

Correlations in Interfaces with Surfactants¹

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The existence or nonexistence of the bending coefficient in liquid interfaces, as well as the applicability of the Helfrich free energy, is examined by comparing correlations in the interfaces with or without a weak surfactant. In the latter case, the formation of a bilayer is studied and density–density correlations and height–height correlations are reported, analyzed, and compared with “normal” liquid interfaces. In particular, the role of lateral tension is discussed.

KEY WORDS: bilayer interfaces; structure factor; surfactants.

1. INTRODUCTION

In our previous work we have investigated the structure of interfaces between two immiscible liquids and between a liquid and its vapor [1–3]. We used the computer simulation and the method of molecular dynamics; the liquids were formed by spherical particles interacting with Lennard–Jones potentials, and only single planar interfaces were studied. It is worthwhile to realize that this was but one particular case and that liquids, in particular, multicomponent mixtures, can form a great variety of most exotic phases. One such large group of systems is those containing a surfactant as one component. A rather brief review [4] summarizes the basic theoretical understanding of these systems. The references by Nelson et al. [5] and the work of Dietrich and Napiorkowski [6] can additionally be consulted.

In particular, two immiscible liquids, on the addition of surfactant, can form microemulsions and lamellar phases. These phases, formed often in a narrow range of state parameters (such as temperature T , pressure p , and

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concentrations x_1, x_2, \dots) have *many* interfaces in their bulk, held in place by their mutual repulsion among other factors, and are successfully described by assuming their surface tensions to be *vanishing* or almost vanishing. Their fluctuations are, therefore, ruled not by the ordinary capillary waves and the underlying surface (interfacial) tension, but by the rigidity (bending) coefficient and changes in curvature.

Similarly, liquid membranes and bilayers are described by a particular set of concepts such as area per head-group, spontaneous curvature, bending (rigidity) coefficient, and Gaussian curvature. To describe these objects, of great common interest to physicists and biologists, a number of phenomenological theories have been proposed, many of them based on the Hamiltonian associated with the names of Canham and Helfrich [7].

An immediate question arises: If these membranes, bilayers, and interfaces in lamellar phases are ruled by their curvatures and associated elasticity coefficients, what about the normal interfaces? Surely they are capable of bending and of having nonzero curvature; it is, therefore, legitimate, to search for presence or absence of the same effects in ordinary interfaces.

And a related question is, What *is* a “normal” interface and what is a membrane? What is it that makes an interface “normal” and what makes it a membrane?

To understand better the transition from normal interfaces with nonzero surface tension to those with a vanishing surface tension, we have studied immiscible liquids with a weak surfactant as the third component. Here we report results of MD simulations for an easier and simpler system, a binary system solvent + surfactant in which the surfactant molecules form a single bilayer. Our results include the correlations as given by the structure factor.

In Section 2 we give a simple theoretical introduction; in Section 3 we describe the model and the simulations and then we show and discuss the interfacial structure factors. In Section 4 we discuss the conclusions.

2. BACKGROUND: FREE ENERGY, SURFACE TENSION, AND CORRELATIONS

The product γA of the surface (interfacial) tension γ and the area A is the contribution of the interface to the total free energy F of the system; thus $F = F_b + \gamma A$, and since γ is positive, lowering of the free energy can normally be achieved by making A as small as possible. Hence, the plot of F versus A looks like the straight line labeled A in Fig. 1. A membrane or a bilayer has an optimal surface area a_h per surfactant head: if $A > Na_h$, the object is stretched, if $A < Na_h$, it is laterally compressed, and, therefore, the

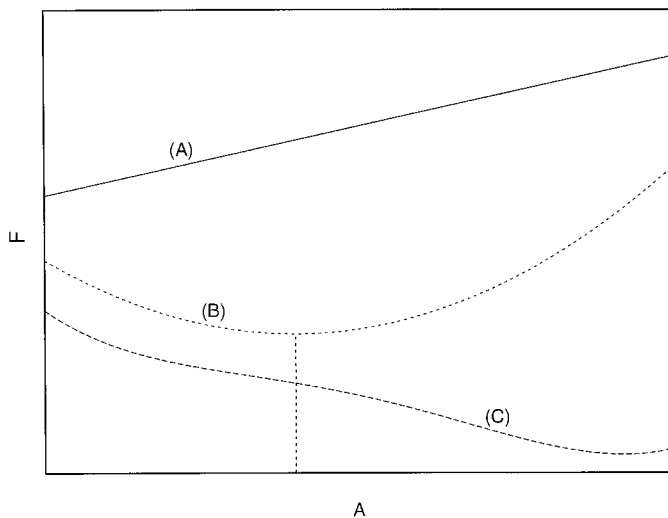


Fig. 1. Total free energy dependence on A , the area of the interface or of the membrane-like object. (A) The normal interface: $F = F_b + \gamma A$ and γ , the slope, is constant. (B) What is predicted for a membrane-like object for which $F(A)$ has a minimum at a specific area per head. (C) The general shape if coexistence of domains is assumed. Then γ is constant in the two-phase region, i.e., in the region of constant γ .

hypothetical dependence of F on A looks like the curve marked B in Fig. 1. Once we have allowed such possibilities, various other shapes of $F(A)$ can be invented [5, 8]. Still another $F(A)$ dependence is suggested in Section 3. If the existence of a minimum in $F(A)$ is allowed, we reach the unsettling conclusion that the surface tension defined as dF/dA can be positive or negative:

$$A > A_0 \equiv Na_h, \quad \gamma = dF/dA > 0 \quad (1a)$$

$$A = A_0 \equiv Na_h, \quad \gamma = dF/dA = 0 \quad (1b)$$

$$A < A_0 \equiv Na_h, \quad \gamma = dF/dA < 0 \quad (1c)$$

This, however, can be explained as follows. Consider a definite setup, like the one illustrated in Fig. 2, where the bilayer fills the periodic simulation box, dividing the solvent into the upper and lower parts of the figure. The interfacial tension can be readily calculated by the Kirkwood–Buff formula [9, 10]

$$\gamma = \bar{p}_{zz} - \bar{p}_{xx} \quad (2)$$

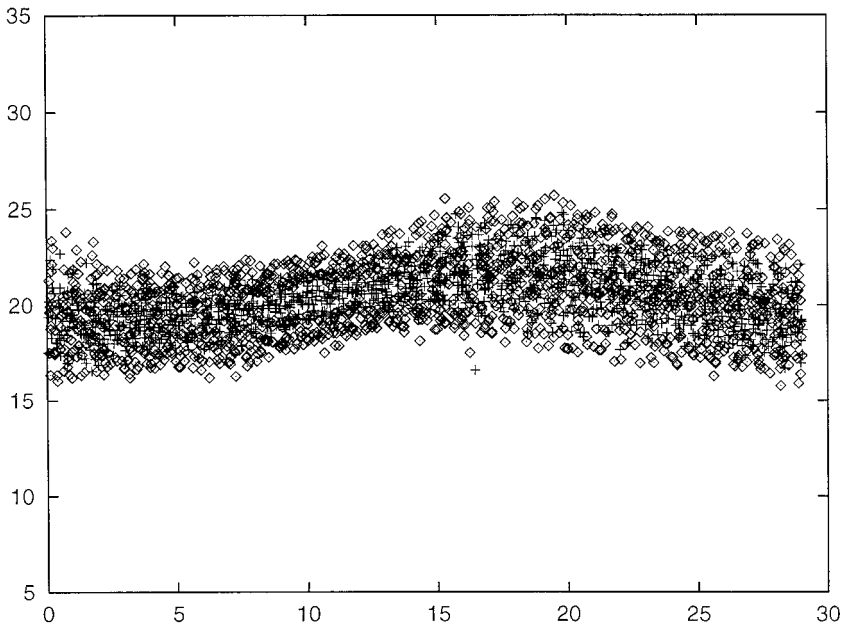


Fig. 2. A typical snapshot configuration of a bilayer; the “a” ends of dimers are marked with diamonds, the “b” ends are marked with crosses, and the free “a”’s (the solvent particles) are marked with dots. Here $kT/\epsilon = 0.75$, and there are 1440 dimers; the lengths are in units of Lennard–Jones σ —the collision diameter of the molecules.

where

$$\bar{p}_{\alpha\alpha} = \int_0^{L_z} dz p_{\alpha\alpha}(z) \quad (\alpha = x, y, z) \quad (3)$$

and $p_{\alpha\alpha}$ is the $\alpha\alpha$ component of the stress tensor. Of course $p_{yy}(z) = p_{xx}(z)$ by symmetry. If $\bar{p}_{zz} < \bar{p}_{xx}$, then $\gamma < 0$, and conversely. But no reason can be found why \bar{p}_{zz} should not be smaller than \bar{p}_{xx} .

In fact, for a bilayer immersed in a solvent, γ loses its physical meaning developed for normal surfaces. It is directly related to the lateral compressibility K [11] by

$$KA_0 = (d\gamma(A)/dA)|_{A=A_0} \quad (4)$$

Such is the quintessential difference between membranes/bilayers and liquid–vapor or liquid–liquid interfaces. For discussions concerning the role of diffusion (particle exchange), various ensembles, different types of bilayers, membranes, and/or vesicles, the specialized literature [4, 5, 8]

can be consulted. Note that when developing a description of Langmuir monolayers, we also change the physical meaning (and the name) of the derivative dF/dA .

Either object can and does fluctuate owing to thermal motion, and the long-wavelength modes are clearly associated with a fluctuation in the surface area A . For normal interfaces the free energy cost of a fluctuation is γdA and γ in the standard theory does not vary. This leads to the interfacial Hamiltonian

$$\mathcal{H}[h] = \frac{1}{2} \int dx dy [\gamma(\nabla h)^2 + V_2 h^2] \quad (5)$$

and to the height–height correlation function (in Fourier-transformed form)

$$\langle |h_q|^2 \rangle = \frac{kT}{\gamma q^2 + \gamma \xi^{-2}} \quad (6)$$

where the parallel correlation length is

$$\xi^2 = \frac{\gamma}{V_2} \quad (7)$$

Here V_2 is a coefficient resulting from the external potential stabilizing the planar interface [10]. If the capillary-wave, or interfacial, Hamiltonian is improved by the addition of further terms, then the denominator in Eq. (6) contains more than just γq^2 . Offhand, one expects this term to be the second term D_2 in a power series such as $D_0 + D_2 q^2 + D_4 q^4 + \dots$, but Dietrich and Napiorkowski [6] have shown that such a power series diverges and should be replaced by $D_0 + D_2 q^2 + D_4 (q^4 \log q) + \dots$ (strictly speaking for long-range potentials like r^{-6}). It is, therefore, safer to write

$$1/\langle |h_q|^2 \rangle = D_0 + \beta \gamma q^2 + q^4 f(q) \quad (8)$$

where $\beta = 1/kT$, $D_0 = \beta V_2$, $D_2 = \beta \gamma$, and $f(q)$ is unknown. Mecke and Dietrich [12] defined the combination $\beta \gamma + q^2 f(q)$ as the effective surface tension $\beta \gamma_{\text{eff}}(q)$ and based their calculation on the density functional theory, in which the rotation of the fluctuating density profile was (for the first time) taken into account. Calculations become straightforward when using the approach pioneered by Robledo et al. [13], based on the interfacial Hamiltonian derived in a clear way from the exact second-order free-energy

difference due to density fluctuations $\delta\rho(\mathbf{r})$ in terms of the inhomogeneous direct correlation function $C(1, 2)$,

$$\delta F = \frac{1}{2} \iint d(1) d(2) C(1, 2) \delta\rho(1) \delta\rho(2) \quad (9)$$

from which, in one approximation

$$\mathcal{H}[h] = \sum_{\mathbf{q}} \bar{C}(|q|) h_{\mathbf{q}} h_{-\mathbf{q}} \quad (10)$$

and

$$1/\langle |h_q|^2 \rangle = \bar{C}(q) \quad (11)$$

The function \bar{C} of one variable q is a projection of $C(z_1, z_2, q)$ [13]. It results when $\delta\rho$ is parametrized as a small shift of the density profile [3, 10, 13]. We have determined [3] this function from our simulations [3], and we have shown unequivocally that there exists an initial region $q \in [0, q^*]$, where $C(q) = C_0 + q^2 C_2$ —i.e., a region of capillary waves that furthermore is terminated by a sharp maximum near $q^* \sim 1\sigma$, after which, $C(q)$ falls to reach a broad minimum near $q \sim 2\pi/\sigma$. If one wishes to construct a power series $C = C_0 + C_2 q^2 + C_4 q^4 + \dots$, it is clear that C_4 *must be negative*, and, moreover, from the general discussion of Stecki [3], it follows that it is *general feature* of the liquid–vapor interface.

We can also make contact now with the theory of Mecke and Dietrich [13] and with the experimental results [14] where the concept of the effective interfacial tension, in the sense of Eq. (8), is used. From our data for $\bar{C}(q)$ we can construct this quantity by simple division by q^2 : $\beta\gamma_{\text{eff}} = (\bar{C}(q) - \bar{C}(0))/q^2$. Another possible definition is $\beta\gamma_{\text{eff}}(q) = (d/d(q^2)) \bar{C}(q)$, and there are still others. Figure 3 shows a plot of $\beta\gamma_{\text{eff}}(q)$ and the characteristic fall with the increase in q ; the confirmation of this result by recent experimental data [14] is very gratifying. These results also mean that all attempts to interpret C_4 as a kind of bending coefficient are doomed because C_4 is *always* going to be negative in a liquid–vapor interface. In a liquid–liquid interface [1] the agreement with the standard capillary-wave theory was excellent but the extraction of the D_4 term was not so unequivocal (although a renewed interpretation of our data with the aid of the theory of Dietrich and Napiorkowski [6] remains to be done).

Such was one way of representing and interpreting the scattering factor $S(q) \sim \langle |h_q|^2 \rangle$, i.e., through the representation

$$1/S = D_0 + D_2 q^2 + D_4 q^4 + \dots = D_0 + D_2 q^2 + q^4 f(q) \quad (12)$$

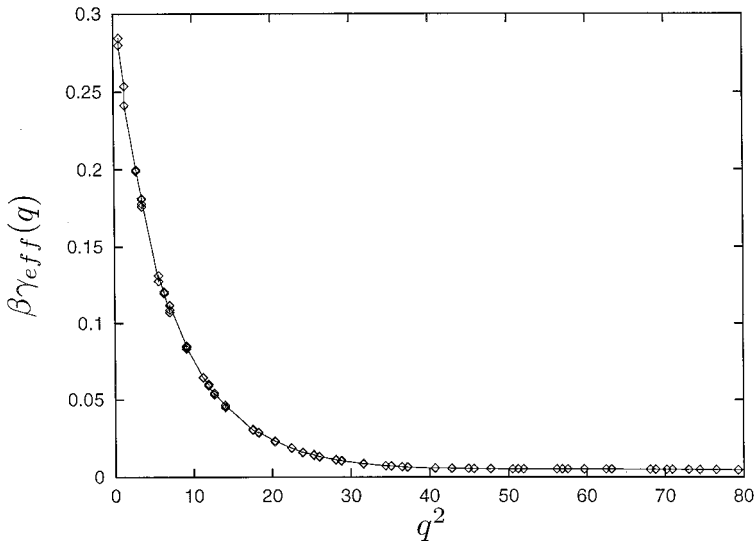


Fig. 3. The “effective q -dependent surface tension” calculated by dividing by q^2 the function $C(q)$ discussed and shown earlier [3]. Its shape as a function of q is identical to that found in a real experiment [14] and calculated from density-functional theory with rotation of intrinsic profile, except for the limiting region $q \rightarrow \infty$, where in our case the finiteness is ensured by the general properties of the Ornstein–Zernicke function c for $r_{12^-} > 0$.

Quite another representation has been used [11] for the height–height correlation function of a simulated bilayer, namely,

$$S(q) \sim a/q^4 + b/q^2 \quad (13)$$

We do not know of any theoretical justification of this form. For normal interfaces statistical mechanics predicts Eq. (6) as “the most divergent term” [9, 10]. It is a broader issue that we do not address here. Certainly, as an empirical formula, Eq. (13) is very successful and in what follows, we have applied both of these representations to our new data on a liquid bilayer formed by a weak surfactant in a one-component solvent. We generalize Eq. (13) in an obvious manner,

$$S(q) \sim (a/q^4) + (b/q^2) + A + Bq^2 + \dots \quad (14)$$

adding more empirical terms for a better representation of the data.

3. MODELING OF INTERACTIONS AND RESULTS

We use the model of spherical particles interacting with the Lennard–Jones (6, 12) potentials with cutoffs. To have the simplest possible system without unnecessary complications, we choose equal masses and equal sizes but different cutoffs in the spirit of the WCA theory, used often in other work [15, 16]. The interaction potential is

$$u_{\alpha\beta}(r_{ij}) = 4\varepsilon [((\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6) - ((\sigma/r_{\alpha\beta}^c)^{12} - (\sigma/r_{\alpha\beta}^c)^6)] \times \eta(r_{\alpha\beta}^c - r_{ij}) \quad (15)$$

with species index $\alpha = 1, 2$ for species a and b, respectively, and similarly for species index β . $\eta(x)$ is the Heaviside function. The cutoff distance is $r_{\alpha\beta}^c = 2.5\sigma$ if $\alpha = \beta$ and $r_{\alpha\beta}^c = r^* \equiv 2^{1/6}\sigma$ if $\alpha \neq \beta$. All lengths are measured in units of σ . We model the surfactant as a dimer made of unlike particles that interact with monomers according to the same interaction potential. The inner bond interaction is $u_{12}(r)$ if $r < r^*$ and $u_{12}(2r^* - r)$ if $r > r^*$. This model was proposed by S. Toxvaerd [17]. But it was Smit [18] who first modeled in a simulation the surfactant as a dimer and has shown that it already has some semblance to reality.

The “standard” version of our model is the one with equal masses and with the same ε for all pairs. The solvent is made of a’s, and the bilayer is made of bound a–b pairs. Therefore, the a end of the dimer plays the role of the “head” in contact with the solvent (since the a–a pairs are favored energetically) and the b end of the dimer plays the role of the hydrocarbon part and likes to stay inside the bilayer, away from the solvent. This is shown in Fig. 2. We have also investigated a few modifications. First, the heads are often polar, as is the solvent, whereas the cohesive energy of the hydrocarbon environment is low; we can thus make the “a” free–“a” bound interaction stronger than the rest. This did not enhance the formation of the bilayer in any visible way but it did result in filling the bilayer with solvent, to a large extent. We can also make the “b” ends heavier to slow down the motions of the bilayer. Finally, we can add an additional repulsion of longer range between the b ends and the free a’s so as presumably to chase any solvent particles out of the inside of the bilayer; the latter interaction can be a repulsive r^{-9} potential [11]. In the end, we did not continue with these modified versions because the essential features of the bilayer were not changed much. We did some simulations with a long-range repulsive potential [11], because we found that it enhanced the q^{-4} contribution to the scattering factor $S(q)$. [cf. Eqs. (13) and (14)].

We report here simulations with a periodic box with $N = 40,000$ particles and $N_d = 1440$ dimers, with box dimensions about $30 \times 30 \times 50$, at

temperature $kT/\varepsilon = 0.75$. The molecular dynamics was performed with the Verlet leap-frog algorithm and the Nose–Hoover thermostat [19]. The preassembled bilayer adapted its own configuration very quickly, but, as we started from a surface area of 50×50 , the surfactant dimers aggregated into domains. These grew in tune, though very slowly. An x, y projection of an early structure with domains is shown in Fig. 4. If left to equilibrate, a large connected domain resulted and one or two big holes filled with solvent. This suggested that there might exist a membrane-like quantity, the area per “a” head. Compressing the system in the lateral x, y directions with a simultaneous expansion in the z -direction changes the surfactant domains; eventually the x, y cross sections become homogeneous at an area at which γ is still positive. This is reminiscent of the two-dimensional domain coexistence, known very well for monolayers. If this is the case, the $F(A)$ dependence might have a shape like the double inflexion curve (C) in Fig. 1. Further lateral compression brings about an increase in $\bar{p}_{xx} = \bar{p}_{yy}$ and a decrease in \bar{p}_{zz} , hence, a decrease in γ and a change in the x, y morphology. Further compression diminishes γ , and eventually very low values of γ can be reached. Such states appear to be stable. Compression

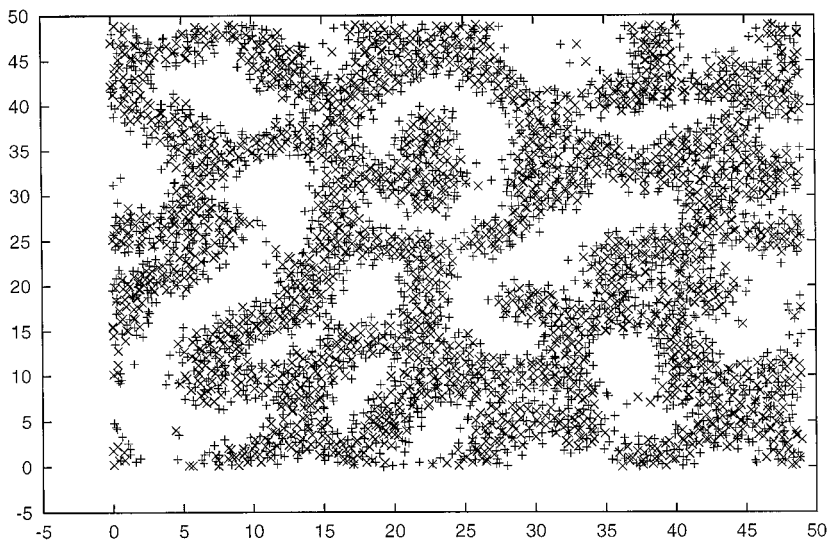


Fig. 4. Lateral domains of surfactant heads and tails formed when the surface area is too large and the bilayer would be under stretching tension were it homogeneous. Solvent molecules, which fill the holes, are not shown for clarity. All data shown are for $N = 40,000$, $T^* = 0.75$, and the “standard” model described in Section 3.

to still lower areas produced a negative γ but such states were not stable. At most, it was found possible to maintain a bilayer with γ about -0.01 (in LJ units). The bilayer reorganized itself, doubling its thickness in most cases and restoring γ to positive values. Also, it was not clear whether the bilayer with slightly negative γ was not a metastable state. It would persist for 10^6 time steps, but this is no proof. The reorganized bi-to-quad layer was very stable.

We have taken the view that the positions of the centers of mass of the dimers determine the instantaneous surface [5] or, rather, two instantaneous surfaces of “up-dimers” and “down-dimer.” From these, two correlation functions were constructed, the dimer–dimer density–density correlation function,

$$H_{dd} = \langle \rho_d(\mathbf{r}_1) \rho_d(\mathbf{r}_2) \rangle$$

or, rather, its two-dimensional Fourier transform $H(q)$, and the height–height correlation function $S(q) \equiv \langle h_q h_{-q} \rangle$. Each z -coordinate of a dimer is treated as height $[x, y, z] \rightarrow [x, y, h(x, y)]$. For each set of positions at a given time, the average heights are calculated and the actual heights are measured with respect to this instantaneous average. These two functions do not differ much so we choose $S(q)$ for the discussion. We wish to discriminate between the two mathematical forms, given by Eqs. (12) and (14). We note that Eq. (13) can be rewritten as $(a + bq^2)/q^4$, which implies a limit of the expression $S(q) q^4$. Therefore, we have analyzed the following quantities: S , Sq , Sq^2 , Sq^3 , Sq^4 , and their inverses. Taking the limit $q \rightarrow 0$, for the damped ($D_0 \neq 0$) and free ($D_0 = 0$) cases, we calculate the limits of the analytical forms of Eqs. (12) and (14) and test these detailed predictions on our data. The expressions given by Eqs. (12) and (14) lead to different behavior of such derived functions, as $q \rightarrow 0$.

Figure 5 shows a plot of the height–height correlation $S(q)$ for a bilayer with a small positive γ ; due to the smallness of the capillary-wave contribution, the plot is dominated by the approach to the first nearest-neighbor peak seen near $q = 2\pi/\sigma$. The capillary-wave divergence is very weak. Of the analysis outlined above, we show only one plot in Fig. 6; if the “traditional” expression, Eq. (12), were appropriate, a plot of Sq^2 versus q^2 should be linear with a value at zero $D_2 = \beta\gamma$ and slope $D_4 > 0$. Clearly this is not the case. Alternatively, Eq. (13) requires that Sq^4 should reach a constant, and, for data shown in Figs. 5 and 6, this is not the case. Detailed analysis is showed that data in Figs. 5 and 6 are well represented (for not-too-large q) by Eq. (14), *though with* $a = 0$, i.e., by $S \sim (b/q^2) + A + Bq^2$.

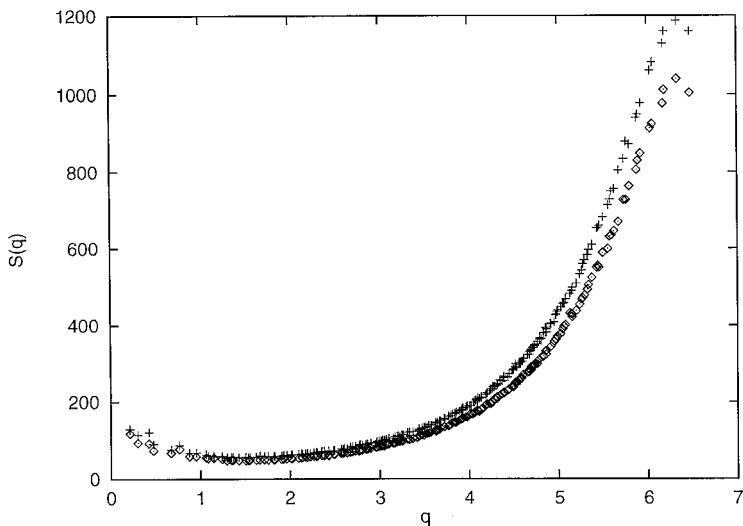


Fig. 5. A typical plot of $S(q)$ versus q for a bilayer (nearly tension-free, i.e., with γ near zero). Note the position of the first peak near $q=2\pi/\sigma$ and the barely visible capillary-wave (or bending wave) divergence near $q=0$. The two curves refer to two layers of the bilayer.

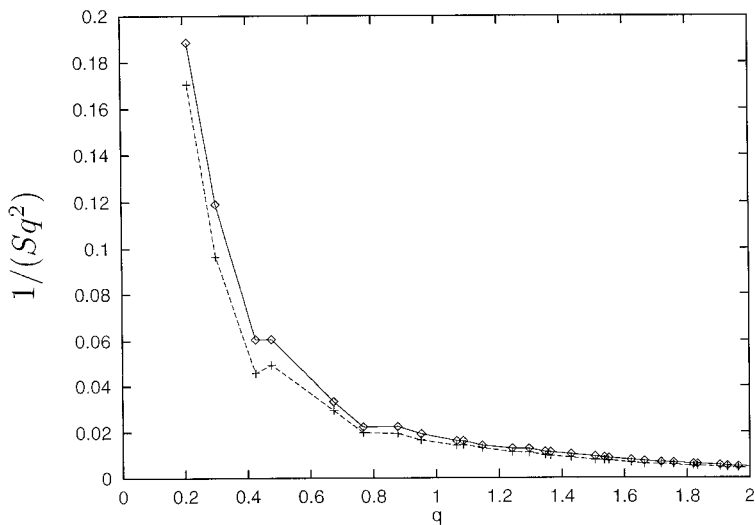


Fig. 6. A typical plot of $1/(Sq^2)$ versus q . It is well represented by $1/(2.5 + 60q^2 + 0.05q^4)$. The two curves refer to two layers of the bilayer. The plot also shows how difficult it would be to reconcile it with the predictions of Eq. (12), for any choice of parameters.

4. CONCLUSIONS

Our results seem to confirm the view expressed above, namely, that the membrane-like approach to interfaces is valid if there exists a series of stable states with a minimum of free energy at a surface area A_0 of a tension-free state. For our weak surfactant modeled by a dimer, it appears that the compressed states with $A < A_0$ are not stable, and the expanded state are stable within a narrow range of areas. For higher A 's the bilayer breaks into domains. For lower A 's it reorganizes itself into a quad-layer with a positive γ . Then the expected bending modes in *either* Eq. (12) ($D_4 \neq 0$) or Eqs. (13) and (14) ($a \neq 0$) do not appear. It may well be, in line with the qualitative discussions [20], that a long chain length or a double chain length is needed for the formation of a stable bilayer, i.e., such that it would be stable in an interval of areas including the equilibrium tensionless state, compressed states, and expanded states. Such a bilayer was constructed [11], but the role of the additional special repulsive (r^{-9}) potential introduced in that work [11] in stabilizing the expanded and compressed states is not clear.

Finally, we find it relatively straightforward to determine correlation functions such as those reported here and we expect to study these correlations in other surfactant systems.

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