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Electrostatic Interactions, Curvature Elasticity, and Steric Repulsion in Multimembrane Systems.

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Abstract. – The effects of electrostatic interactions on steric repulsion and curvature elasticity are considered for dilute multimembrane systems as a function of the electrolyte strength, surface charge and inter-membrane spacing. In the strong electrolyte limit, the electrostatic interactions are screened and the steric repulsion dominates. For weak electrolytes, the electrostatic interactions cut-off the out-of-plane undulations and change significantly the membrane bending constant in qualitative agreement with recent experiments.

Amphiphiles in solution show a wealth of self-organizing structures [1]. For example, natural phospholipids or artificial surfactants dissolved in water can form multilamellar or multivesicular structures consisting of a stack of alternating lipid and water layers. Their precise structure and stability depend on the lipid chemical character, temperature, lipid concentration and surface charge, ionic strength of the aqueous solution (salt concentration) and in some cases the type and amount of an added co-surfactant (usually a short-chain alcohol). In the lamellar phase, the inter-membrane interactions arise from attractive van der Waals and repulsive electrostatic interactions [2]. In addition, for very small inter-lamellar spacing of less than 20 Å, it has been shown [2-4] that repulsive hydration forces play an important role in preventing membranes from adhering to one another. One of the unique features of fluid lipid membranes is their extremely low surface tension leading to strong out-of-plane undulations governed by the membrane bending rigidity [5-12], k_c which can be made quite small, *e.g.*, by adding a co-surfactant [8, 11] (pentanol) and producing a stack of very flexible membranes.

In 1978, Helfrich [5] argued that the entropically induced out-of-plane fluctuations of a stack of membranes cause an effective repulsion due to the reduction in fluctuation entropy experienced by each membrane bounded between its two adjacent neighboring membranes. The predicted repulsion interaction per unit area varies as

$$F_u \simeq T^2/k_c d^2 \tag{1}$$

or equivalently the disjoining pressure $\Pi_d = -\partial F_u/\partial d \sim 1/d^3$, where d is the average inter-membrane distance, T is the temperature in units where the Boltzmann constant is set to be unity.

More recently, Helfrich's predictions have been tested experimentally using X-ray [8, 10, 11] and light scattering [8, 12] experiments. For a lamellar phase diluted with oil [12], the analysis of the structure factor, $S(q)$, gives an agreement with the Helfrich interactions $\sim 1/d^2$. In a different series [10-12], when the lamellar phase was diluted with pure water, electrostatic interactions dominated over the Helfrich interactions (the membranes were charged). However, when a substantial amount of salt was added, so that the Debye-Hückel screening length was a few angströms, the signature of the Helfrich interactions prevailed again [10]. One of the important features of the entropically-induced repulsion is its *universality*; namely, the interactions do not depend on any microscopic parameters [11].

In this letter, we address specifically the cases studied in the experiments: how would electrostatic interactions of *fluctuating* lamellar phases combine with the entropic-driven Helfrich interactions? Motivated by the above-mentioned experiments, we study the relatively larger inter-lamellar distances and neglect van der Waals and hydration forces. Previous studies on how the direct interactions affect the steric repulsion exist [13, 14] also in connection with the unbinding transition [15, 16]. We discuss electrostatic interactions in two cases: i) within a local approximation valid for weakly fluctuating membranes; ii) a more elaborate calculation is done for the high salt case, where the linearized Poisson-Boltzmann (PB) equation is solved for fluctuating membranes. In addition, the electrostatic contribution to the bending constant k_c is also estimated for strong and weak electrolytes.

In order to estimate how the electrostatic interactions modify the membrane fluctuations, we imagine one of the membranes fluctuating against curvature with small displacement $u(x, y)$ relative to a reference plane. The increment in the free energy of the fluctuating membrane (per unit area) is [17]

$$F_u = F_{\text{bend}} + \Delta F_{\text{el}}, \tag{2}$$

where $\Delta F_{\text{el}} = (1/2)(\partial^2 F_{\text{el}}/\partial d^2)\, u^2$, and F_{bend} is the cost in curvature energy $(1/2)\, k_c(\nabla^2 u)^2$ where surface tension is explicitly taken to be zero. Estimation of the electrostatic term relies on a Deryagin-like approximation [2], in which an expansion about the flat result is performed. In Fourier space

$$F_u = \frac{1}{2} k_c \sum_q \tilde{u}_q^2 (q^4 + \xi^{-4}), \tag{3}$$

where $\xi^{-4} = k_c^{-1}\, \partial^2 F_{\text{el}}/\partial d^2$ and ξ is the in-plane electrostatic correlation length.

In the limit of small fluctuations, we determine ξ from the solution of the Poisson-Boltzmann (PB) equation [18, 2] for two flat and charged plates with surface charge σ and separation d. Figure 1 shows the various crossover regimes in the PB equation as a function of the three relevant lengths: the separation d, the Debye-Hückel screening length,

$\varkappa^{-1} = (8\pi n_\infty l)^{-1/2}$, and the Gouy-Chapman length, $\lambda = e/2\pi l\sigma$, where n_∞ is the bulk electrolyte concentration, $l = e^2/4\pi\varepsilon\varepsilon_0 T \simeq 7$ Å is the Bjerrum length for an aqueous solution of dielectric constant, $\varepsilon = 80$. Four regions are seen in fig. 1: i) the Debye-Hückel region (IV), where the PB equation can be linearized $\varkappa d > 1$ and $\lambda > \varkappa^{-1}$, or $\varkappa d < 1$ and $\varkappa^2 \lambda d > 1$. ii) The intermediate nonlinear but weak overlap region (III), $\varkappa d > 1$ and $\lambda < \varkappa^{-1}$. iii) The ideal-gas region (I) $\varkappa d < 1$, $\lambda > d$, $\varkappa^2 \lambda d < 1$, and iv) the Gouy-Chapman region (II) $\varkappa d < 1$, $\lambda < d$.

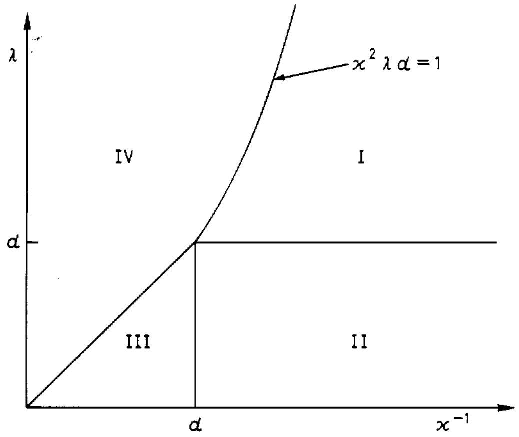

Fig. 1. – Various regimes for the electrostatic interaction between two flat and charged plates in an electrolyte. Region I: the ideal-gas regime, with a free energy of interaction between the plates, $F_{\mathrm{el}} = (T/\pi\lambda l) \log d$. Region II: Gouy-Chapman regime with $F_{\mathrm{el}} = \pi T/2ld$. Region III: the intermediate regime with $F_{\mathrm{el}} = (8T\varkappa/\pi l) \exp[-\varkappa d]$. Region IV: the linear Debye-Hückel regime, $F_{\mathrm{el}} = (T/\pi l \lambda^2 \varkappa)(\mathrm{ctgh}\, \varkappa d/2 - 1)$.

In experiments [8-12], the charge density is one unit charge per polar head, *i.e.* $e/\sigma \simeq (30 \div 100)$ Å^2, and $\lambda \simeq (2 \div 3)$ Å is much smaller than the inter-lamellar spacing 20 Å $< d <$ 800 Å. Thus, we concentrate only on the three regions (II, III, IV) with $d > \lambda$. In the Gouy-Chapman region (II), $F_{\mathrm{el}} = \pi T/(2ld)$, leading to $\xi = d(k_c l/\pi T d)^{1/4}$. Assuming (and later checking) that we are in the small fluctuation limit, *i.e.* the r.m.s. fluctuation $\langle u^2 \rangle$ is much smaller than d^2, the equipartition of energy gives

$$<u^2(x,y)> = \frac{1}{\text{Area}} \frac{T}{k_c} \sum_q \frac{1}{q^4 + \xi^{-4}} = \frac{T}{8k_c} \xi^2 = \frac{d^2}{8} \left(\frac{T}{k_c} \frac{l}{\pi d} \right)^{1/2}. \qquad (4)$$

For flexibile and dilute lamellae [12], $k_c \simeq T$ and $l < d$ so that from (4) $\langle u^2 \rangle \ll d^2$.

Comparing the electrostatic and undulatory parts of the free energy, $F_{\mathrm{el}} = \pi T/2ld$ and $F_{\mathrm{u}} = T/(8\xi^2)$, we get $F_{\mathrm{u}}/F_{\mathrm{el}} = (1/4\pi)(ld/\xi^2) \simeq (Tl/k_c d)^{1/2} < 1$. Therefore, in the limit of weak-electrolyte concentrations ($\varkappa \to 0$), and nonscreened electrostatic interactions, the bending repulsion and the correction to the electrostatic interaction can be treated as small perturbation since $\langle u^2 \rangle = (T/8k_c)\xi^2 < d^2$. The hard-wall repulsion between neighboring membranes has up to now been neglected; as soon as the fluctuation $\langle u^2 \rangle$ is smaller than d^2, it gives an exponentially small correction to the bending energy.

We now turn to the limit of screened electrostatic interactions, $\varkappa d \gg 1$. As shown in fig. 1, there are two different regimes in this limit: for $\varkappa^{-1} > \lambda$ (region III), the PB equation is nonlinear and $F_{\mathrm{el}} = (8T\varkappa/\pi l) \exp[-\varkappa d]$, whereas for the Debye-Hückel regime, $\varkappa^{-1} < \lambda$

(region IV), $F_{\mathrm{el}} = 2T/(\pi\varkappa l\lambda^2)\exp[-\varkappa d]$. Calculating ξ from (4) we get

$$\xi = (\pi l k_c/8\varkappa^3 T)^{1/4}\exp[\varkappa d/4], \qquad \varkappa^{-1} > \lambda, \tag{5a}$$

$$\xi = (\pi l\lambda^2 k_c/2\varkappa T)^{1/4}\exp[\varkappa d/4], \qquad \varkappa^{-1} < \lambda. \tag{5b}$$

Clearly, in this limit the dominant interaction is the steric repulsion calculated by imposing the constraint $\langle u^2\rangle \simeq d^2$. One of the ways to estimate the effect of the constraint is by an addition of a $A\int u_q^2\,\mathrm{d}\boldsymbol{q}$ term (Lagrange multiplier) in the free energy and adjusting the value of A to satisfy the constraint $\langle u^2\rangle \simeq d^2$

$$F_{\mathrm{u}} \simeq \frac{T^2}{k_c d^2}\left[1 - \mathrm{const}\left(\frac{k_c}{T}\right)^2\left(\frac{d}{\xi}\right)^4\right]. \tag{6}$$

The undulating forces are thus reduced by the electrostatic interactions. Since $\xi \sim \exp[\varkappa d/4]$, the correction term in (6) is exponentially small and the main contribution to the undulation free energy is the Helfrich steric repulsion.

To complete the calculation presented above within the Deryagin approximation, we study the linearized version of the PB equation (region IV) for the electric potential ψ, $\nabla^2\psi = \varkappa^2\psi$, valid for concentrated electrolytes. For simplicity, a one-dimensional membrane described by a displacement $u(x)$ is considered. One of the boundary conditions is the discontinuity of the normal component of the electric field on the membrane, and the other is chosen to be the vanishing of the z-component of the electric field at the midplane between membranes.

Looking at a single q-mode undulation of the membrane $u(x) = u_q\cos qx$, and solving the Debye-Hückel equation up to second order in the undulation amplitude, the resulting electrostatic free energy of the membrane (bilayer) is

$$F_{\mathrm{el}} = \frac{\sigma^2}{\varepsilon\varkappa}\,\mathrm{ctgh}\,\frac{1}{2}\varkappa d\left[1 + \frac{u_q^2\varkappa}{4}\left(\frac{q^2}{\varkappa^2} - 2 + 2\frac{\varkappa}{\varkappa_1}\,\mathrm{ctgh}\,\frac{1}{2}\varkappa_1 d\,\mathrm{ctgh}\,\frac{1}{2}\varkappa d\right)\right], \tag{7}$$

where $\varkappa_1^2 = \varkappa^2 + q^2$.

It is useful to expand (7) in powers of q. The zeroth-order term is the overall electrostatic contribution, and the second-order term renormalizes the surface tension but is dropped altogether, since we assume a zero surface tension

$$F_{\mathrm{el}}(q=0) = \frac{\sigma^2}{\varepsilon\varkappa}\,\mathrm{ctgh}\,\frac{1}{2}\varkappa d\left[1 + \frac{1}{2}u_q^2\varkappa^2\sinh^{-2}\frac{1}{2}\varkappa d\right]. \tag{8}$$

The fourth-order term in q in (7) renormalizes the bending constant, $k_c' = k_c + \delta k_c|_{\mathrm{el}}$, where for $\varkappa d > 1$

$$\delta k_c|_{\mathrm{el}} = 3\sigma^2/4\varepsilon\varkappa^3 \simeq T/\varkappa^3 l\lambda^2 \tag{9}$$

and for $\varkappa d < 1$, $\varkappa^2\lambda d > 1$

$$\delta k_c|_{\mathrm{el}} \simeq (T/\varkappa^3 l\lambda^2)(\varkappa d)^{-3}. \tag{10}$$

Using (8) and (3), the in-plane correlation length is then given by

$$\xi^{-4} \simeq \frac{\sigma^2\varkappa}{\varepsilon k_c'}\cosh\frac{1}{2}\varkappa d\,\sinh^{-3}\frac{1}{2}\varkappa d. \tag{11}$$

We note that in the limit $\varkappa d \gg 1$, (11) reduces to the previously obtained result, eq. (5*b*), with the renormalized k'_c replacing k_c.

Equation (9) is in agreement with a previous solution of the electrical bilayer problem for a single charged cylinder or sphere [19, 20]. Moreover, it reveals an additional important effect of electrostatic interactions. Not only they introduce a cut-off in q-space for the undulations, but they change the bending constant as well. In the above results, one should thus replace the bending constant k_c by a renormalized one $k'_c = k_c + \delta k_c|_{el}$, where $\delta k_c|_{el}$ is the electrostatic contribution. In recent studies [21, 22], $\delta k_c|_{el}$ has been calculated in the intermediate regime (region III) and found to be

$$\delta k_c|_{el} = T/\varkappa\pi l, \qquad \varkappa\lambda < 1 \text{ and } \varkappa d \gg 1. \tag{12}$$

For the no-electrolyte limit (region II), we estimate $\delta k_c|_{el}$ using scaling and continuity arguments

$$\delta k_c|_{el} \simeq Td/l. \tag{13}$$

This result crosses over smoothly to the intermediate-regime result (12) by replacing d by $\varkappa^{-1}$. It is also in agreement with an expansion of the exact result of an aqueous solution in between cylinders [23]. Similarly, in the ideal-gas limit (region I), $\delta k_c|_{el}$ is conjectured to be $\sim T\lambda/l$ with a correct crossover into the Gouy-Chapman (region II) and Debye-Hückel (region IV) regimes. We note that for any physical system, there is a finite amount of ions in solution and (13) holds only for small enough d.

To summarize, we have investigated the effect of electrostatic interactions on undulating lamellar phases. When the interactions are screened ($\varkappa d \gg 1$), the long-range steric repulsion is dominant and the change in the bending constant is small, $\delta k_c|_{el}/k_c \ll 1$. As $\varkappa d$ decreases by decreasing d or reducing the salt concentration, we expect a crossover first into an intermediate regime and then into the strong overlap Gouy-Chapman regime where the electrostatic repulsion controls the membrane undulations. For $d = 20$ Å, $\delta k_c|_{el}$ is estimated to be of the order of T from (13) in qualitative agreement with experiments [12], where the increase of the bending constant in the nonscreened electrostatic case compared with the screened one can be interpreted as an increase due to electrostatic interactions. This increase has been estimated experimentally to be about 0.8 T.

On the theoretical side, a more refined calculation for $\delta k_c|_{el}$ is desirable in the Gouy-Chapman regime, since it was obtained only through scaling arguments. On the experimental side, a systematic study of undulations and changes in k_c as function of electrolyte strength is needed to check some of our findings. It will be interesting to see if the two crossovers for $d > \lambda$ can be observed.

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