Dynamic Light Scattering Study of Dilute Lamellar Phases

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Dynamic light scattering measurements on oriented samples of lyotropic smectics have been performed. The layer compressibility modulus B is extracted from the anisotropic dispersion relation of the so-called slip mode, which arises from the coupling between concentration and layer displacement fluctuations. The samples are diluted with three different solvents (repeat distances 50 to 800 Å): The behavior of B suggests either undulation or electrostatic repulsions between membranes, depending on the swelling solvent.

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A lot of interest is currently focused on the understanding of the physics of fluctuating surfaces.[1] In the absence of surface tension, deformation of surfaces is governed by elastic bending energy. Thermal fluctuations leading to undulations of the membrane may have important consequences when the bending modulus is of the order of k_BT. Dilute lamellar phases are particularly interesting systems for the study of fluctuating surfaces. Indeed, in some favorable cases, multimembrane lyotropic smectics with repeat distances of hundreds and even thousands of angströms can be prepared with addition of suitable solvents.[2-6] It has been recently demonstrated that in many cases these extreme dilutions result from the existence of a universal repulsive interaction due to the steric hindrance to thermal fluctuations.[4,5] This purely entropically driven interaction first proposed by Helfrich[7] is long range and keeps the layers apart even for such large distances. These dilute lamellar phases are also a unique example of colloidal smectics. The very large repeat distances one can obtain are responsible for very low elastic constants. The layer compressibility modulus B may vary continuously over about 6 orders of magnitude along the dilution range and the layer bending modulus over 2 orders of magnitude.[5]

We have carried out a dynamic light scattering study of lamellar samples derived from a unique basic system but located on three distinct dilution paths. The system consists of a concentrated lyotropic smectic (repeat distance about 40 Å) of water-pentanol-SDS (sodium dodecyl sulfate). It has been swollen by (1) a mixture of dodecane and pentanol ("oil dilution"), (2) a 0.4*M* sodium chloride solution in water ("brine dilution"), and (3) pure water ("water dilution"). The limiting repeat distances that can be obtained are 460, 800, and 80 Å, respectively. These three dilution paths have been previously investigated by a high-resolution x-ray technique.[4,5] However, because of experimental limitations, x-ray experiments have been restricted to repeat distances smaller than 200 Å. Here, our light scattering method allowed us to get data through the whole dilution range.

We recall the theoretical basis of the hydrodynamics of a two-component smectic-*A* liquid crystal, due to Brochard and de Gennes.[8] In addition to the classical six modes of an ordinary (one-component) smectic *A*, an additional mode (called the slip mode in Ref. 8) comes into existence for lyotropic systems, arising from the coupling between concentration (a conserved quantity) and layer displacement (a broken symmetry variable). These seven modes may be sorted into two groups: a "high-frequency," four-mode group which comprises sound, a thermal wave, and a shear wave; a "low-frequency," group of three modes, the slip mode and second sound, with highly anisotropic properties (the second sound degenerates into an undulation mode and a shear wave when the wave vector **q** is parallel to the layers, or into a permeation mode and a shear wave when **q** is normal to the layers). In the high-frequency group there is essentially no coupling to layer displacement nor to concentration fluctuations and thus little scatter of light. On the other hand, all three modes of the low-frequency group may, in principle, be studied by light scattering. Whereas the second sound is propagative (when **q** is *oblique*), the slip mode is always diffusive; its anisotropic dispersion relation has two simple limiting expressions.[8]

(i) When **q** is parallel to the layers, the relaxation frequency ω is given by $\omega = \mu D_{33} q^2$, where μ is a dissipative coefficient, D_{33} is the inverse of the osmotic compressibility, and q is the modulus of the wave vector. In this limit, concentration and layer displacement fluctuations get uncoupled and the slip mode degenerates into the usual mutual diffusion mode of a two-component system. The slip mode has been experimentally observed in this geometry by Chan and Pershan.[9]

(ii) When **q** is oblique with respect to the layers, $\omega = \mu \Xi q_\perp^2$, where $q_\perp$ is the modulus of the projection of q along the layers, and Ξ is a reactive coefficient which reduces to B, the layer compressibility modulus at constant chemical potential, in the limit $B/D_{33} \ll 1$. The spectral analysis of the light scattered by the slip mode

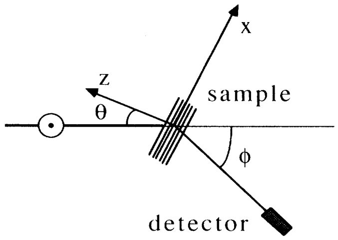

FIG. 1. Geometry of the experimental setup: the normal to the layers z, the incident light, and the scattered beam are in the same plane. The incident light is polarized perpendicularly to this plane.

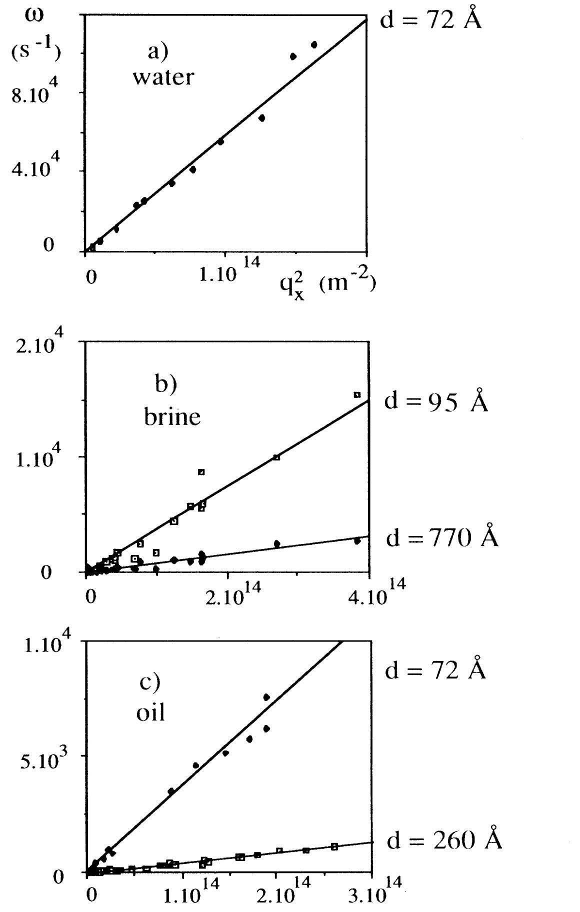

FIG. 2. Representative anisotropic dispersion relations for the three dilution paths: (a) water dilution, (b) brine dilution, and (c) oil dilution. The relaxation frequency ω is a linear function of the squared x component of the wave vector: $\omega = Dq_x^2$ (d is the repeat distance of the multimembrane stacking).

in a geometry where the wave vector is oblique may thus be a way to measure B in lyotropic smectics. Note that this mode reduces to the usual peristaltic mode in two-dimensional soap films.[10]

The experiments have been done as follows: cylindrical glass capillaries with a rectangular section (about 100 μm thick, 1 mm wide, and 35 mm high) are filled by capillarity, then sealed. This procedure leads to unoriented samples. A good orientation is obtained by a thermal treatment: heating the sample through the lamellar-isotropic phase transition (which takes place at a temperature ranging from 30 °C to 100 °C), then cooling it very slowly (0.2° per minute) leads often to an almost perfect homeotropic orientation. The geometry of the light scattering setup is described schematically in Fig. 1: The sealed capillary can rotate around its vertical long axis (angle θ) which is kept perpendicular to the scattering plane, i.e., the normal to the layers is always within the **q** plane. The polarization of the incident light (ionized krypton laser operating at $\lambda = 647.1$ nm) is vertical. For such a configuration, there is no scatter of light originating from layer displacement fluctuations. In a normal run, we do not analyze the polarization of the scattered light, but we do check that depolarized scattering is negligible, as expected from concentration fluctuations. The wave vector **q** is defined by the angle ϕ between the detector and the laser beam. Its three components are $q_x = q\cos(\theta - \phi/2)$, $q_y = 0$, $q_z = q\sin(\theta - \phi/2)$, with $q = 4\pi n/\lambda \sin(\phi/2)$.[11] A typical experiment is done with ϕ fixed (constant modulus q of the wave vector) and θ increasing from $\phi/2$ to $\phi/2 + \pi/2$. This allows us to scan the entire range of accessible wave vectors $q_\perp$ for this geometry. We then proceed to other angles ϕ. Data are recorded at three to five different ϕ angles ranging from 15° to 160°. The signal is analyzed with a Brookhaven Instruments digital correlator (72 channels) which gives the time correlation function of the signal. Except for the limiting values of θ (close to $\phi/2$ or $\phi/2 + \pi/2$), the dynamic part of the signal is easily recovered from the static one: for θ approaching $\phi/2 + \pi/2$ ($q_x = 0$) the specular reflection on the capillary gets close to the scattered beam and no measurements are possible; for θ approaching $\phi/2$ ($q_z = 0$) the dynamic part of the signal decreases significantly and its characteristic frequency gets very large.

Between these two extreme limits the characteristic relaxation frequency ω of the signal is obtained by means of a first-order cumulant expansion. Since the heterodyning conditions are not well controlled (static scattering by remaining dislocations and by the walls of the cell), we also processed the data under the assumption of a mixture of heterdyne and homodyne components: The resulting relaxation frequencies were not affected by the fitting procedure, within the experimental accuracy. Figure 2 shows some $\omega(q_x^2)$ curves representative of the behavior observed for the three sample families: The dispersion relation is well described by the equation $\omega = Dq_x^2$, as expected for the slip mode in the case of an

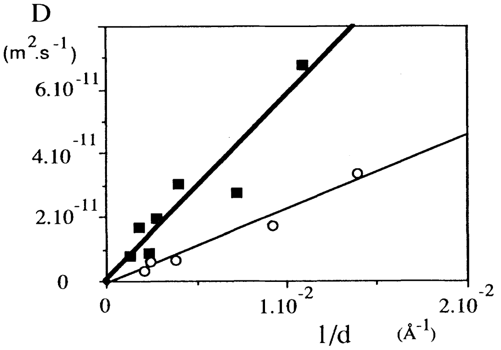

FIG. 3. Plot of the "diffusion" coefficient D as a function of the inverse d spacing for the oil and brine dilutions. The linear behavior is the signature of the undulation interactions. The measure of the slopes leads to $k_c = 1.6 k_B T$ (oil dilution, open circles) and $k_c = 0.8 k_B T$ (brine dilution, filled squares).

oblique wave vector. As is apparent in Fig. 2, D decreases as the interlayer spacing d increases for the brine and oil dilutions. This behavior is linked to the interactions between the membranes constituting the lamellar phase, as we argue later on.

Figure 3 shows for two dilutions (brine and oil) the evolution of D as a function of the interlayer distance d. Values of d smaller than 200 Å have been obtained from x-ray measurements; larger ones are deduced from the composition of the samples, with use of the x-ray result that the mean area per polar head is essentially constant upon dilution (i.e., the osmotic compressibility D_{33}^{-1} is very small).[5] The experimental data hint at a d^{-1} behavior for D which can be interpreted within the Brochard–de Gennes description of the slip mode. Proceeding further, we are led to write $D = \mu B$. To get the layer compressibility modulus B, we need an expression for the dissipative coefficient μ. It has been worked out by Brochard and de Gennes, who modeled the dissipation as due to the Poiseuille flow of the solvent between plane parallel membranes. In the limit of a large repeat distance d, the following expression is obtained[8]: $\mu = d^2/(12\eta_s)$, where η_s is the shear viscosity of the swelling solvent.

Our results thus suggest that B is inversely proportional to d^3 for the dilution with oil or brine. This behavior may be understood with a proper description of the interactions between membranes: as proposed first by Helfrich,[7] the steric hindrance to the thermally excited undulations of the membranes in a lamellar phase lead to a long-range repulsive entropically driven interaction. If this steric interaction is the only *dominant* one (no long-range electrostatic interactions: uncharged membranes or high ionic strength), the layer compressibility modulus is[7,12]

$$B_{\rm st} = \frac{9\pi^2 (k_B T)^2 d}{64 k_c (d-\delta)^4},$$

where k_c is the bending constant of the membrane and δ is its thickness. If there are *unscreened* electrostatic interactions, they always dominate at large distances; the layer compressibility modulus becomes[5,12]

$$B_{\rm elec} = \frac{\pi k_B T d}{2 L_B (d-\delta)^3},$$

where L_B is the Bjerrum length of water (≈ 7 Å).

The experiments support this analysis: Brine and oil dilutions, where no electrostatic interactions are expected, have B linear in $1/d^3$ or D linear in $1/d$ (the inequality $\delta \ll d$ is thoroughly fulfilled since $\delta \approx 20$ Å)[5]; from the slopes we get $k_c \approx 1.6 k_B T$ for the oil dilution and $k_c \approx 0.8 k_B T$ for the brine one. The layer compressibility modulus B ranges from about 10^4 Pa (less dilute "oil" sample) down to 10 Pa (most dilute "brine" sample), typically 10^3 to 10^6 times smaller than the values encountered in usual thermotropic smectics but comparable to the helix compressibility modulus of cholesterics. We shall not draw quantitative conclusions in the water dilution case, since our data are yet scarce and scattered: With d ranging from 50 to 80 Å, measured values for D are between 4×10^{-10} and 7×10^{-10} m^2 s^{-1}. Note, nevertheless, that the correct order of magnitude for D ($D \approx 8\times10^{-10}$ m^2 s^{-1}) is given by the use of the expression $B_{\rm elec}$.

We have demonstrated the feasibility of the dynamic light scattering method for studying interactions between membranes in lyotropic dilute lamellar phases. Indeed, the relaxation frequency of the slip mode at oblique wave vectors is simply related to the layer compressibility modulus (at constant chemical potential) B, i.e., to the intermembrane interactions. In contrast with previous x-ray measurements, this technique allows us to scan the whole dilution range of the system investigated. In these series of experiments we were able to confirm, and extend to far larger dilutions, the x-ray results on less dilute samples, namely that undulation forces always dominate for oil and brine dilutions of the water-pentanol-SDS system. Moreover, electrostatic interactions dominate when charged membranes are swollen with pure water.

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[11] The exact formula for $\mathbf{q}$ is complex in general because of the optical anisotropy of the medium; if both incident and scattered waves have their polarization perpendicular to the optical axis (uniaxial medium), the formula given in the text obtains, where n should be taken as the ordinary index of refraction n_0. Since the birefringence is small and the samples dilute, a very good approximation is $n_0 \approx n_e \approx n_s$, with n_s the index of refraction of the solvent (oil: 1.42; brine: 1.34; water: 1.33).

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