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Abstract. The effect of water thickness on the mean curvature modulus κ of an inverted bilayer has been investigated. Our system is a lamellar phase made up of a series of water films each surrounded by two ionic surfactant monolayers and separated with hydrophobic solvent. The elastic constant κ has been estimated using the excess-area method and it is shown to decrease when the thickness of the water layer increases. This result cannot be interpreted in terms of electrostatic effects—an *increase* of κ is expected instead—but may arise from a coupling between short-range surfactant interactions and curvature strains.

The elastic bending constant κ of membranes is a key parameter in the understanding of the stability and thermodynamic properties of surfactant phases made up of flexible membranes [1, 2, 3, 4]. Many systems such as microemulsions [1, 5], dilute lamellar phases [6, 7], sponge [8, 9] and vesicle phases [10, 11] can indeed be considered as phases of fluctuating surfaces. Their thermodynamic properties can be described in terms of a competition between curvature energy and entropy coming from the fluctuations of the film. Several microscopic parameters are supposed to control the absolute value of the elastic constant κ, among which the bilayer thickness is one of the most easily accessible experimentally [12]. Moreover a number of theoretical predictions have emphasized the role of the electrostatic contribution in relation to κ [13–18]. According to the relative values of three characteristic lengths (Debye–Hückel, Gouy–Chapman and water thickness) several regimes can be described (see [17]). One of the most interesting regimes is the so-called Gouy–Chapman regime where the contribution of the electrostatic interactions to the bending modulus is a *linearly increasing* function of the water thickness [17, 18]. This regime is expected to be found when no electrolyte is added to the polar solvent of the ionic surfactant molecules [18]. To our knowledge, no experimental measurement has been made aiming at checking this theoretical prediction.

In order to investigate the eventual effect of electrostatic interactions on the bending elastic constant, we have studied an *inverted* bilayer system: two (charged) surfactant films surround a water layer without any added electrolyte. There is a weakly screened electrostatic interaction between two adjacent surfactant films through the water layer they share, but no long-range electrostatic interaction between different bilayers since they are globally charge neutral. We have worked with the lamellar (smectic A) phase obtained in the *quaternary* sodium dodecylsulphate (SDS)–pentanol–water–dodecane system—see

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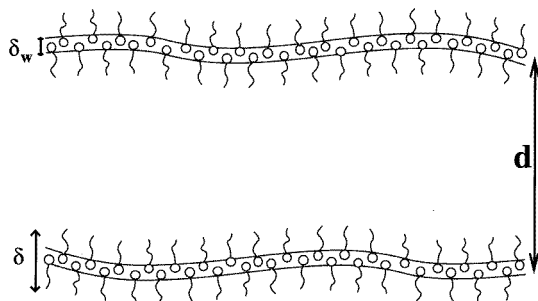
Figure 1. A schematic representation of the inverted lamellar phase: a water film of thickness δ_w is surrounded by two surfactant films. The—undulating—membranes (their geometric thickness is δ) are separated with dodecane. The repeat distance of the smectic A liquid crystal is d.

figure 1 for a geometrical schematic representation of the structure. The surfactant film is a mixture of SDS and pentanol. A small amount (about 8%) of pentanol also gets dissolved in dodecane, and a negligible amount (less than about 1.5%) in water. The complete phase diagram may be found elsewhere [19, 20]. In this system the lamellar phase can be significantly swollen with dodecane for a wide range of water-to-SDS ratios (W/S, in weight, varying typically from 1 to 4). Undulation interactions were shown to be responsible for the relatively high dilutions observed [7], indicating that the inverted bilayers are rather flexible objects. Varying the water content of the bilayers, we induce a significant variation of the water thickness δ_w and therefore of the electrostatic interaction between the surfactant films. On theoretical grounds [17] we expect in our system the following electrostatic contribution $\delta\kappa_e$ to the mean curvature modulus:

$$\delta\kappa_e \propto \frac{\delta_w}{L_B} k_B T \tag{1}$$

where L_B is the Bjerrum length of the solvent, i.e. about 7 Å at room temperature for pure water. Note that the prefactor in equation (1) is not known numerically in the planar geometry of the lamellar phase. However, a rather small value, namely $1/\pi - \pi/12 \approx 0.06$, was obtained in the simple case of cylindrically wrapped films [17].

Different methods have been used in the literature to gain access to the value of κ. The most direct methods are either local ones based on the measure of the amplitude of the membrane normal fluctuations [21, 22] or more collective ones, analysing the long-wavelength modes of the smectic phase [23]. A simpler method, while more indirect, has been suggested and is related to the *excess area* arising in the membrane crumpling. It consists in measuring precisely the position of the first-order Bragg peak of the lamellar samples along a dilution line. A logarithmic deviation from the ideal swelling law is expected in lamellar systems stabilized by undulation forces [24] and indeed experimentally observed with flexible enough membranes [25, 26, 27]. The best estimate for this effect gives—for small enough membrane volume fractions ϕ—the following swelling law for the smectic period d [28]:

$$d = \frac{1}{\phi}(A - B\log\phi) \tag{2}$$

where the constants A and B are expressed in terms of the membrane geometric thickness

δ and of the elastic constant κ by

$$A = \delta\left(1 + \frac{k_B T}{4\pi\kappa} \log\left[\sqrt{\frac{32\kappa}{3\pi k_B T}} \frac{\delta}{a}\right]\right) \tag{3}$$

and

$$B = \delta\frac{k_B T}{4\pi\kappa}. \tag{4}$$

The molecular length a in equation (3) corresponds here to the short-wavelength cut-off of the in-plane fluctuations. In what follows we take $a \approx \sqrt{\Sigma} = 5$ Å (Σ being the area per polar head in the surfactant layers).

We have used the above-outlined excess-area method to determine the evolution of κ as a function of the bilayer water content. Peak positions were measured with an in-house high-resolution x-ray spectrometer. Both the monochromator and the analyser are triple-bounce germanium channel-cut crystals, leading to a narrow in-plane resolution function (half-width at half-maximum of the order of 0.002 Å^{-1}).

In the data analysis we assume that, for a given dilution line (i.e. for a given water-to-SDS ratio W/S), the geometric membrane thickness δ is equal to the smectic period of the *dodecane-free* sample. In order to precisely estimate δ, we measure as a function of the water content the first-order Bragg peak position q_0 of such samples, defining δ as $2\pi/q_0$. The lamellar phase of this SDS–water–pentanol ternary system is stabilized by electrostatic interactions and consequently does not exhibit logarithmic corrections. As previously shown [29], the swelling law relating the smectic period δ of this ternary system to the *water* volume fraction is

$$\delta = \frac{2\delta_S}{1 - \phi_w} \tag{5}$$

with δ_S the surfactant film thickness. Since we are working mainly with rather concentrated ternary systems ($\phi_w > 0.30$), we ignore the small amount of pentanol dissolved in water (we checked that this has no consequences on the results) and find $\delta_S = 10.1$ Å.

Table 1.

δ (Å)	$d\phi$ (Å)	$\kappa/k_B T$ (from equation (4))	$\kappa/k_B T$ (from equation (6))
32.0	$32.2 - \log\phi$	2.56	2.39
32.6	$32.4 - 2.27\log\phi$	1.14	0.95
35.7	$32.8 - 3.3\log\phi$	0.85	0.63
38.7	$35.6 - 7.9\log\phi$	0.39	0.24
39.1	$37.8 - 11.05\log\phi$	0.28	0.17
40.2	$37.0 - 10\log\phi$	0.31	0.19
46.0	$44.6 - 11.4\log\phi$	0.32	0.19

Seven dilution lines were followed, adding dodecane and pentanol to the initially ternary systems. The inverted bilayer thicknesses δ vary from 32 Å to 46 Å, corresponding to a water layer thickness δ_w ($\delta_w = \delta - 2\delta_S$) in the range 12–26 Å. The smectic repeat distance d along a given dilution line increases typically from 50 to 200 Å. The dilution lines were chosen to be straight lines located exactly in the middle of the smectic phase domains [19, 20]. Figure 2 shows the evolution of d for four dilution lines (corresponding to $\delta = 32$, 32.6, 35.7 and 39 Å respectively) as a function of the reciprocal of the bilayer volume fraction
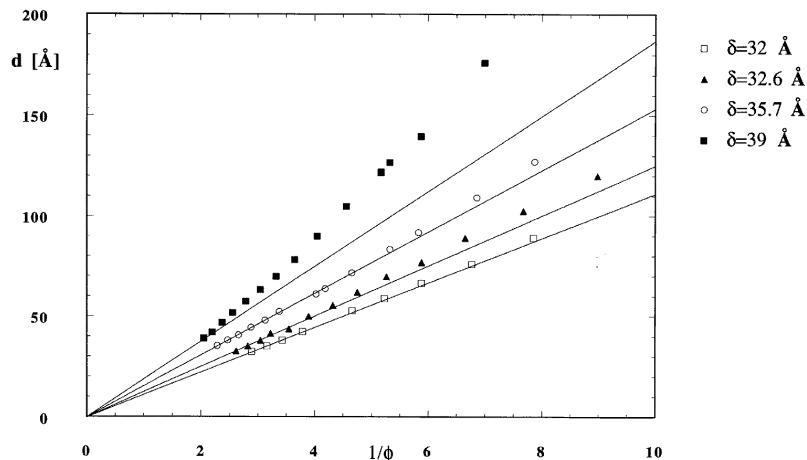
Figure 2. The evolution of the repeat distance d (from small-angle x-ray scattering) as a function of $1/\phi$ (ϕ is the membrane volume fraction). The solid lines correspond to ideal swelling laws: $d = \delta/\phi$ with δ taken from x-ray data on dodecane-free ternary samples (see the text). For the smallest water thickness (open squares) the data follow basically an ideal swelling law; in contrast, a large deviation obtains at large water content (filled squares).
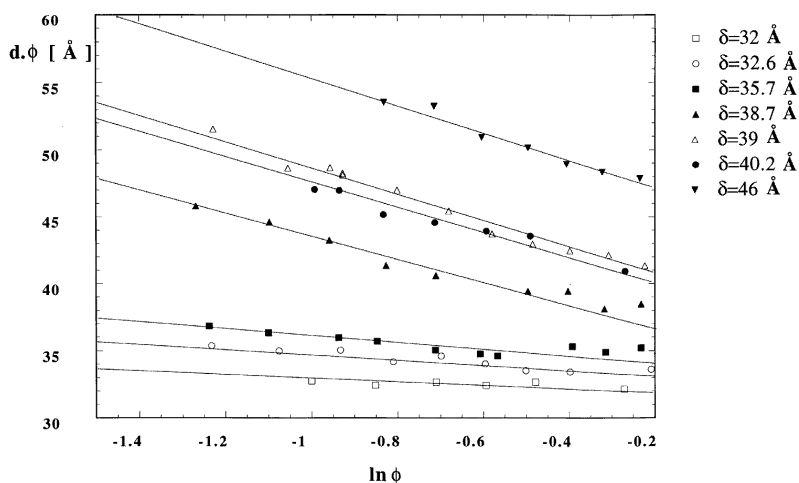

Figure 3. A semi-logarithmic plot of the deviation from ideal swelling ($d\phi$) as a function of the membrane volume fraction ϕ. The linear behaviour observed is consistent with equation (2).

ϕ. Solid lines in figure 2 correspond to ideal swelling laws ($d = \delta/\phi$), using the previously determined values of δ. It is readily observed that for the smallest bilayer thicknesses δ the deviation from the ideal swelling is rather small. On the other hand, a large deviation (more than 20%) is seen at larger δ. We present in figure 3 a different representation of the same data—$d\phi$ as a function of $\log \phi$—emphasizing the *deviation* from ideal swelling. The linear behaviour observed in this semi-logarithmic plot is attributed to membrane crumpling. We easily estimate the parameters A and B of equation (2) from a fit; see table 1. In principle, we can extract from the coefficients A and B two independent values for the elastic constant

κ, with the parameters δ and a given. However, we think that owing to the uncertainties inherent to any acceptable definition of the in-plane cut-off a, the slope B (equation (4)) gives *a priori* a more reliable estimate for κ. It should be noted that this estimate still depends on the value chosen for the membrane thickness. Another estimate of κ, which is not sensitive to the choice of δ, results from the following combination of A and B:

$$\frac{A}{B} - \log\left[\sqrt{\frac{32}{3\pi}}\frac{4\pi B}{a}\right] = \frac{4\pi\kappa}{k_BT} + \frac{3}{2}\log\frac{\kappa}{k_BT} \qquad (6)$$

with the membrane thickness δ eliminated in equation (3) with the help of equation (4). The values for κ arising from solving equation (4) or equation (6) are given in table 1. The two methods yield rather similar values for the most *rigid* membranes and differ increasingly with more flexible bilayers. The trends are *qualitatively* the same, however: there is a significant decrease of κ when the bilayer thickness increases.
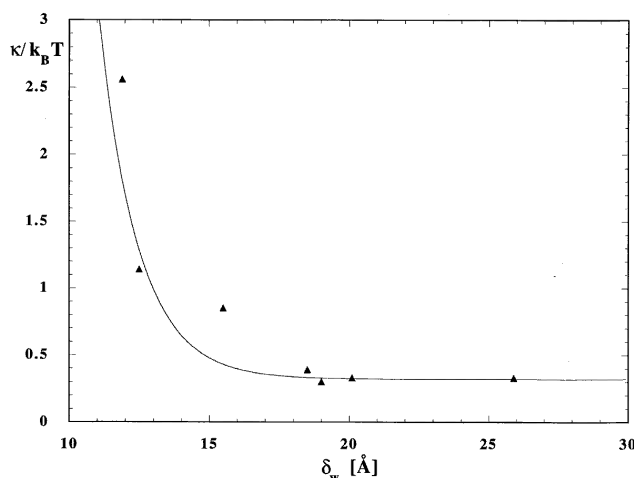

Figure 4. The evolution of the bending constant κ as a function of the water thickness δ_w. The solid line is a guide to the eyes rather than an explicit fit.

The variation of the membrane mean curvature modulus κ (using the first estimate) as a function of the water layer thickness δ_w is displayed in figure 4: there is first a sharp decrease of κ at small thicknesses, followed by a kind of plateau around $0.3k_BT$ at larger δ_w. The electrostatic contribution should lead, according to equation (1), to a *linear increase* of κ with δ_w which is obviously *not* observed in our data. This suggests that—in our case—the electrostatics is, unexpectedly, not relevant for controlling bilayer elasticity. In order to understand the functional dependence of κ, it seems therefore reasonable to look for non-electrostatic phenomena. Taking into account the relatively short distances below which the increase in κ starts to be noticeable (below 15 Å), one may invoke a contribution to the bending elasticity originating in a coupling between short-range surfactant interactions and curvature strains. Indeed, an exponential repulsion between polar heads has been measured in water for distances as small as the ones considered here [30]. This so-called 'hydration force' could explain the short-range nature of the effect. The physical origin of this interaction remains, however, the subject of debate [31, 32]. Our results will probably not help in solving this interesting problem. To our knowledge, there has been no calculation of the consequences for the bending constant in any of the models for 'hydration forces'.

Beside the puzzle of the origin of the large variation of κ at small membrane thicknesses, it should again be emphasized that there are no observable electrostatic contributions. This may be considered as an indication of the magnitude of the (poorly known) numerical prefactor in equation (1). Assuming the prefactor to be equal to 1 would lead to an electrostatic contribution of the order of $0.14 k_B T$ Å^{-1}, i.e. a global variation for the bending rigidity $\Delta\kappa = 2 k_B T$, clearly too large to be compatible with our data. On the other hand, the value $1/\pi - \pi/12$ calculated on the basis of a cylindrical geometry in [17] leads to $\Delta\kappa = 0.1 k_B T$, undetectable with our present experimental precision. More experiments and theoretical consideration are undoubtedly still needed to help in clarifying the relative roles of electrostatics and other interactions in bilayer curvature elasticity.

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