



HAL
open science

Vesicles and onion phases in dilute surfactant solutions

B. Simons, M. Cates

► **To cite this version:**

B. Simons, M. Cates. Vesicles and onion phases in dilute surfactant solutions. *Journal de Physique II*, 1992, 2 (7), pp.1439-1451. 10.1051/jp2:1992211 . jpa-00247741

HAL Id: jpa-00247741

<https://hal.science/jpa-00247741>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
 Physics Abstracts
 64.70J – 64.70M – 82.60L

Vesicles and onion phases in dilute surfactant solutions

B. D. Simons and M. E. Cates

Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, G.B.

(Received 25 February 1992, accepted 8 April 1992)

Abstract. — We study theoretically the stability of phases of unilamellar and multilamellar vesicles in bilayer-forming surfactant solutions. It is argued that these are likely to arise, instead of a bicontinuous “sponge” phase, when the elastic constants of the bilayer are chosen so that the curvature energy of a sphere is small. At very low volume fractions we predict a phase of noninteracting vesicles; as the concentration is increased these reach an overlap threshold, beyond which “nesting” can occur, giving a multilamellar vesicle or “onion” phase. At higher concentration still, a transition to the smectic (L_α) phase is predicted. This transition may be rather weak if the mean curvature rigidity is small. The relevance of our results to recent experimental work is briefly discussed.

1. Introduction.

Recent work on various surfactant systems has revealed the existence of isotropic liquid phases in which the local structural unit is a bilayer [1-4]. These typically arise in materials for which the lamellar phase (smectic liquid crystal) remains stable under strong dilution as a result of the entropic pressure between neighboring sheets in the smectic stack. The most common bilayer liquid phase is called usually L_3 ; in this phase it is known that the bilayer forms a continuous web or “sponge” [1-4] that apparently divides the solvent into two distinct regions. This leads to some unusual light scattering properties and novel phase behaviour [1, 5]. In many systems (those where Coulomb or van der Waals forces do not dominate), the transition from smectic (L_α) to sponge (L_3) can be rationalized in terms of the Helfrich Hamiltonian for bilayers, [6] which expresses the elastic energy in terms of the local principal radii of curvature R_1 and R_2 :

$$\mathcal{H} = \int dS \left[2\kappa H^2 + \bar{\kappa}K \right]. \quad (1.1)$$

This contains two elastic constants, κ and $\bar{\kappa}$, which control respectively the mean curvature $H = \frac{1}{2}(1/R_1 + 1/R_2)$ and the gaussian curvature $K = 1/(R_1R_2)$. According to the Gauss-Bonnet theorem the latter, when integrated over the entire surface becomes a topological

invariant [7]:

$$\bar{\kappa} \oint K \, dS = 4\pi\bar{\kappa} (n_c - n_h), \quad (1.2)$$

where n_c denotes the number of components and n_h the number of handles of the surface. For stability one requires $-2\kappa \leq \bar{\kappa} \leq 0$.

The sponge phase arises when a stable lamellar phase, which can be diluted down to volume fractions in the few percent range, is diluted further. The random surface structure is then stabilized by configuration entropy of the interface. If even more solvent is added to a sponge phase, theory predicts a breakup into disconnected vesicles, stabilized by entropy of translation [2]. However, sponge phases exist also at much higher concentrations in certain systems. These are usually "adjacent" to a lamellar phase in a pseudoternary phase diagram and the transition from lamellar to sponge is driven by tuning (say) the amount of alcohol. It is thought [3, 8, 4] that the alcohol acts as a cosurfactant, so that small changes in its bulk concentration can lead to shifts in the effective elastic constants of the bilayers. In these cases it has been proposed that the transition from lamellar to sponge is controlled mainly by variation of $\bar{\kappa}$, [3, 8] which couples to the difference in topology between the L_3 and L_α phase. If so, the L_3 phase becomes stable as $\bar{\kappa}$ becomes less negative.

With this trend in mind, it is natural to enquire what should happen if, starting from a lamellar phase, the alcohol content is now tuned in the opposite direction ($\bar{\kappa}$ more negative). In several systems, this has also been shown to lead to an isotropic phase, sometimes referred to as L_4 [9] (or L_3^* [10]). In contrast to the sponge phase, this phase can be significantly viscoelastic at high concentrations. It also has other characteristic features that differ from the sponge. In particular, there is now clear evidence that at low enough concentrations, the L_4 phase consists of dilute large vesicles [9, 10]. In the system SDS/dodecane/octanol/ H_2O , conductivity, light scattering and other studies all suggest that at less than 2.5 weight percent, noninteracting vesicles of radius a few hundred Angstroms are present [9]. Likewise for the system DDAO/hexanol/ H_2O , freeze fracture studies show clearly vesicle-type structures of a similar average size [10].

Throughout this paper, we assume (as suggested by the above discussion) that the behaviour of the system on varying alcohol content can be understood in terms of a competition between entropy, and the elastic properties of homogeneous bilayers. A different possibility is that the stability of any vesicle or onion phase depends on an unequal distribution of one of the components (e.g. the alcohol) between the two halves of the bilayer; this mechanism is known to be relevant in phases of large vesicles formed in some mixed surfactant solutions [11].

That the dilute L_4 phase consists of vesicles is a fairly natural idea when we consider the Gauss-Bonnet theorem, (1.2). It is known that for $\bar{\kappa} < -2\kappa$, the system becomes unstable to the formation of extremely small vesicles (whose size is limited only by anharmonic corrections to (1.1) which we have ignored). For $\bar{\kappa}$ close to but larger than -2κ , the net energy to form a vesicle, $4\pi(2\kappa + \bar{\kappa})$ is small and positive, so by tuning $\bar{\kappa}$ into this range one may expect to see a stable vesicle phase, where translational entropy balances the small energy of formation, even at moderate volume fractions. The renormalization of the elastic constants at large length scales [12, 13] can also favour the occurrence of vesicles of reasonable size (in contrast to the very small vesicles which may arise on ultimate dilution of a sponge phase, for example).

In this paper, we give a more detailed analysis of how the vesicle phase can arise, and for what range of parameters. This builds on earlier work by Huse and Leibler, [14] among others. However, we also address a more difficult issue, namely the character of the L_4 phase at higher concentrations. In this regime, the vesicles cannot be dilute. We investigate here the possibility that at higher concentrations (above a suitably defined overlap threshold), the vesicles become "nested" into multilamellar vesicles or small spherulites (Fig. 1). We shall argue that a state

in which each of these “onions” contains between 2 and 5 layers is thermodynamically feasible for typical parameters. This seems to be roughly consistent with the observed properties of the L_4 phase above the overlap threshold. The possibility of much larger mean layer numbers is also addressed.

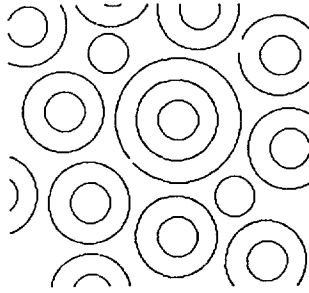


Fig. 1. — Typical vesicle configuration in the proposed onion phase.

We do not consider the dynamics of the system in this paper; however, it seems possible that the even the small multilamellar structures proposed here could be rather stable objects dynamically – with a behaviour similar to deformable elastic spheres at similar volume fractions. If so, it might explain the relatively high viscosity (and near-yield behavior) reported in some concentrated L_4 phases [9, 10]. At present, experimental data is not precise enough to determine whether the L_4 phase is more or less viscous than one would expect for a system of hard spheres with a similar (effective) volume fraction – the comparison is made harder by polydispersity effects, and the very strong volume-fraction dependence of the viscosity in the hard sphere case as close-packing is approached.

In the next section we will formulate a simple model of the vesicle and onion phases and compare the relative phase stability around the critical concentration at which vesicles interact, ϕ^* .

2. Vesicles and onions.

Formally, the energy to create a perfect sphere of radius r is given by $4\pi\tilde{\kappa}(r)$, where we have defined an appropriate bend modulus of $\tilde{\kappa}(r) = 2\kappa(r) + \bar{\kappa}(r)$. Fluctuations of the fluid membrane at small length scales lead to a renormalisation of the modulus given by ($k_B = 1$),

$$\tilde{\kappa}(r) = \tilde{\kappa}_0 - \gamma \frac{T}{4\pi} \log \frac{r}{a}, \quad (2.1)$$

where $\tilde{\kappa}_0$ denotes the bare value, a denotes the monomer size, and present estimates suggest that $\gamma = (d - 2) 8/3$ (i.e. $\gamma = 8/3$ for $d = 3$) [7]. For $\tilde{\kappa}_0 < 0$ there is an instability towards forming vesicles of vanishingly small radius. However, as $\tilde{\kappa}_0$ is increased it becomes favourable (in terms of bending free energy) to form vesicles only above some finite radius. Then, if the mass fraction, ϕ of surfactant is sufficiently small, a phase of dilute, independent vesicles will remain the stable equilibrium phase. However, as the mass fraction is increased, the vesicles begin to interact through contact and approach close-packing. Beyond this critical

concentration denoted by the mass fraction ϕ^* , there are several possible ways in which the system may react to accommodate the additional surface area. The first is simply to form a lamellar phase. The second is for the vesicles to shrink in size and so accommodate the extra mass fraction while remaining at the overlap threshold. Finally, the vesicles may become nested in the form of spherulites or onions and thereby sustain a high mass fraction while maintaining a large vesicle radius. However, there is a penalty arising from the cost in entropy in removing translational degrees of freedom. Nevertheless, we suggest that there is a region of the phase diagram in which the latter phase becomes stable, and that this may account for the observed properties of the L_4 phase at high concentrations.

In what follows we propose a model with which to study this scenario. Initially we investigate a system of unilamellar vesicles which exclude all surfactant from the volume they enclose, so for the purposes of packing they can be thought of as solid. We examine both the dilute and interacting regime around the concentration at which unilamellar vesicles become close packed, ϕ^* . Thereafter we study a phase in which the exclusion is relaxed, allowing the vesicles to become nested into "onions."

2.1 UNILAMELLAR VESICLES. — For a number density $c(m)$ of spherical vesicles of aggregation number (or "mass") m , the bending energy of a unilamellar vesicle phase is given by,

$$\frac{E_{\text{Ves}}}{V} = \int dm \, 4\pi\tilde{\kappa}[r(m)] c(m), \quad (2.2)$$

where the radius $r(m)$ is related to the vesicle mass by $m = 4\pi(r/a)^2$. Here a is a molecular length. For a system of non-interacting vesicles a lattice-gas description provides a reliable estimate of the entropy. The cell size is set by the monomer size of the solvent, which we take to be of order the surfactant size a . (Later we will discuss the validity of this approximation, which is questionable when the vesicles become more densely packed). For low concentrations we have the usual expression for the ideal entropy of mixing,

$$\frac{S_m}{V} = - \int dm \, c(m) [\log(c(m)a^3) - 1]. \quad (2.3)$$

Finally including a chemical potential for the total mass of surfactant, and minimising the grand potential, $\Phi_{\text{Ves}} = E_{\text{Ves}} - TS_m - \mu N$, where the total number of monomers is given by $N = V\phi/a^3$, we find an equilibrium concentration of vesicles,

$$c(m)a^3 \approx \exp[-(4\pi\tilde{\kappa}[r(m)] - \mu m)/T]. \quad (2.4)$$

where μ is determined as usual from the constraint,

$$\phi = \int dm \, m \, c(m)a^3 \quad (2.5)$$

The renormalisation of the bending modulus leads to a prefactor $m^{\gamma/2}$ in the concentration, so that the mass distribution, $c(m) \sim m^{\gamma/2}e^{-\mu m}$ becomes peaked around $m \approx \gamma/2\mu$. Applying the constraint (2.5) on the total mass fraction, we obtain the chemical potential,

$$\frac{\mu}{T} = -C_1(\gamma) \exp\left[-\frac{1}{2+\gamma/2} \frac{4\pi\tilde{\kappa}_0}{T}\right] \phi^{-1/(2+\gamma/2)}, \quad (2.6)$$

where $C_1(\gamma)$ is a constant ⁽¹⁾. (For $\gamma = 8/3$, $C_1 = 0.494$.) From this we can determine the

⁽¹⁾ In fact $C_1(\gamma) = [\Gamma[2 + \gamma/2]/(4\pi)^{(\gamma/2)}]^{1/(2+\gamma/2)}$

total free energy $F_{\text{Ves}} = \Phi_{\text{Ves}} + \mu N$, with result:

$$F_{\text{Ves}} = -\frac{VT}{a^3} \left(\frac{2 + \gamma/2}{1 + \gamma/2} \right) \frac{\mu}{T} \phi \quad (2.7)$$

Thus (combining (2.6) and (2.7), for $\gamma = 8/3$) the free energy density scales with volume fraction as $\phi^{7/10}$

As the volume fraction ϕ of surfactant is increased, the free energy continues to become more negative. However, for a sufficiently large volume fraction the vesicles begin to interact. The corresponding volume fraction can be estimated by calculating the equivalent solid volume fraction (ESVF) of the vesicles. Taking the volume enclosed by a vesicle of mass m to be $v(m) = (4\pi/3)(m/4\pi)^{3/2}$, the total ESVF is defined by

$$\begin{aligned} \psi &= \int dm v(m) c(m) a^3, \\ &= C_2(\gamma) \phi^{(5+\gamma)/(4+\gamma)} \exp\left[\frac{1}{4+\gamma} \frac{4\pi\tilde{\kappa}_0}{T}\right], \end{aligned} \quad (2.8)$$

where $C_2(\gamma)$ is a constant ⁽²⁾. (For $\gamma = 8/3$, $C_2 = 0.235$.) With the renormalization factors included, the ESVF of the vesicles is a weakly increasing function of ϕ . This increase arises purely by mass action effects.

We now define the overlap threshold ϕ^* , at which the vesicles become strongly interacting, by equating ψ to the volume enclosed by vesicles occupying a cubic close-packed lattice with an intervesicle spacing of (say) three times the vesicle radius. We thus obtain an ESVF at overlap of $\psi^* = 8\pi/81\sqrt{2} \sim 0.22$. In terms of surfactant volume fraction this yields, for example, $\phi^* = 0.025$ (the value estimated for SDS/dodecane/octanol/water by Hervé and Roux [9]) when $\tilde{\kappa}_0/T \sim 2.2$.

Let us now consider the region in which $\phi \gtrsim \phi^*$. First we might suppose that the vesicles simply shrink to accommodate the additional mass but remain unilamellar. In this case we should add an additional Lagrange multiplier to the grand potential to enforce the constraint that $\psi = \psi^*$. Minimizing $\Phi_{\text{Ves}} = F_{\text{Ves}} - \mu N - \lambda V\psi$ we obtain the equilibrium concentration,

$$c(m)a^3 \approx \exp[-(4\pi\tilde{\kappa}[r(m)] - \mu m - \lambda v(m))/T], \quad (2.9)$$

where μ and λ are determined by combining equation (2.5) with the constraint equation:

$$\psi^* = \int dm v(m) c(m) a^3 = 0.22. \quad (2.10)$$

Of main interest is the region in which $\phi \gtrsim \phi^*$. The behaviour in this region has been studied numerically. Qualitatively, very close to ϕ^* , λ becomes non-zero and cuts off the distribution at high m . As ϕ is increased above ϕ^* , μ soon becomes positive and the size distribution becomes very sharply peaked; much of the entropy associated with polydispersity is lost as a result. The natural tendency (from mass action effects) of vesicles to increase in size as ϕ is raised, becomes reversed by steric forces in this region.

A numerical calculation of the free energy $F_{\text{Ves}}(\phi)$ of a phase of unilamellar vesicles, found by determining μ and λ self-consistently from the constraint equations, (2.5) and (2.10) is shown for different values of $\tilde{\kappa}$ in figure 2. (The free energy for an onion phase, calculated below, is also plotted). We see that for $\phi \geq \phi^*$ the free energy very rapidly increases with volume fraction. For ϕ more than about 3/2 times ϕ^* , this phase would be unstable with respect to

⁽²⁾ In fact $C_2(\gamma) = (1/3(4\pi)^{2/(4+\gamma)}) (\Gamma[5/2 + \gamma/2]/\Gamma[2 + \gamma/2])^{(5+\gamma)/(4+\gamma)}$

a lamellar phase (whose free energy is discussed in more detail below). The fact that we have probably overestimated the translational entropy of the phase (by using (2.3) even near ϕ^*) simply reinforces this prediction. We conclude that a phase of *unilamellar* vesicles, so long as they remain spherical, will not be stable at volume fractions larger than the natural overlap threshold.

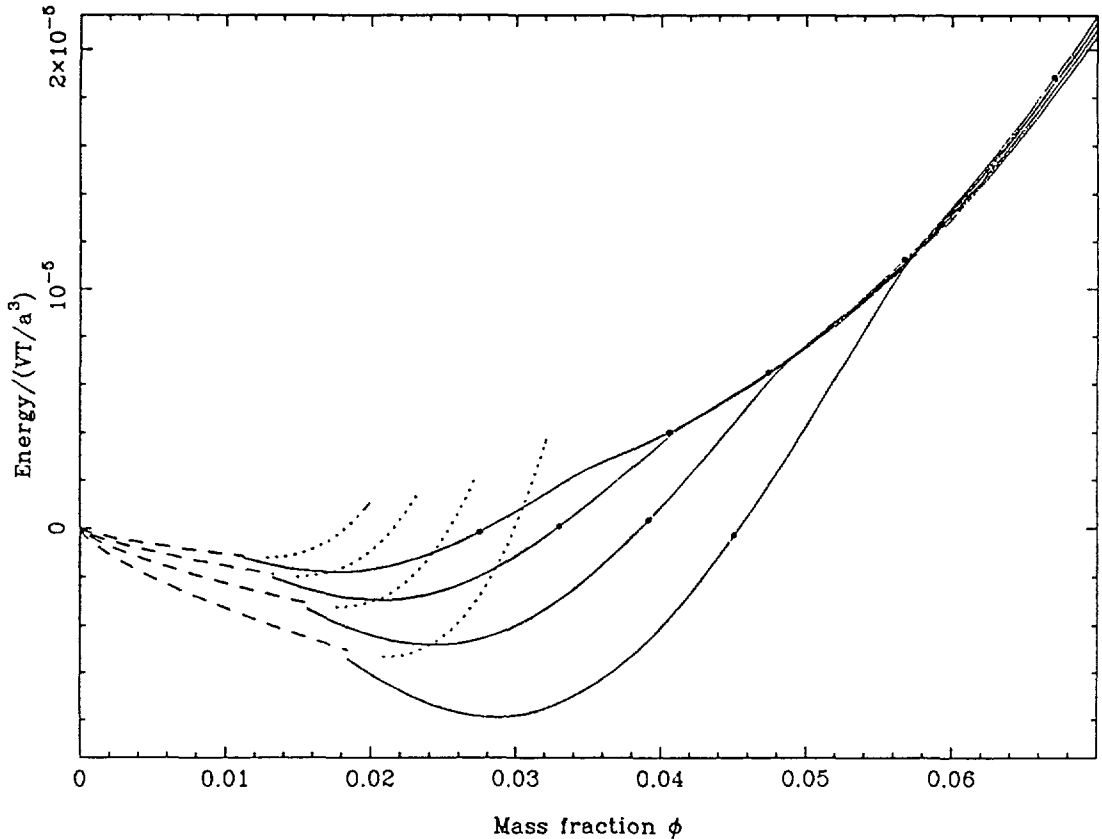


Fig. 2. — Free energy of the unilamellar vesicle and onion phase as a function of the mass fraction, ϕ at fixed $\tilde{\kappa} = -5k_{\text{B}}T$, and for values of κ of $3.7k_{\text{B}}T$, $3.75k_{\text{B}}T$, $3.8k_{\text{B}}T$, and $3.85k_{\text{B}}T$ going from the lower to the uppermost curve. The free energy of the unilamellar vesicle phase is shown dashed below ϕ^* , and dotted above. The free energy of the onion phase (including the Helfrich contribution; see Sect. 2.2.3) is shown as a continuous line for $\phi \geq \phi^*$ with the points of common tangency denoted by filled circles.

Another possibility is that above ϕ^* the vesicles could deform into ellipsoidal shapes (rather than simply shrink). The result might be some sort of nematic phase; calculation of the free energy is very difficult and we do not attempt it here. Formally, we can in any case prohibit such a phase by increasing κ to a large value while maintaining the same value of $\tilde{\kappa}$ (which is the only control parameter for phases based on spherical structures, as shown above). For simplicity therefore, we exclude the possibility of a nematic phase, in what follows.

2.2 MULTILAMELLAR VESICLES (ONIONS). — Rather than constraining two vesicles to exclude one another entirely from the volume enclosed by each, let us now allow the possibility of nesting. In this case, the mean vesicle size can continue to increase for $\phi \geq \phi^*$, though at the expense of some entropy. Our aim is to construct a simple model which qualitatively predicts the equilibrium phase diagram in the system. In doing so we will make several approximations which we will argue become reliable in limiting cases. We pay most attention to the regime where ϕ exceeds ϕ^* by a factor of about 1—4. In this region we argue that multilamellar vesicles, or “onions” of several layers are formed. For simplicity we neglect non-uniform nestings in which a single shell of membrane can enclose two or more internal onions ⁽³⁾.

Since it arises when unilamellar vesicles would become sterically overpacked, we may assume that any phase of onions maintains an essentially close-packed geometry (Fig. 1). The onions are assumed to be configured to fill space with a mean separation between their surfaces of order $d = a/\phi$, which is the smectic layer spacing of an equivalent lamellar phase. The average spacing between layers within an onion is also of order d . These assumptions are a natural consequence of the Helfrich repulsion, [15] which gives in a smectic phase an osmotic penalty for any strong departure of the local layer spacing from its mean value. Thus the proposed onion phase can be considered as a lamellar phase whose long range order is destroyed while maintaining a reasonably uniform mean spacing between layers. This is analagous to the sponge phase L_3 , but with a totally different local topology.

To be consistent, we must now take into account that the undulations of each membrane or shell within an onion are constrained by its neighbours, implying that the appropriate renormalized bending moduli (2.1) are those corresponding to the length scale of order d . Actually, this is a slight underestimate: the scale at which undulations become hindered is not d but the “transverse correlation length” $\xi_{\perp} \sim d(\kappa_0/T)^{1/2}$ [15]. This means that for onions of small size (a few times d), the Helfrich repulsion between neighboring shells is rather weak.

2.2.1 Bending energy. — In estimating the bending energy of an onion, we will assume that the vesicles within it are spheres. As the onions become larger, this assumption is increasingly incompatible with our previous argument that the spacing between membrane layers is of order d at all points in space. To calculate the effect of this on the free energy requires a careful consideration of polydispersity (small onions can fill the interstices between larger ones), but it seems probable that the extra bending energy involved would ultimately destabilize a phase of very large onions (or true spherulites) with respect to a lamellar phase. However, our main predictions concern phases where the mean number of layers in each onion remains small, and the size of the interstices remains on the order of the d -spacing. We therefore ignore any asphericity of the onions in our calculations.

For an onion comprised of n shells, with mean intershell spacing d , the total aggregation number (mass) is given approximately by $m = (4\pi/3)n^3/\phi^2$, a formula which would be exact for very large n . Therefore, the total bending energy of a phase of onions at concentration $c(m)$ can be estimated as

$$\frac{E_{\text{On}}}{V} = \int dm 4\pi n(m) \tilde{\kappa}[d] c(m). \quad (2.11)$$

To this must be added various entropy contributions, which we now calculate.

2.2.2 Entropy of onions. — To estimate the entropy of an onion phase, we consider three contributions. First, there is contribution, S_m , from the translational entropy of each species

⁽³⁾ Such configurations should anyway only arise for large layer numbers, and should incur a large bending energy.

of aggregate, which we assume is given by (2.3). The second entropy contribution arises from fluctuations in the mass of the individual layers within each onion. We assume that each internal shell can have any radius r in the range $r_0 - \alpha d \leq r \leq r_0 + \alpha d$ where α is a parameter (we set $\alpha = 1$ for numerical work) and d is the mean layer spacing. Here r_0 is the nominal radius, which for the l th shell in an onion is simply given by ld . Hence there are roughly $16\pi\alpha l/\phi^2$ different choices of mass for the l th shell. If there are n shells on a vesicle in total, whose mass m is also specified, then there are only $n-1$ independent contributions of this sort; for simplicity we assume that the outermost vesicle has fixed mass but that the inner ones can fluctuate. The fluctuations in mass of all the internal vesicles then provides

$$(n-1)! \left(\frac{16\pi\alpha}{\phi^2} \right)^{(n-1)} \quad (2.12)$$

different ways of making up an onion of mass m . Thirdly, there is a finite translational entropy from the relative displacements of the centres of mass of each shell within the onion. Each spherical shell can typically be displaced of order d before colliding with its inner or outer neighbour; the resulting multiplicity is of order $(2d/a)^3$ where a is a molecular size. This can be combined with the previous contribution (2.12) to give a total entropy S_I from the internal degrees of freedom within each onion. The result is

$$\frac{S_I}{V} = \int dm [\log(n-1)! - (n-1) \log g(\phi)] c(m), \quad (2.13)$$

where $g(\phi) = \phi^5/2^7\pi\alpha$. The total entropy of the onion phase is then estimated by $S_I + S_m$, with S_m obeying (2.3).

These three entropy estimates all involve some degree of approximation. Firstly, (2.3) for S_m is the expression for noninteracting spheres; in neglecting the effects of crowding, it overestimates the entropy. However, we have checked that an alternative *underestimate* of S_m yields similar results to those presented below. Our underestimate is obtained by replacing the characteristic molecular length a which appears in (2.3) by a length of order the mean vesicle size nd . In effect, we confine vesicle centres to lie on a lattice of this size [16]. In this way, the purely translational part of S_m is eliminated, and for monodisperse onions we would have $S_m = 0$. (This is clearly an underestimate since in reality some translational freedom remains). For polydisperse aggregates, as here, there remains a large contribution to S_m which comes from multiple ways of assigning vesicles of different mass between our coarse-grained lattice sites.

Our estimate of the internal entropy S_I assumes that the radius and centre of mass position of a given shell can both fluctuate by amounts of order d , the mean spacing between sheets in the system. This is not true for large vesicles, since the Helfrich repulsion will provide a confining potential that forces a shell to fluctuate weakly about its nominal position, rather than explore all (spherical) configurations that can be fitted between an inner and an outer spherical boundary. But at least formally, this effect can be ignored for shells smaller than the transverse correlation length ξ_{\perp} which may be large compared to d if $\kappa \gg kT$. Thus for onions of moderate size (say, 2–5 layers), the internal entropy should not differ too much from our estimate (2.13).

Minimizing the grand potential $\Phi_{On} = E_{On} - T(S_I + S_m) - \mu N$ over the concentration distribution $c(m)$, we obtain for the concentration of onions of mass m the following result:

$$c(m)a^3 \approx \exp\left[-\frac{4\pi n\tilde{\kappa}_{\text{eff}}(n)}{T} - \frac{\mu}{T}m\right], \quad (2.14)$$

which we have written in terms of an effective n -dependent bend modulus,

$$\tilde{\kappa}_{\text{eff}}(n) = \tilde{\kappa}[d] + \frac{T}{4\pi} \left(\frac{n-1}{n} \log[g(\phi)] - \frac{\log[(n-1)!]}{n} \right), \quad (2.15)$$

which includes the various entropic contributions.

The chemical potential is again determined by (2.5), but we now introduce a cutoff on the lower limit of integration at $m_0 = 4\pi/3\phi^2$, corresponding to an onion having a single layer with radius of order d (4).

Evaluation of the free energy of the onion phase F_{On} is performed by substitution of (2.14) for the size distribution together with the appropriate chemical potential, μ into the equation $F_{\text{On}} = \Phi_{\text{On}} + \mu N$. This confirms the presence of only a slight mismatch at ϕ^* with the free energy F_{Ves} of the unilamellar vesicle phase calculated in section 2.1 above (see Fig. 2). Fortunately the mismatch is unimportant in calculating phase equilibria since the free energy in the immediate vicinity of ϕ^* has upward curvature (according to either estimate). Thus the transition from vesicles to onions is by means of a smooth crossover without phase separation.

As in the previous discussion of the unilamellar case, the integration (2.5) can only be performed analytically in certain asymptotic limits, and in the region around ϕ^* it is necessary to resort to a numerical computation of μ and the total free energy. However, it is possible to qualitatively understand the behaviour directly from the mass distribution (2.14). For ϕ small the effective bend modulus, $\tilde{\kappa}_{\text{eff}}$ becomes negative. The distribution becomes peaked at some value of $n > 1$ and the chemical potential μ truncates the distribution. As ϕ increases so $\tilde{\kappa}_{\text{eff}}$ becomes more positive, μ becomes smaller and the weight of the distribution moves slowly to higher n . Eventually there is a crossover in the distribution to a region where the factorial term in the exponent becomes dominant, typically at a large value of n . This crossover occurs extremely rapidly, and the optimal n quickly becomes extremely large, as shown in figure 3 on a log plot (5).

2.2.3 Free energy, and phase diagram. — To compare the free energy of an onion phase, as calculated above, with that of a lamellar phase, a naive argument would be to say that the lamellar phase has neither bending energy nor entropy so that $F_{\text{Lam}} = 0$. However, it has been shown [16] in the context of L_3 phases and microemulsions that this is a very unrealistic choice, mainly because $\partial^2 F / \partial \phi^2$ vanishes identically, which means that phase diagrams cannot be constructed. To obtain sensible results it is necessary to include the Helfrich free energy arising from repulsion of two neighbouring layers due to the constraints on the amplitude of the undulations. This free energy has been calculated as [15]

$$F_{\text{Hel}} = \frac{VT}{a^3} \frac{3\pi^2}{128} \frac{T}{\kappa} \phi^3. \quad (2.16)$$

It seems clear that such a contribution should also be added to any onion phase containing very large spherulites, since locally these are the same as a lamellar phase. On the other hand, for small onions or vesicles that arise at low ϕ , the Helfrich repulsion is very small as argued in section 2.1 above. In fact it is easily checked that the contribution of (2.16) is negligible in comparison to the other terms in the free energy in this region. Therefore it is a good enough approximation simply to add the Helfrich term, (2.16) to the free energy estimate F_{On} given previously, not only at high volume fractions but over the whole range of ϕ . The free energy

(4) This low m cut-off prevents a collapse of the distribution into a mathematically artefactual phase where the onions possess only a fraction of a layer each; it is necessary because in the concentrated regime we impose a space-filling requirement on the onions.

(5) In practise, however, the free energy in this region is likely to exceed that in a lamellar phase, for reasons discussed below.

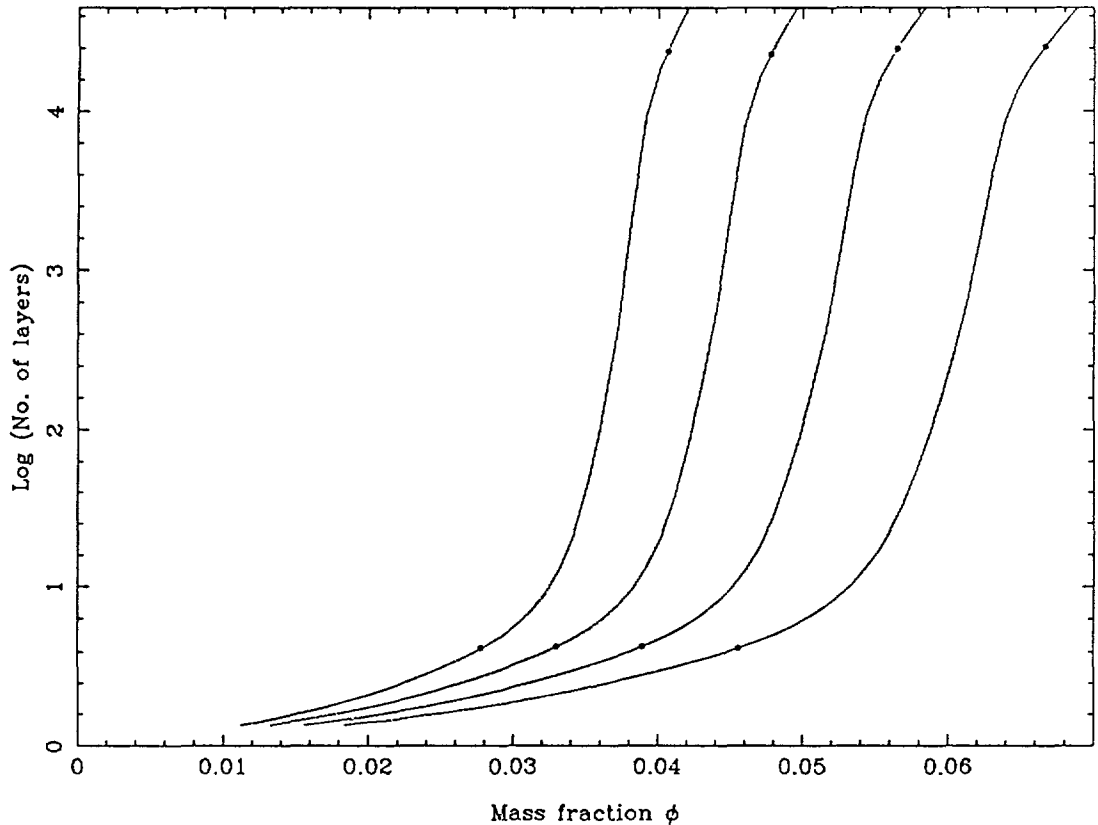


Fig. 3. — Log plot of mean number of layers in the onion phase as a function of the mass fraction, ϕ at fixed $\bar{\kappa} = -5k_B T$, and for values of κ of $3.7k_B T$, $3.75k_B T$, $3.8k_B T$, and $3.85k_B T$ going from the right to left most curve. The boundary of the two-phase coexistence region is denoted by filled circles.

curve found by this procedure, $F(\phi) = F_{\text{On}} + F_{\text{Hel}}$ is our final estimate for the onion phase. Note that the first contribution depends on the elastic constants only in the combination $\tilde{\kappa} \sim 2\kappa + \bar{\kappa}$, whereas the second depends on κ alone. Figure 2 shows the free energy as a function of volume fraction for a given value of $\bar{\kappa}$ and various values of κ .

With this final form for $F(\phi)$, we can now construct phase diagrams for our system as a function of ϕ , κ and $\bar{\kappa}$. For reasonable parameters we find numerically a two-phase coexistence between an onion phase of typical number of shells n which is larger than unity (though not by a large factor) and a coexisting denser phase. Typical cuts through the phase diagram at fixed values of both $\bar{\kappa}$ and κ are shown in figures 4a,b. In figure 4c is a plot with $2\kappa + \bar{\kappa}$ and ϕ as the variables. In this representation, there is a strong degree of universality (since F_{On} depends only on this combination) with a weaker residual $\bar{\kappa}$ dependence as shown.

According to our calculations, the dense phase at coexistence is an onion phase of very large mean layer number n : the difference in free energy between this phase and the lamellar phase is extremely small, that of the onion phase being marginally lower. However, the apparent stability of this phase with very large n at high volume fraction is probably an artefact arising from our neglect of any bending energy needed to deform the onions so as to satisfy the space-

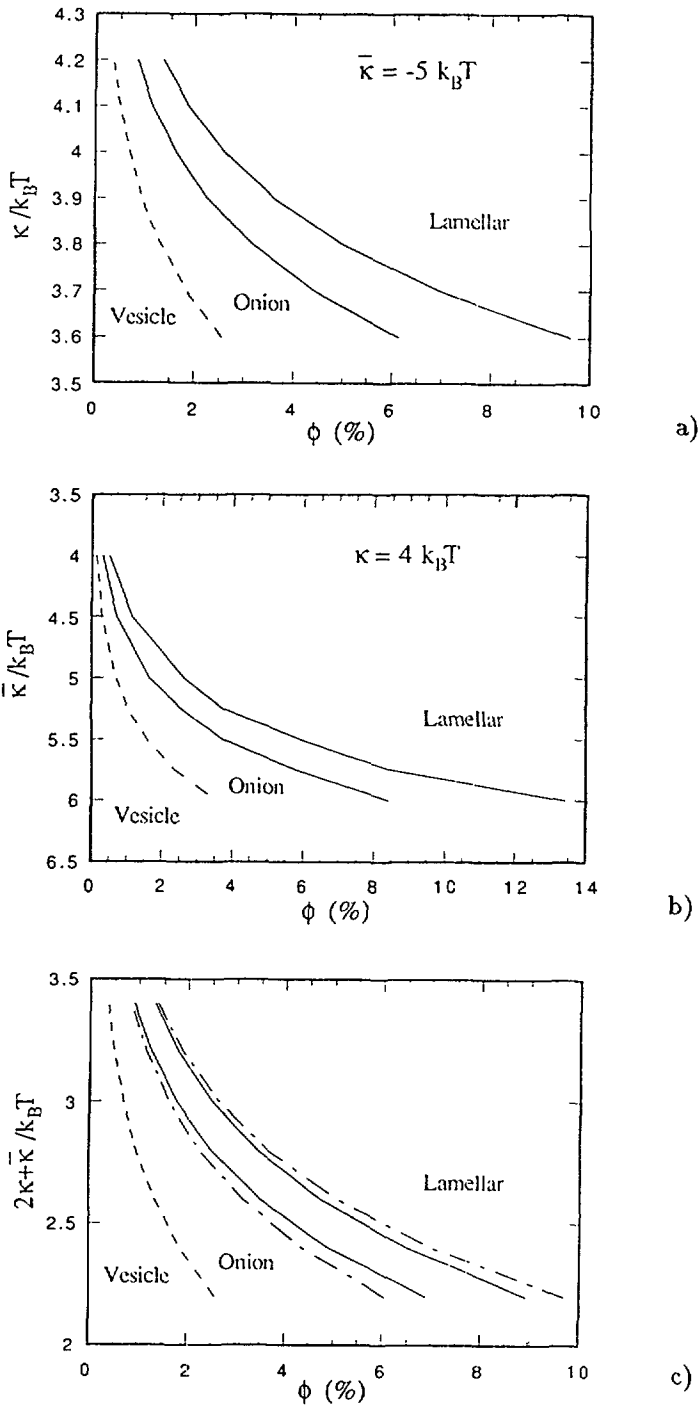


Fig. 4. — Phase diagram (a) in (ϕ, κ) plane at fixed $\bar{\kappa}$, and (b) in $(\phi, \bar{\kappa})$ plane at fixed κ showing the two-phase coexistence region. The line ϕ^* which separates the interacting and non-interacting unilamellar vesicle phase is shown dashed. (c) Phase diagram in $(\phi, 2\kappa + \bar{\kappa})$ representation for $\bar{\kappa} = -2k_B T$ (continuous) and $\bar{\kappa} = -6k_B T$ (dash-dotted). (Note that ϕ^* is a function only of $2\kappa + \bar{\kappa}$).

filling constraint (see Sect. 2.2 above)⁽⁶⁾. Moreover, our estimate of the internal entropy S_I is also optimistic in the regime of large n , as discussed already in section 2.2.2. These two factors mean that the free energy of a large n onion phase is almost certainly underestimated by our theory. By comparison with figure 2, we conclude that in practical cases the coexisting dense phase is more likely to be an ordinary lamellar phase than a phase of extremely large onions.

The low- n onion phase at coexistence has n values in the range 1-3. Although very large n values are not predicted, there should still be a clear difference in physical properties between a phase with $n \simeq 3$ and a noninteracting vesicle phase. We note that the freeze fracture studies of reference [10] show some nesting, with an average n somewhat greater than unity, although in this system the L_4 (L_3^*) phase does not persist to very high concentration. Freeze fracture studies on the SDS system [9] would be very interesting and should not be too difficult since the phase is very viscous.

As κ is decreased (at fixed $\tilde{\kappa}$), there is a tendency for the transition to a dense phase to become weaker. Ultimately, the region of two-phase coexistence terminates in a line of critical points at $\kappa \sim 0.8$ and approximately independent of $\tilde{\kappa}$ beyond which a second order transition from onions to lamellae is predicted by our theory. Taken literally, our calculations predict at small κ a continuous transition from an isotropic to a lamellar phase via a thermodynamically stable phase of spherulites of diverging mean layer number n . This is an intriguing scenario. However, as mentioned in the previous paragraph, the apparent stability of onion phases with very large n at high volume fraction is likely to be an artefact. Therefore we expect in practise a weak first order transition to a lamellar phase for all parameter values. Nonetheless the trend toward a weaker transition at smaller κ (when Helfrich forces are larger) is a clear prediction of the model.

3. Discussion.

In this paper, we have presented results that suggest the existence of a phase of dilute vesicles when the bending energy of a sphere $\tilde{\kappa}$ is not too large compared to $k_B T$. This idea is not new [14, 2] and the existence of such structures, stabilized by entropy, seems to be established by the very recent experiments of Hervé *et al.* and Thunig *et al.* [9, 10]. More controversial is our prediction that at higher concentration (and in a certain range of κ and $\tilde{\kappa}$) a stable phase of *multilamellar* vesicles or "onions", each with a small number of concentric shells, can arise. These strongly interacting assemblies may have quite different properties from a noninteracting dilute vesicle phase, and we propose this as a model for the L_4 phase above the overlap threshold ϕ^* for the constituent vesicles. Note that even a phase with $n = 2$ or 3 should be clearly distinguishable in physical properties from a phase of unilamellar vesicles; for example, the hydrodynamic radius found in light scattering will be incompatible with a unilamellar geometry, as will the conductivity (which is determined by the fraction of connected space exterior to the vesicles). It is tempting also to invoke "nesting" of vesicles to explain the novel viscoelasticity [9, 10] of the L_4 phase.

Our approximations are numerous and hard to quantify, but the results nonetheless intriguing, especially in view of the freeze fracture experiments of reference [10] which do appear to show some nesting. Both the dilute (vesicle) and the semidilute (onion) phase are stabilized by entropy, and by the renormalization of the elastic constants which favours curvature at large length-scales. The onion phase is stable only over a relatively narrow range of parameters and

⁽⁶⁾ The alternative is to have a layer spacing within onions significantly less than d . This leads to an increase in F_{Hel} by an order unity factor which is a very large penalty compared to other energy scales in the problem.

it is not surprising if to observe it one has to carefully tune the elastic constants of the bilayer (such as $\tilde{\kappa}$). This is consistent with the observed narrow stability range of the semidilute L_4 phase [9].

We have not, in this paper, explicitly considered the relative stability of the onion phase with respect to a sponge phase (L_3). However, at all but the lowest concentrations the sponge is seen on the opposite side of the lamellar phase to L_4 , and therefore it should not interfere much with the relative stability of the latter two phases as discussed here. Put another way, we can argue for stiff or concentrated films ($\kappa(d)$ large) that the onion phase will only arise roughly for $2\kappa + \bar{\kappa} \leq k_B T$ whereas in the handle-rich sponge phase, the criterion is roughly $\bar{\kappa} \geq -k_B T$ [8]. Of course, for rather flexible films both criteria could be obeyed simultaneously, and in this case a more complicated phase diagram could result.

We have predicted that as κ is reduced, the phase transition from small onions ($n = 2, 3$) to very large spherulites or (more realistically) a lamellar phase becomes weaker. This is consistent with the preliminary work of the Bordeaux group [9, 17] which suggests a much weakened transition in the SDS/dodecane/water system when the alcohol octanol is replaced by pentanol. (This change is known to soften the film). The theoretical prospect of a *continuous* transition from an isotropic to a lamellar phase via onions of ever-increasing size remains interesting although, as we have discussed, the stability of large onions is probably limited in practice by the problem of filling space at uniform density with such objects, without incurring a large deformation energy.

Acknowledgements.

We are grateful to H. Hoffmann, P. Hervé and, especially, D. Roux for communicating experimental results prior to publication and for valuable discussions on many aspects of this work.

References

- [1] For a review see Roux D., Coulon C. and Cates M.E., *J. Phys. Chem.* in press.
- [2] Cates M.E., Roux D., Andelman D., Milner S. and Safran S., *Europhys. Lett.* **5** (1988) 733; *erratum ibid.* **7** (1988) 94.
- [3] Porte G., Marignan J., Bassereau P. and May R., *J. Phys. France* **49** (1988) 511.
- [4] Gazeau D., Bellocq A.M., Roux D. and Zemb T., *Europhys. Lett.* **9** (1989) 447.
- [5] Roux D., Cates M.E., Olsson U., Ball R.G., Nallet F. and Bellocq A.M., *Europhys. Lett.* **11** (1990) 229.
- [6] Helfrich W., *Z. Naturforsch* **28c** (1973) 693.
- [7] David F., in *Statistical mechanics of membranes and surfaces*, D. Nelson, T. Piran and S. Weinberg Eds. (World Scientific, Singapore, 1989).
- [8] Porte G., Appell J., Bassereau P. and Marignan J., *J. Phys. France* **50** (1989) 1335.
- [9] Hervé P., Roux D. and Bellocq A.M., (1991) *to be published*.
- [10] Thunig C., Platz G. and Hoffmann H., (1991) *to be published*.
- [11] Safran S.A., Pincus P., Andelman D., *Science* **248** (1990) 354.
- [12] Helfrich W., *J. Phys. France* **46** (1985) 1263.
- [13] Peliti L. and Leibler S., *Phys. Rev. Lett.* **54** (1986) 1690.
- [14] Huse D.A. and Leibler S., *J. Phys. France* **49** (1988) 605.
- [15] Helfrich W., *Z. Naturforsch* **33a** (1978) 305.
- [16] Andelman D., Cates M.E., Roux D. and Safran S., *J. Phys. Chem.* **87** (1987) 7229; see also *Phys. Rev. Lett.* **57** (1986) 491.
- [17] Roux D., Private communication.