

## Random bilayer phases of dilute surfactant solutions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 SA339

(<http://iopscience.iop.org/0953-8984/2/S/053>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:17

Please note that [terms and conditions apply](#).

## Random bilayer phases of dilute surfactant solutions

M E Cates<sup>†</sup> and D Roux<sup>‡</sup>

<sup>†</sup> Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

<sup>‡</sup> Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence Cédex, France

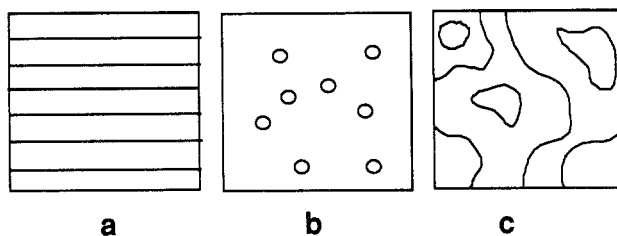
Received 9 July 1990

**Abstract.** Surfactant molecules in dilute solution may aggregate reversibly into extended structures. For suitably chosen molecules, the preferred packing involves a locally flat bilayer, which tends to wander entropically at large distances. At low temperatures (and/or high concentrations) the system forms a stack of flat sheets with one-dimensional quasi-long range order (a smectic liquid crystal), but at high temperatures or low concentrations, the stack can melt into a random surface structure that resembles a multiply connected labyrinth or 'sponge' of bilayer in a sea of solvent. Recent theoretical and experimental progress in understanding the properties of the sponge is reviewed. We argue that the sponge phase may provide a good system for the study of various liquid-state critical phenomena.

### 1. Introduction

Due to their amphiphilic property, surfactant molecules in solution aggregate reversibly, and can form a large variety of phases. For suitable molecular geometry these include phases in which the local structural unit is a semiflexible bilayer. When the characteristic distance scale of the structure we are considering is large compared to the bilayer thickness, the appropriate description involves the statistical physics of thin two-dimensional fluid films embedded in a three dimensional space. This limit is approached when the volume fraction of bilayer-forming material is small compared to unity, which we assume from now on. We also assume that the free energy penalty per unit length for tearing the bilayer is large enough for us to neglect the presence of edges in our two-dimensional film. The same applies to seam-like defects in which three or more pieces of bilayer meet along a line. (In practice, of course, defects such as these do have some finite energy scale, and their effects will be discussed in section 7.)

To arrange a given volume fraction of self-avoiding, flexible bilayer, with no edges or seams, in three-dimensional space is not easy. Two trivial solutions spring to mind: a one-dimensional stack of infinite sheets (the lyotropic smectic A phase, figure 1(a)) and a phase of closed vesicles (figure 1(b)). Another, less obvious, choice is to make a labyrinth or sponge-like phase of random surface (figure 1(c)) [1], which can also be thought of as a defect-ridden version of a cubic 'minimal surface' phase [2] (having lost all long-range order). We have proposed this as the structure of the so-called 'anomalous isotropic' or 'L<sub>3</sub>' phase that has been described in a number of dilute surfactant solutions [3–6]. Conductivity, neutron scattering and flow-birefringence data are all consistent



**Figure 1.** (a) Smectic liquid crystal. (b) Dilute vesicles. (c) Symmetric sponge. These are all cuts through a three-dimensional structure. In each case, if a point is chosen arbitrarily and labelled  $\text{i}$  (inside) the surface uniquely partitions the rest of space into  $\text{i}$  and  $\text{o}$  (outside) regions. These have the same statistics in (c) (and also (a)) but different statistics in (b). See section 3.

with this idea, but the strongest evidence is now from small-angle light scattering measurements [7], reviewed in section 4 below.

## 2. Elasticity of bilayers

The relative stability of the sponge phase can be explained in terms of the entropy and elastic energy of the bilayer [1]. Within a harmonic approximation the elastic energy of a fluid film can be written as [8–10]

$$E = \int (\kappa H^2 + \bar{\kappa} K) dS \quad (1)$$

where  $H$  is the mean curvature and  $K$  the gaussian curvature of the film. The parameter  $\kappa$  is the mean bending constant, which is positive, and  $\bar{\kappa}$  is the gaussian bending constant, which obeys  $-2\kappa < \bar{\kappa} < 0$  (required for stability of the film [9]). It is known (Gauss–Bonnet theorem [9, 10]) that

$$\int K dS = 4\pi(n_c - n_h) \quad (2)$$

where  $n_c$  is the number of disjoint pieces or ‘components’ of the film, and  $n_h$  its number of handles. Both of these vanish (per unit volume) in a perfect smectic, although a more realistic description allowing neck-like defects will give a small negative value for  $n_c - n_h$ . For vesicles the corresponding sum is positive, whereas for a randomly connected sponge it may be moderately negative, if there is on average more than one handle per component. Typically a sponge will have one infinite and many finite components [1].

The rigidities  $\kappa$  and  $\bar{\kappa}$  have units of energy, and can be considered as of comparable magnitude (under most conditions). When  $\kappa$  is not too large compared to  $k_B T$ , we expect thermal fluctuations to become important, and in fact they lead to a ‘softening’ of the bilayer at large distances. Within perturbation theory, an effective rigidity can be calculated [9–12]:

$$\kappa(\xi) = \kappa - (3/4\pi)k_B T \log(\xi/a) \quad (3)$$

(with a similar equation for  $\bar{\kappa}$ , [10]). In (3),  $\xi$  is some length scale corresponding to a coarse-grained bend and  $a$  is the bilayer thickness, which provides a short cutoff on the

thermal undulations of the film. The decrease of the elastic constant with  $\xi$  means that over a certain distance the bilayer will tend to lose its orientational order. This persistence length  $\xi_k$  can be (crudely) equated to the length at which the effective bending constant goes to zero [13]:

$$\xi_k = a \exp(4\pi\kappa/3k_B T). \quad (4)$$

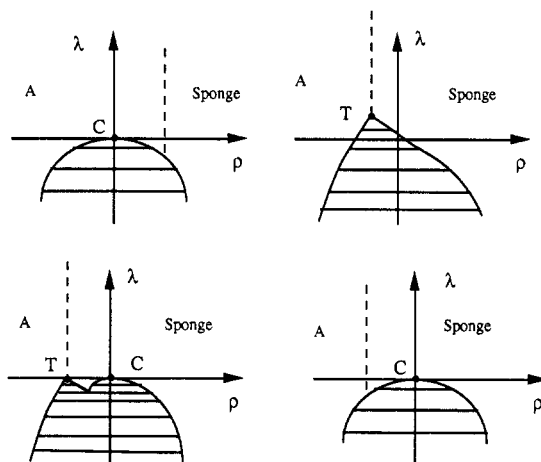
We might expect that a smectic phase of bilayers will ‘melt’ into a sponge-like phase, when its mean layer spacing  $d = a/\varphi$  is of order  $\xi_k$ . For suitable bilayer-forming surfactants, this may be of order 500–1000 Å; the corresponding volume fraction  $\varphi$  is then a few per cent. The characteristic pore size of the sponge so formed will be of order the persistence length of the bilayer. (This argument is rather oversimplified, as the gaussian rigidity term may also favour melting to a handle-rich sponge [2, 18]; experimentally the phase often remains stable to quite high concentrations.) If the sponge is diluted further, one may expect it to fragment into a phase of small droplets or vesicles, which are ultimately favoured by translational entropy [1, 14, 15].

A closer examination shows that these transitions under dilution are linked to the renormalization of the elastic constants [1, 2, 14], and that the boundaries of stability the sponge phase should be nearly straight lines if the phase diagram is plotted as a function  $\log(\varphi)$ . This is because the characteristic pore size of the sponge,  $\xi$ , varies as  $a/\varphi$ , and the phase boundaries depend on  $\varphi$  mainly through the  $\log(\xi)$  corrections to the elastic constants (equation (3)) [16]. This unusual scaling has now been confirmed to reasonable accuracy, for the  $C_{12}E_5$  system in water [17].

### 3. Structure and symmetry of the sponge phase

The convoluted film structure (without seam or edge defects) assumed to arise in a sponge phase has a very special property. Such a film (in three dimensions) divides space into two disjoint regions. These may be arbitrarily labelled ‘inside’ (i) and ‘outside’ (o). The partitioning is unique up to a global interchange of i and o. Thus the bilayer can be imagined to lie everywhere at the interface of two ‘different’ solvents (i and o), although these are constituted of identical material. (Viewed this way, the structure closely resembles a microemulsion [14–16], in which i and o regions really are different solvents: water and oil.)

This analogy is useful for estimating the entropy of the random bilayer, for example in the context of a lattice model [1]. It also reveals a very profound fact. The sponge has a hidden degree of freedom, and a special symmetry, associated with the equivalence of i and o. In a ‘symmetric’ sponge there are equal amounts of i and o, which is natural since the bilayer Hamiltonian (1) is symmetric under interchange of i and o (as is any other Hamiltonian that respects the equivalence of opposite sides of a bilayer). On the other hand, it is possible to envisage a state with different amounts of i and o, for example with much less solvent ‘inside’ the film than ‘outside’. In the limit of large asymmetry, one recovers the dilute vesicle structure of figure 1(b). The transition from a symmetric sponge to a weakly asymmetric state (which has only a small difference between the total volumes of i and o regions), or a strongly asymmetric one (vesicles), is an example



**Figure 2.** Several different types of pseudobinary phase diagram in the  $\rho, \lambda$  plane. These have the same topology when plotted in the usual  $\varphi, T$  plane. The broken line is a line of second-order phase transitions from a symmetric sponge to an asymmetric one.  $\tau$  is a tricritical or higher-order critical point and  $c$  a liquid/gas critical point.

of spontaneous symmetry breaking. This special Ising-like symmetry of the sponge has major experimental consequences, as we now describe.

#### 4. Landau theory

Due to the special symmetry, the Landau free energy of a sponge phase depends on two order parameters [7, 18, 19]. This is true even in a binary system of surfactant + solvent. One order parameter is the volume fraction of bilayer  $\varphi$  (or its departure from a reference value  $\rho = \varphi - \varphi_0$ ) and the other one is a parameter  $\eta$  which we may take as the difference in volume fraction of the ‘inside’ (i) and ‘outside’ (o) regions of solvent. This parameter vanishes in a symmetric state and, since i and o are made of identical material, it can enter only in even powers in the Landau expansion. We expect  $\rho$  and  $\eta$  to be coupled at the lowest order allowed by symmetry. This argument gives the following Landau expansion of the thermodynamic potential [18, 19]:

$$\Delta\Phi = \mu\rho + \lambda\rho^2 + \alpha\rho^4 + \beta\eta^2 + \delta\eta^4 + \nu\rho\eta^2 \quad (5)$$

where  $\mu, \lambda, \alpha, \beta, \delta$  and  $\nu$  are numerical coefficients that can be estimated, for example, from the lattice model of [1, 15].

Under variation of these coefficients, several different types of ‘pseudobinary’ phase diagram can be generated (figure 2) [19]. The transition between the sponge and the dilute phase can be either first order or second order; in fact we predict (even in a binary system) a line of second order transitions on the  $\varphi, T$  plane at which the i/o symmetry is spontaneously broken. In addition, a regular liquid gas critical point can exist either between two symmetric sponge phases, or two broken symmetry phases, of different volume fraction. Symmetric tricritical behaviour [20] should be unusually easy to obtain in these systems. It should also be relatively easy to study various other higher order critical points. The great advantage of bilayer containing systems over other multi-

component liquids is that the Ising-like I/O symmetry remains exact over a finite range of temperatures and compositions. In contrast, for most other systems there is some composition-dependent analogue of the magnetic field which must carefully be tuned to zero at each temperature [20]. (An exception is the  $^3\text{He}/^4\text{He}$  system [21].)

### 5. Small angle light scattering

By adding suitable gradient terms to (5), we may generate a Landau Ginzburg theory and compute correlation functions, as are probed by SALS [7, 19]. Experimentally the only observable fluctuations are in the surfactant density, since clearly there is no scattering contrast between I and O regions (which contain identical matter). Suppose that we are in the symmetric sponge state, approaching the I/O symmetry-breaking line, but not too closely, in which case we may keep a gaussian treatment of the fluctuations. So long as  $\lambda > 0$ , we can write:

$$\Delta\Phi = \mu\rho + \lambda\rho^2 + \beta\eta^2 + \nu\rho\eta^2 + \gamma(\nabla\eta)^2 + \tau(\nabla\rho)^2 + \xi\nabla\eta\nabla\rho. \quad (6)$$

Far from any tricritical point, we can drop the last two terms [7, 19], in which case the fluctuations of the  $\eta$  order parameter are of the usual Ornstein–Zernicke type. However, these cannot be measured. What we can measure (and predict) is the correlation function  $J(q) = \text{constant} \times \langle \rho_q \rho_{-q} \rangle$ , which does probe (indirectly) the long-wavelength correlations of  $\eta$ , via the  $\eta^2\rho$  coupling term in (6). The calculation gives [7]

$$I(q) = A[B + 2 \tan^{-1}(q\xi_\eta/2)/q\xi_\eta] \quad (7)$$

where  $A$  and  $B$  are combinations of the previous parameters, and  $\xi_\eta$  is the correlation length for I/O density fluctuations. At this level of approximation,  $\xi_\eta$  should diverge like  $(\varphi - \varphi_c)^{-1/2}$  near the symmetry-breaking line. There are two contributions in (7): one from the intrinsic fluctuations of  $\rho$  controlled by  $\lambda$ , and the other from fluctuations induced by the coupling to  $\eta$  in (6). The second contribution varies (within the Gaussian approximation) like  $q^{-1}$  near the critical point, which is a most distinctive behaviour. This unusual scattering signature has indeed been observed, and we regard it as decisive evidence for some sort of sponge-like bilayer arrangement that divides space symmetrically [7].

### 6. Critical and tricritical effects

More generally, the scattering functions on the asymmetric side of the transition can also be predicted, as can those in the vicinity of a tricritical point, using an extension of the Gaussian fluctuation approach [19]. Although the published data [7] is for a system in which the transition is weakly first order, there is a closely related system in which a continuous transition is apparently seen [19], and for which these (more complicated) predictions are relevant. This system consists of aqueous SDS bilayers slightly swollen with dodecane and pentanol [4, 5]; to the accuracy so far measured it does show a divergence in the osmotic compressibility and the correlation length as one crosses a line in the pseudobinary phase diagram [19].

Close to a tricritical point, a mean-field approach (plus Gaussian fluctuations) should be quite accurate [20], but on the second-order I/O line far from tricriticality the usual

non-Gaussian critical fluctuations should play a role, just as in any other three-dimensional system with Ising-like symmetry. However, the critical behaviour of the sponge system is unusual for two reasons. Firstly, unless measurements are made at fixed surfactant chemical potential  $\mu$ , the Ising-like exponents associated with the I/O symmetry breaking transition (as given in [14], say) are subject to Fisher renormalization, and therefore increased by a factor  $(1 - \alpha)^{-1}$  [22]. (This reflects the singularity in  $\mu$  that arises as the transition is approached by varying either  $T$  or  $\varphi$  with the other one fixed. The effect is present even for a binary system at the I/O symmetry-breaking line.)

The second unusual aspect, mentioned above, is that experimentally one cannot observe the I/O order parameter directly, only its effect on the surfactant density  $\rho$ . In the symmetric sponge this is quadratic in the order parameter, which gives a further change in the exponents measured in light scattering. In terms of the usual  $d = 3$  Ising exponents (not to be confused with coefficients in the Landau expansion, equation (6)) results are easily obtained for the dependence on  $\Delta$ , the distance from the critical line either in  $\varphi$  or in  $T$ . For the correlation length, we find  $\xi \sim \Delta^{-\nu/(1-\alpha)}$ . The surfactant osmotic compressibility diverges as  $\chi_s \sim \Delta^{-(2\gamma-d\nu)/(1-\alpha)}$  when approaching the transition from the symmetric side; when approaching from the broken symmetry phase we find instead  $\chi_a \sim c_1 \Delta^{-(\gamma-2\beta)/(1-\alpha)} + c_2 \Delta^{-(2\gamma-d\nu)/(1-\alpha)}$ , with  $c_1$  and  $c_2$  non-singular constants. Inserting the numerical values, we get  $\xi \sim \Delta^{-0.71}$  ( $\sim \Delta^{-1/2}$ );  $\chi_s \sim \Delta^{-0.60}$  ( $\sim \Delta^{-1/2}$ ) and  $\chi_a \sim \Delta^{-0.66}$  ( $\sim \Delta^{-1/2}$ ) where the values in parentheses are those from the mean-field/Gaussian fluctuation approach [7, 19]. For the scattering at criticality, the result [23] is  $I(q \neq 0, \Delta = 0) \sim q^{d-4+2\eta} \sim q^{-0.93} (q^{-1})$ .

## 7. Defects

In presenting these exponents for our second order phase transition, we should consider again the role of edge and seam defects in the bilayer. These were neglected above, and in their absence the partitioning of space into I and O regions is well-defined. If defects are very rare (which we expect to often be the case on energetic grounds) our description remains valid over very large regions of space. On the other hand, if defects are very common (for example if there is a large hole through the bilayer, on average, in every two or three ‘pores’ of our sponge) the I/O symmetry will no longer play a role, and most of the effects we have discussed in this paper will disappear. This crossover is a remarkable one since puncturing the bilayer does not actually break the I/O symmetry, it just makes it less and less clearly defined. At present we have no real theoretical understanding of this unusual crossover; however, we may advance a conjecture that defects, by leading to the ‘abolition’ of I/O symmetry at large length scales, cause the second order phase transition to become slightly rounded [7, 18]. If so, the critical exponents discussed above may be hard to measure unless care is taken to ensure that the defect energies are genuinely large. (They may be hard to measure anyway, since the ‘bare’ correlation length in the system is large ( $\sim \xi_\kappa$ ) even before any critical phenomena set in.) In fact for the aqueous SDS dodecane pentanol system discussed above, there is some prospect of deliberately decreasing the defect energy by varying the salt content of the aqueous phase. This should allow the crossover region to be explored in more detail.

## 8. Conclusions

We have seen that in certain systems, an isotropic liquid phase made of random connected bilayers is expected. The bilayer film divides space into two domains arbitrarily

labelled inside (i) and outside (o). The symmetry of the bilayer Hamiltonian with respect to i and o may be spontaneously broken, but even in the unbroken phase it leads to some novel effects. The concentration fluctuations for the surfactant are not Ornstein–Zernike but have a strikingly different  $q$  dependence (at least in certain parts of the phase diagram) due to the coupling between the i/o order parameter and the surfactant concentration.

One may also observe, in suitable systems [5, 19], a critical line between two isotropic liquids. Starting with such a system, it should not be too hard to attain a symmetrical tricritical point. Another interesting prospect is the smooth abolition of the critical line (perhaps we should more accurately call it a ‘pseudocritical’ line!) as defect energies are reduced. Finally, we should add that the dynamical properties of the sponge phase, especially near the i/o symmetry breaking line [24], and near the transition to the smectic state [25] are the subject of current theoretical and experimental study.

### Acknowledgments

We would like to thank many of our colleagues for stimulating discussions, especially the following: R C Ball, A M Bellocq, S T Milner, F Nallet, U Olsson, S Ramaswamy and D F K Shim.

### References

- [1] Cates M E, Roux D, Andelman D, Milner S and Safran S 1988 *Europhys. Lett.* **5** 733 (erratum 794).  
See also  
Cates M E 1989 *Proc. NATA ASI on Phase Transitions in Soft Condensed Matter* ed D Sherrington and T Riste (New York: Plenum) pp 179–93
- [2] Porte G, Appell J, Bassereau P and Marignan J 1989 *J. Physique* **50** 1335
- [3] Harusawa F, Nakumara S and Mitsui T 1974 *Colloid Polym. Sci.* **252** 613  
Mitchell D J, Tiddy G J T, Waring L, Bostock T and McDonald M P 1983 *J. Chem. Soc. Faraday Trans. I* **79** 1975  
Lang J C and Morgan R D 1980 *J. Chem. Phys.* **73** 5849  
Laughlin R G 1978 *Advances in Liquid Crystals* ed G H Brown (New York: Academic) pp 41, 99  
Nilsson P G and Lindman B 1984 *J. Phys. Chem.* **88** 4764  
Benton W J and Miller C J 1983 *J. Phys. Chem.* **87** 4981
- [4] Bellocq A M and Roux D 1987 *Microemulsions, Structure and Dynamics* ed S Friberg and P Bothorel (Boca Raton, FL: Chemical Rubber)
- [5] Gazeau D, Bellocq A M, Roux D and Zemb T 1989 *Europhys. Lett.* **9** 447
- [6] Porte G, Marignan J, Bassereau P and May R 1988 *J. Physique* **49** 511
- [7] Roux D, Cates M E, Olsson U, Ball R C, Nallet F and Bellocq A M 1980 *Europhys. Lett.* **11** 229
- [8] Helfrich W 1973 *Z. Naturf. c* **28** 693
- [9] Leibler S 1989 *Statistical Mechanics of Membranes and Surfaces* ed D Nelson, T Piran and S Weinberg (Singapore: World Scientific) pp 45–103
- [10] David F 1989 *Statistical Mechanics of Membranes and Surfaces* ed D Nelson, T Piran and S Weinberg (Singapore: World Scientific) pp 157–223
- [11] Helfrich W 1985 *J. Physique* **46** 1263
- [12] Peliti L and Leibler S 1986 *Phys. Rev. Lett.* **54** 1690
- [13] de Gennes P G and Taupin C 1982 *J. Phys. Chem.* **86** 2294
- [14] Huse D and Leibler S 1988 *J. Physique* **49** 605
- [15] Golubovic L and Lubensky T 1989 *Europhys. Lett.* **10** 513
- [16] Andelman D, Cates M E, Roux D and Safran S 1987 *J. Chem. Phys.* **87** 7229  
Cates M E, Andelman D, Safran S A and Roux D 1988 *Langmuir* **4** 802
- [17] Strey R, Shomaker R, Roux D, Nallet F and Olsson U 1990 *J. Chem. Soc. Faraday Trans. II* at press



- [18] Roux D and Cates M E 1990 *Proc. 4th Nishinomyia–Yukawa Symp.* (Heidelberg: Springer) at press
- [19] Roux D, Coulon C and Cates M E in preparation
- [20] Knobler C M and Scott R L 1984 *Phase Transitions and Critical Phenomena* vol 9, ed C Domb and J L Lebowitz (New York: Academic)
- [21] Blume M, Emery V J and Griffiths R B 1971 *Phys. Rev. A* **4** 1071
- [22] Fisher M E 1968 *Phys. Rev.* **176** 257  
See also  
Bergman D and Halperin B 1976 *Phys. Rev. B* **13** 2145
- [23] Ball R C 1989 private communication  
Ramaswamy S 1990 private communication
- [24] Milner S T, Cates M E and Roux D 1990 *J. Physique* at press
- [25] Cates M E and Milner S T 1989 *Phys. Rev. Lett.* **62** 182  
Marques C M and Cates M E 1990 *J. Physique* **51** 1733  
Roux D and Knobler C M 1988 *Phys. Rev. Lett.* **60** 373