Direct Measurement of the Interaction between Two Ordering Surfaces Confining a Presmectic Film

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With a surface forces apparatus, we have investigated the isotropic and the nematic phases of a lyotropic solution near its lamellar phase. A smectic ordering shows up near walls, giving a specific oscillatory force profile which is shown to be the sum of two contributions. The symmetric distribution of the smectic order between the walls leads to an attractive background upon which oscillations arising from the elastic response of the layers are superimposed. In the isotropic phase, the oscillatory force is preceded by an attractive regime. We ascribe the attraction to a deeper penetration of the orientational ordering compared to the positional ordering range.

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Since the pioneering work of Sheng [1] concerning the effect of surface confinement on molecular ordering, many studies have probed the spatial dependence of the order parameter for liquid crystals in contact with surfaces [2–6]. Much attention has also been devoted to phase transitions of confined liquid crystals [1,7,8] showing a strong dependence on surface anchoring [9,10], the geometry of enclosure [9,11–13], and the order of the transition [10].

Specific interactions between ordering surfaces confining liquid crystal molecules have been studied only theoretically [7,14]. A natural approach is to describe the induced ordering in terms of a Landau order parameter and to approximate the interaction potential using a mean field free energy. The interaction between two parallel walls, generating a smectic layering parallel to the surfaces while the bulk phase is not yet smectic (presmectic film), has been addressed by de Gennes [14]. The order parameter describing the presmectic film was chosen to be the usual complex 1D density wave $\Psi = \psi e^{i\phi}$. De Gennes retained only the quadratic terms in the free energy [14], and therefore only the onset of a second-order transition was implicitly investigated. Symmetric boundary conditions were considered with a contact potential (zero range) between the surfaces and the liquid crystal particles. In that case, the magnitude of the smectic density modulation $\psi(x)$ decreases exponentially from the ordering surfaces to the mid-plane with a decay length $\xi = \xi_{\parallel}$, known as the order parameter correlation length. When the separation between the walls d is not an integral multiple of the smectic layer thickness a_0, $d \neq na_0$, a strain is applied to the presmectic film. The phase $\phi(x)$, related to the layer displacement $u(x)$ by $\phi(x) = 2\pi u(x)/a_0$, describes the local elastic deformation and is not uniform between the walls. The distortion is mainly undergone by the central layers where the smectic order is poorly established. Moreover, when the applied strain is half a layer, the central layer melts, $\psi(x = 0) = 0$, allowing the system to transit continuously from n to $n \pm 1$ layers. In short, a presmectic film confined between parallel walls is elastically equivalent to a series of springs of different stiffness. The stiffer ones are close to the walls, while the weaker ones lie at the center. The spring stiffness varies with the applied strain, especially the modulus of the central spring which vanishes as the strain tends to $a_0/2$. This mechanical response of a presmectic film is quite original and very different from the elastic behavior of a regular smectic stack [15,16]. Consequently, the specific interaction between the two ordering surfaces would have two distinct contributions: an attractive background due to the distribution of the magnitude $\psi(x)$ and oscillations resulting from the elastic stress of the smectic layers.

In this Letter we report the first experimental characterization of such a presmectic interaction. Using the surface forces apparatus (SFA) [17,18], we have investigated a lyotropic solution near the lamellar phase. This instrument allows one to measure the force between two mica surfaces immersed in a solution. The molecularly smooth sheets of freshly clived mica are glued to cylindrical lenses of perpendicular axes. To account for the data with much accuracy, we have slightly revised the early de Gennes model [14] by choosing more suited boundary conditions and by supplementing the de Gennes asymptotic calculation down to the small separations.

The system studied was a mixture of water and an anionic surfactant, caesium perfluorooctanoate (CsPFO) [19]. The micelles formed above the critical micellization concentration (CMC) are anisotropic with a disklike shape. At high micelle concentration, three distinct phases are found [19]: an isotropic phase (L_1) at high temperature, a smectic or a lamellar phase (L_α) at low temperature, and a nematic phase (N_D) for an intermediate range of temperature. At fixed composition, the N_D range is about 7 °C. Note that the L_1-N_D transition is weakly first order, while the N_D-L_α transition is second order over most of the N_D composition range. To measure the presmectic interaction, we have approached the lamellar phase from high temperatures, adjusting chemical compositions from one experiment to another so that the transitions were accessible around room temperature, i.e., between 18 and 31 °C, always above the Krafft temperature which is about 13 °C at the studied concentrations. $\Delta T = T - T_0$, the temperature difference from the smectic transition, is then chosen as the control parameter. The temperature was controlled to ±0.02 °C outside the SFA, but stability was better in the SFA due to its large mass and thermal inertia. Although the temperature between the mica surfaces was not probed during the experiments, previous evaluations have shown a constant offset of 0.1–0.2 °C compared to the outside temperature.

Figure 1 shows the qualitative evolution of the profiles in the nematic and in the isotropic phases as ΔT is decreased. Since one surface is suspended at the end of a spring of stiffness K, unstable regimes without data are seen when the force slope is greater than K [17]. The curves display the expected oscillatory interactions with a period that is quite constant. The oscillations superimpose over an attractive background (defined as the envelope of the minima), while the maxima describes a smooth decreasing function. Further away from the smectic phase, a smaller number of oscillations are seen concordant with a decreasing smectic correlation length. Between successive measurements performed with the same sample and at the same contact position, the oscillation amplitude decreases as the ΔT is lowered. Likewise, the attractive background holding up the oscillations weakens progressively as illustrated in Fig. 1. We have observed, however, some scattering on the amplitudes for similar samples studied at comparable ΔT [compare Fig. 1(c) and Fig. 2(b)]. Previous studies on simple liquids consisting of isotropic [20] or anisotropic [21] molecules that have some tendency to align parallel to the surfaces have shown force profiles similar to the curves of Fig. 1. A small number of oscillations were obtained giving the so-called solvation forces [18]. Moreover, Horn, Israelachvili, and Perez have studied the interaction between two surfaces confining a droplet of a thermotropic nematic at fixed temperature [22]. From a not well understood long-range repulsion, they observed the emergence of a structural interaction with up to six oscillations at short separations.

Force profiles recorded close to the N_D-L_α transition at the same contact position and with the same chemical composition allow a quantitative analysis (Fig. 2). When the bulk phase is lamellar [Fig. 2(a)], the force profile is a long-range oscillatory curve. This is the periodic profile expected for a smectic sample confined with a homeotropic alignment [23,24]. The distance between two successive minima must be equal to ba_0 (Fig. 3), where b is the Burgers vector of the edge dislocation loop, allowing the system to release the elastic stress by adjusting the number of layers from n to $n \pm b$ when the applied strain is $d \approx (n \pm b/2)a_0$ [15,16]. Since the oscillation period is found to be 6.3 ± 0.1 nm (Fig. 3), in agreement with the reticular

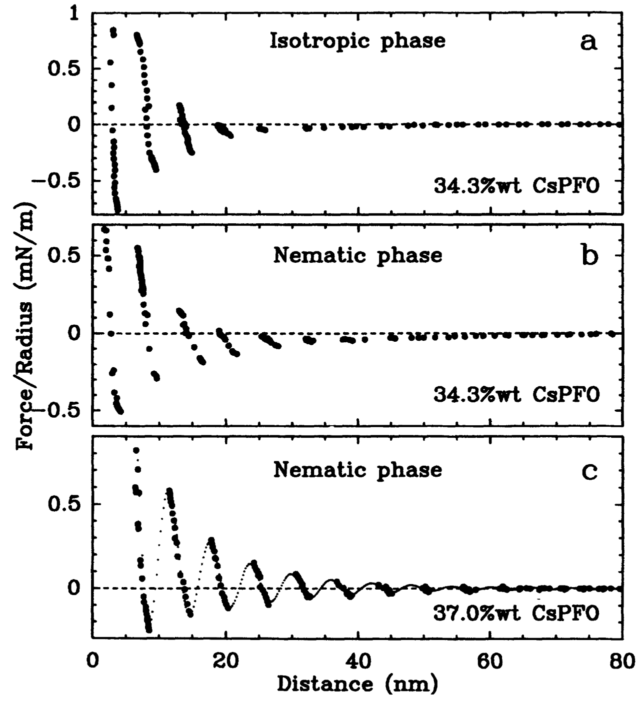

FIG. 1. Presmectic force profiles upon increasing the temperature (a) in the isotropic phase, 9 °C above the bulk lamellar transition (T_0), (b) close to the nematic-isotropic transition, 7 °C above T_0, and (c) in the nematic phase, 1.7 °C above T_0. The dotted line represents a fit using Eq. (2) giving $\xi_\parallel = 13.5$ nm.

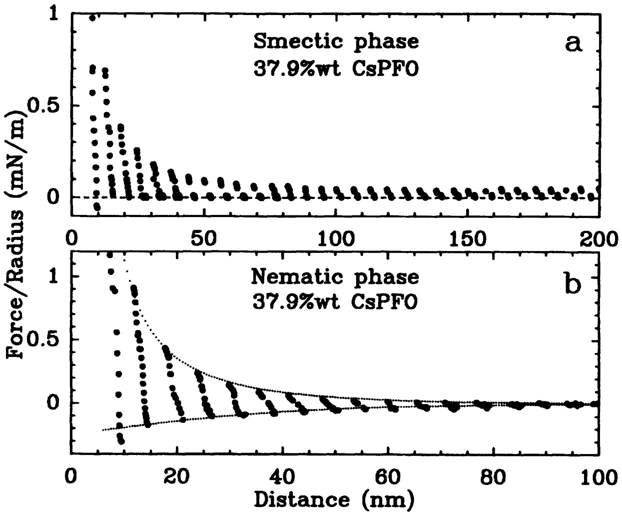

FIG. 2. Force profiles on both sides of the lamellar-nematic transition (a) in the lamellar phase, 3 °C below the smectic transition (T_0). The curve is a long-range oscillatory profile with a constant (zero) background and (b) in the nematic phase, 1.7 °C above T_0. The curve is a short-range oscillatory profile. The dotted lines are best fits using the modeling force (2) with $[\phi] = 0$ and π, respectively, for the attractive background and the maximum envelope giving $\xi_\parallel = 20.5$ nm.

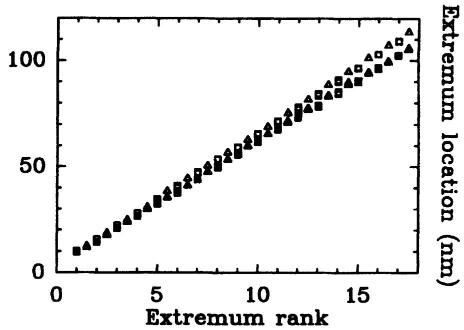

FIG. 3. Periodicity of the n first oscillations of the profiles of Fig. 2. Seventeen oscillations have been recorded in the presmectic interaction. The minimum positions (square) are plotted vs n and the maximum positions (triangle) are plotted vs $n + \frac{1}{2}$. The slopes give a period equal to 6.3 ± 0.1 nm for the smectic film (open symbols) and 5.9 ± 0.1 nm for the presmectic film (solid symbols) with similar intercept.

distances reported in the literature [25], we conclude that b is equal to 1 (pore defect) at short separations. Comparison of the contact position at equilibrium in surfactant solution with that of bar micas indicates that a uniform surfactant bilayer (or micelles) is adsorbed on the two surfaces. The contact shift was about 6.2 nm in direct agreement with the intercept of the coordinate axis in Fig. 3, which was found to be 3.0 ± 0.2 nm. However, this adsorption seems to occur only at low temperature near the lamellar phase as illustrated in Fig. 1. In the first two curves no adsorption was measured, explaining the shift in oscillation positions with the last profile. No systematic study of the adsorption conditions has been done. In Fig. 2(a) the oscillations lie down on a zero background. The attractive background present in the presmectic regime vanishes only between 2 and 3 °C below the N_D-L_α transition in accordance with its second-order nature. As mentioned earlier, this attraction results from the enhancement of the smectic order near the surfaces. In the lamellar phase the bulk-order parameter moves continuously toward the surface-order parameter. When the two parameters are similar, the interaction potential between the surfaces is dominated by the elastic behavior yielding the long-range oscillatory profile.

Figure 2(b) displays a presmectic force profile obtained just above the N_D-L_α transition showing a large number of oscillations (17 recorded). The oscillation period was found to be 5.9 ± 0.1 nm (Fig. 3), comparable to the previously measured smectic thickness. The small decrease in the period from one phase to another is in agreement with structural measurements reported in the literature [25]. Above the transition, homeotropic alignment is preserved and the thickness of the adsorbed surfactant layer remains the same.

In the de Gennes model [14], the ordering interaction between the walls and the anisotropic fluid is assumed to be a contact potential, expressed by a linear coupling term between the order parameter and a conjugate field, $-h_s[\Psi(-d/2) + \Psi(d/2)]$. In fact, this surface potential fixes the amplitude slope of the order parameter profile at the surfaces, whatever the separation between the walls, $\nabla_x\psi(-d/2) = -\nabla_x\psi(d/2)$. At large separations (the asymptotic regime considered by de Gennes [14]) the model predicts that the interaction between the walls averaged over the oscillations is zero [26], but at short separations the averaged free energy becomes attractive. If we change the boundary conditions in assuming a fixed smectic density on the surfaces, $\psi(-d/2) = \psi(d/2)$ (strong anchoring), the averaged interaction in the asymptotic regime remains neutral, but at short separations it becomes repulsive. From the presmectic curves of Fig. 1 and Fig. 2, on average, the measured forces are repulsive. A larger portion of the last oscillations stands above zero. Since a surfactant layer adsorbs on the mica surfaces near the lamellar phase (strong anchoring), the revised boundary conditions seem well suited for our experiment.

With the smectic density fixed at the surfaces, the de Gennes model can be solved exactly. The interaction between the walls can be written as the sum of two terms, one involving the amplitude and another involving the phase of the complex order parameter. In the de Gennes notation, the free energy is

$$f(d) = \alpha\xi_{\|}\rho_s\left(\tanh(d/2\xi_{\|}) + \frac{1 - \cos([\phi])}{\sinh(d/\xi_{\|})}\right), \qquad (1)$$

where $\rho_s = \psi_s^2$, $\xi_{\|}$ is the smectic correlation length, $\alpha = a(T - T_0)$ is the driving parameter, while $[\phi] = \phi(d/2) - \phi(-d/2) = 2\pi(d - na_0)/a_0$ is related to the strain applied to n presmectic layers when the separation d is not an integral multiple of a_0. The first term is the very general attractive amplitude contribution arising from the symmetric nonuniform distribution of a scalar order parameter as calculated first by Marčelja and Radić [27]. The second term is the elastic contribution of the presmectic film, a damped oscillatory function of period a_0. The maxima of the elastic contribution occur when the applied strain is half a layer $a_0/2$, $[\phi] = \pi$, and the central smectic layer melts, allowing the system to adjust the number of layers from n to $n \pm 1$. In the asymptotic regime, when $d \gg \xi_{\|}$, both the attractive background $f_{[\phi]=0} = \alpha\xi_{\|}\rho_s\tanh(d/2\xi_{\|})$ and the maximum envelope $f_{[\phi]=\pi} = \alpha\xi_{\|}\rho_s\coth(d/2\xi_{\|})$ follow an exponential law with a decay length $\xi_{\|}$. This interaction potential between two plates is short-range interaction as long as the system is not too close to a second-order transition. In this close vicinity, the higher order terms ($\Psi^4, \Psi^6, \cdots$) can no longer be neglected in the free energy [14].

The surface geometry in the SFA is not two parallel plates but two crossed cylindrical surfaces [17]. For the present case, we can use the Derjaguin approximation [28], $F(d) = 2\pi Rf(d)$, linking the force $F(d)$ between two identical crossed cylinders of radius R and the interaction potential $f(d)$ between two parallel plates when

$d \ll R$ ($R \approx 2$ cm). Indeed, the Derjaguin approximation is expected to hold because Eq. (1) falls off sufficiently rapidly (exponentially) with the distance. The model predicts the following force for the experiment:

$$F = 2\pi R \alpha \xi_{\|} \rho_s \left(\tanh[(d - d_a)/2\xi_{\|}] + \frac{1 - \cos([\phi])}{\sinh[(d - d_a)/\xi_{\|}]} - 1 \right), \quad (2)$$

where d_a is the zero stress separation without any smectic layer given by the intercept of Fig. 3. The third term arises from the geometry integration, ensuring a zero force at large separations. In Fig. 2(b), we present the result of a numerical fit performed both on the background and the maximum envelope using (2) with $[\phi] = 0$ and π, respectively. The modeling force is in remarkable agreement with the measured profile, except for the first minimum, but such a departure from the theoretical zero background was already present for the regular smectic force in Fig. 2(a). The correlation length $\xi_{\|}$ extracted from the fit was 20.5 ± 1 nm, which is between 2 or 3 times the layer thickness. The same fit procedure has been carried out with the curve of Fig. 1(c), where the full modeling force is displayed.

The temperature range over which the fit can be performed is quite limited (no more 3 °C). In most of the N_D phase and in the L_1 phase, the oscillatory presmectic forces are preceded by a weak attractive regime as illustrated, for instance, in Fig. 1(b) for separations between 40 and 80 nm or in Fig. 1(a) for separations between 30 and 50 nm. Accordingly, the first oscillations that follow are often fully negative. On approaching the N_D-L_1 transition from the L_1 phase, the range of the attractive regime increases continuously. It reaches a maximum value at about 40 nm, close to the transition [Fig. 1(b)]. Below the transition, the strength of the attraction decreases progressively and disappears definitively about 3 or 4 °C beneath it. A likely interpretation is that a prenematic film precedes the presmectic film. Near the ordering walls there exists the presmectic film with both an orientational and positional order. Recalling that both bulk transitions are either second order or weakly first order, we can suppose that while the positional order is lost outside the presmectic film, the orientational order is kept over a thicker layer giving a prenematic film. Its thickness depends on the distance from the N_D-L_1 transition. Under this picture, an attraction is expected before the presmectic oscillatory force when the prenematic films of each surface overlap first. When the nematic order can be described by a scalar order parameter (uniaxial), the interaction between the two confining surfaces would be identical to the amplitude term of (2) giving the attractive background [7,27]. Even in the nematic phase the attraction would be effective so long as the nematic order parameter in the bulk is weaker than the value imposed at the interface of the presmectic and prenematic films.

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