Forces Measured in a Swollen Lyotropic Lamellar Mesophase Confined between Solid Surfaces

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The measured force as a function of separation between two mica surfaces immersed in a swollen lyotropic lamellar mesophase (interlamellar spacing 25–30 nm) is an oscillatory function of distance superimposed on a background attraction. The periodicity of the oscillations matches the bulk layer spacing at large surface separations, but it decreases at smaller separations, suggesting that the interlayer repulsion is due to fluctuations of the interfaces. The solid walls reduce these fluctuations, leading to a negative disjoining pressure.

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Amphiphilic molecules made of polar heads attached to apolar tails to form condensed phases where polar/apolar contacts are avoided. These phases can be seen as arrays of polar/apolar interfaces, with separations of the order of molecular lengths.[1] The "simplest" of these mesophases are the lyotropic lamellar phases, where flat amphiphilic bilayers are separated by thin water layers in a one-dimensional stacking. However, some lamellar mesophases can be swollen by an appropriate diluent, either water or oil. In the system of water, sodium *n*-octylbenzene sulfonate (SOBS), and 1-pentanol, the lamellar mesophase can incorporate large quantities of a decane-pentanol mixture while retaining the lamellar structure[2]—the very extensive swelling is found up to a repeat distance of 1100 nm.[3] The stability of the stacking with such a huge spacing, far beyond the range of usual surface interactions (van der Waals, electrostatic, hydration, hydrophobic forces), has been analyzed by by Helfrich:[4] He has suggested that out-of-plane thermal fluctuations of membranes would generate the required long-range interaction. This entropically induced interaction originates from the steric hindrance of the thermal undulations of the membrane bound between two neighbors. X-ray, neutron, and light scattering experiments have recently been used to study highly swollen lamellar mesophases.[3,5,6] In particular, high-resolution x-ray scattering experiments have yielded values of the elastic constants of the bulk layered system from the thermal-diffuse-scattering profile around the Bragg diffraction point.[5]

In an attempt to provide information on the existence of steric fluctuation forces, a series of force measurements has been carried out. Two solid surfaces were immersed in a swollen lamellar mesophase of the above system and their interaction measured as a function of the surface separation. The experiments employed a technique[7] which has previously been applied to nematic and smectic thermotropics,[8] and the lamellar phase of the egg-lecithin–water system.[9]

The sodium *n*-octylbenzene sulfonate (SOBS) was a gift from Larché.[2] The water was doubly distilled while the pentanol and decane (Sigma) were distilled once. The samples were prepared by weighing the four components and mixing them in a sealed tube by repeated centrifugation. Expressed in g/g the weight fractions were the following: water 10.04%, SOBS 9.23%, 1-pentanol 12.78%, and *n*-decane 67.94%.

Molecularly smooth sheets of muscovite mica were glued to curved (radius ~ 2 cm) silica disks and mounted in a surface force apparatus.[7] This instrument allows the force F between the surfaces to be measured to within 10^{-7} N by monitoring the deflection of a double-cantilever spring on which the lower surface is mounted, and the surface separation D to be independently controlled by the expansion of a piezoelectric crystal and measured to within 0.2 nm by an optical-interference technique. Since one of the mica surfaces is suspended at the end of a spring stiffness $K \sim 10^2$ N/m, forces can be measured only in regions where $\partial F/\partial D < K$. When the gradient of the force $\partial F/\partial D$ exceeds the stiffness K, instabilities occur, leading to jumps.[7] The results of the force measurements are given as F/R (measured force normalized by the mean radius of curvature R of the surfaces) and this is equal to $2\pi E$, where E is the corresponding interaction free energy per unit area between flat surfaces.[10] The validity of this relationship in the case of multilayered systems has been discussed in detail by Horn, Israelachvili, and Perez.[8]

The experiments were performed with both mica surfaces immersed in a bath[11] filled with bulk mesophase. The thermal drift of the surfaces was less than ± 2 Å per min. In order to align the layers parallel to the mica surfaces, the surfaces were moved very slowly back and forth over separations of several tens of microns. This method, equivalent to shearing the mesophase, is commonly used to produce homeotropic alignment in thermotropic[12] or lyotropic lamellar mesophases.[13] The system was then left to equilibrate overnight at a separation of a

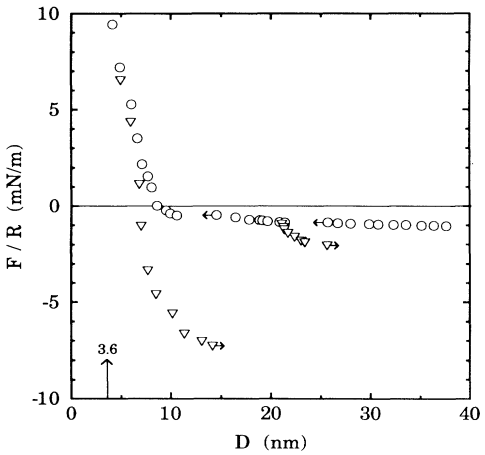

FIG. 1. Measured force F (normalized by the mean radius of curvature R of the surfaces) as a function of the separation D between crossed mica cylinders immersed in a swollen lamellar mesophase of the system of water, SOBS, 1-pentanol, and decane ($D=0$ is at bare-mica contact). The arrows, indicating inward jumps (←) and outward jumps (→) from unstable to stable positions, have a slope of $K/R \sim 7\times10^3$ N/m^2. Measurements during an inward run are represented by circles (○), while outward data are plotted as triangles (▽). The contact position of the surfaces (located 3.6 nm out from bare-mica contact) in the liquid crystal is reached under large applied forces (~20 mN/m) not shown here.

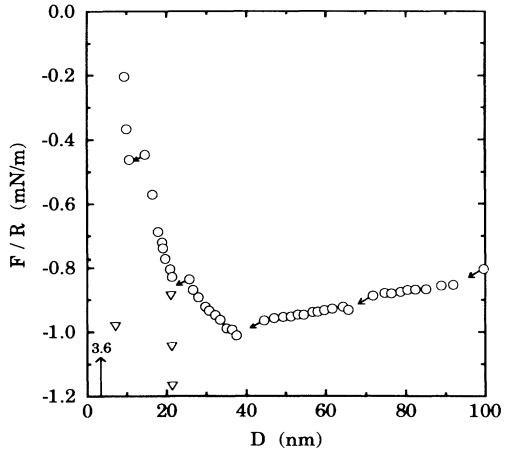

FIG. 2. Same as in Fig. 1 but for larger separations (up to 100 nm) and on an expanded scale. The periodicity of the oscillations calculated from the contact position (3.6 nm out from bare mica) are 10.9 ± 0.5, 12.2 ± 0.5, 19 ± 1, 27 ± 1, and 27 ± 1 nm.

few microns.

Because of the viscosity of the mesophase and the slow reequilibration of the confined structure as the separation between the mica surfaces is changed, care must be taken to ensure that equilibrium results are obtained.

The viscous drag effect was estimated using the calculations of Chan and Horn[14] and the more recent analysis of Horn *et al.*[15] To get an accuracy in spatial distance of 0.2 nm, the required waiting period between two of our experimental inward steps (~3 nm) during a force run is estimated to be about 3 s at 300-nm separation, 15 s at 100 nm, increasing to 100 s at 10 nm, and 200 s when the surfaces are close to contact. We point out here that these estimated times are based on a viscosity (0.15 cP measured with a viscosimeter) which averages in a complicated manner the different components of the anisotropic viscosity due to the slip of layers over each other.

In order to maximize the time for achievement of thermodynamic equilibrium, the inward runs were carried out as slowly as the thermal drifts would permit: 4–6 h were taken to decrease the separation from 300 nm down to contact. Outward runs were only started after maintaining the surfaces at a given separation for about 4 h.

The following are the general features of the results (Figs. 1–3):

(i) The measured refractive index of the mesophase is 1.42 ± 0.01, and independent of the surface separation.

(ii) The contact between the surfaces is shifted from bare mica by 3.6 ± 0.1 nm indicating that a monolayer of surfactant was adsorbed on each mica surface. It seems likely that the polar heads are next to the mica surfaces (otherwise twice the layer thickness would be measured), since the small quantity of water is used only to hydrate the polar heads. We could not detect any double-layer force between the mica surfaces, although it should be noted that if a double-layer force has an extremely long Debye length, as expected for the very low electrolyte concentrations possible in a low dielectric

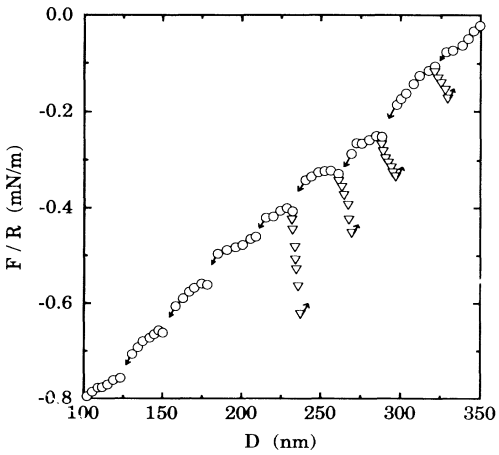

FIG. 3. Same in in Figs. 1 and 2 but for larger separations (100–350 nm). Beyond 350 nm from contact, no force (<0.01 mN/m) is detected. The periodicity of the oscillations correlates well with the expected mean layer spacing in a bulk sample (28 nm).

constant medium, it would give an almost constant background repulsion which would not be detected by our force measuring technique.

(iii) The spatially decaying oscillatory forces are measurable up to about fourteen layers, i.e., 350 nm of separation between the surfaces. These oscillations are superimposed on a long-range attractive background force.

(iv) The first three oscillations have a periodicity (11, 12, and 19 nm, respectively) much smaller than the periodicity observed beyond the fourth oscillation, about 27–29 nm. Statistical analysis of the results of five different experiments show that, starting from $D=3.6$ nm, successive oscillations have a period of 10.9 ± 0.5, 12.2 ± 0.5, 19 ± 1, 27 ± 1, 27 ± 1, 28 ± 1, 28 ± 1, 28 ± 1, 28 ± 1, 28 ± 1, 29 ± 1, 29 ± 2, and 29 ± 2 nm. The values at large distances correlate well with the expected mean layer spacing as measured by x-ray diffraction in a bulk sample of the same concentration (28.0 ± 0.1 nm).[2,3]

(v) On separation the surfaces can be moved some distance—typically 1%–2% of the total—before they jump apart. This feature is presumably related to the elastic properties of the lamellar structure. The depths of the force minima are dependent on the time allowed for the system to equilibrate. As an example, if the surfaces were separated just after having been brought into contact, almost no adhesion was observed; if the surfaces were separated after 1 h a pulloff force of $F_0/R=1$ mN/m was measured, increasing up to 7.5 mN/m if the surfaces were separated after 4 or 12 h. Obviously, this time dependence is related to equilibration effects and rearrangement of the lamellar structure. As it is very difficult to stabilize the system at a given separation during more than a couple of hours due to drifts, only the outward-run data for the smallest separations (where the forces become repulsive) or for the largest ones (where the forces are only weakly attractive) are reported here.

(vi) The individual oscillations do not appear to be sinusoidal: The two first oscillations have a steeply rising repulsive part wherein the positions of all the minima $n-1$ are at about the same separation as the next maxima n.

These results show that the force between two molecularly smooth solid surfaces separated by a slightly swollen lyotropic lamellar mesophase exhibits spatial oscillations with periodicity equal to the expected bulk spacing, but that this periodicity decreases when the surface separation becomes of the same order of magnitude as the spacing. These spatial oscillations indicate that the confined system retains its lamellar structure even though the layers have to contour the curved mica surfaces ($\sim$1–2 cm). On going outwards from the point of closest approach the surface separation increases and consequently dislocations must appear to relax the stress in the lamellar structure.[16,17] When the mica surfaces are brought together the dislocations move away from the point of closest approach, and the spacing between the confined layers decreases due to the compressibilty of the system which also reduces the fluctuations of its interfaces. Spontaneous pinching of the bilayer interfaces (which has already been observed in classical lyotropic lamellar mesophases[18]) causes a breakdown into parts of the layer located midway between walls, and the pieces are expelled into the surrounding bulk sample. An alternative way to squeeze out a layer on approach would be to nucleate an elementary edge dislocation.[17] This process is certainly likely in order to incorporate a supplementary layer on separation: As the surfaces are taken apart two half layers move in as the loop of the dislocation becomes smaller.

This is the first experimental report of the dependence of layer thickness on separation between solid surfaces in a swollen lyotropic liquid crystal. For the last three lamellae the periodicity of the oscillations departs strongly from the bulk layer spacing. This is due to a reduction of fluctuations of the interfaces when the separation between the surfaces corresponds to the thickness of only a few lamellae, as predicted by recent Monte Carlo simulations.[19]

In a smectic structure, the amplitude of the oscillations is related to the compressional modulus of the layered system, if the energy associated with the displacement of dislocations is assumed to be negligible. Because most of the minima are experimentally inaccessible and their magnitudes show a significant time dependence we cannot be certain of the amplitudes of the oscillations. This precludes any meaningful comparison with expected values of the compressional modulus for similar systems.[5,6]

The shape of the repulsive parts of the force profile should be related to the steric fluctuation forces between the interfaces of the layers. In the case of hard interfaces, which are sterically repulsive, Helfrich predicts a parabolic profile of the force as a function of the distance.[4] Unfortunately, our data do not permit a comparison to be made, for the reasons given above. Moreover, any such comparison would be difficult as the oscillatory forces are superimposed on a general attractive background force. Furthermore, we cannot be certain of the true magnitude of the background attraction due to the very long equilibration times required in this system.

The long-range background attraction is far stronger than predicted by the Lifshitz theory of van der Waals forces.[20] To interpret the extra attraction observed, Marcelja has suggested[21] considering the ordering potential exerted on the lamellae by the walls in contact with the confined sample: These walls reduce the amplitude of fluctuations of the confined membrane interfaces compared to those exhibited in a bulk sample. It is analogous to finite-size nematic sample between two parallel ordering walls, first studied theoretically by Sheng[22] and

reanalyzed by Poniewerski and Sluckin.[23] The force, sometimes called disjoining force or pressure, exists because each wall independently affects the structure of the adjacent fluid; the presence of a second wall changes this effect slightly, and hence the free energy changes with separation. Because this force is an increasing function of the wall separation and is zero at infinite separation[23] the disjoining force is always negative, and the plates attract each other. This type of attractive force is conceptually similar to the attractive entropic depletion force associated with changes in the density of solute molecules between two surfaces as they approach each other.[24] We hope to calculate the order of magnitude of this disjoining force to establish whether or not the background attraction is related to it.

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