
COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in the Physical Review. Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

**Comment on “Light scattering from the L_3 (sponge) phase:
Evidence against logarithmic corrections to ideal scaling”**

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We discuss the above referenced article by Daicic *et al.* and show that the light-scattering data measured by them on the L_3 phase of the sodium bis(2-ethylhexyl)sulfosuccinate–brine system are essentially similar to those presented previously by us for the same system. After reanalyzing the thermodynamic model of the authors, we show that their data do not bring convincing evidence against logarithmic correction to ideal scaling. [S1063-651X(97)15106-6]

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In a recent article [1], Daicic *et al.* present a light scattering study of the sponge phase of the sodium bis(2-ethylhexyl)sulfosuccinate (AOT)–NaCl–water system. The data are treated in the frame of a thermodynamic theory that they have presented in a previous article [2]. The authors conclude that their study provides “definitive experimental evidence that the renormalization effects, so often invoked as an important thermodynamic feature of fluid membrane phases, do not, in fact, appear.” They expressed strong reservations about data that we had collected earlier on the same system [3]. In this Comment, we first point out inconsistencies in the authors’ theory and then observe that their data are, in fact, essentially similar to ours in the relevant dilute range.

The theory of the authors relies on expression (1) for the free energy density g of the sponge phase as function of the volume fraction ϕ of membranes:

$$g = 2\kappa \left(\frac{H_0}{l^2} \phi^3 + \frac{1}{4l^3} \phi^5 \right), \quad (1)$$

where H_0 , κ , and l are, respectively, the spontaneous curvature, the mean curvature bending constant, and the thickness of the individual monolayers stuck opposite to one another so to make the bilayer. Expression (1) is based upon the treatment of the midsurface of the multiply connected, disordered bilayer as a minimal surface and the elastic energy is determined by the fact that each monolayer is displaced by l from the midsurface.

In other words, the thermodynamics of the sponge phase is treated in [1] as that of a cubic crystal of membrane at zero temperature. But a crystalline structure would lead to sharp Bragg diffraction peaks, while the neutron scattering patterns of all sponge phases studied to date only show a smooth maximum with no Bragg singularity (Fig. 6 in [3(b)]): the structure is liquidlike and not crystalline. Therefore, position

correlations in the multiconnected membrane are weak and conformational entropy is large. Considering these facts, we see no reason to believe that the contribution of fluctuations [4] to the free energy is negligible compared to the elastic terms retained in Eq. (1). Note that if such an approximation were applied to the swollen lamellar phase, the Helfrich steric interaction should be simply neglected.

Our second point is related to the ϕ^5 term in Eq. (1). As well as the cubic term, it is calculated from the bending energy of the surfactant monolayers as defined up to the harmonic order (quadratic in curvature) by H_0 and κ . However, it is clear from simple dimensional analysis that the neglected anharmonic terms (quartic in curvature) will also bring finite contributions into the ϕ^5 term in g . Here again there is no reason to presume that these contributions are small compared to those arising from the only harmonic term retained in Eq. (1). So in order to remain consistent within the harmonic starting point, the calculations in g should not be pushed beyond the ϕ^3 term. Furthermore, the conformational fluctuations will presumably also bring in an uncontrolled contribution to the ϕ^5 term. In this context, the coefficient taken in Eq. (1) for the quintic term is quite arbitrary.

Finally, in order to evaluate the evolution of H_0 and κ as function of the salinity, the authors have fitted the experimental lamellar- L_3 coexistence line in terms of the theoretical expressions of the free energy densities in the two phases. For the L_3 phase they took g as given from Eq. (1), thus neglecting all bending fluctuations. For the lamellar phase they used the classical Helfrich steric energy which entirely arises from bending fluctuations. This means that the free energy densities of the two phases are not compared at the same level of approximation.

These are the three weak points that we see in the authors’ conceptual framework. The situation would certainly not be so serious if the purpose were to give a qualitative interpretation of the general phase behavior. In this respect, we ac-

knowledge that the general basis of the authors' approach is indeed appealing. We ourselves explicitly pointed out the role of H_0 in a very similar manner in our previous article [5]: the prefactor of ϕ^3 in Eq. (1) is in fact a simple translation of our previous expression (8) in [5]. But the aim is to treat data quantitatively so to reject definitely the renormalization scheme. For this purpose, the accuracy of the theory is crucial: the data being explicitly taken at the phase boundaries, they bear by themselves no significance regarding log correction unless they are treated quantitatively within a consistent thermodynamic theory. Therefore, in our view the unjustified approximations mentioned earlier produce a real problem: as a matter of fact, we note that the data shown by the authors deviate considerably at low concentrations from the model predictions (up to 1000% in Fig. 3).

As regards the log correction, it is true that no scaling of the form

$$g = A \phi^3 \log(\phi/\phi^*) \quad (2)$$

for the free energy density of the L_3 phase has never been clearly demonstrated. Nevertheless, Eq. (2) has good chance of being reliable because it incorporates only extremely general features of fluid bilayers: the main ϕ^3 dependence is an immediate consequence of the scale invariance of the bending elasticity and the log correction is expected from the renormalizations of area and rigidities which have a priori no reason to cancel exactly. These renormalizations have been calculated on very general and rigorous theoretical grounds [6]. However, Eq. (2) is an asymptotic expression that only stands for diluted samples where the local curvatures are small. Therefore, it makes no sense to compare Eq. (2) against experimental data taken at concentrations up to 40%

for which the radii of curvature are comparable to the thickness l of the bilayer. This is the reason why our data in [3] are shown at low volume fractions only (data at higher concentrations are reported in [7] having identical behavior as those of the authors in [1]). They are plotted in the representation appropriate to emphasize log deviations to the ideal dependence (Fig. 9 in [3(b)]): a reasonably straight line being obtained, there is no contradiction with the renormalization scheme. Moreover, one easily checks that, restricted to the same concentration range, the data of Daicic *et al.* in [1] have a behavior identical to ours: plotted in the same representation, they even extrapolate to zero at the same $\log \phi = -1.8$ value. So we completely disagree with the statement that "the results are in clear contradiction to those previously published."

There is one point, however, where we acknowledge the criticism of Daicic *et al.*: our dilution line suffers from a lack of specifications of the compositions of the samples. Hence, we have no guarantee of invariance for the elastic properties of the bilayer upon dilution. Furthermore, the L_3 phase of the sodium bis(2-ethylhexyl)sulfosuccinate-brine system cannot be diluted below 5%: this is not an ideal situation when the purpose is to check scaling predictions for high dilution only. So our data should not be considered as a definite proof of the log corrections; actually, we did not make a conclusive statement in [3]; and we pointed out explicitly that dynamical properties are not consistent with the log scheme. The criticisms raised in the articles of Daicic *et al.* indicate that the sodium bis(2-ethylhexyl)sulfosuccinate system is not very appropriate for that purpose and that measurements remain to be done on a system where the L_3 phase is stable at much higher dilution. In our opinion, the issue is still open.

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