Electrostatic interactions in two-component membranes

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Abstract. — The effect of electrostatic interactions on membrane undulations is examined. We consider a mixed membrane consisting of neutral and charged amphiphiles in an aqueous solution. In general, this system may exhibit a non-uniform surface charge density. Two limiting cases are distinguished: quenched surface–charge distribution; and annealed inplane distribution which is coupled to an undulation mode. For the former case the electrostatic free energy of an undulating membrane is calculated in the limit of strong ionic solution. Spatial modulations of the surface charge density are found to induce a local spontaneous curvature in a single mono-layer. In addition, the electrostatic contribution to the elastic bending modulus is obtained for a general non-uniform surface-charge density. In the latter case of a self-adjusting (annealed) membrane, an electrostatic coupling between the inplane distribution and the membrane curva-ture produces an added effective interaction which stabilizes modulated phases.

1. Introduction.

Aqueous solutions of amphiphiles exhibit a variety of self-assembling structures. As an example, we mention the lamellar phase consisting of alternating amphiphilic *bilayers* and coherent water regions where the hydrophobic tails of the two membrane layers are packed together away from the water regions. In some cases, when a second (insoluble) solvent like oil is added, the lamellar order persists and amphiphilic *monolayers* separate alternating regions of water and oil [1].

The thermodynamics of the formed *fluid* amphiphilic membrane is controlled by out-of-plane thermal undulations governed by surface tension, in situations where the total area covered by the membrane can vary, and by the curvature elastic energy of each membrane. The free energy we use is

$$\gamma \int dS + \frac{1}{2}\kappa_c \int dS \,(c_1 + c_2 - c_0)^2 \; + \; \tilde{\kappa}_c \int dS \, c_1 c_2 \qquad (1.1)$$

where we add a surface tension term (the γ term) to the elastic free energy originally proposed for fluid membranes by Helfrich [2]. The principle curvatures are c_1, c_2, the spontaneous

curvature is c_0 (it vanishes for symmetric membranes), and κ_c and $\bar{\kappa}_c$ are the moduli of the bending rigidity and Gaussian curvature, respectively. The latter is relevant only when different topologies are considered and will, therefore, be neglected in our treatment of lamellar phases.

The electrostatic contribution to the bending moduli, κ_c and $\bar{\kappa}_c$, has been the focus of several recent papers [3-12] and has been obtained for different electrostatic boundary conditions: constant potential, constant surface charge; as well as for different geometries: undulating planar membranes, cylindrical and spherical shapes, etc.

To the best of our knowledge previous approaches accounted only for *homogeneous* electrostatic boundary conditions with either constant surface potential or surface charge density. The one exception [5] will be discussed separately below. The aim of the present work is to consider the electrostatics of *inhomogeneous* amphiphilic membranes immersed in an electrolyte. The novelty is the possibility of inhomogeneous surface-charge distribution for *two-component* membranes having both electrostatic as well as other inplane degrees of freedom. Two different limits are investigated. For the first, the surface charge distribution is *quenched* ("frozen"), whereas for the second, the membrane is *annealed* and the inplane degrees of freedom, such as surface concentration and out-of-plane undulations are coupled and mutually adjusted.

Our theoretical study of mixed amphiphilic solutions is motivated by recent experiments on mixtures of charged and non-charged amphiphiles. For example, mixtures of PC (phosphatidyl-choline) which is a neutral (polar) amphiphile and PG–Na⁺ (phosphatidyl-glycerol sodium salt) which is (monovalently) charged, are commonly found in biological membranes. It was reported [13-15] that by lowering the temperature, a phase with non-uniform surface charge density is formed (i.e., non-uniform partitioning of the charged and neutral amphiphiles on the membrane). Moreover, many phospholipid membranes, including mixtures of charged and neutral lipids, have been observed to exhibit an intermediate "ripple" phase, denoted $P_{\beta'}$ [13, 16-19]. Other systems, consisting of mixtures of oppositely charged amphiphiles have been shown to produce equilibrium phases of vesicles [20]. The local interaction between the different amphiphiles (e.g., differently charged) has been shown to affect the spontaneous curvature of the monolayer [21]. A somewhat similar effect, so-called synergism, has been reported with respect to micelle formation [22]. Mixtures of two differently charged amphiphiles have been found to stabilize micelles as compared to single-component micelles, with respect to the free amphiphile in the bulk, i.e., the electrostatic interaction lowers the critical micellization concentration (cmc) of the bulk solution. Another example is that of mixtures of ionic and zwitterionic (dipolar) amphiphiles, where lamellar phases as well as rod-like and spherical micellar phases are influenced by electrostatic effects. For instance, the rod-like micellar growth and their observed transition to a nematic phase depend on the ionic strength of the solution as well as the mixing ratio of the two species [22]. All these observations imply that the internal structure of the membrane is related to the shape by means of the electrostatic interaction. It is this relation we aim to study and at present we limit ourselves to lamellar phases.

The outline of this paper is the following: sections 2 and 3 deal with the cases of frozen and annealed surface-charge distributions, respectively. In section 2 we show that electrostatic interactions give rise to a local spontaneous curvature in the membrane when a non-uniform surface-charge density is imposed and we also obtain the electrostatic contribution to κ_c. In section 3, a phenomenological free energy, incorporating an electrostatic coupling of curvature and inplane order, produces stable modulated phases. Conclusions and a general discussion are presented in section 4.
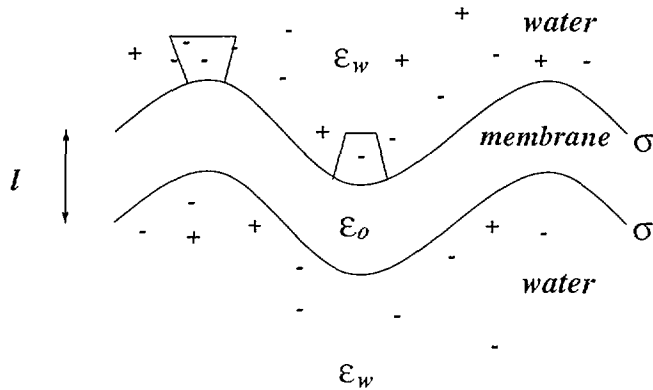
Fig.1. — A bilayer consisting of two electrically decoupled monolayers undulating *in-phase* with a separation l. The water and the "oily" lipid chain permittivities are $\varepsilon_{\rm w}$ and $\varepsilon_{\rm o}$, respectively, and σ is the surface-charge density. Notice the larger volume per unit surface area, accessible to the ions in the solution, in the convex parts as compared to the concave parts.

2. Quenched membranes.

In this paper we consider only one single membrane embedded in a liquid environment. Two experimental situations can be realized: an amphiphilic monolayer separating two different solvents (for example, a monolayer at the oil/water interface) or a bilayer separating an aqueous solution on "top" from one on "bottom", figure 1. In the latter case we assume that the two monolayers do not interact electrically across the "oily" region. The limit in which the two monolayers are electrically decoupled has been discussed in reference [5] and is reached when $\frac{\varepsilon_{\rm o}}{\varepsilon_{\rm w}}/\kappa l \ll 1$, where $\varepsilon_{\rm o}/\varepsilon_{\rm w}$ is the ratio of the oil (inside) to water (outside) permittivities, l the width of the "oily" region and κ^{-1} the Debye-Hückel screening length defined below. This limit is valid even for very low electrolyte concentrations and, therefore, is a good approximation for biological systems in physiological conditions. Throughout this paper, the membrane is assumed to be weakly undulating around a *flat* reference plane so that the membrane shape and energetics can be expressed as an expansion around the averaged flat plane. The membrane is characterized by a height profile $u(x)$ which, for simplicity, is taken to vary only along one dimension.

We now consider the case of a membrane with a quenched spatial structure and composition. To further simplify, we analyze only one specific undulation mode, $u(x) = u \cos qx$, with an imposed spatially-varying but frozen surface charge density $\sigma(x)$. In our model the electrolyte occupies the half plane $z > u(x)$ and the electric field is assumed to be zero for $z < u(x)$, corresponding to the decoupled limit mentioned above. The electric potential ψ is determined by the Poisson–Boltzmann (PB) [23-25] equation

$$\nabla^2 \psi(x, z) = \frac{8\pi n_\infty e}{\varepsilon_{\rm w}} \sinh \frac{e\psi(x, z)}{k_{\rm B}T} \qquad (2.1)$$

where $e > 0$ is the electronic charge unit, T is the temperature, $k_{\rm B}$ is the Boltzmann constant, and the water permittivity is $\varepsilon_{\rm w}$. At $z \to \infty$ the bulk electrolyte concentration is n_∞ and the potential vanishes. The electrostatic boundary conditions on the membrane are of the

Neumann type (fixed surface charge)

$$\mathbf{n} \cdot \boldsymbol{\nabla}\psi(x, z = u(x)) \;\; = \;\; -\frac{4\pi}{\varepsilon_{\mathrm{w}}}\sigma(x). \tag{2.2}$$

Equation (2.2) relates the normal derivative of the potential to the non-uniform surface charge $\sigma(x)$. A further simplification is to consider only the linearized Debye-Hückel (DH) approximation valid in the strong electrolyte or weak surface-charge density limit (corresponding to surface potentials less than 25 mV). Solving the *full* non-linear PB equation with undulating boundary conditions and variable surface-charge density is a tremendous task. Our results, hence, are valid only for screened electrostatic interactions and maybe overlook some features of unscreened long-range electrostatic interactions. On the other hand, our results are of relevance to systems in physiological conditions where some salt is always present.

In the linear approximation equation (2.1) reduces to $\nabla^2\psi = \kappa^2\psi$, and the Debye-Hückel screening length $\kappa^{-1} = (8\pi n_\infty e^2/\varepsilon_{\mathrm{w}} k_{\mathrm{B}}T)^{-1/2}$ is small, typically in the range of several Angströms. The free energy of the system is given by an integral over the membrane surface S:

$$F = \frac{1}{2}\int_S \mathrm{d}S\,\psi(x)\sigma(x) \tag{2.3}$$

and the free energy of a decoupled bilayer is the sum of the free energy of the two monolayers. The calculation is carried out in Fourier space to 2nd order in the undulation. We choose

$$u(x) \;\; = \;\; u\cos qx \tag{2.4}$$

$$\sigma(x) \;\; = \;\; \sigma_0 + \sum_{n=1}^{\infty}\left[\sigma_n^1(z)\sin nqx + \sigma_n^2(z)\cos nqx\right] \tag{2.5}$$

where $\sigma_0^1 = 0$ and $\sigma_0^2 \equiv \sigma_0$ is the average surface-charge density. The resulting average free energy per unit area is $f = f_0 + f_1 u + f_2 u^2$ where

$$f_0 = \frac{\pi}{\varepsilon_{\mathrm{w}}}\left[\frac{2(\sigma_0)^2}{\kappa} + \sum_{n=1}^{\infty}\sum_{i=1}^{2}\frac{\sigma_n^i\sigma_n^i}{\kappa_n}\right] \tag{2.6}$$

$$\kappa_n^2 \equiv \kappa^2 + n^2 q^2 \tag{2.7}$$

and the full expressions for f_1 and f_2 are given in appendix A.

The electrostatic free energy of a *flat* membrane ($u = 0$) with non-uniform (periodic) surface charge and the corresponding ionic layer is f_0. The correction of the nth inplane mode, σ_n, to the uniform surface charge term σ_0 is positive and a decreasing function of the wave number nq. Therefore, the energetically preferred state of a flat membrane has a uniform surface-charge density, $\sigma = \sigma_0$.

For membranes that modulate both in u and σ, the periodic modulation introduces another characteristic length scale — the wavelength $2\pi/q$ — in addition to the screening length κ^{-1}. The terms f_1 and f_2 of the free energy, which pertain to an undulating surface, are examined as a function of the ratio of the two length scales q/κ. Since the full expressions, equations (A15, A16), are rather cumbersome, we discuss here the limits $q/\kappa \ll 1$ and $q/\kappa \gg 1$. In the limit of small q, $q/\kappa \ll 1$, $f_1(q)$ becomes

$$f_1(q) = -\frac{\pi}{2\varepsilon_{\mathrm{w}}}\sum_{n=0}^{\infty}\sum_{i=1}^{2}\left(\frac{q}{\kappa}\right)^2\sigma_n^i\sigma_{n+1}^i \tag{2.8}$$

and for $q/\kappa \gg 1$

$$f_1(q) = -\frac{\pi \kappa^2}{2\varepsilon_w q^2} \sum_{n=0}^{\infty} \sum_{i=1}^{2} \frac{1}{n^2(n+1)^2} \sigma_n^i \sigma_{n+1}^i \tag{2.9}$$

For $f_2(q)$ we obtain in the limit of small q, $q/\kappa \ll 1$

$$\begin{aligned}
f_2(q) &= \frac{\pi \kappa}{4\varepsilon_w} \sum_{n=0}^{\infty} \sum_{i=1}^{2} \left[\sigma_n^i \sigma_n^i - \sigma_n^i \sigma_{n+2}^i \right] \left(\frac{q}{\kappa} \right)^2 \\
&+ \frac{\pi \kappa}{16\varepsilon_w} \sum_{n=0}^{\infty} \sum_{i=1}^{2} \left[(2n^2+3)\sigma_n^i \sigma_n^i - (2n^2+4n-3)\sigma_n^i \sigma_{n+2}^i \right] \left(\frac{q}{\kappa} \right)^4
\end{aligned} \tag{2.10}$$

and for $q/\kappa \gg 1$

$$f_2(q) = \frac{\pi |q|}{2\varepsilon_w} \sum_{n=0}^{\infty} \sum_{i=1}^{2} \left[\frac{1}{n} \sigma_n^i \sigma_n^i - \frac{n+1}{n(n+2)} \sigma_n^i \sigma_{n+2}^i \right] \tag{2.11}$$

Note that an additional specific contribution to $n = 0$ in (2.8-2.11) is omitted for clarity purposes. It appears in appendix A in the formulation of the general expression. In the above limits f_1 and f_2 can be shown to be finite for any physical well-behaved $\sigma(x)$.

The free energy per unit area of a single undulated monolayer is given by $f = f_0 + f_1 u + f_2 u^2$. The existence of a linear term in u ($f_1 \neq 0$) indicates that there is a dependence of the free energy on the *sign* of the local curvature with respect to the ionic solution. The origin of this term is in the asymmetry across the monolayer. Since the ionic solution occupies only half the space on one side of the monolayer, convex parts of the surface with respect to the electrolyte are better screened than concave parts. This is due to the larger volume accessible to counterions per unit area of membrane at convex parts of the surface (see Fig. 1). It follows from equations (2.8, 2.9) that a variation in the charge density, corresponding to a higher charge density at convex parts and lower densities at concave parts, will reduce the average free energy.

For example, if the modulation in $\sigma(x)$ follows the undulation $u(x) = u \cos qx$, i.e., $\sigma(x) = \sigma_0 + \sigma_1 \cos qx$ with $\text{sign}[\sigma_0] = \text{sign}[\sigma_1]$, $f_1 u$ is negative (in the limits $q/\kappa \gg 1$ and $q/\kappa \ll 1$), and the total free energy per unit area of the curved membrane is lowered (to 1st order in u) with respect to the flat membrane. On the other hand, if $\sigma(x)$ and the undulation are out-of-phase $\text{sign}[\sigma_0] = -\text{sign}[\sigma_1]$, $f_1 u$ is positive, favoring no undulation (note that in the quenched limit the system is inhibited from readjusting its surface charge). Support to the above argument lies in the fact that in the limit $q/\kappa \gg 1$, $f_1 \to 0$. This limit suggests that the undulation wavelength $2\pi/q$, is smaller than the DH screening length. Therefore, the ability of the ionic solution to distinguish between positive and negative curvature diminishes, leading to a vanishing linear term.

This linear term also vanishes when considering the somewhat artificial case of a symmetric bilayer, comprised of two in-phase monolayers (Fig. 1) charged identically. In this case the curvature sign is irrelevant since a convex deformation of the "top" monolayer is concave for the "bottom" one. Indeed, the total free energy for such a bilayer is $f = 2(f_0 + f_2 u^2)$. A more realistic bilayer would consist of two monolayers undulating with different charge densities since they are considered decoupled.

An electrostatic contribution to the spontaneous curvature c_0 of the membrane can be obtained from equation (2.8), using the definition given in equation (1.1). Due to the choice of a unique q-mode in the undulation, $u(x) = u \cos qx$, it is easy to show that the most general spontaneous curvature $c_0(x)$ has the form $c_0(x) = c_0 \cos qx$. In this case the term $\kappa_c \, c \, c_0$ in equation (1.1) is proportional to $u q^2$ (since $c \approx \mathrm{d}^2 u/\mathrm{d}x^2$) yielding $c_0 = -(\pi/\varepsilon_w \kappa_c \kappa^2) \sum \sigma_n \sigma_{n+1}$.

This is another manifestation of the asymmetry due to different chemical conditions on the two sides of the membrane. In this representation, when the surface-charge density follows the undulation, the local spontaneous curvature follows the imposed curvature leading to a favorable state. In the opposite situation $\text{sign}[\sigma_0] = -\text{sign}[\sigma_1]$, $\text{sign}[c(x)] = -\text{sign}[c_0(x)]$ which is obviously unfavorable.

The 2nd order term in the free energy, $f_2(q)$, is insensitive to the curvature sign and may be related to the bending energy of the membrane. The electrostatic contributions to the mean bending modulus is obtained by comparing $f_2(q)$ in the limit $q/\kappa \ll 1$ with equation (1.1). The elastic energy per unit area of one monolayer is $\frac{1}{4}\kappa_c u^2 q^4$. Hence, we obtain for a single monolayer

$$\delta\kappa_c^{\text{el}} = \frac{3\pi}{2\varepsilon_w\kappa^3}[\sigma_0\sigma_0 + \sigma_0\sigma_2^2]$$
$$+ \frac{\pi}{4\varepsilon_w\kappa^3}\sum_{n=1}^{\infty}\sum_{i=1}^{2}\left[(2n^2+3)\sigma_n^i\sigma_n^i - (2n^2+4n-3)\sigma_n^i\sigma_{n+2}^i\right]. \qquad (2.12)$$

The bending constant $\delta\kappa_c^{\text{el}}$ can be shown to converge for well-behaved surface-charge densities. Equation (2.12) is a generalization of previously obtained result [3-12] for the electrostatic contribution to κ_c of a homogeneous surface-charge density (in the decoupled monolayer limit). Taking $\sigma(x) = \sigma_0$, all but the first term of equation (2.12) vanishes yielding the known result $\delta\kappa_c^{\text{el}}\{\sigma_0\} = 3\pi\sigma_0^2/(\varepsilon_w\kappa^3)$ for a symmetric bilayer. For simple perturbations of the homogeneous surface-charge distribution, the correction to the (positive) homogeneous bending modulus due to the charge density modulation is positive, i.e., $\delta\kappa_c^{\text{el}}\{\sigma(x)\} - \delta\kappa_c^{\text{el}}\{\sigma_0\} > 0$. For instance, the surface-charge density

$$\sigma(x) = \sigma_0 + \sigma_1\cos qx + \sigma_3\cos 3qx$$

inserted into equation (2.12) leads to

$$\delta\kappa_c^{\text{el}} = \frac{\pi}{4\varepsilon_w\kappa^3}\left[6\sigma_0\sigma_0 + 21\sigma_3\sigma_3 + \sigma_1(5\sigma_1 - 3\sigma_3)\right]$$

which is positive for any σ_0, σ_1 and σ_3. In this case the electrostatic energy rigidifies the membrane and damps thermal undulations. General surface-charge densities must be evaluated individually.

In equation (2.11), f_2 diverges linearly as the wavenumber $q \to \infty$. This divergence represents the breakdown of the continuum approach as the wavelength becomes comparable to the molecular size. Note also that the first term in equation (2.10) is related to the change in area due to the undulation ($\Delta S \propto q^2 u^2$) and may be regarded as an electrostatic contribution to the surface tension. If we assume a free membrane, the effective membrane surface tension γ vanishes and we may disregard this term [8].

In this section we have demonstrated the relation between the surface-charge density and the membrane curvature. We identified an electrically induced spontaneous curvature in f_1 and the electrostatic contribution to the bending modulus in f_2. When the membrane is annealed this implies a *coupling* between the surface-charge density and the curvature. We have found that in the DH approximation the electrostatic free energy of the membrane is quadratic in the surface charge density to 2nd order in the undulation. This dependence is used to suggest the coupling term for the annealed case discussed in the following section.

3. Annealed membranes.

Consider a two–component membrane undulating along one dimension where the constraint on the amphiphile surface concentration (and charge) is relaxed. For simplicity we regard the membrane as a single amphiphilic monolayer. If only electrostatic interactions are taken into account, disregarding all short-range interactions and allowing an *annealed* surface-charge density, (i.e., dependent on the geometry) it has been shown [5] that the most general surface-charge density which minimizes the PB free energy is equivalent to an equipotential surface. However, when other surface interactions of the amphiphiles are present, the monolayer free energy depends both on electrostatic and non-electrostatic interactions, like steric and van der Waals interactions between the amphiphilic tails. The optimal monolayer shape and surface charge distribution can be obtained by applying a variational principle on the total free energy consisting of three parts: $F^{\text{tot}} = F_{\text{out}} + F_{\text{in}} + F_c$. The first accounts for the elastic energy of out-of-plane undulations; the second for the *inplane* degrees of freedom (mixture of two components); and the third is an electrostatic coupling term between the inplane distribution and the monolayer shape. Electrostatic interactions also contribute to the first two terms.

The free energy F_{out} that pertains to the out-of-plane undulation $u(x)$ is given by equation (1.1) as an expansion about a flat reference plane by

$$F_{\text{out}} = \frac{1}{2}\gamma \int \left(\frac{du}{dx}\right)^2 dx + \frac{1}{2}\kappa_c \int \left(\frac{d^2u}{dx^2}\right)^2 dx \qquad (3.1)$$

where $(du/dx)^2$ is the relative change of area to 2nd order in $u(x)$ and γ is the effective surface tension (including the electrostatic contribution identified in the previous section). The local curvature $c \approx d^2u/dx^2$ is expanded about a flat reference plane, and κ_c is the bending modulus including contributions from short-range interactions. Electrostatic corrections to κ_c are evaluated separately.

The internal structure of the flat monolayer is described by F_{in}. The most natural order parameter in the case of two-component mixing is the relative concentration of the two constituent molecules, A and B, accounting for both short–range and electrostatic interactions. In the case where A is *neutral* and B is *charged*, $(\Sigma/e)\sigma(x)$ is the relative composition of the A/B system, where Σ is the area per headgroup (A and B are assumed to have the same Σ) and e the electron charge unit. The order parameter ϕ can be conveniently related to the surface-charge density in a simple way

$$\phi(x) = \frac{\Sigma}{e}\sigma(x) - \frac{1}{2} \qquad (3.2)$$

The general free energy of a partially miscible A/B system can be expressed as a Ginzburg–Landau (GL) expansion in the order-parameter $\phi(x)$ about the critical point,

$$F_{\text{SR}} = \int dx \left[\frac{1}{2}d(\nabla\phi)^2 + \frac{1}{2}t\phi^2 + \frac{1}{4}\lambda_4\phi^4 - \mu\phi\right] \qquad (3.3)$$

accounting for short-range (SR) interactions. The coarsed-grain coefficients $t = a(T - T_0)$, λ_4 and d are determined by the inter-molecular interactions, and μ is the chemical potential of the A/B mixture. Note that the chemical potential is coupled only to the average of the order parameter, $\langle\phi\rangle$. This average can be controlled by changing the relative concentration of the A/B mixture. For d and λ_4 positive, the critical point occurs at $T = T_0$ (around room temperature for typical amphiphiles) and $\mu = 0$. Below T_0 the homogeneous phase separates into two phases.

The next step is to include for the one dimensional flat monolayer the inplane electrostatic interactions. For any periodic surface charge distribution $\sigma(x)$, the inplane electrostatic free energy f_0 is given by equation (2.6). However, it is more convenient to consider the continuum limit of f_0

$$f_0 = \int \mathrm{d}q\, \Gamma_1(q)\sigma_q\, \sigma_{-q}$$

where $\Gamma_1(q) = 1/(\varepsilon_{\mathrm{w}}\sqrt{\kappa^2 + q^2})$ and $\sigma_q = \int \mathrm{d}x\, \sigma(x)\mathrm{e}^{iqx}$. Note that the electrostatic interaction on the surface is strongly screened and effectively short-ranged. This is a result of the DH assumption of high screening/weak surface-charge density. Including electrostatic contribution from f_0 to the GL expansion and using equation (3.2) to express it in terms of the order parameter, equation (3.3) yields the following total inplane free energy for the flat monolayer:

$$F_{\mathrm{in}} = F_{\mathrm{SR}} + f_0 = \int \mathrm{d}q\, g(q)\phi_q\, \phi_{-q} + \int \mathrm{d}x[\frac{1}{4}\lambda_4\phi^4(x) - \tilde{\mu}\phi(x)] \tag{3.4}$$

where the small-q expansion of $g(q)$ is $\frac{1}{2}\tilde{t} + \frac{1}{2}\tilde{d}q^2 + O(q^4)$ and $\tilde{\mu}$ is the renormalized chemical potential. The renormalized GL coefficients are

$$\tilde{t} = 2\pi t + \frac{2}{\kappa\,\varepsilon_{\mathrm{w}}} \tag{3.5}$$

$$\tilde{d} = 2\pi d - \frac{1}{\kappa^3\varepsilon_{\mathrm{w}}} \tag{3.6}$$

$$\tilde{\mu} = \mu - \frac{1}{\kappa\,\varepsilon_{\mathrm{w}}} \tag{3.7}$$

The competition between short–range and electrostatic interactions in the flat monolayer is manifested by a shift in the transition temperature, and by a renormalized coefficient $\tilde{d}$. As long as $\tilde{d}$ is positive, equation (3.5) represents a downward renormalization of the critical temperature due to inplane electrostatic interactions. When the electrostatic correction to the gradient coefficient induces an *instability* with respect to the homogeneous phase, $\tilde{d} < 0$, then the phase diagram is more complicated.

We now turn to the coupling term, F_{c}. This phenomenological term represents the relation between the monolayer curvature and its surface-charge density mediated by the electrolyte. The specific dependence of F_{c} on $u(x)$ and $\sigma(x)$ is motivated by the electrostatic free energy $f(\sigma, u)$ calculated in the previous section. A detailed argument based on a similar calculation of $f(\sigma, u)$ but allowing for an annealed surface-charge density [i.e., $\sigma = \sigma(u)$] is given in appendix B and results in the following coupling term to lowest order

$$F_{\mathrm{c}} = \frac{\Lambda\Sigma^2}{e^2} \int \mathrm{d}x\, c(x)\sigma^2(x). \tag{3.8}$$

This coupling term F_{c} is a generalization of the spontaneous curvature term c_0. Note that in the quenched limit we identified the f_1 as a contribution to the spontaneous curvature. Inserting (3.2) into (3.8) yields

$$F_{\mathrm{c}} \simeq \Lambda \int \mathrm{d}x\, \frac{\mathrm{d}^2 u}{\mathrm{d}x^2}\left[\phi^2(x) + \phi(x)\right] \tag{3.9}$$

The coupling term includes both linear and quadratic orders in $\phi(x)$.

The total free energy of the undulating monolayer can be expressed in Fourier space by taking the proper Fourier transform of (3.1, 3.4, 3.8). Since our $F^{\mathrm{tot}} = F_{\mathrm{out}} + F_{\mathrm{in}} + F_{\mathrm{c}}$ is

bilinear in u_q [the Fourier transform of $u(x)$] we can conveniently "trace out" the out-of-plane degrees of freedom by minimizing F^{tot} with respect to u_q. The resulting optimal u_q is:

$$u_q = \frac{\Lambda}{\gamma + \kappa_c\, q^2}\left[\phi_q + \int dq_1\, \phi_{q_1}\phi_{q-q_1}\right] \qquad (3.10)$$

which relates the undulation mode to the inplane order parameter. Inserting (3.10) back into F^{tot} yields the total free energy as a function of only the inplane order parameter, $\phi(x)$.

$$\begin{aligned}
F^{tot}[\phi(x)] = & \int dq\left[g(q) - \frac{1}{2}\Gamma_2(q)\right]\phi_q\,\phi_{-q} \\
& - \int dq \int dq_1\, \Gamma_2(q)\phi_q\,\phi_{q_1}\phi_{-q-q_1} \\
& - \frac{1}{2}\int dq \int dq_1 \int dq_2\, \Gamma_2(q)\phi_{q_1}\phi_{q-q_1}\phi_{q_2}\phi_{-q-q_2} \\
& + \int dx\left[\frac{1}{4}\lambda_4\phi^4(x) - \tilde{\mu}\phi(x)\right]
\end{aligned} \qquad (3.11)$$

where

$$\Gamma_2(q) = \frac{\Lambda^2 q^2}{\gamma + \kappa_c\, q^2} = \frac{\Lambda^2}{\kappa_c} - \frac{\gamma}{\kappa_c}\frac{\Lambda^2}{\gamma + \kappa_c\, q^2}. \qquad (3.12)$$

represents an effective, curvature induced, interaction introduced by the coupling. According to (3.12) it falls off over long distances ($q \to 0$). The range of this interaction is determined by the ratio between the surface tension γ and the bending modulus κ_c. Equation (3.11) is the main result of this section. In particular, the effective interaction $\Gamma_2(q)$ produces a mechanism which stabilizes modulated phases. An expansion of $\Gamma_2(q)$ in powers of q leads to an enhancement of the instability of the homogeneous phase induced by $\Gamma_1(q)$ (Eq. (3.6)), as $\tilde{d}$ is reduced by an additional negative factor $(-\Lambda^2/\gamma)$. In reference [26, 27] and references therein, a similar study has been done for a simpler coupling term which was linear in the inplane order parameter. In the present work, the coupling to ϕ^2 is more complicated.

It is instructive to examine the electrostatic contributions to the free energy [i.e, $\Gamma_1(q)$ and $\Gamma_2(q)$] in real space. Thus, neglecting the bare inplane terms and transforming back equation (3.11) to real space we obtain

$$\begin{aligned}
F = & \int dx \int dx'\, \Gamma(x - x')\phi(x)\,\phi(x') \\
& - \int dx \int dx'\, \Gamma_2(x - x')\phi(x)\,\phi^2(x') \\
& - \frac{1}{2}\int dx \int dx'\, \Gamma_2(x - x')\phi^2(x)\phi^2(x')
\end{aligned} \qquad (3.13)$$

where

$$\Gamma(x) = (2\pi)^{-1}\int\left[\left(\frac{e}{\Sigma}\right)^2\Gamma_1(q) - \frac{1}{2}\Gamma_2(q)\right]e^{iqx}dq \qquad (3.14)$$

We see that the (local) electrostatic coupling produces a non-local (but exponentially decaying) effective interaction. Transforming $\Gamma_1(q)$ and $\Gamma_2(q)$ to real space we obtain for a one dimensional monolayer that $\Gamma_1(x)$ is proportional to the hyperbolic Bessel function $K_0(\kappa x)$. In the limit $\kappa x \gg 1$

$$\Gamma_1(x) \propto \frac{1}{\sqrt{\kappa x}}e^{-\kappa x} \qquad (3.15)$$

Similarly, for the effective interaction $\Gamma_2(x)$

$$\Gamma_2(x) = \frac{\Lambda^2}{\kappa_c}\delta(x) - \frac{\Lambda^2}{2\kappa_c\,\xi}e^{-|x|/\xi} \tag{3.16}$$

where $\xi = \sqrt{\kappa_c/\gamma}$ is the decay length to be distinguished from the DH screening length, κ^{-1} Thus, in addition to the GL short-range interactions we have an electrostatic interaction originating in the flat monolayer and characterized by the DH screening length κ^{-1}, and an effective short-range interaction due to the coupling which decays with a curvature dependent decay length ξ.

4. Discussion.

We have explored the interplay between inplane ordering and out-of-plane undulations of a two–component charged amphiphilic monolayer, mediated by screened electrostatic interactions. The inplane surface-charge distribution may, in general, be non-uniform. We considered two cases: *i*) a quenched ("frozen") amphiphile charge distribution; and *ii*) an annealed distribution which is determined by the electrostatic and short–range inplane interactions.

In the case of quenched surface charges we find that for a single *flat* monolayer, a homogeneous surface-charge density is electrostatically favorable over a periodic density modulation. An undulating monolayer is found to be advantageous, with respect to a planar membrane, provided an appropriate modulation is introduced in the ("frozen") surface-charge density. The latter case can be represented in terms of a local spontaneous curvature induced by the electrostatic interactions. In the limit of long wavelength undulations, we obtain the electrostatic contribution to the bending modulus κ_c of the membrane for a non-uniform fixed surface-charge density. For simple perturbations of an average homogeneous surface-charge distribution, which is known to rigidify the membrane, the electrostatic interaction acts to further enlarge κ_c. In future work, it will be also interesting to obtain the electrostatic contribution to the Gaussian curvature modulus $\bar{\kappa}_c$.

Bilayers are discussed only in the context of electrically decoupled monolayers, which is a good approximation for biological systems. In a rather artificial symmetric case, where the membrane is composed of two equally charged in-phase monolayers, the electrostatic interaction produces a positive contribution to the free energy, thus rigidifying the membrane. The general non-symmetric case can, however, exhibit electrically favorable undulations, though it is not entirely clear how to prepare two decoupled monolayers where each of them has the necessary quenched surface-charge density. The analysis presented here may be extended to various bilayer topologies with charge partitioning between the monolayers. In particular, electrostatically driven vesicle formation may be analyzed using similar ideas as Safran *et al.* [21] used for short-range interactions.

In the case of annealed surface charges, all constraints on inplane and out-of-plane configurations are relaxed. The order parameter $\phi(x)$ represents the spatially varying A/B relative concentration (as well as the local charge density since A is taken as neutral and B as charged). In an experimental setup, the average of ϕ is fixed. In our model this is achieved by tuning the chemical potential μ.

We obtain a phenomenological free energy incorporating short-range molecular interactions as well as the (screened) long-range electrostatic one. The coupling induces an effective interaction which decays exponentially with a curvature dependent length, $\xi = \sqrt{\kappa_c/\gamma}$ in addition to the electrostatic screening length κ^{-1} Similar coupling for short-range (non-electrostatic) interactions has been previously obtained [26, 27]. Here we directly calculate a coupling mechanism arising from the electrostatic interaction and find it to destabilize the homogeneous phase

as the effective stiffness coefficient $\tilde{d}$ can become negative. Note that as the surface tension becomes smaller, the range of the effective interaction ξ diverges.

The case of vanishing surface tension, $\gamma = 0$, needs a separate consideration. Here, the electrostatic coupling with the out-of-plane undulations (Eq. (3.9)) only changes the inplane transition temperature, without affecting the stability of homogeneous phase. Modulated phases can be stabilized only in the presence of an *inplane* instability, i.e., when the Γ_1 contribution to $g(q)$ yields a negative $\tilde{d}$ (Eq. (3.6)).

The quenched and annealed cases discussed are extreme limits as far as real phospholipid membranes are concerned. Biological membranes exhibit a wide range of inplane mobility from nearly static to ≈ 5 μm/s [16]. The membrane can be considered quenched (annealed) if the inplane relaxation time is larger than (comparable to) the relaxation time of the ions in the solution and the characteristic time scale related to the thermal undulations. In this sense the quenched limit may be valid for *fluid* membranes, e.g., consisting of slowly inter-diffusing fluid domains (A/B). Furthermore, exchange of phospholipids with the solution takes place on time scales of hours, leading to a rearrangement of the surface-charge density to a more favorable state. We would like to emphasize that throughout this work the membrane was assumed to be fluid-like, whereas in experiments on mixed membranes such as the PC/PG membranes [13-15], the membrane probably has solid-like domains embedded in a fluid membrane. This may result in other coupling terms between concentration and curvature.

The electrostatic calculations have been performed in the Debye-Hückel approximation, where the electrostatic equation of state is linearized. This limit of screened electrostatics is of relevance in biological systems characterized by an ever present electrolyte concentration. The electrostatic effects are generally found to be weak and $\delta\kappa_c^{el}$ for homogeneous systems is typically of the order of $k_B T$ or lower. In order to detect the effect of a non-uniform charge distribution on thermal undulations, flexible membranes are needed. Mixing charged cosurfactants with polar surfactants will lower κ_c and enable a non-uniform surface-charge density. Tuning the electrolyte concentration, pH and temperature, can result in a change in the rigidity. Another assumption made throughout the present work is that the phospholipids and electrolyte are monovalent. However, in many systems divalent ions are present and these ions are found to bind to the charged surface, forming (solid-like) clusters of ionic domains [13-15]. Hence, it may be necessary to use the full non-linear PB equation where the multivalency of the charged groups enters in a non-trivial fashion. Alternatively, one may need to go beyond the continuum description of the PB equation [28].

For the sake of simplicity we considered only one scalar inplane order parameter. We did not account for other degrees-of-freedom, such as a variable area per phospholipid headgroup, which is obviously affected by the electrostatic repulsion, and the hydrocarbon chain interaction. These factors dictate the packing of the amphiphile molecules and thus affect the spontaneous curvature and bending moduli. Furthermore, the aliphatic tails play a major role in the inplane structuring. In a more detailed description of the membrane structure, one can include additional order parameters, e.g., a tilt order parameter coupled to curvature [29].

Appendix A. Electrostatic free energy-the quenched limit.

We derive the free energy of the system described in section 2.1. The calculation is carried out in Fourier space to 2nd order in the undulation amplitude u. We choose

$$u(x) = u \cos qx \tag{A1}$$

$$\sigma(x) = \sum_{n=0}^{\infty} \left[\sigma_n^1(z) \sin nqx + \sigma_n^2(z) \cos nqx \right]. \tag{A2}$$

The electrostatic potential is a solution of the linearized PB equation, given in a dimensionless form by

$$\nabla^2 y(x, z) = \kappa^2 y(x, z) \tag{A3}$$

where $y = e\psi/k_B T$ is the dimensionless potential. In Fourier space the potential is

$$y(x, z) = y_0(z) + \sum_{n=1}^{\infty} \left[y_n^1(z) \sin nqx + y_n^2(z) \cos nqx \right]. \tag{A4}$$

Inserting equation (A4) into equation (A3) we obtain

$$y_n''(z) - \kappa_n y_n(z) = 0 \tag{A5}$$

$$\kappa_n^2 \equiv \kappa^2 + (nq)^2. \tag{A6}$$

Since y_n^1 and y_n^2 have the same expansion we omit the superscripts of y_n in the following.
The boundary conditions, given at infinity and on the membrane, are:

$$y(x, z \to \infty) = 0$$

$$\mathbf{n} \cdot \nabla y(x, z = u(x)) = -\frac{4\pi}{\varepsilon_w} \frac{e\sigma(x)}{k_B T} \tag{A7}$$

where $\mathbf{n}$ is the normal to the undulating surface $z = u(x)$

$$\mathbf{n} = \frac{(uq \sin qx, \, 1)}{\sqrt{g}} \tag{A8}$$

and $g = 1 + u^2 q^2 \sin^2 qx$ is the determinant of the curved surface metric. Solving equation (A5) with the boundary condition at $z \to \infty$ yields

$$y_n(z) = B_n \exp(-\kappa_n z) \tag{A9}$$

The dependence on the undulation mode, imposed by the second boundary condition, is in the coefficient $B(u)$, expanded consistently to 2nd order in u:

$$B_n(u) = B_n^{(0)} + B_n^{(1)} u + B_n^{(2)} u^2 \tag{A10}$$

Inserting equations (A4, A6, A8 and A9) into the boundary condition (A7) and expanding to 2nd order in u results in an equation for the coefficients $B_n^{(\iota)}$:

$$B_n^{(0)} = \frac{4\pi}{\varepsilon_w \kappa_n} \frac{e\sigma_n}{k_B T} \tag{A11}$$

$$
B_n^{(1)} = \frac{2\pi e}{\varepsilon_{\mathrm{w}} k_{\mathrm{B}} T} \left(\frac{\kappa_{n-1}^2 + (n-1)q^2}{\kappa_n \kappa_{n-1}} \sigma_{n-1} + \frac{\kappa_{n+1}^2 - (n+1)q^2}{\kappa_n \kappa_{n+1}} \sigma_{n+1} \right) \tag{A12}
$$

$$
\begin{aligned}
B_n^{(2)} = {} & \frac{\kappa_{n-1}^2 + (n-1)q^2}{2\kappa_n} B_{n-1}^{(1)} + \frac{\kappa_{n+1}^2 - (n+1)q^2}{2\kappa_n} B_{n+1}^{(1)} \\
& - \frac{(n-2)q^2 \kappa_{n-2} + \frac{1}{2}\kappa_{n-2}^3}{4\kappa_n} B_{n-2}^{(0)} + \frac{(n+2)q^2 \kappa_{n+2} - \frac{1}{2}\kappa_{n+2}^3}{4\kappa_n} B_{n+2}^{(0)} \\
& + \frac{\pi e}{\varepsilon_{\mathrm{w}} \kappa_n k_{\mathrm{B}} T} q^2 [\sigma_n - \tfrac{1}{2}\sigma_{n+2} - \tfrac{1}{2}\sigma_{n-2}] - \tfrac{1}{4}\kappa_n^2 B_n^{(0)} \tag{A13}
\end{aligned}
$$

We omitted the index i in σ_n^i since the results are the same for $i = 1, 2$. Substituting equations (A10 - A13) into (A4) determines the electrostatic potential. To calculate the free-energy per unit area we use equation (2.3). The integration is on the surface, thus $\mathrm{d}S = \sqrt{g}\,\mathrm{d}x$ as the system is invariant in the y direction. The free energy per unit area (averaged over the x coordinate) can be written in the following way:

$$
f = f_0 + f_1 u + f_2 u^2
$$

where

$$
f_0 = \frac{\pi}{\varepsilon_{\mathrm{w}}} \left[\frac{2(\sigma_0)^2}{\kappa} + \sum_{n=1}^{\infty} \sum_{i=1}^{2} \frac{\sigma_n^i \sigma_n^i}{\kappa_n} \right] \tag{A14}
$$

$$
f_1 = \frac{\pi}{2\varepsilon_{\mathrm{w}}} \sum_n \sum_{i=1}^{2} \left(\frac{\delta_n^+ + \delta_{n+1}^-}{\kappa_n \kappa_{n+1}} - 2 \right) \sigma_n^i \sigma_{n+1}^i \tag{A15}
$$

$$
\begin{aligned}
f_2 = {} & \frac{\pi}{4\varepsilon_{\mathrm{w}}} \sum_n \sum_{i=1}^{2} \left(\frac{\delta_{n-1}^+ \delta_n^-}{\kappa_n^2 \kappa_{n-1}} + \frac{\delta_{n+1}^- \delta_n^+}{\kappa_n^2 \kappa_{n+1}} - \frac{2\kappa_n^2 - 2q^2}{\kappa_n} \right) \sigma_n^i \sigma_n^i \\
& + \frac{\pi}{4\varepsilon_{\mathrm{w}}} \sum_n \sum_{i=1}^{2} \left(\frac{\delta_{n+1}^+ \delta_n^+ + \delta_{n+1}^- \delta_{n+2}^-}{\kappa_n \kappa_{n+1} \kappa_{n+2}} \right. \\
& \left. - \frac{\kappa_{n+2}^2 + \kappa_n^2 - 2q^2}{2\kappa_{n+2}} - \frac{\kappa_{n+2}^2 + \kappa_n^2 - 2q^2}{2\kappa_n} \right) \sigma_n^i \sigma_{n+2}^i \tag{A16}
\end{aligned}
$$

where $\delta_n^\pm \equiv \kappa_n^2 \pm nq^2$. In the expressions for f_1 and f_2 different charge-density modes $\{\sigma_n\}$ are coupled. This coupling emerges from the boundary condition at the surface, equation (2.2), which is not bilinear in u and σ. The limits of small and large q-vectors of equations (A15, A16) are discussed in section 2. Also note that the first terms in the sum, $n = 0$ and 1, have to be calculated separately. For example, for $\sigma(x) = \sigma_0 + \sigma_2^2 \cos 2qx$ the calculation of f_2 yields

$$
\begin{aligned}
f_2 = {} & \frac{\pi}{\varepsilon_{\mathrm{w}}} \left(\frac{\delta_1^- \delta_0^+}{\kappa^2 \kappa_1} - \frac{\kappa^2 - q^2}{\kappa} \right) \sigma_0 \sigma_0 \\
& + \frac{\pi}{2\varepsilon_{\mathrm{w}}} \left(\frac{\delta_1^+ \delta_0^+ + \delta_1^- \delta_2^-}{\kappa \kappa_1 \kappa_2} \right. \\
& \left. - \frac{\kappa_2^2 + \kappa^2 - 2q^2}{2\kappa_2} - \frac{\kappa_2^2 + \kappa^2 - 2q^2}{2\kappa} \right) \sigma_0 \sigma_2^2 \tag{A17}
\end{aligned}
$$

where an additional $\sigma_2\sigma_2$ term (same as in equation (A16)), is omitted from equation (A17) for clarity purposes. Note that this f_2 (Eq. (A17)) is used to calculate the first two terms of $\delta\kappa_c^{el}$, equation (2.12), and not the $n = 0$ term of equation (A16).

Appendix B. Motivation for the coupling term.

The phenomenological coupling term F_c of section 3 represents the relation between the membrane curvature and its surface-charge density mediated by the electrolyte. The specific dependence of the coupling term F_c on the undulation and the surface-charge density is motivated by the following considerations. Using the linear PB equation, the electrostatic free energy of an undulating membrane with a general *annealed* surface-charge density may be obtained for a single undulation mode [5]. The derivation is similar to the one performed in section 2. However, since the charge density and the undulation are allowed to mutually adjust, one must *consistently* expand $\sigma(x)$ in the undulation amplitude, in addition to the Fourier expansion $\sigma(x) = \sum_{n=0}^{\infty} \sigma_n \cos nqx$. Expanding in powers of κu

$$\sigma_n = \sum_{i=0}^{\infty} (\kappa u)^i \sigma_{in}$$

where σ_{in} is the ith Taylor coefficient of the nth Fourier mode of the surface-charge density. The solution for the electrostatic potential, in the limit of decoupled monolayers, is

$$\psi = \psi_0 + u\frac{4\pi}{\varepsilon_w}\left[\left(\sigma_{11} - \frac{1}{2}\sigma_{00}(\frac{\kappa_1}{\kappa} - 1)\right)I_1\cos qx + \sum_{n=2}^{\infty}\sigma_{1n}I_n\cos nqx\right] + O(u^2)$$

where

$$I_n = \left(\frac{\kappa_n}{\kappa} + \frac{nq\varepsilon_o}{\kappa\,\varepsilon_w}\right)^{-1} \quad;\quad \kappa_n \equiv \sqrt{\kappa^2 + (nq)^2}$$

and ψ_0 is the potential of the flat membrane. The free energy may readily be calculated using the charging method [25]. Applying a variational principle to the free energy with respect to the surface-charge density, has been shown to correspond to an electric equipotential surface [5]. For our purpose, we are interested in the u-dependent energy terms prior to the minimization, since they may be interpreted as *electrostatic coupling terms* of the surface-charge density and the undulation. For the sake of simplicity, we limit ourselves to the linear term in u denoted $\tilde{f}_1$

$$\tilde{f}_1 = \frac{\pi}{\varepsilon_w}\left[I_1\left(\sigma_{11} - \frac{1}{2}\sigma_{00}(\frac{\kappa_1}{\kappa} - 1)\right)\sigma_{01} + \sum_{n=2}^{\infty}I_n\sigma_{0n}\sigma_{1n}\right]. \tag{B1}$$

Expanding equation (B.1) in powers of q/κ, we identify the coupling of the curvature and the surface-charge density since the curvature is proportional to uq^2. This implies that the coupling is quadratic in the surface-charge density, in agreement with equation (A15) obtained for the quenched case. However, equation (B.1) was derived for a single mode undulation, as it is difficult to obtain such a term for a general annealed undulation using the PB equation. The coupling term can thus only be inferred from the q/κ expansion of the single-mode result, and to lowest order in curvature we choose:

$$F_c = \frac{\Lambda\Sigma^2}{e^2}\int \mathrm{d}x\, c(x)\sigma^2(x) \simeq \frac{\Lambda\Sigma^2}{e^2}\int \mathrm{d}x\, \frac{\mathrm{d}^2 u}{\mathrm{d}x^2}\,\sigma^2(x) \tag{B2}$$

which, as implied, is linear in the curvature and quadratic in the surface-charge density. The 2nd order term in equation (B1) contributes a coupling term of higher order in curvature, or it may be interpreted as an electrostatic contribution to κ_c in equation (3.1). For a general undulation $u_q = \int dx \, u(x) e^{iqx}$ we find that $F_c \sim \int dq \, u_q q^2 \sigma_q^2$. Comparing this to equation (B1) in the limit of small q implies that the coupling coefficient scales as $\varepsilon_w^{-1} \kappa^{-2}$ for long wavelength undulations in agreement with equation (2.8).

References

[1] Safinya C. R., in Phase Transitions in Soft Condensed Matter, T. Riste and D. Sherrington Eds. (Plenum, N.Y., 1990).

[2] Helfrich W., Z. Natureforsch. 28c (1973) 693.

[3] Winterhalter M., Helfrich W., J. Phys. Chem. 92 (1988) 6865.

[4] Kiometzis M., Kleinert H., Phys. Lett. A 140 (1989) 520.

[5] Fogden A., Ninham B. W., Langmuir 7 (1991) 590.

[6] Fogden A., Mitchell. D. J., Ninham B. W., Langmuir 6 (1990) 159.

[7] Pincus P., Joanny J. -F., Andelman D., Europhys. Lett. 11 (1990) 763.

[8] Bensimon D., David F., Leibler S., Pumir A., J. Phys. France 51 (1990) 689.

[9] Lekkerkerker H. N. W., Physica A 159 (1989) 319.

[10] Duplantier B., Goldstein R. E., Pesci A. I., Romero-Rochin V., Phys. Rev. Lett. 65 (1990) 508.

[11] Kantor Y., Kardar M., Europhys. Lett. 9 (1989) 53.

[12] Harden J. L., Marques C., Joanny J. -F., Andelman D., Langmuir 8 (1992) 1170.

[13] Findlay E. J., Barton P. G., Biochemistry 17 (1978) 2400.

[14] Swanson J. E. , Feigenson G. W., Biochemistry 29 (1990) 8291.

[15] Galla H. J., Sackmann E., Biochem. Biophys. Acta 401 (1975) 509.

[16] Gebhardt C., Gruler H., Sackmann E., Z. Natureforsch. 32c (1977) 581.

[17] Janiak M. J., Small D. M., Shipley G. G., J. Bio. Chem. 254 (1979) 6068.

[18] Parsegian V. A., Biophys. J. 44 (1983) 413.

[19] Wack D. C., Webb W. W., Phys. Rev. Lett. 61 (1988) 1210.

[20] Kaler E. W., Murthy A. K., Rodriguez B. E., Zasadzinski J. A. N., Science 245 (1989) 1371.

[21] Safran S. A., Pincus P., Andelman D., Science 248 (1990) 354;
Safran S. A., Pincus P., Andelman D., MacKintosh F. C., Phys. Rev. A 43 (1991) 1071.

[22] Hofmann S., Rauscher A., Hoffmann H., Ber. Bunsenges. Phys. Chem. 95 (1991) 153.

[23] The valency of the electrolyte and counter-ions has been taken as one. In the linear regime the valency does not have any major effect.

[24] Israelachvili J. N., Intermolecular and Surface Forces (Academic Press, London, 1990).

[25] Verwey E. J. W., Overbeek J. Th. G., Theory of the Stability of Lyophobic Colloids (Elsevier, N.Y., 1948).

[26] Leibler S., Andelman D., J. Phys. France 48 (1987) 2013.

[27] Andelman D., Kawakatsu T., Kawasaki K., Europhys. Lett. 19 (1992) 57.

[28] Attard P., Mitchell D. J., Ninham B. W., J. Chem. Phys. 88 (1988) 4987.

[29] MacKintosh F. C., Lubensky T. C., Phys. Rev. Lett. 67 (1991) 1169;
MacKintosh F. C., Lubensky T. C., unpublished.