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## Comment on “Thermodynamics of the $L_3$ (Sponge) Phase in the Flexible Surface Model” by John Daicic *et al.*

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In a recent article [1] Daicic *et al.* have proposed a new model for the stability of the sponge phase. They claim that the free energy per unit volume can be written

$$f = 2\kappa \frac{H_0}{l^2} \Phi^3 + \kappa \frac{\Phi^5}{2l^3} \quad (1)$$

where  $\kappa$  is the mean curvature rigidity,  $H_0$  the spontaneous curvature, and  $l$  the molecular thickness of a monolayer.

This model assumes in effect that the bilayer midplanes in the sponge phase lie on a surface that has zero mean curvature (ZMC) *everywhere*; the stability and thermodynamics of the phase are then controlled by the fact that each monolayer is displaced by  $l$  from the bilayer midplane. The resulting energy terms are found by expanding to the two leading orders the elastic energy of the monolayers, based on this construction. The authors explicitly neglect terms involving *fluctuations* in local curvature, which arise because the bilayer midplane does not, in a sponge phase, lie everywhere on a ZMC surface (although its *spatially-averaged* mean curvature will indeed vanish in a symmetric sponge).

Previous models [2,3] are based on a quite different physical picture in which the dominant elastic energy of bilayers comes from the fluctuations in local mean curvature; this is balanced by entropic contributions. To this basic picture, as pointed out by Porte [4], a Gaussian curvature contribution should be added; this was subsequently done quantitatively within the same framework [5]. In this approach, the mean and Gaussian curvature elastic energy terms are respectively of order  $\kappa\Phi^3/l^3$ ,  $\bar{\kappa}\Phi^3/l^3$  where  $\bar{\kappa}$  is the Gaussian rigidity of a bilayer. There are two entropic contributions, one from the randomness on the scale of the pore size, and another from microscopic undulations (which lead in effect to a logarithmic renormalization of the elastic constants), respectively of order  $k_B T \Phi^3/l^3$  and  $k_B T \ln(\Phi)\Phi^3/l^3$ . The resulting free energy is then of the form  $f = (A + B \ln(\Phi))\Phi^3/l^3$  where  $A$  and  $B$  depend on  $\kappa$ ,  $\bar{\kappa}$ ,  $k_B T$  which are all of a comparable magnitude in most surfactant systems.

Daicic *et al.* make it clear that they do not believe in the logarithmic entropy term. However, they do accept that the remaining (pore-scale) entropy contribution, and that from fluctuations in mean curvature, should both be present: however, since both have  $\Phi^3$  scaling they argue that their inclusion would not qualitatively alter their results.

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We wish to point out that:

(1) The  $\Phi^3$  term of equation (1) is simply one contribution, from monolayer spontaneous curvature, to the Gaussian rigidity  $\bar{\kappa}$  of the bilayer. (The  $\Phi^5$  part is then an anharmonic correction to this.) As shown by Porte [4], this contribution is of order  $\bar{\kappa} \approx \kappa l H_0$ . There is also another contribution, from monolayer Gaussian curvature, which is  $\bar{\kappa} \approx \bar{\kappa}_{\text{mono}}$ . This term should be included.

(2) The resulting contribution and, even more importantly, those arising from pore-scale entropy and from fluctuations in mean curvature, are respectively of order

$$\bar{\kappa}_{\text{mono}}\Phi^3/l^3, k_B T\Phi^3/l^3, \kappa\Phi^3/l^3$$

Although these all have  $\Phi^3$  scaling, such terms are not (as claimed by Daicic *et al.*) comparable to, but *much larger than*, the term  $\kappa H_0\Phi^3/l^2$  which is retained in equation (1). This is because, for the sponge phase to exist at all, the product  $lH_0$  must be much smaller than unity. (If it is not, then a micellar phase would be stable instead.) This point is tacitly accepted by Daicic *et al.* who, in their numerical examples of phase diagrams, use values of  $lH_0$  in the range 0.01-0.05. Hence the  $\Phi^3$  term retained by these authors is at least one and probably two orders of magnitude smaller than terms they neglect.

(3) Restoring the neglected terms would, in contrast to the claims of reference [1], totally change the predicted behaviour. In particular, the occurrence of a sponge phase at low volume fractions arises in the model of reference [1] from the balance of a  $\Phi^3$  term which is unreasonably small (by a factor  $H_0$ ), against a more realistic  $\Phi^5$  term arising from higher order elasticity. This leads to a stable sponge extending down to  $\Phi \approx (lH_0)^{1/2}$  (for which Eq. (1) is minimized). When a  $\Phi^3$  term of realistic magnitude is instead used, the sponge phase is only stable for  $\Phi$  of order unity. This is of course what one would expect from a model that is ultimately stabilized by anharmonic elasticity (which should only be important when the pore size is of order  $l$ , that is  $\Phi \approx 1$ ). Clearly, for relatively concentrated sponges (say  $\Phi \geq 10\%$ ) anharmonic terms should become important, but if so equation (1) includes only one of several such contributions. In any case, as shown above, such terms cannot in reality explain the existence of the sponge phase at lower concentrations. The claim of Daicic *et al.* to have explained the behaviour of sponge phases “*over all concentration regimes*” without recourse to logarithmic corrections stems directly from their arbitrary selection of an unrepresentatively small  $\Phi^3$  term.

(4) In reference [1], experimental data is presented on relatively concentrated sponges ( $\Phi \geq 10\%$ ) using dilution paths corresponding to the phase boundaries at high and low salinity and one intermediate line. These show no evidence of logarithmic terms in the free energy. To observe the logarithm, it is necessary in principle to perform the dilution at constant  $\kappa, \bar{\kappa}$ . In previous work on more dilute systems ( $\Phi \leq 10\%$ ), dilution paths were chosen along which the *bilayer composition* is expected to be constant [6]. (The authors of Ref. [1] appear to suggest that these paths were entirely uncontrolled; this is not the case.) This seems more appropriate than choosing the phase boundaries, along which the elastic constants may be varying. Low volume fraction and constant bilayer composition may both be needed to observe the logarithms; however this point deserves closer investigation.

To summarize, the model presented by Daicic *et al.* does not stand up to close scrutiny: it can “explain” the existence of dilute sponge phases only by balancing small terms in the free energy while neglecting much larger ones. Daicic *et al.* go on to make very strong criticisms of earlier work, rejecting with particular emphasis the evidence for logarithmic correction terms in the free energy. Without wishing to belabour the point, logarithmic corrections have been predicted theoretically on very general grounds [7], observed experimentally to high precision (along dilution curves where constant bilayer composition is expected) [6], and, as shown above,

so far provide the only feasible explanation of the stability of sponges at high dilution [2,3]. We therefore believe that Daicic *et al.* are misguided in their rejection of these terms.

On a more positive note, we can agree nonetheless with Daicic *et al.* that monolayer spontaneous curvature should be involved (if only through its influence on the Gaussian rigidity of bilayers) in the remarkable narrowness of the sponge phase [4], and certain other features of the phase diagram; that higher order curvature terms may become important at high concentration, perhaps dominating the logarithmic terms in this regime; and that a more careful study of the influence of the dilution line on the measured osmotic compressibility would be worthwhile.

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