

Direct Observation of Shear-Induced Orientational Phase Coexistence in a Lyotropic System Using a Modified X-Ray Surface Forces Apparatus

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The second generation x-ray surface forces apparatus (XSFA-II) allows for the first time simultaneous *in situ* small-angle x-ray scattering and surface force measurements. We have used the XSFA-II to monitor shear-induced orientational transitions in a lyotropic model lubricant system. Upon applying small shear amplitudes ($\sim 20 \mu\text{m}$) to a relatively thick ($\sim 800 \mu\text{m}$) film, we observed evidence for the formation of an orientational boundary layer at the shearing surface. Time-resolved x-ray diffraction revealed the gradual transition to shear-favored orientation by growth of the boundary layer.

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The structure of liquid crystals under confinement and shear has been studied extensively in the last 20 years [1]. The viscoelastic properties of these structured fluids were found to be highly dependent on the molecular orientation. In fluids where the molecules are either arranged in layers (smectic or lamellar phase) or as hexagonal arrays of cylindrical micelles, very low frictional forces were measured [2]. This has been attributed to molecules realigning under shear to low frictional states, such as the “sliding layer” arrangement in the lamellar phase and the “rolling cylinder” arrangement in the hexagonal phase. Earlier work using an x-ray Couette shear cell has shed some light on the structure of bulk molecular fluids under shear [3].

The development of techniques that can directly probe structural and chemical evolution in shearing contacts at real time is essential for understanding complicated tribological processes. Consequently, there has been considerable effort in recent years in coupling friction experiments with a variety of *in situ* probes [4]. The first generation of the x-ray surface forces apparatus (XSFA), adapted directly from the SFA-III surface forces apparatus (SFA) [5], allowed for the first time x-ray structural measurements to be carried out on confined complex fluid samples using a synchrotron source [6]. In the initial experiments, the XSFA was successfully used to study effects of shear and confinement in liquid crystalline films [7–9]. These experiments demonstrated the unique advantage of combining the SFA methodology with *in situ* x-ray small-angle scattering, which provide direct information on molecular arrangements in the confined sample. However, the first generation XSFA did not permit white light interferometry or direct force measurements to be made simultaneously with x-ray diffraction experiments.

Recent developments have led to the second generation x-ray surface forces apparatus (XSFA-II), with normal and shear force measurement capabilities coupled with *in situ* small-angle x-ray scattering experiments under static

confinement and oscillatory shear conditions in a well-defined environment [10]. Figure 1 shows a schematic diagram of the experimental setup of the XSFA-II, which was designed to allow simultaneous use of multiple beam interferometry (using white light) and x-ray diffraction, and equipped with a piezoelectric bimorph slider [11] for shearing one of the surfaces in the v direction. The second generation XSFA-II chamber was redesigned and completely sealed to allow structure measurements in a controlled temperature, humidity, and chemical environment and was equipped with two Al-coated Mylar mirrors

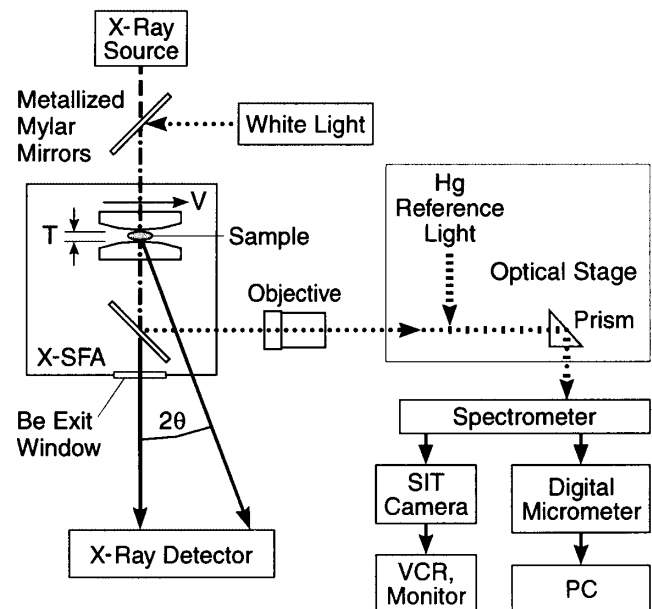


FIG. 1. Experimental setup of the XSFA-II, which was redesigned for direct normal and lateral force measurements coupled with *in situ* x-ray scattering experiments. White light interferometry was used for measuring the gap separation T . All components are portable, to allow the setup of the XSFA-II at synchrotron radiation sources.

mounted at 45° before and after the sample. These mirrors were used in order to deflect the (optical) white light while allowing monochromatic x rays to pass with reasonable loss. A side port (not shown) was used to inject the sample in between two molecularly smooth mica surfaces. The back of the mica sheets was coated with a semitransparent silver layer, attached to ultrathin quartz sheet supports and mounted onto curved aluminum disks fitted with $500\ \mu\text{m}$ pinholes [7]. For measuring the sample thickness T , the fringes of equal chromatic order obtained were analyzed in a portable grating spectrometer and recorded using a low-light silicon intensified tube camera. For the experiments described here, the XSFA-II was mounted on a small-angle x-ray spectrometer equipped with an 18 kW Rigaku rotating anode x-ray source and a 2D image plate detector. For measurements of confined thin films, the XSFA-II is a powerful tool because of its capability to measure structural and orientational changes in the sample upon shear at well-defined gap separations.

In this work, we have chosen to study the behavior of lamellar fluid samples in relatively large gaps ($\sim 800\ \mu\text{m}$) in order to maximize the scattering signal with the in-house rotating anode x ray set up. The XSFA-II was used for studying a four-component lyotropic model lubricant system composed of sodium dodecyl sulfate [SDS (surfactant)], pentanol (cosurfactant), dodecane (oil), and water. This system has a well-characterized, rich phase diagram, which allows one to access a variety of molecular structures by simply changing the composition [1,7]. The data shown below were obtained from a lamellar (L_α) phase sample which was composed of 28.18% SDS, 20.91% pentanol, 7.19% dodecane, and 43.72% water (in percent by weight). This sample was chosen because in the L_α region of the phase diagram, the molecules are arranged in stacked layers which are intrinsically anisotropic, and the application of external shear is expected to induce rearrangement of domains into energetically favorable (low friction) structures. By applying small shear amplitudes ($\sim 20\ \mu\text{m}$) to a relatively thick ($\sim 800\ \mu\text{m}$) film, we observed evidence for the formation of an orientational boundary layer at the shearing surface, which realigned in a shear-favored orientation. Time-resolved x-ray diffraction revealed the gradual transition, which proceeded by growth of the boundary layer and a simultaneous decrease of the original orientation in the bulk sample.

The three possible orientation directions “a,” “b,” and “c” of the smectic layer domains with respect to the shear are illustrated in Fig. 2 [3,12]. In orientations a and c, the velocity vector \vec{V} is in the plane of the layers, while in orientation b, \vec{V} intersects the layers. For this reason, shearing a surface confining a b-oriented sample will cause the layer stacks to distort and therefore the b orientation is expected to become unstable upon the onset of shear.

The x-ray diffraction pattern obtained from a lamellar fluid sample under static conditions showed a single ring

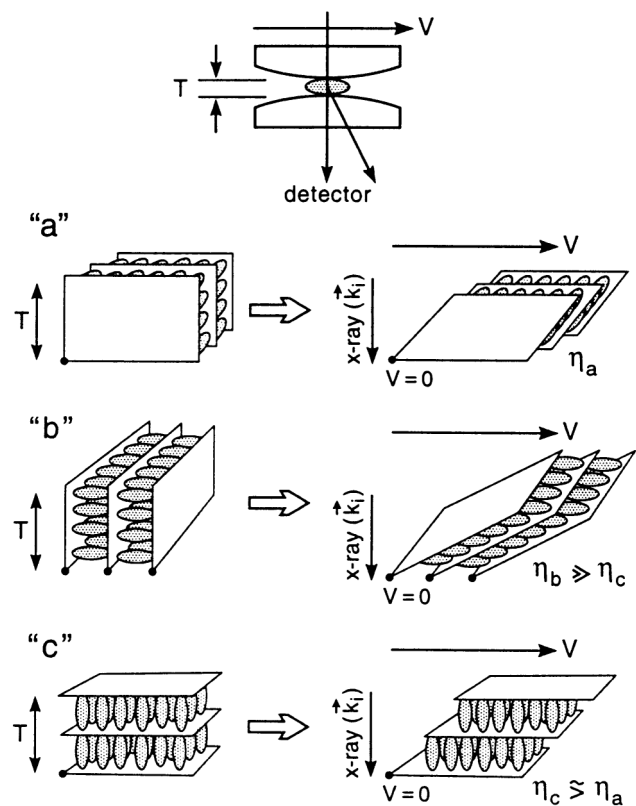


FIG. 2. Three possible domain orientations with respect to shear. The shear vector \vec{V} is perpendicular to the incident x-ray path (\vec{k}_i). The wave vector $\vec{q} \equiv \vec{k}_f - \vec{k}_i$ is in the plane that contains \vec{V} and the neutral direction with respect to the shear plane ($\vec{V} \cdot \nabla \vec{V}$). Orientations a and c are allowed with respect to shear. Orientation b is expected to be unfavorable with respect to shear due to distortion of the layer stacks. η is the standard notation for viscosity.

of scattering intensity which corresponds to the first order (001) peak of the smectic layer spacing. A ring of uniform radial intensity would suggest isotropically distributed membrane domains. However, two prominent arcs obtained at $\phi = 0^\circ$ and $\phi = 180^\circ$ indicated that the smectic layers were already aligned in a preferred orientation even before shear was applied [13]. The plots of x-ray intensities as a function of the ϕ angle on the diffraction ring (in-plane orientation) are shown in Fig. 3. From curve I in Fig. 3(a) (taken under static conditions), it is evident that the layers are initially oriented in the b direction ($\phi = 0^\circ$), which is unfavorable at high shear rates. Since the azimuthal orientation of the mica surfaces was kept constant during the experiment, it is possible that the initial alignment of the sample is due to a well-defined orientation relationship with the mica substrate. Additionally, the direction of the sample injection through the sample injection port, which was always done along the shear direction, might also be responsible for the initial sample alignment. Note that the same static measurement (curve I) is shown for reference in Figs. 3(a)–3(c).

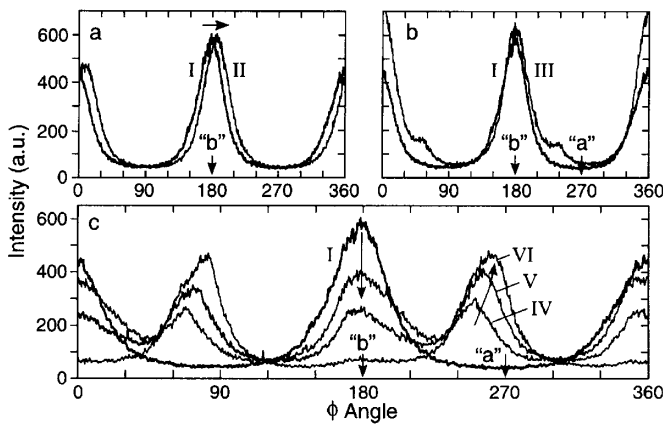


FIG. 3. Dynamic behavior as monitored from time-resolved small-angle x-ray scattering spectra. Data are presented as scattering intensity of the first order (001) peak of the smectic layer spacing versus rotational ϕ angle. Acquisition time was 30 min for all spectra (a) under static conditions (curve I) and after 30 min of oscillatory shear (curve II). (b) Appearance of a distinct orientation after 240 min of shear (curve III). At this point, the b orientation relaxes back to its initial position. (c) Same, after 630 and 900 min of shear (curves IV and V, respectively). With shearing time, the b intensity gradually decreased while a simultaneous increase in the a orientation intensity was observed, accompanied by a shift towards the precise a orientation at $\phi = 90^\circ$ and 270° . After recording curve V, the shear oscillations were stopped. Interestingly, the transition continued and appeared to be completed after an additional 900 min (curve VI). For all curves, oscillating shear amplitude was ca. $20 \mu\text{m}$; frequency was 1 Hz. Note that curve I is shown for reference in (a)–(c).

Because of the relatively small shear amplitude and large gap size, the effective shear rate was very low. Interestingly, the sample *did* respond to this perturbatory shearing, albeit on a very long time scale. Figure 3(c) shows the radial plots obtained with the same sample after 630 and 900 min after the onset of oscillatory shearing at a frequency of 1 Hz (curves IV and V, respectively). The data indicate the existence of two orientation populations of the smectic stacks, which are just about orthogonal to each other. Since the data are on the same intensity scale, the decreasing intensity of the peak at 0° and 180° and subsequent increasing intensity of the peak at 90° and 270° strongly suggests that part of the initial b oriented domains have rotated towards the shear-favored a orientation. After the measurement of curve V, the shear oscillations were stopped, and the x-ray measurements were continued under static conditions in order to monitor possible further changes in orientation. Interestingly, the transition from b to a continued also after the shear was stopped and appeared to be completed after 900 min of static measurements (curve VI).

Fortuitously, the long time scale of the orientation transition provided us with the opportunity to follow and resolve the dynamic behavior of the transition. X-ray diffraction data taken continuously in 30 min intervals after the onset of shear gave a clear evolutionary picture of the process,

as shown in Fig. 3. After 30 min of shear, the initial orientation of the domains (curve I) shifts slightly towards a larger angle (curve II), which is consistent with the shear-unfavorable b oriented domains being strained by the shear field and tilting towards the a orientation (Fig. 4, illustrations I and II). After 240 min, a distinct second peak sets in [curve III in Fig. 3(b)], indicating the appearance of a new orientation which is closer to a. It is important to note the initial peak (b domains) in curve III, which *relaxes back* to the original b position. This strongly suggests the formation of a distinct shear-induced boundary layer at the shearing surface, which gradually shifts towards the shear-favorable a direction (illustration III in Fig. 4), while the bulk of the film can relax back to the initial b orientation. From this point, the intensity of the second peak grows during continued shear and shifts continuously towards the shear-favorable a orientation, while the number of the original b-oriented domains decreases correspondingly, as depicted in Fig. 4. This is consistent with a gradual increase in the thickness of the boundary layer as depicted in illustrations III and IV in Fig. 4, as discussed below.

More than one scenario can be suggested for the interpretation of the small-angle x-ray scattering data in Fig. 3. The phase separation observed can be interpreted as

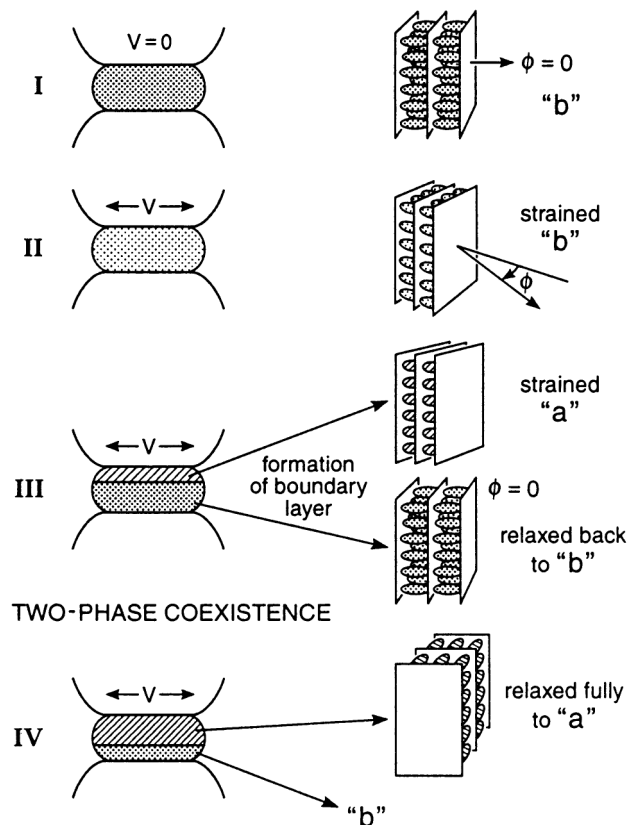


FIG. 4. Schematic illustrations showing the morphology evolution via formation of an orientational boundary layer, as suggested from the diffraction data in Fig. 3. Note the relaxation of both orientations towards the precise a and b orientations after orientational phase separation occurs.

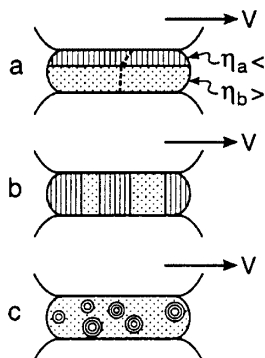


FIG. 5. Schematic illustrations showing (a) horizontal two phase (dashed line denotes velocity gradient along the cross section). (b) Vertical (in-plane) two phase. (c) Multilamellar vesicle ("onion") phase.

boundary layer formation (horizontal two phase, as shown in Fig. 4), or as coexistence of in-plane a and b domains (vertical two phase), as illustrated in Figs. 5(a) and 5(b), respectively. With respect to shear, the effective viscosity of the b oriented material is much higher than the effective viscosity of the same material when a oriented, so that $\eta_b \gg \eta_a$. Since the stress is continuous across the boundary ($\gamma_b \eta_b = \gamma_a \eta_a$), it is clear that the shear rate must be different in the a and b domains. Moreover, the relaxation of the strained b oriented material back to the initial b direction when the a peak emerges cannot be explained by the vertical domain case. For these reasons, it is reasonable to rule out the possibility depicted in Fig. 5(b). Another option to be considered is the possible formation of a multilamellar vesicle phase, known also as an "onion" phase [Fig. 5(c)]. Upon applied shear, this system was previously reported to form such "onions" with sizes determined by the shear rate, which can vary from a few microns to a tenth of a micron [14,15]. However, the clear anisotropy seen in our x-ray data is not consistent with a phase of spherical vesicles. Additionally, onions were not seen in optical microscopy in these samples after the XSFA experiments.

To our knowledge this is the first experimental evidence for orientational "phase" separation behavior and the formation of a shear-induced boundary layer via an interfacial "moving front," which advances with the increase in a orientations and subsequent decrease in b. Work is under way to improve the spatial resolution of the x-ray probe by using microfocusing x-ray optics for separately probing distinct sections in the contact. The use of a third generation synchrotron source will improve the time resolution of the x-ray experiments and allow combined structural and direct force measurements of films confined in much smaller gaps.

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