR two-dimensional image plate detector to yield a diffraction pattern showing the sample alignment.

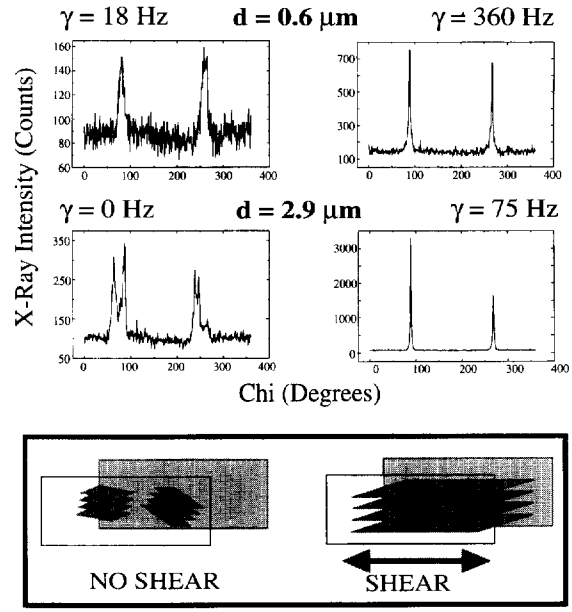

Fig. 6. X-ray diffractograms of 8CB confined between soft surfaces at different gaps and shear rates. These one-dimensional scans were derived from 2D images. (Top) The gap is 6000 Å for shear rates of 18 and 360Hz. (Middle) The gap is 2.9 μm with shear rates of 0 and 75 Hz. In both cases, it can be seen that shear aligns the smectic domains significantly. (Bottom) Schematic of the domain orientation occurring as a function of shear.

the mosaic improves substantially to 2°, thus providing an extremely well oriented phase, indicating the onset of orientational coarsening (domain orientational ordering). Surprisingly then, as the gap is decreased to 1.0 μm, the orientational ordering decreases as the mosaic increases to 7°, effectively destroying the previous order. In contrast, the same measurements taken for 8CB confined between two hard surfaces show that the mosaic is essentially constant, increasing from 6.4° at a gap of 6.0 μm to 8.5° at 0.8 μm. These measurements demonstrate the power of the XSFA in allowing a gap to be easily and smoothly changed.

A comparison of surface elasticity and the sample elasticity can be used to examine the effect of the surface stiffness. In the case of traditional hard silica disks used in SFA experiments, the sample is always much more elastic than the confining surfaces, and is therefore forced to conform to the shape of the surfaces. The viscous force of a fluid sample can increase as the confining gap decreases. If this sample is then confined between two surfaces that are relatively stiff so that at large gaps the sample is more flexible and at small gaps less flexible than the surfaces, the nature of the confinement has fundamentally changed. In this case, the surface can be deformed by the elastic fluid.

If a liquid crystal sample is confined between two surfaces, the alignment at small gaps would be determined both by the surface geometry and the "epitaxial" orientational ordering [25,26] 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. If the gap is increased, the grain boundary energy arising from the different domains present would be expected to increase with the gap size. In the case of hard surfaces, that do not distort during their approach, domains cannot easily align and fuse, as the gap is decreased, resulting in a roughly constant mosaic spread with changing gap thickness.

But in the case of soft surfaces, the initially curved surfaces deform and flatten on approach. 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, allowing domain coarsening to occur. However, as the gap is further reduced, observation of the surfaces with Newton's rings revealed that highly localized surfaces distortions, resulting from the competition between surface elasticity and the increasing rigidity of the confined fluid, become enhanced, forcing

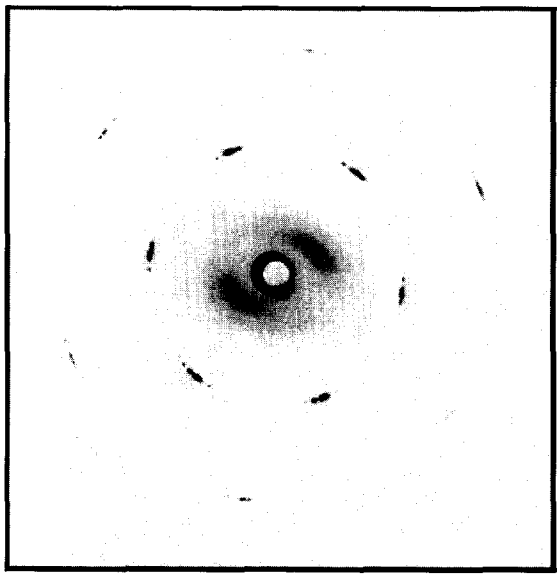

Fig. 7. Two-dimensional X-ray diffractogram of the SDS lyotropic liquid crystal sample illustrating the beautiful six-fold hexagonal symmetry. The shadow near the beam stop comes from the scattering of the mylar mirrors used for optical access to the sample.

the singly oriented domains to fracture into many smaller grains. The interaction between a sample and its confining surface is not solely determined by the microscopic nature of the surface; in addition, the bulk macroscopic properties, such as elasticity, play a crucial role in studying these phenomena.

The unique ability to readily vary the separating gap can be further exploited to perform sample alignment. A two-dimensional X-ray diffractogram of the SDS-pentanol–water system in its hexagonal phase is shown in Fig. 7. This outstanding domain growth was achieved in minutes by simply placing the sample between the two surfaces, squeezing the surfaces into contact, and then separating the surfaces approximately 30 μm over 30 min. This alignment technique is similar to the strand drawing (pin and cup) technique [27,28] which has been used to align discotic liquid crystals, but it allows easy X-ray access to the 2D lattice which is forbidden by the pin and cup method. This resulting six-fold scattering pattern is one of the very few that have been observed in lyotropic liquid crystals with X-rays in this orientation and is reproducible and simple to obtain.

4. Conclusion

The X-ray surface forces apparatus is still a relatively new technique whose full power is yet to be harnessed. In this article, confinement has been shown to orient a smectic liquid crystalline sample that was then reoriented with shear flow. We have demonstrated that the domain orientational structure of a confined model boundary lubricant depends critically on the mechanical properties, such as the flexibility, of the confining surfaces. The removal of the hard wall constraint and the resulting competition between surface and sample elasticities has caused the emergence of new structural behaviour. Further work is under way to study the effects on confinement of different types of surfaces, for instance atomically rough surfaces. This technique has widespread potential: as a means of aligning otherwise difficult systems such as zwitterionic samples [15], or the lyotropic system described above. It is also useful as a simple probe of the effects of confinement; or even for studying biological processes that occur in confined spaces. New third generation synchrotron facilities, such as the European Synchrotron Radiation Facility and the Advanced Photon Source, will greatly contribute to the ability to study confinement at much smaller gaps, approaching true molecular confinement.

Acknowledgements

We gratefully acknowledge conversations with P. Pincus. We thank R. Hill for technical assistance. C.R.S. and J.N.I. gratefully acknowledge partial support by the office of Naval Research under grant N00014-93-1-0269. C.R.S. and S.H.J.I. also gratefully acknowledge partial support from the Los Alamos–UC Campus Collaborative Research Initiative (LACOR) under award UC-94-8-A-221.P.D gratefully acknowledges support from a NATO Research Fellowship. The synchrotron X-ray scattering experiments were carried out at beamlines 6-2 and 10-2 at the Stanford Radiation Laboratory, which is supported by the US Department of Energy.

References

[1] M. Schoen, D.J. Diestler and J.H. Cushman, J. Chem. Phys. 87 (1987) 5464.
[2] C.L. Rhykerd Jr., M. Schoen, D.J. Diestler and J.H. Cushman, Nature 330 (1987) 461.
[3] P.A. Thompson, G.S. Grest and M.O. Robbins, Phys. Rev. Lett. 68 (1992) 3448.
[4] J.M. Drake, J. Klafter and P. Levitz, Science 251 (1991) 1574.
[5] T. Bellini, N.A. Clark, C.D. Muzny, L. Wei, C.W. Garland, D.W. Schaefer and B.J. Oliver, Phys. Rev. Lett. 69 (1992) 788.
[6] M.Y. Lin, S.K. Sinha, J.M. Drake, X.-I. Wu, P. Thiyagarajan and H.B. Stanley, Phys. Rev. Lett. 72 (1994) 2207.

[7] P. Lambooy, T.P. Russell, G.J. Kellogg, A.M. Mayes, P.D. Gallagher and S.K. Satija, Phys. Rev. Lett. 72 (1994) 2899.
[8] J.N. Israelachvili, A.M. Homola and P.M. McGuiggan, Science 240 (1988) 189.
[9] J. Klein, D. Perahia and S. Warburg, Nature 352 (1991) 143.
[10] J. van Alsten and S. Granick, Phys. Rev. Lett. 61 (1988) 2570.
[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 and J.N. Israelachvili, Science 264 (1994) 1915.
[13] S.H.J. Idziak, C.R. Safinya, E.B. Sirota, R.F. Bruinsma, K.S. Liang and J.N. Israelachvili, in: Structure and Flow in Surfactant Solutions, eds. C.A. Herb and R.K. Prud'homme (American Chemical Society, Washington, 1994) pp. 288–299.
[14] S.H.J. Idziak, I. Koltover, K.S. Liang, J.N. Israelachvili and C.R. Safinya, Int. J. Therm. 16 (1995) 299.
[15] I. Koltover, S.H.J. Idziak, C.R. Safinya, S. Steinberg, J.N. Israelachvili and K.S. Liang, in: Dynamics in Small Confining Systems II (Materials Research Society, 1995).
[16] S.H.J. Idziak, I. Koltover, J.N. Israelachvili and C.R. Safinya, Phys. Rev. Lett. 76 (1996) 1477.
[17] C.R. Safinya, E.B. Sirota, R. Plano and R.F. Bruinsma, J. Phys.: Condens. Matter 2 (1990) SA365.
[18] C.R. Safinya, E.B. Sirota and R. Plano, Phys. Rev. Lett. 66 (1991) 1986.
[19] C.R. Safinya, E.B. Sirota, R.F. Bruinsma, C. Jeppesen, R.J. Plano and L.J. Wenzel, Science 261 (1993) 588.
[20] R.J. Plano, C.R. Safinya, E.B. Sirota and L. Wenzel, Rev. Sci. Instrum. 64 (1993) 1309.
[21] M. Miecowicz, Nature 158 (1946) 27.
[22] C.R. Safinya, D. Roux, G.S. Smith, S.K. Sinha, P. Dimon, N.A. Clark and A.M. Bellocq, Phys. Rev. Lett. 57 (1986) 2718.
[23] D. Roux, C.R. Safinya and F. Nallet, in: Micelles, Membranes, Microemulsions, and Monolayers, eds. W.M. Gelbart, A. Ben-Shaul and D. Roux (Springer, New York, 1994).
[24] J.N. Israelachvili and P.M. McGuiggan, J. Mater. Res. 5(10) (1990) 2223.
[25] P. Pieranski and B. Jerome, Phys. Rev. A 40 (1989) 317.
[26] B. Jerome, Rep. Progr. Phys. 54 (1991) 391.
[27] C.S. Safinya, K.S. Liang, W.A. Varady, N.A. Clark and G. Anderson, Phys. Rev. Lett. 53 (1984) 1172.
[28] E. Fontes, P.A. Heiney, M. Ohba, J.N. Haseltine and A.B.S. III, Phys. Rev. A 37 (1988) 1329.