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Isotropic phases of self-assembled amphiphilic aggregates

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An account is given of recent theoretical and experimental progress in understanding isotropic phases of amphiphilic molecules in solution. The viewpoint is mainly that of equilibrium statistical mechanics, but with some discussion of dynamical features, such as viscoelasticity. We start by discussing spherical and anisometric micelles, especially rigid rod micelles, and their interactions with each other and with perturbing fields. Flexible worm-like micelles are next considered, emphasising their length distribution and its kinetics; their linear (and, briefly, nonlinear) viscoelasticity; tracer diffusion, including anomalous diffusion; and the role of equilibrium crosslinks. The aggregation of amphiphiles into bilayers is then discussed. The elastic curvature energy of bilayers is used to account for the stability of the sponge phase (L_3). Scaling laws for dilution of this phase are given, and its unusual symmetry pointed out. The role of edge- and line-defects in the sponge phase is outlined, along with preliminary ideas concerning its dynamical properties. Finally, the possible stability of other isotropic bilayer phases, containing equilibrium vesicles and/or onion-like structures, is briefly examined.

1. Introduction

This paper reviews recent work on the various isotropic phases of amphiphilic molecules, such as detergents, in solution. The word ‘phase’ here is used loosely since (with one remarkable exception) all the isotropic phases considered here have the same symmetry as a simple liquid, and can in principle run smoothly into one another without any form of phase transition. Throughout, the emphasis is on simple models, in which the detailed molecular specification of the amphiphile(s), solvent, and their mutual interactions, are encapsulated in a small number of phenomenological parameters. By thus limiting our ambitions, more can be achieved in terms of a general description of self-assembly and its consequences, than if we attempt to base our models directly on fundamental molecular chemistry. In fact, the models described may be relevant not only to conventional surfactant molecules, but also more complex materials including dyes (Attwood *et al.* 1990), metallic complexes (Terech *et al.* 1992), phospholipids (Leibler 1989), Lecithins (Schurtenberger *et al.* 1989, 1990) and liquid sulphur (Cates 1987*a*).

2. Principles of self-assembly: spherical micelles

Amphiphilic molecules, such as soaps, can in solution self-assemble into a variety of aggregated structures. The aggregation is usually fully reversible: this allows one to apply the laws of statistical mechanics. A typical amphiphile consists of a polar head group attached covalently to a hydrocarbon tail. In aqueous solution, these

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molecules will aggregate spontaneously so as to avoid hydrocarbon/water contacts. The usual structure is a small spherical micelle (or, in an organic solvent, a reverse micelle) of 20–50 molecules.

The basic compromise the system has to make is between translational entropy, which favours the maximum number of small objects, and the (free) energy of packing (Israelachvili *et al.* 1976). We choose to work at fixed volume, in which case the natural thermodynamic potentials are F (Helmholtz free energy) and $\Phi = F - \mu N$. Is it convenient to introduce units of energy such that $k_B T = 1$. For a dilute solution of micelles, the thermodynamic potential Φ per unit volume as a function of the concentrations c_n of n-mers, is then

$$\Phi = \sum_{n=1}^{\infty} c_n (\ln c_n + f(n) - \mu n), \tag{1}$$

where $f(n)$ is the local packing energy of an n-mer whose centre of mass position is specified. The $c \ln c$ terms are the entropy of translation of the aggregates; a phenomenological microscopic length, of order the amphiphile size, has been set equal to unity. To find the equilibrium size distribution, the potential Φ must be minimized at fixed μ with respect to all the concentrations c_n. This gives a standard result (recalling $k_B T = 1$):

$$c_n = e^{-(f(n) - \mu n)}, \tag{2}$$

where μ is determined, for a closed system, from the constraint that

$$\sum_{n=1}^{\infty} n c_n = \phi, \tag{3}$$

where ϕ (in suitable units) is the volume fraction of amphiphile.

What happens, as μ is increased, depends on the shape of $f(n)$. For spherical micelles, this function typically has negative curvature at small n, a minimum at some $n = n_m$, and then rises steeply at large n (reflecting the fact that a hole at the centre is very unfavourable). If so, a fairly sudden proliferation of micelles of size n_{cmc} occurs near a well defined chemical potential $\mu = \mu_{cmc}$, where cmc denotes critical micellization concentration. The total amount of material contained in micelles rapidly becomes very large as μ passes μ_{cmc}. Conversely, the chemical potential μ becomes almost independent of the concentration for $\phi > \phi_{cmc}$. Note that the micelles formed are always somewhat smaller than the optimal packing size (n_m). This reflects the compromise between packing energy and translational entropy. If, in contrast to our assumption, $f(n)$ does not have negative curvature at small n, the mean micellar size instead evolves smoothly away from zero as ϕ is increased; there is no sudden onset. This scenario appears to be common for (reverse) micelles in organic solvents (see, for example, Mittal & Bothorel 1986).

Phases of spherical micelles are of some interest, especially in the 30–70% volume fraction range where they share some of the static and dynamical properties of interacting colloidal suspensions (Kotcharlyk *et al.* 1984). However, since the basic micellar shape is roughly constant, there is not much direct influence of self-assembly on solution properties.

3. Anisometric micelles

(*a*) *Rods and discs*

In addition to the spherical case, rod-like and disc-like micelles can both be envisaged. For a single species of amphiphile, the linear size of the aggregate in its shortest direction is basically controlled by the length of the molecule. Subject to this, spheres, cylinders and sheets have decreasing surface to volume ratio, and therefore one expects a progression through this sequence as the ratio of head group size to that of the tail is decreased (Israelachvili *et al.* 1976). The same arguments can be used to explain the role of cosurfactants and mixtures of surfactants.

For the case of rod-like assemblies, the packing energy $f(n)$ takes the form (for n large)

$$f(n) = An + E, \tag{4}$$

where the first term arises from the cylindrical body of the micelle, and the second is the excess packing free energy of two end-caps. For surfactant assemblies, this end-cap energy is typically in the range 5–$25k_B T$ (Cates & Candau 1990). If we assume that micelles are dilute enough not to interact (via steric, van der Waals, or Coulomb forces) we can continue to use (1) but with this new form of $f(n)$. The result is then

$$c_n = \mathrm{e}^{-E}\,\mathrm{e}^{-n/\bar{n}}, \tag{5}$$

where $\bar{n} = (A - \mu)^{-1}$ is the mean aggregation number. Solving for μ then shows that $\bar{n}$ depends on volume fraction ϕ according to (Mukerjee 1972)

$$\bar{n} \sim \mathrm{e}^{E/2}\,\phi^{\frac{1}{2}}. \tag{6}$$

The rod size thus evolves smoothly with volume fraction. This result has been confirmed experimentally for large aggregates in dilute conditions (Young *et al.* 1978; Missel *et al.* 1983), though ignores any correction to (4) arising at small n, and thus does not describe systems in which rods form with an aspect ratio of, say, two or three (which may still be governed by a CMC type evolution).

The case of disc-shaped micelles is completely different. For a flat disc, the packing free energy becomes $f(n) = A'n + Bn^{\frac{1}{2}}$ where the second term is a perimeter contribution. Repeating the previous argument gives $c_n = \mathrm{e}^{-(Bn^{\frac{1}{2}} - (\mu - A')\,n)}$. In this case, negligible aggregation occurs so long as $\mu \leqslant A'$ (since c_n is then maximum for $n = 1$). However, for $\mu > A'$, c_n is unbounded at large n. Therefore $\mu = A'$ formally marks the onset of an abrupt transition from monomers to a phase of infinite discs, or more realistically a smectic liquid crystalline phase (Israelachvili *et al.* 1976). However, for disc-like aggregates of moderate size, the shape can be more like an oblate ellipsoid, to which this argument does not apply. Such micelles are indeed found, and show a variety of interesting phases, including (at high concentrations) exotic phases of columnar, discotic, and even smectic order (see, for example, Boden *et al.* 1987).

(*b*) *Interactions among rods*

Returning now to rod-like micelles, we note that long rods will tend to overlap even at quite low total volume fractions of amphiphile. By overlap we mean that the sphere swept out by one rod typically contains (parts of) several other rods: this defines the 'semidilute' régime, $\phi \geqslant \phi^*$ (Doi & Edwards 1986). The effect of interactions on the size distribution for rods calculated previously is somewhat delicate. But any interaction which depends only on the total amount of material, ϕ, can be shown to be irrelevant in determining the size distribution. Thus the calculation leading to (5) and (6) is not necessarily invalidated simply because rods overlap in space.

In practice, though, there are two important types of interaction that do not depend only on the total amount of material present. The first is the orientational interaction which causes nematic ordering at high concentrations (de Gennes 1974).

Near any nematic transition, the size distribution of micelles may be strongly coupled to the state of local order (McMullen *et al.* 1985; Herzfeld & Taylor 1988). However, for long uncharged rods, there is in principle a large concentration range between the onset of rod overlap ($\phi \approx \phi^*$) and the onset of strong nematic interactions at $\phi \approx \phi^{**} = \phi^* L$, where L is the aspect ratio of a typical rod (Doi & Edwards 1986).

The second interaction of this type is the Coulomb force, which is important in ionic surfactant systems at low ionic strengths. The effect of this force on the size distribution has been studied for the case of no added salt (Safran *et al.* 1990; MacKintosh *et al.* 1990; see also Odijk 1989). Below the overlap threshold, micellar growth is suppressed, with a slower increase of mean micelle size with ϕ than given by (6), and a narrower size distribution than predicted by (5). Close to ϕ^*, a collective screening of the Coulomb force sets in, and the mean rod length increases very rapidly, approaching from below an asymptotic behaviour governed by (6) and (5) in the semidilute régime. This is consistent with some evidence from dynamical studies (see, for example, Wunderlich *et al.* 1987). In practice, however, the behaviour near ϕ^* may be yet more complex, due to a strong coupling between the relative orientations of neighbouring micelles and their centre of mass positions (Canessa *et al.* 1991). The characterisation and modelling of charged rod-like micelles at or above the overlap threshold remains an important challenge for future research.

(*c*) *Rod micelles under fields and flow*

In this section we ignore the complications of rod–rod interactions and discuss some unusual features that arise from self-assembly in systems subjected to an external field. This will generally tend to align the micellar axes along the direction of the field, which reduces the entropy of rotation of any given rod. The rotational entropy, like the translational kind, is involved in a competition with the local packing preference of amphiphiles. The imposition of a field interferes with this balance and will tend to favour longer rods: this is the phenomenon of *alignment induced growth.*

The simple case of non-interacting rod-like micelles in an external electric or magnetic field can be solved using the methods of §3*a*. For micelles without permanent dipole moments (the usual case) we can write in place of (2)

$$c(n,\alpha) = \exp\left[-(E-\mu n-\mathscr{E}^2 n\alpha^2)\right], \tag{7}$$

where $c(n, \cos\theta)$ is the concentration of rods of ‘length’ n at an angle θ to the applied field. The end-cap energy is again denoted E whereas $\mathscr{E}$ is a field strength measured in reduced units which incorporate various microscopic factors of polarizability, etc. From (7) one can calculate any desired thermodynamic properties of a solution of non-interacting rod-like micelles in a field (Drye & Cates 1993).

For the case of monodisperse, unbreakable rod-like particles, a similar thermodynamic argument can be used to calculate the response of rods to an applied *flow* field (Doi & Edwards 1986). This works only for the case of potential flows (such as elongational flow); shear flow is excluded. The case of self-assembling rods under flows is more complex, since in principle there is not only a rotational torque from the flow but also a coupling between the flow of the micelles and the kinetics of their aggregation and breakdown. None the less, an effective-field model has been proposed for the self-assembled case in both elongation (Wang *et al.* 1990) and shear (Wang 1990, 1991). This gives quite reasonable predictions: for example in elongation, some increase in micellar length at modest flow rates is followed by an eventual decrease as rods are torn apart by the flow. However, there are fundamental difficulties with this approach, which involves implicit (and arguably unrealistic) assumptions concerning the dependence of the fusion rates for rods on their angle to the flow direction.

An alternative approach is based on the direct analysis of rate equations for breakdown and (collinear) fusion of micelles. The main effect of flow is now to enhance reactions by increasing the number of parallel rods that can fuse. For elongational flow, the analysis can be carried out in detail if one assumes that micellar reactions are frequent on the timescale of rotation of an average micelle (Cates & Turner 1990). Some asymptotic results for shear flows, and for the opposite limit of slow reactions, have also been obtained (Turner & Cates 1992*a*). In all cases, substantial micellar growth is predicted at high flow rates; for elongational flow the behaviour can mimic a phase transition, at a critical flow rate, to rods of virtually infinite length.

So far, neither theory has been very successful in explaining shear-flow experiments on stiff rod-like micelles. In reality, many systems show (in flow birefringence and stress measurements) a fraction of strongly aligned material at much lower shear rates than predicted by theory (Rehage *et al.* 1986; Wunderlich *et al.* 1987). The resulting shear-induced state can take seconds or even minutes to build up after flow is started (Hofmann *et al.* 1991). In apparent contradiction, neutron scattering data has been used to argue against any form of alignment-induced growth (Cummins *et al.* 1987, 1992). To explain these strange effects, a more detailed account of (Coulombic) micellar interactions, perhaps in the framework of a kinetic coagulation model (Bruinsma *et al.* 1992), will be needed.

4. Worm-like micelles

In many surfactant systems, very long, flexible one dimensional micelles are formed, for example by adding excess salt to a system of short rodlike micelles (Porte and Appell 1981, Candau *et al.* 1985; Ikeda *et al.* 1980; Hoffmann *et al.* 1983). The salt reduces the effective head group size (by screening of Coulomb forces), destabilizing the hemispherical end caps relative to the cylindrical body of the micelle, and so causing an increase in length. (At the same time, the screening leads to a much reduced micellar stiffness (Odijk 1979).) The overlap threshold can then be very low (a few percent). The resulting phase of entangled micelles is viscoelastic and strongly resembles a polymer solution. This suggests the application of semidilute polymer solution theory (de Gennes 1979), which predicts certain scaling laws. For example, the osmotic pressure Π and high-frequency shear modulus (plateau modulus) G_0, should each vary approximately as $\phi^{2.25}$. These laws (and similar ones concerning light scattering) are not sensitive to the individual lengths of the polymers, but only to the total volume fraction of chains present. In practice such laws are obeyed fairly well by viscoelastic surfactant phases (see Cates & Candau 1990), confirming the presence of entangled polymerlike objects.

(*a*) *Micellar length distribution*

The molecular weight distribution for semidilute self-assembling polymers can be calculated in a mean-field (Flory–Huggins) approach (Scott 1965). We may write

$$\Phi = \sum_{n=0}^{\infty} c(n)\,(\ln c(n) + E - \mu n) + \Delta\Phi(\phi), \tag{8}$$

where E is again the (free) energy of two end-caps. Terms linear in n have been incorporated into μ. The last term in (8) represents interactions; it is a feature of the mean-field treatment that this depends only on the total volume fraction, ϕ. The minimization to find the size distribution $c(n)$ proceeds exactly as in §3*a*, with the same results, (5) and (6). In principle, these are now liable to corrections from three sources. First, for solutions of ionic micelles at low ambient salinity, the micelles themselves contribute to the ionic strength so that E in (8) becomes ϕ-dependent (Mackintosh *et al.* 1990; Porte 1984; Odijk 1989). This effect leads to an enhanced concentration dependence of the mean worm-length $\bar{n}$. The mean-field treatment neglects a second ϕ-dependent correction to E, from excluded volume correlations (Cates 1988). This too leads to a slight shift in the power-law exponent (0.5 → 0.6) for the dependence of $\bar{n}$ on ϕ in (6). Finally, we have ignored the presence of closed rings, which should have only weak effects (Cates 1988; Petscheck *et al.* 1986).

(*b*) *Dynamics of micellar breakdown*

The main differences between worm-like micelles and conventional polymers is in the reversibility of the aggregation process. In many systems, reversible breakdown and fusion occur on timescales comparable with, or more rapid than, those associated with chain diffusion. Hence the dynamics (self-diffusion and viscoelasticity) are strongly sensitive to the micellar kinetics. These can also be probed directly using the T-jump technique (Lang & Zana 1987). In this method, a small change in temperature is made (rapidly) by discharging a capacitor through the sample. The light scattering signal is then monitored as it relaxes to a new equilibrium value.

Three different model schemes for the kinetics of micellar fusion and breakdown have been analysed (Cates 1987*b*; Turner & Cates 1990, 1991, 1982*b*; Turner *et al.* 1993); these are reversible scission, end-interchange and bond-interchange (figure 1). For each scheme, there is a characteristic time τ_{break} for changes in micellar size. The case of a T-jump measurement turns out to be unexpectedly simple (Turner & Cates 1990). For reversible scission, the scattering signal is predicted to decay mono-exponentially (with relaxation time $\frac{1}{2}\tau_{\text{break}}$); this behaviour has indeed been observed in the system CTAB/KBr (Candau *et al.* 1990). For the other two reaction schemes, T-jump corresponds to a zero mode (not decay of the signal), which can be traced to the fact that these schemes preserves the overall number of chains. This is consistent with observations on CTAC/NaSal/NaCl (Kern *et al.* 1991), for which the end-interchange mechanism has been suggested.

(*c*) *Viscoelastic spectra*

The most spectacular property of entangled micellar solutions is their viscoelasticity. Viscoelastic surfactant phases are used in a number of domestic and industrial applications, where their unique rheology, as well as their detergent activity, are exploited. The relaxation time for stress response to an applied shear is typically about 1 s.

Of interest is the function $\mu(t)$, the fraction of shear stress remaining at time t after a small step strain is made. For unbreakable polymers, this can be predicted using the reptation model. In this model, each chain is viewed as trapped in a tube, representing entanglements with its neighbours (de Gennes 1979). The chain can diffuse only along its own length (reptate); its escape from the tube is characterized by a time τ_{rep} which varies roughly as $\phi^2 n^3$. (The exponent for ϕ is slightly model dependent.) If a step strain is applied at time zero, the chain creeps out of its original

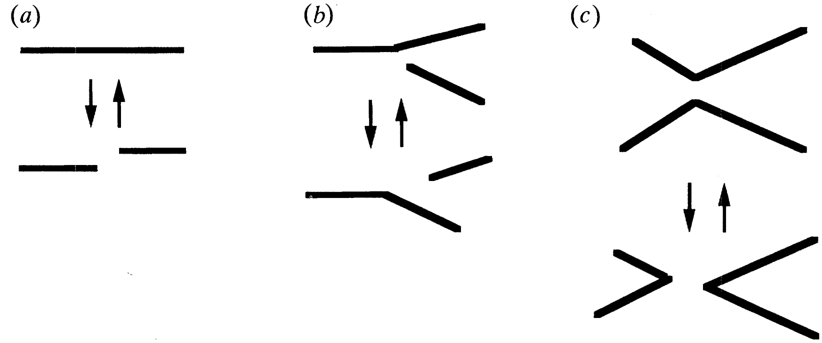

Figure 1. (*a*) Reversible scission, (*b*) end-interchange and (*c*) bond-interchange.

tube gradually into a new environment, creating new tube as it goes. The new tube is in equilibrium in the strained environment, and therefore carries no stress. In this model, therefore $\mu(t)$ is given by the fraction of the original ($t=0$) tube through which neither end of the chain has passed before time t. This can be calculated by casting the problem as a one-dimensional stochastic process (see Doi & Edwards 1986).

The resulting stress relaxation function $\mu_n(t)$ for unbreakable polymers of length n is close to single exponential. This, along with many other predictions of the reptation model, has been confirmed in experiments on conventional polymers. Within the reptation picture it is straightforward to include polydispersity; for an exponential distribution of chain lengths (as predicted by (5)) the result is the weight average:

$$\mu(t) \approx \phi^{-1}\sum_{n} c(n)\, n\mu_n(t) \approx \exp\left[-(t/\tau_{\mathrm{rep}})^{\frac{1}{4}}\right] \tag{9}$$

where from now on τ_{rep} denotes $\tau_{\mathrm{rep}}(\bar{n})$. This broad relaxation spectrum seems to be approached in some micellar systems, such as CPyCl/NaSal with low added salt (Rehage & Hoffmann 1988, 1991). Equation (9) assumes that the micellar kinetics are so slow as to not influence the reptation process itself, in which case polydispersity is the sole effect of self-assembly.

However, there is a (much larger) class of micellar systems which show experimentally, instead of (9), behaviour approaching a simple Maxwell fluid (see, for example, Rehage & Hoffmann 1988, 1991; Shikata *et al.* 1987, 1988*a*, *b*),

$$\mu(t) \sim \mathrm{e}^{-t/\tau}. \tag{10}$$

This can be explained by a model in which the reptation process is coupled to the kinetics of micellar breakdown. Chains move by reptation but are also subject to intermittent changes in length, brought about by micellar reactions. It turns out that the coupled reptation–reaction model can again be cast as a one-dimensional stochastic process, from which $\mu(t)$ can be efficiently computed (Cates 1987*b*; Turner & Cates 1991).

For negligibly slow micellar kinetics ($\tau_{\mathrm{break}} \gg \tau_{\mathrm{rep}}$), the result (9) is recovered, whereas in the opposite limit of rapid reactions, near-Maxwell behaviour, (10), is indeed found. In this limit the Maxwell time τ obeys asymptotically $\tau \sim (\tau_{\mathrm{rep}}\,\tau_{\mathrm{break}})^{\frac{1}{2}}$ for both reversible scission and end-interchange, whereas for bond interchange, $\tau \sim \tau_{\mathrm{rep}}^{\frac{2}{3}}\tau_{\mathrm{break}}^{\frac{1}{3}}$ (Turner & Cates 1992*b*). The approach to a single exponential stress decay can be explained by noting that the relaxation time τ for stress relaxation

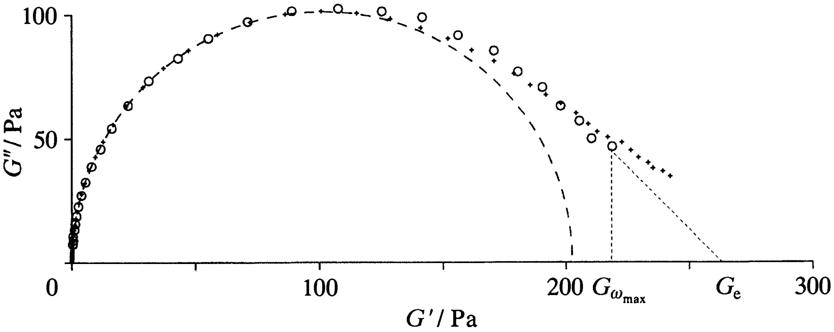

Figure 2. Cole–Cole plot of complex modulus for a CTAB/KBr system (Turner & Cates 1991; Kern *et al.* 1991). Crosses: theory, circles: experiment. $\zeta = \tau_{\text{break}}/\tau$ is fitted.

remains much greater than the breaking time τ_{break}. On a time scale of a few τ_{break}, any given tube segment loses all memory of its initial position relative to the ends of the chain which occupies it. For later times, all tube segments are equivalent, and relax with an equal rate. The resulting relaxation is thus nearly monoexponential, but with departures at short times ($t \leqslant \tau_{\text{break}}$).

Within the model, a quantitative analysis of these departures may be made. They are most visible when the complex elastic modulus $G^*(\omega)$ is plotted in the Cole–Cole representation, that is, the imaginary part of G^* (loss modulus) against the real part (storage modulus) (Doi & Edwards 1986). Here $G^*(\omega)$ is related to the fourier transform of $G(t) = G_0 \mu(t)$, where G_0 is the high-frequency ‘plateau’ modulus of the system, whose scalings was discussed earlier. By comparing the departures seen experimentally with those calculated in the model, an estimate of τ_{break} can be deduced from the viscoelastic spectrum (see figure 2). This has been done for a CTAB/KBr system (Turner & Cates 1991; Kern *et al.* 1992); the result for $\tau_{\text{break}} \approx 0.1$ s is very close to that determined independently by T-jump measurements (Candau *et al.* 1990). This is strong evidence that the model is correct for the system studied.

Another interesting estimate can be extracted from the viscoelastic spectrum: that of the mean micellar length. The procedure here is more complicated but again involves analysing the shape of the Cole–Cole plot (Granek & Cates 1992). The resulting length estimates are typically in the micron range for CTAB/KBr, CTAC/NaSal/NaCl, and CPyCl/NaSal systems (Kern *et al.* 1991), but for the most extreme cases (e.g. 15 mM CPyCl + 12.5 mM NaSal (Hoffmann & Rehage 1988)) estimated mean contour lengths of more than 0.1 mm are obtained.

We conclude this section with a brief discussion of *nonlinear* viscoelastic phenomena. Although they approach a simple Maxwell relaxation in linear response to applied shear, the behaviour of viscoelastic surfactant solutions under high shear conditions is far from simple. None the less, a nonlinear constitutive equation has been proposed (Cates 1990), and solved for the case of steady shear (Spenley *et al.* 1993). The equation exhibits a flow instability, and (for $\tau_{\text{break}} \ll \tau$) predicts a constant shear stress of $\sigma^* = 0.67 G_0$ over a wide range of shear rates. The theoretical shear stress curve is compared with that found experimentally by Rehage & Hoffmann (1991) for a CPyCl/NaSal system in figure 3; there are no adjustable parameters. Over the same range of shear rates, the first normal stress difference is predicted to increase (roughly linearly) towards a very large value; this is also observed. These are obviously encouraging results. Experimentally, a wide range of

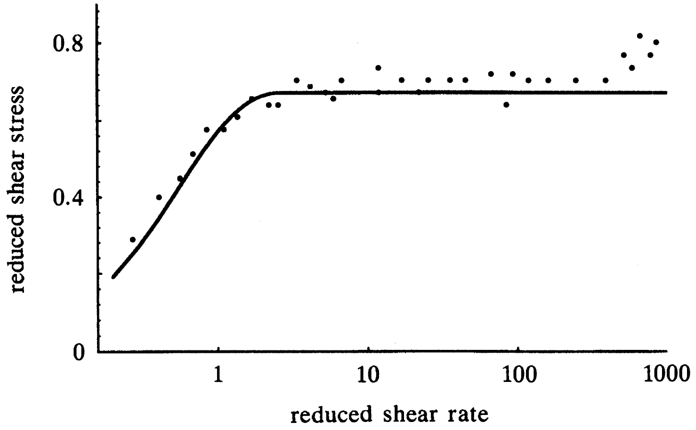

Figure 3. Reduced shear stress σ/G_0 against reduced shear rate $\dot{\gamma}\tau$ for a CPyCl/NaSal system (Spenley *et al.* 1993; Rehage & Hoffmann 1991). Solid line, theory; points, experiment.

unusual stress effects have also been seen in non-steady flows, such as startup (Shikata *et al.* 1988*b*; Rehage & Hoffmann 1988, 1991), which remain to be analysed theoretically.

(*d*) *Self-diffusion*: *Levy-flight anomaly*

The reptation–reaction model can be used to calculate the diffusivity D of individual amphiphiles (Cates 1987*b*); the prediction is $D \sim \phi^{-y}$, with y in the range 1.3–1.7, depending on the kinetic scheme. The exponent is sensitive to the precise dependence of $\bar{n}$ on ϕ (which may depart from theory due to Coulomb effects) and a wider range of values have been obtained in experiment (Ott *et al.* 1990*a*). These do come close to the predicted value for ionic surfactants at moderately high ambient salt, as well as in an uncharged (lecithin in oil) system (Ott *et al.* 1990*b*).

The calculation of D (Cates 1987*b*) assumed that the diffusion is a gaussian process. However, the motion of a given tracer is made up of a sequence of intervals spent on chains of different lengths. There is a disproportionate contribution to diffusion from rare visits to very short chains, which move very quickly. This can lead to a breakdown in gaussian statistics, if the typical motion is dominated by these rare events. The motion is then described instead by a Levy-flight: a sequence of random steps whose length distribution has no second moment (Bouchaud & Georges 1990).

This anomalous behaviour has indeed been observed in fluorescence recovery after photobleaching (FRAP) measurements (Bouchaud *et al.* 1991). The anomaly shows up as an unexpected power law dependence of the relaxation time on wavevector: $\tau_{\text{frap}}(k) \sim \boldsymbol{k}^{-m}$, with m around 1.6–1.8, rather than the usual $m = 2$. The facts can be accounted for by assuming a slightly stronger dependence of D_{rep} on n (over some range of chain lengths) than the usual reptation prediction. Such a correction has previously been suggested in the context of unbreakable polymers (see, for example, Deutsch 1987).

(*e*) *Role of crosslinks*

So far we have neglected any possibility that the micelles form crosslinks with one another to form a real network (rather than merely a network of entanglements). Whether such crosslinks actually are important, depends on their relative packing energy compared with that of end caps. In ionic surfactant solutions, it is known that the end-cap energy, and hence the mean chain length, increases with salinity. Since crosslinks and end caps have the opposite local curvature, one may expect the relative stability of crosslinks to increase under the same conditions, in which case a crossover towards network behaviour is expected at high enough salt levels (Porte *et al*. 1986).

Equilibrium crosslinks have two main consequences, one static and one dynamic. In terms of static equilibria, the main effect is from three-fold junctions, which become increasingly important as the concentration is decreased. Formation of such a link increases the entropy of the system, by an amount that increases with the mesh size (Drye & Cates 1992). Crosslink formation can ultimately defeat excluded volume repulsions, leading to a phase-separation, in which the network avoids further dilution by expelling solvent.

The effect of crosslinking on dynamics is also interesting. In the régime where crosslinks are sparse compared with entanglements, it has been shown that the previous reptation–reaction model can be applied, so long as the mean chain length $\bar{n}$ is replaced by a (smaller) effective value n^*, which is the average strand length between crosslinking points (Lequeux 1992). Hence crosslinks tend to *decrease* the stress relaxation time of the system, in marked contrast to their effect on conventional polymers. This calculation suggests a possible connection between crosslink formation, and anomalously weak viscoelasticity. The latter is seen experimentally in a number of systems at high salt (Khatory *et al*. 1993; Candau *et al*. 1993). An extreme example is $\mathrm{CPyClO_3/NaClO_3}$, which shows perfect polymer scaling behaviour in static and dynamic light scattering (Appell & Porte 1990), and yet is almost completely inviscid (Appell *et al*. 1992). The system also seems to be close to a phase separation (G. Porte, personal communication), which could also be a sign of crosslink formation (see above). It is possible that in this material nearly all the entanglements have been replaced by equilibrium crosslinks. It has been argued that such a network can flow easily by a continuous sliding of junction points (Appell *et al*. 1992).

5. Bilayer-forming surfactants

We now turn to systems in which the locally stable structure is a fluid bilayer. This can be arranged by tuning parameters, such as salinity, to reduce the relative size of the surfactant head-group. The resulting bilayer can support elastic deformations (curvature) and, in principle, two types of line-defect: ‘edges’ and ‘seams’. An edge consists of a sharply curved region where one face of the bilayer folds over to join the other; in a seam, three sections of bilayer meet along a line. (There is again strong local curvature, but in the opposite direction.) For the moment, we rule out such defects; their role is considered briefly in §5*e*. Hence our bilayers must be closed (the case of vesicles: see §5*a* below) or infinite, as in the dilute smectic (L_α) phase. We assume that the area per surfactant is constant, so that the film surface area is ϕ/a, where ϕ is the volume fraction and a the bilayer thickness. With these simplifications, we are left to deal with a fundamental competition between the curvature energy of bilayers (favouring flat films) and entropy (favouring random structures).

(*a*) *Elastic free energy*

Within the harmonic approximation, the packing energy of a bilayer is (Helfrich 1973)

$$E = \int (2\kappa H^2 + \bar{\kappa} K)\,\mathrm{d}s, \tag{11}$$

where $H = \frac{1}{2}(1/R_1 + 1/R_2)$ is the mean curvature, and $K = 1/R_1R_2$ is the gaussian curvature. Here R_1 and R_2 are the two local principal curvature radii, assumed large compared with a, whereas κ and $\bar{\kappa}$ are the mean and gaussian curvature rigidities. Stability conditions (discussed below) require that $\kappa > 0$ and $-2\kappa < \bar{\kappa} < 0$. An interesting topological theorem (see David 1989) states that

$$\int K\,\mathrm{d}S = 4\pi(N_\mathrm{c} - N_\mathrm{h}), \tag{12}$$

where N_c is the number of disconnected pieces of a surface (or 'components') and N_h its number of 'handles'. (For example a torus has one component and one handle.)

The rigidities κ and $\bar{\kappa}$ have units of energy. When κ is comparable with the thermal energy ($k_\mathrm{B}T = 1$, in our units), thermal undulations of the fluid bilayer become significant. These lead to a thermally-induced 'softening' of the bilayer (Helfrich 1983; Peliti & Leibler 1986; Kleinert 1985; David & Guitter 1987). Within perturbation theory, an effective rigidity $\kappa(\xi)$ can be calculated as

$$\kappa(\xi) = \kappa - (3/4\pi)\log(\xi/a) \tag{13}$$

with a similar logarithmic correction expected for $\bar{\kappa}(\xi)$ (see David 1989).

The thermal softening causes a flat piece of bilayer to lose memory of its orientation over a certain 'persistence length', $\xi_\kappa \approx a\exp[4\pi\kappa/3k_\mathrm{B}\mathrm{T}]$ (de Gennes & Taupin 1982). In typical surfactant bilayers, ξ_κ is around 100 nm. For some other systems, such as cell-membrane phospholipids, κ is larger and the persistence length is macroscopic. Even in these systems, thermal undulations can play an important role in the stability of the lamellar (L_α) phase. The tendency of a bilayer to wander in a direction normal to its plane leads to a confinement pressure or 'Helfrich force' (Helfrich 1978) which results from entropic collisions of one bilayer with its neighbours. If the films are even moderately flexible, the repulsive force between adjacent bilayers can overcome the van der Waals attraction between them. In surfactant systems this permits the existence of very dilute smectic phases, typically at volume fractions of 1–10% (see, for example, Roux & Safinya 1988; Bassereau *et al.* 1987).

(*b*) *The sponge phase*

Some years ago, an 'anomalous' isotropic phase was found for bilayer-forming surfactants in either water or oil (Laughlin 1978; Lang & Morgan 1980; Benton & Miller 1983). This phase (also called L_3) exhibits strong birefringence under gentle shearing, suggesting very large aggregates. More recent work using conductivity and other methods (Gazeau *et al.* 1989) has shown that the phase is actually bilayer continuous. It must therefore contain a spongelike web of bilayer which spans the entire sample (figure 4).

Two main theoretical arguments can be used to explain the stability of this phase. Starting from a lamellar phase, one can first consider a dilution experiment, whereby the mean layer spacing $d \sim a/\phi$ is increased more and more. When d exceeds the persistence length, ξ_κ, the driving force for smectic order (local flatness of the bilayers) is lost. Therefore the phase should melt into a more random, sponge-like structure, with a characteristic length scale of order ξ_κ. This is the basic argument of Cates *et al.* (1988), which was supported by a lattice model (see also Golubovic & Lubensky 1989). This model predicts that under even stronger dilution the sponge structure should break up into small aggregates, stabilized by translational entropy.

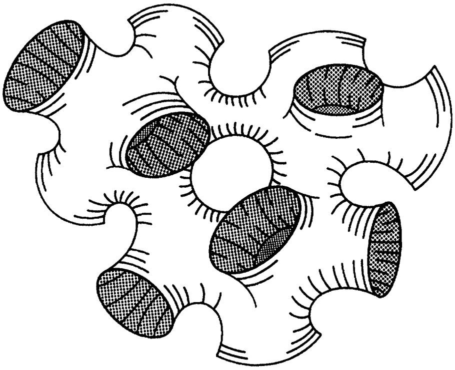

Figure 4. The sponge phase (picture courtesy of G. Porte).

Porte *et al.* (1989) argued somewhat differently, picturing the sponge phase as a molten analogue of the bicontinuous cubic phase. Again starting from a dilute lamellar phase, they argued that by tuning $\bar{\kappa}$ to favour handles (i.e. making it less negative, see (12)), the sponge phase could be reached. In both pictures, the resulting random surface has much more entropy than any ordered phase that would minimise (11). This ordered structure is either lamellar or – if $\bar{\kappa}$ is positive – a cubic phase. (Note that if the *bare* gaussian rigidity is positive, (11) is unstable to a cubic minimal surface phase with a very small lattice parameter, determined by anharmonic corrections. But a larger-length-scale cubic could arise if $\bar{\kappa}(\xi)$ is positive only at large distances.)

The two viewpoints just described are probably both correct, since in many materials the sponge phase can equally well be reached by either route (see Roux *et al.* 1992). Thus the characteristic length scale (or 'pore size') in the sponge (which by simple geometry varies as $\xi \sim a/\phi$) is not necessarily close to the persistence length ξ_κ, and indeed can be varied over a wide range, typically 10–200 nm (Porte *et al.* 1991).

(c) *Scaling laws for the sponge phase*

The fundamental equation of bilayer elasticity, (11), has a remarkable scale-invariant property. If a piece of surface is homogeneously enlarged by a scale factor λ, the energy is unchanged (the factors of λ^2 in the radii of curvature, and the area element, cancel each other out). Porte *et al.* (1989, 1991) emphasized the similarity between the mathematical process of *dilating* the structure, and the physical one of *diluting* the phase. If we compare a given sponge phase, and one in which all length scales are increased by λ, the Helmholtz free energy of the enlarged system is unaltered; hence the free energy *density* follows the law $f \rightarrow f\lambda^{-3}$. This cannot be tested directly since it compares two systems with identical elastic constants but different bilayer thicknesses ($a \rightarrow \lambda a$). However, if we make an ansatz that the free energy (for a fixed area) does not depend on a, then the mapping between a given volume of the initial, and of the final, state can be achieved instead by reducing the concentration of bilayer: $\phi \rightarrow \phi/\lambda$. We thus obtain a scaling law, $f \propto \phi^3$.

This leads to a prediction for the osmotic compressibility, $I(0) \sim \phi^{-1}$. This is quite well-obeyed, though careful measurements expose a clear deviation (Roux *et al.* 1990, 1992; Porte *et al.* 1991). This can be accounted for, by adopting the modified formula

$$f = \phi^3 [A + B \log \phi], \tag{14}$$

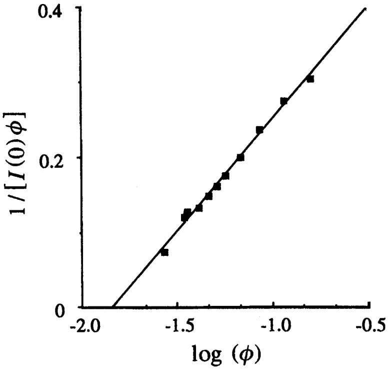

Figure 5. Osmotic compressibility $I(0)$ plotted as $1/(\phi I(0))$ against $\log \phi$, to reveal logarithmic corrections from undulation entropy (from Roux *et al.* 1990).

with A, B constants. This functional form is in fact the one predicted theoretically by the lattice model mentioned earlier, if thermal undulations are treated perturbatively (as in (13)). The logarithmic corrections arise because the ansatz made above, that the bilayer free energy per unit area is independent of thickness a, is not quite correct. Although true of the elastic energy (11), the ansatz is violated by the entropy of undulations (Roux *et al.* 1990). The observation of these delicate corrections (figure 5) is very strong evidence for the correctness of the underlying elastic model as embodied in (11). Scaling laws for various other properties (such as the shape of the scattering function $I(q)$, and various dynamical measurements) have also been confirmed experimentally, though (strangely) the logarithmic corrections are much more prominent in scaling laws for static properties than in those for dynamical relaxation times (Porte *et al.* 1991).

(*d*) *The sponge phase: a hidden symmetry*

The presence in the sponge phase of a continuous two-dimensional film of bilayer has a peculiar consequence. Any such film has the property of partitioning three-dimensional space into exactly two subvolumes. To identify these, we start arbitrarily at some point in space and assign this point to be 'inside' the surface (I). Any point that can be reached from this one without crossing the surface, or by crossing it an even number of times, is also I, whereas any point which is reached by crossing the surface an odd number of times is 'outside' (O). This partitioning is unique, up to a single global interchange of I with O; it applies even if the surface has many components.

We can now distinguish two different types of sponge phase: one in which the two subvolumes are statistically equivalent (the ratio of I to O is 1:1) and one in which they differ. The first, which we have implicitly been discussing so far, is called the symmetric sponge phase, the second is the asymmetric sponge. This latter can be changed continuously into (say) a dilute phase of vesicles by smoothly varying the I/O ratio until it is very small. Therefore, the asymmetric sponge has the same symmetry as an ordinary liquid. The symmetric sponge, however, does not: there is additionally a discrete global symmetry between I and O. In the asymmetric sponge phase, this Ising-like symmetry is *spontaneously broken* (Huse & Leibler 1988; Cates *et al.* 1988; Roux *et al.* 1990).

The extra symmetry of the sponge phase has some important consequences. It permits in principle the existence of a line of second-order phase transitions in the composition/temperature plane of a binary fluid, rather than an isolated critical point as would be normal in such a fluid. There is also a generic tendency toward tricritical (or even higher order) behaviour, with associated regions of parameter space where the transition is first order. Experimentally, first order transitions from the symmetric to an asymmetric phase have definitely been found (Roux *et al.* 1990; Porte *et al.* 1988), as has (in at least one system) a clear turbidity signature (accompanied by apparently divergent light scattering) which is consistent with a line of continuous phase transitions (Coulon *et al.* 1991). The experiments also show some evidence of tricriticality in certain aqueous sponge systems (Roux *et al.* 1991).

These phenomena can be studied using a Landau expansion of the thermodynamic potential in terms of two interacting order parameters, ρ and η. Here ρ represents the surfactant density, and η the degree of asymmetry. A suitable form is (Roux *et al.* 1991)

$$\Delta\Phi = \mu\rho + \lambda\rho^2 + \alpha\rho^4 + \beta\eta^2 + \delta\eta^4 + \nu\rho\eta^2, \tag{15}$$

where $\lambda, \alpha, \beta, \delta$ and ν are expansion coefficients. The surfactant density ρ is measured relative to a reference value, chosen to eliminate any ρ^3 term. The physical content of the Landau expansion is that of a binary-fluid order parameter (ρ) coupled to an Ising like I/O variable (η) by a $\rho\eta^2$ term (this is the lowest order permitted by symmetry). From (15) a number of generic predictions can be obtained concerning phase diagrams, tricriticality, etc., which seem to be generally consistent with observations (Roux *et al.* 1991).

The special I/O symmetry of the sponge phase leads to a very distinctive signature in light-scattering, which probes the correlations of the surfactant density, ρ. This is coupled quadratically to η (see (15)). The scattering signal can be calculated at the level of gaussian fluctuations in η, and for the simplest nontrivial model reduces to the form

$$I(q) \sim \text{const.} + \frac{\arctan(q\xi_\eta)}{q\xi_\eta}, \tag{16}$$

where ξ is the correlation length for η fluctuations (Roux *et al.* 1990). This scattering function has been clearly observed in several different systems (Roux *et al.* 1990; Porte *et al.* 1991), though more complicated functions are sometimes needed, for example in symmetric sponges close to tricriticality, and in asymmetric sponges (Roux *et al.* 1991).

(*e*) *Role of defects*

So far we have assumed that the bilayer in the sponge phase is free of edge and seam defects. In fact the line energy for such defects is not infinite, so they must be present. An important question is whether a small concentration of such defects invalidates the conclusions of our previous discussion. The presence of edges or seams prevents any unique assignment of I and O regions; this might lead, for example, to rounding of any second order transition.

The problem has been studied by Huse & Leibler (1991). These authors used a lattice model which could be written as a gauge theory. They argued on this basis that there was in fact no rounding of the transition until the line energy for defects was so low that *infinite* line defects were present on the percolating bilayer. This suggests that our simpler description in terms of I/O symmetry remains basically reliable unless the line energy for defects is rather small. In this régime, a transition to a new 'seaweed' phase, with the same symmetry as an asymmetric sponge (or an ordinary liquid) was argued to occur (Huse & Leibler 1991); the experimental confirmation of this idea remains a matter of some uncertainty (Porte & Pfeuty 1993).

(*f*) *Dynamics in bilayer-continuous phases*

Theoretically it is not obvious whether the sponge phase, which contains a percolating film of continuous bilayer, should exhibit significant viscoelasticity. On the one hand, the bilayer film is fluid, and this allows transport of surfactant from place to place without rupture or topological change in the film (Snabre & Porte 1990). On the other hand, one might argue that topological features, such as handles, cannot be mutually rearranged without rupture and reconnection of the film (Milner *et al.* 1990). The latter is presumably an activated process which could have a long relaxation time. Experimentally, the situation seems fairly clear: there is negligible viscoelasticity (Snabre & Porte 1990; see also Hoffmann *et al.* 1992).

None the less, the sponge phase has some interesting flow behaviour. For example, in the symmetric sponge, the viscosity is higher by a factor of 3 or so than that of pure solvent. This factor, which remains even if one extrapolates to zero volume fraction, can be explained in terms of an effective 'tortuosity' of local fluid streamlines (Snabre & Porte 1990). The connectivity of the sponge is also exhibited if one tries to pump it through a porous medium (Vinches *et al.* 1992). The strong flow birefringence of the sponge phase has already been mentioned. Indeed, in some systems gentle shearing of the phase in a test tube seems to lead to the formation of a metastable lamellar liquid crystal (see Hoffmann *et al.* 1992). This persists for seconds or (in some cases) very much longer. A theoretical study of the effect of shear on the isotropic to lamellar transition offers a qualitative explanation of this effect (Cates & Milner 1989; Cates 1991), though the details of what happens under controlled laminar flow conditions may be much more complex (Diat & Roux 1993).

Recent temperature jump measurements on sponge phases show a very rich multimode response spectrum (Waton & Porte 1993). An unusual relaxation spectrum has also been predicted for dynamic light scattering in sponge phases near the symmetry breaking transition (Granek *et al.* 1992). Anomalies can also be expected in other aspects of sponge phase dynamics, though most of these remain to be investigated in detail.

(*g*) *Vesicles and onions*

The arguments of Porte *et al.* (1989, 1991) involve stabilising a sponge phase with many handles by increasing the gaussian rigidity $\bar{\kappa}$ to a less negative value (see §5*a*). It is interesting to ask what happens if instead $\bar{\kappa}$ is decreased towards its stability limit of $\bar{\kappa} = -2\kappa$. (When this limit is reached, the bending energy for creating a small sphere is negative and hence one expects proliferation of very small vesicles whose size is limited only by anharmonic corrections to (11).)

The combination of elastic constants which controls the energy of a sphere is $\kappa' = 2\kappa + \bar{\kappa}$; as usual this is logarithmically dependent on the length scale ξ. If the bare value of κ' is slightly positive, there is no instability at short distances but (because of the renormalization effect) $\kappa'(\xi)$ could none the less be negative at large length scales, leading to a proliferation of spheres of an intermediate size. Such a vesicle phase could also be stabilized, relative to the lamellar state, by translational entropy terms (Huse & Leibler 1988). There is now good evidence that an isotropic phase of large (*ca.* 30 nm) vesicles does arise in some systems (Herve & Roux 1993; Hoffmann *et al.* 1992), if one varies the bilayer composition in the opposite direction from the sponge phase.

The properties of this 'L_4' phase are particularly interesting in the semidilute regime (more than 2–3%). Here spherical unilamellar vesicles, if present, would overlap, and theoretical arguments (Simons & Cates 1992) suggest that 'nesting' of vesicles, should occur to form a phase of onion-like aggregates. This seems to be consistent with some experimental data from light scattering and conductivity studies (Herve & Roux 1993). However, detailed experiments on the semidilute L_4 phase have so far proved difficult, partly because any phase separation involving the nearby lamellar phase is extremely slow. The L_4 phase is viscoelastic; details of its behaviour remain to be explored. Somewhat similar viscoelastic phases, containing larger multilamellar vesicles, can also be formed by the ultrasonification or (with much better control of aggregate size) careful shearing of a dilute lamellar phase (Diat & Roux 1993). These long-lived metastable states pose many important challenges for future research.

6. Concluding remarks

Recent work on isotropic phases of self-assembled structured fluids has been reviewed. The emphasis has been on areas where significant understanding has been gained (as judged by the convergence of theoretical and experimental results). But it would be wrong to conclude that all was settled even in these limited areas: many minor (and several major) discrepancies between theory and experiment have been glossed over. For reasons of space, very little detail has been given on the main experimental results and how they were obtained. This belies the fact that recent progress in this area has generally been marked by an unusually strong interplay between theoretical and experimental studies, a trend which seems likely to continue.

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