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Equilibrium onions?

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Abstract. – We demonstrate the possibility of a stable equilibrium multi-lamellar ("onion") phase in pure lamellar systems (no excess solvent) due to a sufficiently negative Gaussian curvature modulus. The onion phase is stabilized by non-linear elastic moduli coupled to a polydisperse size distribution (Apollonian packing) to allow space-filling without appreciable elastic distortion. This model is compared to experiments on copolymer-decorated lamellar surfactant systems, with reasonable qualitative agreement.

Introduction. – The existence of vesicles at thermal equilibrium is a long-standing, and still controversial, problem [1]. Unilamellar and multi-lamellar vesicles (MLVs) were first induced in lyotropic lamellar phases with excess water by adding energy (*e.g.*, shear flow, ultrasound, electric field) [2]. In a very elegant work, using membranes generated by a chemical reaction, Hoffman and co-workers demonstrated that any of lamellae, unilamellar vesicles, or MLVs can be prepared in the same system, depending on the mechanical path chosen [3]. However, in some special cases [4,5] *equilibrium* unilamellar vesicles have been demonstrated. These systems are all in the dilute regime (large excess of water). Some experiments have suggested that MLVs (or onions) can be stabilized in the semi-dilute regime (excess water) [5]. Theories to explain the stability of dilute unilamellar vesicles either describe a competition between the entropy of mixing and the curvature energy of the vesicles [5–7] or a symmetry-breaking instability leading to a spontaneous curvature [8]. Onions are also predicted to be stabilized in the dilute and semi-dilute regimes due to an unstable curvature energy; in these cases, a transition towards unilamellar vesicles is avoided by imposing either a core energy [9] or a cutoff in the entropy of the Helfrich interactions [10]. Indeed, Simons and Cates [10] have discussed the stability of unilamellar vesicles and the transition to onions as the concentration increases even when the curvature energy is unfavorable, due to entropic reasons.

In the concentrated regime (homogeneous lamellar phase with no excess water), very monodisperse onions can be prepared under shear [11–13]. The vesicles fill space and remain in the one-phase region without expelling solvent, by distorting into space-filling polyhedra [14]. The resulting texture is a lattice of disclinations which can be either disordered [11] or ordered [13]. Moreover many experimental systems "spontaneously" exhibit onions in regions of the phase diagrams that seem to be continuously linked to the lamellar phase [15]. This evolution from a texture of polydisperse vesicles to a texture of focal conics upon tuning a parameter, such as a co-surfactant concentration or the volume fraction of solvent, seems to be generic. A striking signature of this evolution is the change in the rheology, from a viscous gel in the "onion" phase to a more fluid phase in the "lamellar" focal conic phase. Thus, whether an onion texture is at equilibrium or not seems yet unclear. In this work we propose a model based on a non-quadratic elastic energy, which shows that a pure lamellar phase, or one of space-filling deformed monodisperse onions, is unstable with respect to a polydisperse space-filling packing (we study an Apollonian packing [16]). We compare these predictions to experiments on copolymer-doped lamellar phases, originally introduced by Ligoure *et al.* [17].

Model. – The bending free energy per area F/A for membranes is usually taken, following Helfrich, as the simplest quadratic function of the mean and Gaussian curvatures, respectively $2H = r_1^{-1}+r_2^{-1}$ and $G = 1/(r_1 r_2)$, where r_1 and r_2 are the two principal radii of curvature [18]. This suffices for large curvature radii $r \gg \delta$, where δ is the layer thickness. However, if onions exist, because of the high concentration of membrane, high curvatures (small r) are expected near the core of the onions. We will thus use the free energy, relative to a flat state, of a symmetric bilayer expanded to quartic order in the curvature radii [19]:

$$\frac{F}{A} = 2\kappa H^2 + \bar{\kappa} G + \frac{1}{4} c_1 H^4 + \frac{1}{4} c_2 G^2 + 2 c_3 G H^2, \tag{1}$$

where κ and $\bar{\kappa}$ are the conventional bending and Gaussian curvature moduli, and the non-linear moduli c_i can be expected to scale as $k_{\mathrm{B}} T \delta^2$.

Stability of a flat membrane requires $2\kappa > -\bar{\kappa} > 0$. For $\bar{\kappa} > 0$, an instability towards a phase with $G < 0$ (*e.g.*, a bicontinuous phase) is possible. However, for $\tilde{\kappa} \equiv 2\kappa + \bar{\kappa} < 0$ spherical shells are stabilized, with free energy (for radius r) $F_{\mathrm{shell}}(r) < 0$ given by

$$F_{\mathrm{shell}}(r) = 4\pi\tilde{\kappa} + \frac{\pi\tilde{c}}{r^2}\,, \tag{2}$$

where $\tilde{c} = c_1 + 4c_2 + c_3$. Positive $\tilde{c}$ stabilizes spherical shells (vesicles) of finite radius. Unilamellar vesicles cannot accommodate volume fractions close to space filling, so we consider the free energy of an onion of radius R, constructed from k shells of discrete radii $r_j = jd$, ($j = 1, 2, 3, \ldots, k$) set by the layer spacing d, which we assume remains fixed:

$$F_{\mathrm{onion}}(R = kd) = \sum_{j=1}^{k} F_{\mathrm{shell}}\big(r_j = jd\big) = \frac{4\pi\tilde{c}}{d^2}\big[\lambda k + S(-2,k)\big], \tag{3}$$

where $\lambda \equiv \tilde{\kappa} d^2/\tilde{c}$ is the balance between the Helfrich and non-linear elastic coefficients and $S(l,m) \equiv \sum_{i=1}^{m} i^l$(1). In the limit $R \gg d$, the second term above, due to the fourth-order coefficients, is equivalent to the core energy introduced by Fournier and Durand [9].

For large dilute monodisperse onions the free energy per unit volume scales as $F/V \sim F_{\mathrm{onion}}(R) \sim \tilde{c}(\lambda + d/R)/(d^3 R^2)$, leading for $\lambda < 0$ to stable onions with size $R \sim d/|\lambda|$.

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(1) There is, generally, a surface energy due to, *e.g.*, van der Waals attraction, but if we assume an inter-onion spacing identical to the equivalent lamellar separation we need not consider such a term.

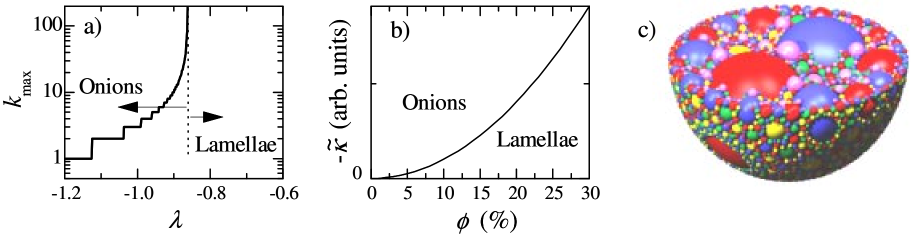

Fig. 1 – (a) Maximum number of layers per onion, $k_{\max}$, as a function of $\lambda \equiv \tilde{\kappa} d^2/\tilde{c}$. Apollonian onions are stable for $-1.125 \lesssim \lambda \lesssim -0.86$. (b) Schematic phase diagram in the $(\tilde{\kappa}, \phi)$-plane, $\tilde{\kappa}^* \sim \phi^2$. (c) Schematic packing of the Apollonian distribution (reprinted with permission from [16]).

However, in the concentrated regime monodisperse onions cannot fill space without non-trivial deformations [14]. Typically, onions formed under shear pack as polyhedra, with the deformation of layer j concentrated along the edges of length r_j with curvatures of order $1/\xi$, where the smectic bending penetration length $\xi = \sqrt{K/\bar{B}}$ depends on the bending $K = \kappa/d$ and compression $\bar{B}$ moduli of the lamellar phase [20]. Summing over all shells in a deformed polyhedron leads to an energy per unit volume that scales as $F_{\mathrm{el}}/V \sim \tilde{c}[\lambda + d^2/\xi^2]/(R\xi d^3)$. For $\lambda + d^2/\xi^2 < 0$, this leads to an unphysical unilamellar vesicle phase with $R = d$ (the lower cutoff). However, a polydisperse phase can relax the deformation, leading, for a broad enough distribution to a space-filling distribution of spheres. A candidate space-filling distribution is the Apollonian packing, for which the number distribution of spheres $n(R) \sim (R/d)^{-D_{\mathrm{A}}}$, with a fractal dimension estimated from simulations to be $D_{\mathrm{A}} \simeq 3.45$ [16, 21, 22] (see fig. 1c). Such a packing has been previously suggested to describe focal conic defects in smectic droplets [23]. In principle we should calculate this distribution from a free energy that incorporates entropy. Although small on the typical scale of the elastic terms, this entropy should widen the parameter range in which onions are stable [10]. Existing equations of state for, *e.g.*, polydisperse hard spheres, fail for widely disperse distributions near space filling [24], so we have been unable to estimate this contribution to any useful accuracy. Entropic effects will most likely influence the upper and lower cutoffs of the distribution, and would eventually lead (for highly fluctuating systems) to an exponential, rather than power law, size distribution away from space filling [7, 9].

The normalized number distribution of onion sizes R_k obeying $\frac{4\pi}{3}\sum_{k=1}^{k_{\max}} n(R_k)R_k^3 = V_{\mathrm{m}}$, where V_{m} is the volume of lamellar material, is

$$\tilde{n}(k = R_k/d) = \frac{3}{4\pi d^3}\frac{V_{\mathrm{m}}}{S(3 - D_{\mathrm{A}}, k_{\max})}\left(\frac{R_k}{d}\right)^{-D_{\mathrm{A}}}. \tag{4}$$

The total energy of the distribution, $F_{\mathrm{tot}} = \sum_{k=1}^{k_{\max}} \tilde{n}(k) F_{\mathrm{onion}}(k)$, is

$$\frac{4\pi d^3 F_{\mathrm{tot}}}{3V_{\mathrm{m}}} = \frac{\lambda\, S(1 - D_{\mathrm{A}}, k_{\max}) + \sum_{j=1}^{k_{\max}} S(-2, j) j^{-D_{\mathrm{A}}}}{S(3 - D_{\mathrm{A}}, k_{\max})}. \tag{5}$$

This energy can then be minimized over the maximum onion size $k_{\max}$ as a function of the single parameter λ to find the lowest free-energy distribution (fig. 1a). Although spherical shells are stable for $\lambda < 0$, the stabilizing elastic constants c_i assure that a finite and negative $\lambda \leq \lambda^* \simeq -0.86$ is required for onion formation. Onions are first stable with "infinite radius", implying a smooth transition from lamellae to onions. However, the scaling

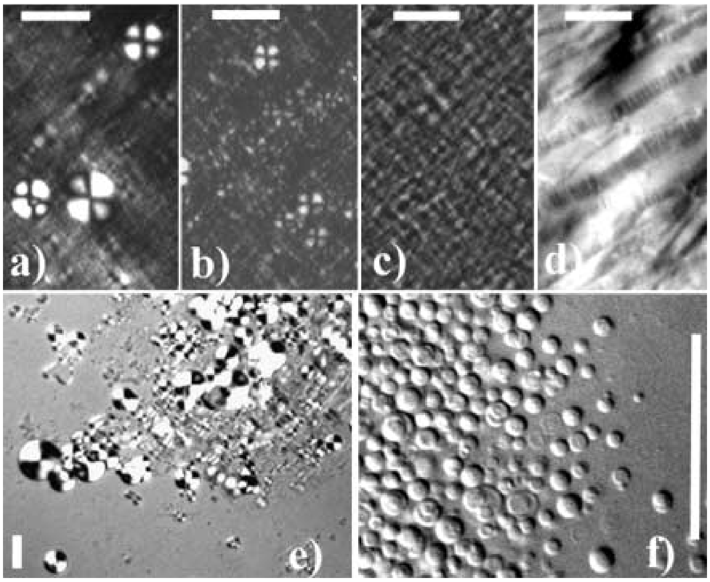

Fig. 2 – Top: gel phase observed between crossed polarizers, for membrane fractions ϕ and copolymer/surfactant weight ratios α of a) $\phi = 16\%$, $\alpha = 0.2$; b) $\phi = 16\%$, $\alpha = 0.4$; c) $\phi = 16\%$, $\alpha = 0.8$; d) $\phi = 22\%$, $\alpha = 0.8$. Bottom: gel phase in contact with water; e) crossed polarizers, $\phi = 16\%$, $\alpha = 0.15$; f) Differential Interference Constrast microscopy, $\phi = 16\%$, $\alpha = 1.6$. Scale bar 50 μm.

$nR^3 \sim R^{3-D_\mathrm{A}} \simeq R^{-0.45}$ implies an unbounded total volume. Hence, the size distribution must have an upper cutoff, which in practice should be the smallest dimension of the sample container. (In fact, the nature of the size distribution for Apollonian packings of spheres is still under debate [21, 22], and appears to depend crucially on the manner in which the packing is constructed.) The maximum onion size then decreases, and for $\lambda \lesssim -1.125$ the stable phase is of unilamellar vesicles. At this point the calculation has presumably broken down, and either another phase such as micelles intervenes(2), or even higher-order curvature terms become important. Because $\lambda = \tilde{\kappa} d^2/\tilde{c}$, and the volume fraction ϕ is of order δ/d, the condition $\lambda < \lambda^*$ implies a phase boundary $\tilde{\kappa}^* \sim \phi^2$, as shown in fig. 1b, in the $(\tilde{\kappa}, \phi)$-plane.

Experiments. – As shown theoretically in [26], adsorption of amphiphilic copolymers to surfactant bilayers is expected to decrease $\tilde{\kappa}$, which eventually becomes negative. We therefore prepare lamellar phases decorated with copolymers [17]. Bilayers of thickness $\delta_0 = 2.8$ nm comprising cetylpyridinium chloride (CpCl) and octanol (Oct) (CpCl/Oct = 0.95 w/w) are diluted in brine ([NaCl] = 0.2 M) and decorated with Symperonics F68 (Serva) ($(\mathrm{EO})_{76} - (\mathrm{PO})_{29} - (\mathrm{EO})_{76}$, where EO is ethylene oxide and PO is propylene oxide) as amphiphilic copolymer. The bilayer volume fraction ϕ and the copolymer/surfactant weight ratio α range from 9 to 23% and 0 to 1.6, respectively. The lamellar structure is preserved upon adding copolymer, with a continuous hardening into a "lamellar gel". The location of this gel in the (α, ϕ) phase diagram was studied by Ligoure *et al.* [17]. They observed gel-like behavior over a range of critical copolymer/surfactant weight ratios that depends on the membrane fraction.

The marked variation of the mechanical properties of the bulk lamellar phase is accompanied by modifications of the optical textures. The pictures shown in fig. 2 demonstrate that

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(2)A cubic phase of unilamellar vesicles has been experimentally observed in the concentrated regime [25].

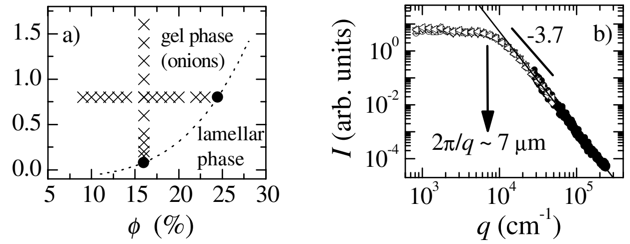

Fig. 3 – (a) Schematic phase diagram, adapted from [17], overlaid with the experimental points (×), where α and ϕ are, respectively, the copolymer/surfactant weight ratio and bilayer volume fraction. Experimental phase boundaries are inferred at •. The dotted line is a guide for the eye. (b) Small- and large-angle static light scattering intensity for $\phi = 16\%$ and $\alpha = 0.8$. A crossover from power law to constant intensity is noted at a length scale of order $7\,\mu$m.

the lamellar gels are onion phases. Onions are clearly obtained for both neat lamellar phases and samples put in contact with solvent. In the latter case, individual onions detach from the solvent/gel interface (figs. 2e, f), while in the former case defect textures characteristic of the onion phase are observed between crossed polarizers (figs. 2a-c). The onions are highly polydisperse, with an apparent maximum size which seems to decrease with increasing α. Different textures and the presence of oily streaks are discerned at higher ϕ (fig. 2d).

While microscopy indicates that the size distribution is very broad and varies with α and ϕ, a quantitative determination of the size distribution using this technique is delicate. However, assuming an Apollonian distribution we can, for example, estimate the macroscopic elastic modulus as a mass (or volume) average of the elastic moduli of onions of different sizes r_i. The elastic energy stored in a linear deformation of strain μ of an onion of radius R is $4\pi\gamma R^2\mu^2$, where the effective surface tension $\gamma = \frac{1}{2}\sqrt{K\bar{B}}$ [27], leading to a modulus $G_R = 3\pi\gamma/R$. Thus, an estimate of the volume-averaged elastic modulus is $G_0 \simeq \frac{1}{V}\sum_i 3\gamma n_i r_i^2$ [20]. Averaging for $R_{\max} \gg d = \delta_0/\phi$, we find $G_0 \simeq \frac{3\gamma}{d}\frac{4-D_{\mathrm{A}}}{D_{\mathrm{A}}-3}(\frac{d}{R_{\max}})^{4-D_{\mathrm{A}}} \simeq 3.67\,\gamma\, d^{-0.45}\, R_{\max}^{-0.55}$ for $D_{\mathrm{A}} = 3.45$. The linear elastic plateau is measured in a Couette rheometer along two lines in the phase diagram at constant α and ϕ (fig. 3a). For fixed ϕ, the modulus G_0 increases monotonically with increasing α, while for fixed α, the modulus varies non-monotonically with ϕ (fig. 4). To extract the maximum onion radius $R_{\max}$ from G_0, we must estimate the surface tension γ. For interlamellar forces dominated by Helfrich entropic undulations, $\sqrt{K\bar{B}} = \frac{3\pi}{8}\frac{k_{\mathrm{B}}T}{(d-\delta)^2}$, with δ the

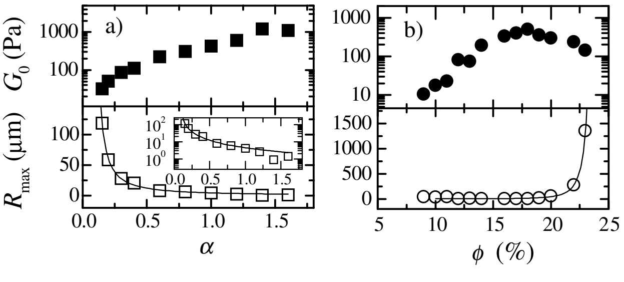

Fig. 4 – Variation of the elastic plateau modulus G_0 (top) and maximum radius $R_{\max}$ (bottom) determined from G_0, for samples with a) $\phi = 16\%$ and various α; b) $\alpha = 0.8$ and various ϕ. Solid lines are fits to $R \sim (\alpha - \alpha_{\mathrm{c}})^{-p}$ and $R \sim (\phi_{\mathrm{c}} - \phi)^{-m}$, with $\alpha_{\mathrm{c}} = 0.08$, $\phi_{\mathrm{c}} = 24.5\%$, $p = 1.3$, $m = 3.0$. Inset in a): same data as in the main figure in a semi-logarithmic plot.

bilayer thickness [17, 28]. Interestingly, it has been shown [17] that for a decorated lamellar phase the inter-bilayer interactions are still of an effective Helfrich form, with an effective bilayer thickness $\delta_{\mathrm{eff}} = \delta_0 + 2 \times h_{\mathrm{pol}}$, where h_{pol} is the apparent thickness of the polymer layer(3). In the experimental range of α we take $h_{\mathrm{pol}} = A\alpha^{1/3}$ with $A = 3.5\,\mathrm{nm}$, although this expression is strictly valid only in the brush regime ($\alpha \geq 0.5$). One can thus calculate the surface tension by taking $\delta = \delta_{\mathrm{eff}}$ and hence extract, from the experimental values of G_0, the variations of $R_{\max}$ with the two experimental parameters ϕ and α. As can be seen in fig. 4, for $\phi = 16\%$, $R_{\max}$ varies between $1\,\mu\mathrm{m}$ and $120\,\mu\mathrm{m}$, with an apparent divergence near $\alpha_{\mathrm{c}} \simeq 0.08$; while for $\alpha = 0.8$, $R_{\max}$ varies between $4\,\mu\mathrm{m}$ and $1400\,\mu\mathrm{m}$, with an apparent divergence near $\phi_{\mathrm{c}} \simeq 24.5\%$(4).

The critical-like behavior of the onion maximum size inferred experimentally is remarkably similar, qualitatively, to the prediction of fig. 1. From the observed critical-like variations in $R_{\max}$ we have identified two points on the boundary between lamellar and onion phases, in the (α, ϕ)-plane (fig. 3a). Using the relation between $\tilde{\kappa}$ and the parameter λ, we can estimate experimental values for $\tilde{\kappa}$. The onion/lamellae phase boundary is given by $\lambda^* = \frac{\tilde{\kappa}^* d^2}{\tilde{c}} = -0.86$ with $\tilde{c} = k_{\mathrm{B}}T\delta_{\mathrm{eff}}^2$. For the two copolymer/surfactant weight ratios α for which the boundary has been determined (fig. 1c), we obtain $\tilde{\kappa} = -0.1k_{\mathrm{B}}T$ for $\alpha = 0.08$ and $\tilde{\kappa} = -0.6k_{\mathrm{B}}T$ for $\alpha = 0.8$. In agreement with theoretical expectations [26], $\tilde{\kappa}$ is found to be negative, of order $1\,k_{\mathrm{B}}T$, and to decrease with increasing copolymer/surfactant weight ratio. Consistent with the theoretical phase diagram (fig. 1b) and with previous experimental observations [17], we also find that the critical value of $\tilde{\kappa}$, below which the onion phase is stable, decreases when ϕ increases.

The radii $R_{\max}$ estimated from the elastic moduli are similar to those observed by microscopy (figs. 2e, f). For $\alpha = 0.15$, the largest observable onion is $R \simeq 35\,\mu\mathrm{m}$ and the calculated $R_{\max}(G_0) = 120\,\mu\mathrm{m}$ (fig. 2e), and for $\alpha = 1.6$, the largest observable onion is $R \simeq 5\,\mu\mathrm{m}$ (in fig. 2f) and the calculated $R_{\max}(G_0) = 1.4\,\mu\mathrm{m}$. We can also compare $R_{\max}$ to static light scattering experiments (fig. 3). The scattering intensity $I(q)$ scales as a power law for large q, $I(q) \simeq q^{-3.7}$, and has a plateau for smaller q, indicating that there is no structure at lengths larger than the crossover length $2\pi/q \simeq 7\,\mu\mathrm{m}$. This provides an estimate for the maximum onion size $R_{\max}$ that is very close to the value obtained from G_0 ($R_{\max} = 6\,\mu\mathrm{m}$). While similar power law behavior for high q has previously been observed for monodisperse onions obtained by shear, the behavior at large q [29] was very different, with a peak characteristic of the onions size observed in that case. The flat intensity obtained here clearly indicates the intrinsic polydispersity of the onions. Figures 2e, f also show wide size distributions.

In summary, we have presented experimental evidence for an equilibrium phase of polydisperse multi-lamellar vesicles (onions), and rationalized this by combining a non-linear Helfrich elastic theory with an assumed polydisperse distribution of onions. Future work should incorporate the entropy and calculate the nature of the space-filling distribution.

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(3)Since the lamellar phase is stabilized by Helfrich interactions, one should in principle incorporate layer undulations into an onion entropy [10]. However, we believe that these effects, important for small onions in dilute systems, would not significantly change the phase diagram at the higher concentrations studied here.

(4)We note that, at small ϕ, $R_{\max}$ is a decreasing function of ϕ, which may be due to the nearby lamellar-to-vesicle phase boundary [17].

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