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Ordered and curved meso-structures in membranes and amphiphilic films

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Résumé. — On étudie ici les instabilités de courbure dans les membranes et les films amphiphiles en introduisant un couplage entre une variable de forme (telle que la courbure) et les degrés de liberté internes (comme l'aire par molécule, l'angle d'inclinaison des chaînes ou la composition locale). L'approximation du champ moyen appliquée à un développement de l'énergie libre de Ginzbourg-Landau, démontre l'existence de différentes phases *ondulées* (sur l'échelle mésoscopique), qui peuvent apparaître entre les phases homogènes condensées (type solide) et diluées (type fluide) de la membrane. Ces phases ondulées sont caractérisées par des modulations locales de leur composition ainsi que de leur courbure locale. Nous trouvons ici deux types de telles phases — en bande et hexagonale — et nous calculons le diagramme de phase de ce système.

Abstract. — Curvature-induced instabilities in membranes and amphiphilic films are investigated by introducing a general coupling between a shape variable (such as curvature) and « internal » degrees of freedom (such as area per molecule, tilt angle, or local composition). A mean-field treatment of the Ginzburg-Landau free energy expansion shows the existence of various undulated phases (on a mesoscopic scale) that can appear between condensed (solid-like) and dilute (fluid-like) homogeneous phases of the membrane. These undulated phases are characterized by undulations in their local composition as well as in their local curvature. We find two types of undulated phases — stripe and hexagonal — and calculate the phase diagram for the system.

A bilayer membrane is one of various structures formed by amphiphilic molecules (e.g. phospholipids) in a solvent (e.g. water) [1]. Such bilayer membranes consist of two opposing layers of amphiphiles that have their polar heads pointed towards the surrounding water, while their hydrocarbon tails overlap and point away from the water due to their hydrophobic character. Membranes are usually found either in the form of closed vesicles or as part of a multilayer stack of lamellae.

Other related structures that can be found in solutions are two-dimensional monolayers of amphiphile molecules. These monolayers reside on interfaces between two immiscible solvents of different character such as water and oil, and they exist

either as a single interface between coexisting water and oil phases, or as an extended interface that separates oil and water regions (e.g. in microemulsion). In the case where the amphiphilic monolayer resides on a liquid/air interface it is known as a Langmuir monolayer.

For the purpose of this paper we will not make the distinction between bilayer membranes and amphiphilic monolayers; our treatment equally applies to both systems, and thus we will use both to illustrate our findings. However, in a more refined model, the difference between membranes and amphiphilic films can be of importance.

One can study the shape of two-dimensional membranes and amphiphilic films [2], their fluctuations [3-5], and their mutual interactions [6], by neglecting completely their *internal degrees of freedom* and by treating them as curved and fluctuating

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interfaces. However, this approach has some limitations since in many physical or biological systems, the degrees of freedom within the amphiphilic film are coupled to global properties of the film. For instance, a phospholipid or surfactant layer can undergo an « internal » phase transformation such as a chain melting (known as the « main transition » [7]), or a lateral (inplane) phase separation [8] in the case where two different types of amphiphiles are present. Clearly, in such cases, it is appropriate to introduce internal variables such as the local area per amphiphile, or the local relative concentration of the two different species.

These internal degrees of freedom, which are connected to the inplane phase-transitions, are, in general, *coupled* to the « external » degrees of freedom that govern the behaviour of the membrane as a two-dimensional, curved, and fluctuating structure. The purpose of this paper is to show, using a simple example, how this coupling is a possible source for a new type of phenomena termed *curvature instabilities* [9]. These instabilities leads to the appearance of ordered meso-structures for which *both* the internal degrees of freedom and the curvature will have modulations with nonzero wavevector around their mean values at thermodynamic equilibrium.

Ordered and curved structures are indeed observed in many different systems of bilayer membranes. For example, in mixtures of amphiphiles of different symmetries, a lateral phase separation with curvature modulation takes place [8]. Moreover, many phospholipid membranes can form a phase known as the « ripple » phase. This phase is usually found [10] for inplane concentrations that are between those of the dilute fluid-like and condensed solid-like (sometimes called the « gel ») phases. By the addition of small amounts of a different (small) molecule that dissolves asymmetrically in the membrane, one can provoke shape transformations, and in some cases, structures that are both ordered and curved [11].

In order to construct a model that exhibits the behaviour discussed above, we make several simplifying assumptions :

i) While allowing the bilayer membrane or the monolayer amphiphilic film to curve (the difference between the two *is not* taken into our model), their shape is assumed to be close to planar ; thus the possibility of having overhangs or discontinuities in the film is neglected. Consequently, a displacement variable $\ell(x, y)$ that measures the displacement of the film from a flat reference plane is a single valued function. We note that a vesicle can be similarly described in the limit where its radius of curvature is large. We can now write an effective Hamiltonian as an expansion in gradients of this variable $\ell(x, y)$

$$H_1 = \int \left\{ \frac{1}{2} \sigma (\nabla \ell)^2 + \frac{1}{2} \kappa (\nabla^2 \ell)^2 + \dots \right\} dx dy \quad (1)$$

where σ is the surface tension and κ is the rigidity modulus [12].

ii) We also assume that the relevant internal degrees of freedom (e.g. the area per amphiphile, the relative concentration for a membrane that is composed of two different amphiphile molecules, or the tilt angle of the hydrocarbon chains) can be described by a single continuous scalar variable $c(x, y)$. Allowing for the possibility of a phase transition *within* the membrane, we take $\Phi(x, y) = c(x, y) - c_0$ as the appropriate order parameter of this transition and writing the corresponding Ginzburg-Landau Hamiltonian as an expansion around the critical point, $c = c_0$

$$H_2 = \int \left\{ \frac{1}{2} b (\nabla \Phi)^2 + \frac{1}{2} A (\nabla^2 \Phi)^2 + \dots + f(\Phi) - \mu \Phi \right\} dx dy \quad (2)$$

where b and A are phenomenological coefficients, μ is the chemical potential, and $f(\Phi) = (1/2) a_2 \Phi^2 + (1/4) a_4 \Phi^4$. Without the gradient terms ($b = A = 0$), equation (2) gives the usual critical point at $\mu = a_2 = 0$, and a line of first-order transitions for : $\mu = 0, a_2 < 0$. All other coefficients (a_4 , etc.) are assumed to be positive for simplicity sake, and the cubic term in Φ in $f(\Phi)$ is omitted since it can be eliminated by redefining Φ .

Finally, the two lowest orders in the coupling between the internal variable Φ and the membrane shape can be written as follows :

$$H_3 = \int \left\{ \Lambda \Phi (\nabla^2 \ell) + \lambda \Phi (\nabla^4 \ell) + \dots \right\} dx dy \quad (3)$$

where the two lowest-order linear terms in both Φ and ℓ are retained. These terms contain only even powers of the gradient operator. In addition, we omit other terms of the same order that can be reduced to the ones in (3) by integration by parts. In (3) we did not, as well, include terms that can be written as the total derivative of some function, since these terms can be re-expressed as boundary terms, using the divergence theorem ; thus they vanish for simple surfaces in the thermodynamic limit, when both ℓ and Φ are continuous and slowly varying functions. An interesting generalization, which is beyond the scope of this paper, would be to include the possibility of defect structures [13] or nontrivial boundary conditions.

Equations (1) to (3) define our model. The total effective Hamiltonian $H = H_1 + H_2 + H_3$, can then be written in momentum space as :

$$\begin{aligned}
H = \int d^2q \left\{ \frac{1}{2} \sigma q^2 \ell_q \ell_{-q} + \frac{1}{2} \kappa q^4 \ell_q \ell_{-q} + \right. \\
\left. + \frac{1}{2} b q^2 \Phi_q \Phi_{-q} + \frac{1}{2} A q^4 \Phi_q \Phi_{-q} + \right. \\
\left. + \Lambda q^2 \Phi_q \ell_{-q} + \lambda q^4 \Phi_q \ell_{-q} \right\} \\
+ \int \{f(\Phi) - \mu \Phi\} dx dy. \quad (4)
\end{aligned}$$

Since (4) contains terms that are at most quadratic in ℓ_q , the integration over the $\{\ell_q\}$ degrees of freedom can be done exactly. Such an integration is performed using a « naive » measure $\int D\ell \equiv \int \Pi_q d\ell_q$, which is justifiable within the approximation that we will use hereafter. If one wants, however, to take into account thermal fluctuations, a more accurate definition of the appropriate measure is needed.

Integrating out the $\{\ell_q\}$, yields the effective Hamiltonian

$$\begin{aligned}
H_{\text{eff}} = \int d^2q \left\{ \frac{1}{2} q^2 \Phi_q \Phi_{-q} \left(b - \frac{\Lambda^2}{\sigma} \right) + \right. \\
\left. + \frac{1}{2} q^4 \Phi_q \Phi_{-q} \left(A + \frac{\Lambda^2 \kappa}{\sigma^2} - \frac{2 \Lambda \lambda}{\sigma} \right) \right\} \\
+ \int \{f(\Phi) - \mu \Phi\} dx dy \quad (5)
\end{aligned}$$

where the bare surface tension σ is assumed to be positive and, for simplicity, we expanded (5) up to forth order in q . The form revealed here (5) has an important consequence : if the value of the coupling constant Λ exceeds a critical value

$$\Lambda > (b\sigma)^{1/2} \quad (6)$$

the coefficient of the term $q^2 \Phi_q \Phi_{-q}$ becomes negative, leading to an *instability* of the homogeneous system with respect to long wavelength fluctuations. The most unstable wavevector q^* is found by minimizing H_{eff} with respect to q , equation (5)

$$q^* = \left| \frac{b\sigma^2 - \Lambda^2 \sigma}{2(A\sigma^2 + \Lambda^2 \kappa - 2 \Lambda \lambda \sigma)} \right|^{1/2} \equiv \left| \frac{B}{2C} \right|^{1/2}. \quad (7)$$

Here the coefficient of the q^4 term in equation (5) is assumed to be positive (otherwise higher order terms in q are needed).

In order to estimate the value of q^* in a real system, we suppose for simplicity, $A = \lambda = 0$. The term $\Lambda \Phi (\nabla^2 \ell)$ in equation (3) is the generalization of the spontaneous curvature energy [14] for nonhomogeneous films, so that $\Lambda c_0 \sim H_0 \kappa$, where H_0 is the spontaneous curvature, and κ is the rigidity modulus. Taking typical values [14, 15] for H_0 , κ ,

and c_0 , and putting $b \sim k_B T \xi_0^4$, with the correlation length amplitude ξ_0 equal to a few angstroms, the undulation periodicity, $\lambda^* = 2 \pi / q^*$, is found to range between 10 and 1 000 Å. These unstable wavelengths should therefore lie in the experimental range, and in fact are comparable to the periodicity of ordered structures observed in several systems [16] (~ 100 -1 000 Å).

In what follows, a mean-field approximation [17] for the effective Hamiltonian, equation (5) is presented. Studies of similar Hamiltonian have been performed previously for quite different systems ; among other these are : smectic phases of liquid crystals [18], thin magnetic films of uniaxial symmetry in a magnetic field [19], convection rolls [20], and polar insoluble monolayers at the liquid/air interface (Langmuir monolayers) [21].

The basic idea consists of comparing the mean-field free energies of the following phases :

i) the stripe phase,

$$\Phi_S = \Phi_0 + \Phi_{q^*} \cos q^* x \quad (8)$$

ii) the hexagonal phase,

$$\Phi_H = \Phi_0 + \sum_{i=1}^3 \Phi_{q^*} \cos (\mathbf{k}_i \cdot \mathbf{r}_i + \delta_i) \quad (9a)$$

where

$$|\mathbf{k}_i| = q^*, \quad \sum_{i=1}^3 \mathbf{k}_i = 0, \quad \delta_i = 0 \quad (9b)$$

and

iii) the homogeneous phases with $q^* = 0$ and $\Phi_I = \Phi_0$. These include both the dilute (fluid) and condensed (solid) phases. Although we refer to the condensed phase as being solid-like and to the dilute one as being fluid-like, there is nothing in our model that takes into account the difference in character between the two phases (such as the existence of long range order in the solid phase).

Only the most unstable wavevector q^* is used in equations (8)-(9). This assumption greatly simplifies the calculations and can be justified [19] close to the homogeneous critical point, $\Lambda = \lambda = 0$.

Figures 1 and 2 show the phase diagrams that has been obtained from equations (5)-(9). In fact, close to the critical temperature these phase diagrams are identical to the ones found in the problem of polar Langmuir monolayers [21]. There, the long-range dipolar and repulsive interactions cause « super structures » with undulating inplane concentration.

Figure 1 shows the phase diagram in the reduced temperature — reduced concentration (ε, m) plane, which is defined by

$$\varepsilon \equiv (2C/B^2) a_2; \quad m \equiv (2a_4 C/B^2)^{1/2} \Phi_0. \quad (10)$$

Close enough to $\varepsilon = 1, m = 0$, there are five distinct

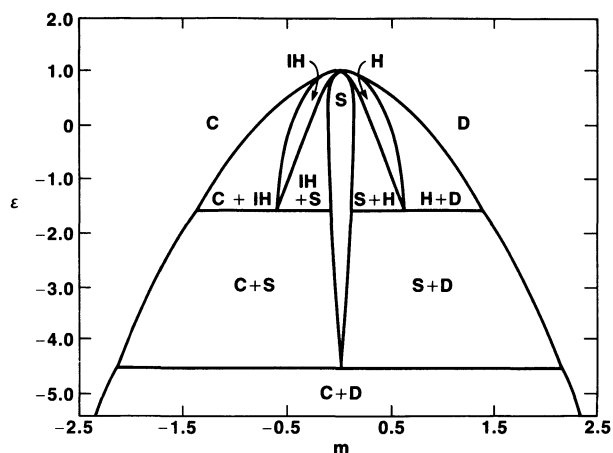


Fig. 1. — Phase diagram in the (m, ε) plane where ε is the reduced temperature and m is the reduced order parameter. Here, as an example, this order parameter is chosen to be the local density of amphiphilic molecules. The two homogeneous phases : dilute (D) and condensed « gel » (C) are separated by the hexagonal (H), stripe (S) and inverted hexagonal (IH) phases. Two-phase coexistence regions between the various single phases are also shown. This phase diagram was obtained from equations (5)-(9) and is valid close to the critical point of the homogeneous system, $\varepsilon = 0$.

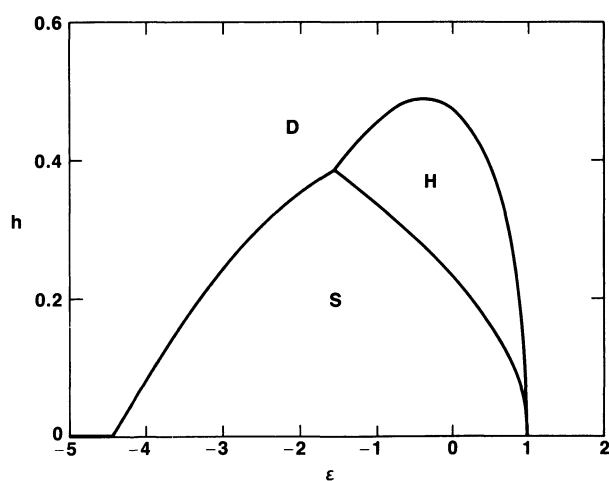


Fig. 2. — The same phase diagram as in figure 1, in the reduced temperature ε — rescaled chemical potential h plane. This phase diagram is symmetric about $h = 0$ and only half of it with $h > 0$ is shown. All transition lines are first order and they terminate at the critical point : $h = 0, \varepsilon = 1$.

phases : a dilute homogeneous fluid (D), a condensed « gel » or solid-like (C), and three undulated phases : a stripe phase (S) consisting of alternating stripes of dilute and condensed regions, as well as hexagonal (H) and inverted hexagonal (IH) phases with triangular symmetry, equation (9). Between the five phases there are four regions of two-phase

coexistence : D-H, H-S, S-IH, and IH-C. At a lower temperature, $\varepsilon \cong -1.6$, the two hexagonal phases : H and IH disappear, and the remaining phases S, C and D have two regions of coexistence : S-D and S-C. At even lower temperatures $\varepsilon \cong -4.45$, the stripe phase itself becomes unstable and one is left with the two-phase coexistence curve $m^2 = \varepsilon$ between the D and C phases.

In figure 2 the same phase diagram is shown in the chemical potential— reduced temperature (h, ε) plane where the rescaled chemical potential h is defined as

$$h \equiv (B^2/2 a_4 C)^{1/2} \mu . \quad (11)$$

At $(h = 0, \varepsilon = 1)$ there are four first-order transition lines that join together. Only two of them are shown in figure 2 (between D-H and H-S) since our phase diagram is symmetric about $h = 0$, and we plotted only the $h > 0$ half of it. In figure 2, two triple points are shown ; the first ($\varepsilon \cong -1.6, h \cong 0.38$) is where the three phases : S, H, and D coexist, whereas the second one ($\varepsilon \cong -4.45, h = 0$) is where the three phases : D, C, and S coexist. A third triple point that is not shown in figure 2 is the one where the phases S, IH, and C coexist ($\varepsilon \cong -1.6, h \cong -0.38$).

In general, several phases with *spatial undulations* of both the internal order parameter Φ and the local curvature, $\nabla^2 \ell$, of the film are found. The undulations in the local curvature are due to the coupling between the local curvature and Φ . Thus undulations of the latter will induce undulations of the former. For the case where Φ represents the relative composition of two species (A and B) of amphiphiles, one (say A) will have higher concentration in regions of higher curvature whereas the other (say B) will have higher concentration in regions of lower curvature. For the predicted hexagonal and inverted hexagonal phases, lower and higher curvature regions correspond to the « mountains » and « valleys » of the film.

The phase diagram presented in figure 2 can be viewed as a cut of a higher dimensional parameter space. If the coefficient of the q^2 term of equation (5) is allowed to vary, a Lifshitz point [22] occurs when $b = \Lambda^2/\sigma$. Such an extended phase diagram is similar [23] to the one obtained for an Ising model with competing axial interactions in the presence of an external field (the ANNNI model [24]). However, the Ising problem is realized on a lattice and thus has commensurate and incommensurate phases. In our case, there is no underlying lattice and the undulation wavelength varies continuously with the coupling strength.

An interesting special case, which merits a separate discussion, is the case of a bilayer membrane (or film) with vanishing surface tension, $\sigma = 0$. This case had already been studied in reference [9].

Setting $\sigma = 0$ in (4) and integrating over ℓ_q , we get that the coefficient of the Φ^2 term is given by

$$a_{\text{eff}} = a_2 - \frac{\Lambda^2}{\kappa}.$$

This means that for $\Lambda^2 > \kappa a_2$, one obtains a curvature instability [9] which is, nevertheless, different from the one we obtained above for $\sigma > 0$ [compare with (6)]. For $\sigma = 0$, the coupling to the curvature increases the critical temperature of the inplane phase separation. No undulated phase becomes stable since $q = 0$ is the most stable wavevector for $\sigma = 0$.

In a recent paper [10], a simple theory was proposed to explain the intermediate ripple phase $P_{\beta'}$ of phospholipid bilayers. A one-dimensional periodic (« single q ») structure appears there as a result of a term in the free energy which couples the order parameter (the bilayer thickness) with its second derivative (curvature); in our notation this term is proportional to $q^2 \ell_q \ell_{-q}$. Our theory can be viewed as a generalization of reference [10] — the periodic structures are not restricted to one-dimensional undulations and the coupling is between two independent thermodynamic variables — the inplane order parameter Φ , and an external shape variable ℓ .

We can obtain the simpler model of reference [10] if a linear relation between the chemical potential h and the reduced temperature ε is imposed. In this case, one obtains a ripple phase lying between the condensed solid-like (« gel ») and dilute fluid homogeneous phases. (For a one-dimensional membrane there is only one type of ripple phase). The transitions between both the ripple and dilute, as well as the ripple and dense phases is always first order. This is easily seen by drawing a straight line with a finite slope on the phase diagram, figure 2, without intersecting the critical point $\mu = 0$, $\varepsilon = 1$.

We would like to stress that although the simple model presented here looks quite appealing as a first step towards understanding the $P_{\beta'}$ phase [10, 13], we believe that our model as well as the models of references [10, 13] represent an oversimplification of

the $P_{\beta'}$ phase. In fact, the order parameter of the $P_{\beta'}$ most likely, is not a scalar. It will rather have to include the conformation degrees of freedom of the amphiphilic chains.

In conclusion, we have constructed a simple continuum theory in which membrane (film) shape is coupled to the internal degrees of freedom of the membrane (or the film). The mean-field treatment of the model leads to the prediction of inplane *meso-structures*, i.e. periodic undulated structures with varying internal order-parameter (such as tilt angle, density of impurities or « fluidity »). Such structures have, indeed, been seen in several experimental situations [8, 16].

Possible extensions of this model include: (i) going beyond mean-field approximation, which would require taking into account critical fluctuations. These fluctuations may, in principle, destroy the undulated phases [19, 25], since the membrane is two dimensional. (ii) Within mean-field theory, finding the most stable solution, without making the one-mode approximation, $|q| = q^*$. This approximation can be justified only close to a critical point [19], and probably fails in some cases [21] at low temperatures. (iii) Even more importantly is to incorporate specific interactions into the model presented here, which probably would require the introduction of several, possibly non-scalar, order-parameters. Such a study is needed before a detailed comparison with experiments is possible. Finally, better experimental estimates of the important parameters in our model (such as the rigidity modulus κ) are needed in order to obtain more precise estimates on the range of the undulation wavevector, q^* .

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