1690 *Langmuir* **1992,** *8,* 1690–1691

Self-Consistent Theory of a Charged Multimembrane System

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Received December 9, 1991. In Final Form: March 13, 1992

Although the theory of isolated curved surfaces bearing charge is developing rapidly,[1–10] the resolution of the problem of interacting surfaces is progressing at a substantially slower pace. Pincus, Joanny, and Andelman[11] have attempted to incorporate charge into the Helfrich theory.[12] They replace the real stack of interacting and fluctuating membranes by one membrane undulating between two charged planes which are postulated to be perfectly flat and fixed in space. Hence, the configurations of the test membrane are constrained by an externally imposed potential which is independent of the undulations. Lipowsky and Leibler have earlier adopted a similar starting point to study the effect of attractive forces.[13] Actually, the two surrounding membranes themselves are not flat but perturbed by thermal fluctuations so in principle the test membrane is restricted by a fluctuating external field. This problem is of course very difficult as it stands, but here I introduce an average of the fluctuating potential which is determined self-consistently at the end of the analysis by minimizing the total free energy. My approach is similar in spirit to a recent theory of the nematic liquid crystal of undulating, semiflexible surfaces in which the fluctuating excluded-volume interactions are also taken into consideration on a mean-field level.[14]

Membranes are often so highly charged that we must use the nonlinear Poisson–Boltzmann equation to calculate the electrostatic potential ϕ. Nevertheless, it is possible to investigate interacting, undulating membranes in the experimentally important case where nonlinear screening does not interfere with the undulations. First, we recall the form of the Poisson–Boltzmann potential at a distance x from a flat plate of positive surface charge density σ (i.e. number of charges per unit area)

$$\Psi(x) = 2 \log \left[\frac{1 + \pi \Sigma_{\mathrm{eff}} e^{-\kappa x}}{1 - \pi \Sigma_{\mathrm{eff}} e^{-\kappa x}} \right] \qquad (1)$$

$$\Sigma_{\mathrm{eff}} \equiv \frac{(1 + 4\pi^2 \Sigma^2)^{1/2} - 1}{2\pi^2 \Sigma} \qquad (2)$$

Here, $\Sigma \equiv Q\sigma/\kappa$ is a dimensionless surface charge density in terms of two basic electrostatic scales (the Bjerrum length $Q = q^2/\epsilon k_{\mathrm{B}}T$ and the Debye length $\kappa^{-1} = (8\pi Q n)^{-1/2}$, where k_{B} is Boltzmann's constant and T the temperature of the system, q is the elementary charge, and the solvent of permittivity ϵ contains an excess of monovalent electrolyte of concentration n) and the dimensionless potential $\Psi \equiv q\phi/k_{\mathrm{B}}T$.

At large distances (i.e. when $\pi\Sigma_{\mathrm{eff}} \exp(-\kappa x) \ll 1$) the potential has a screened form

$$\Psi \approx 4\pi \Sigma_{\mathrm{eff}} e^{-\kappa x} \qquad (3)$$

Furthermore, in the Debye–Hückel approximation valid at low enough charge densities ($\Sigma \ll 1$), the potential is given by eq 3 with $\Sigma_{\mathrm{eff}} = \Sigma$. Therefore, as long as we do not probe the inner double layer, we may as well replace the real plate of charge density σ in the Poisson–Boltzmann approximation by a plate of effective charge density $\sigma_{\mathrm{eff}} \equiv \kappa \Sigma_{\mathrm{eff}}/Q$ in the Debye–Hückel approximation. The effective charge density is lower than σ because a number of counterions are "condensed" within the inner double layer. It is important to realize that eq 3 then results from a *linear* superposition of Debye–Hückel potentials from effective charges on the surface of the plate. In our analysis of the interactions between undulating charged membranes, we require that the average distance D between two membranes is somewhat larger than both the Debye length and the typical amplitude of the undulations. This ensures that the condensed counterions are not perturbed by the membrane fluctuations. Accordingly, in our stack of membranes the actual surface charge density σ is replaced by σ_{eff} and all the effective charges in the system interact by simple superposition.

Next, I assume the reference configuration of the multimembrane system is a stack of equidistant flat planes (distance = D). Smectic director fluctuations are disregarded. A complete theory would include not only these but also their coupling to the undulations of the individual membranes (in a way analogous, say, to a recent theory of directed polymers[15]). At this juncture one might wish to assume that the system is adequately described by a single membrane distribution function f in order to set up a self-consistent field theory. Even this problem turns out to be prohibitively difficult, so instead I postulate a Gaussian Ansatz, presumably correct to the leading order

$$f = (\pi^{1/2} d)^{-1} e^{-x^2/d^2} \qquad (4)$$

which expresses the fluctuations from the reference configuration. It depends on a variational parameter d. Equation 4 is valid for every membrane in the system; x is the distance from a point on the surface of a particular membrane that we happen to consider to its corresponding surface in the reference configuration. The membrane area is presumably very large so that end effects may be neglected and eq 4 pertains to every point of the fluctuating surface. The amplitude of the undulations is of order d, so we must have $d \ll D$ in view of the discussion above. Equation 4 is normalized to unity.

Equation 4 implies a deflection length[12,14] (also termed an undulation length[12] or in-plane correlation length[11]) for a fluid membrane

$$\lambda \approx K^{1/2} d \qquad (5)$$

where K is the elastic bending modulus of the membrane scaled by $k_{\mathrm{B}}T$. If we suppose that the effective platelets are highly ordered ($\lambda \gg d$ or $K \gg 1$), it is straightforward to obtain the electric potential of a particular membrane which is renormalized by its own fluctuations. This is a linear superposition of Debye potentials from all the undulations or equivalently a superposition of flat wall potentials since all points of the surface have the same

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distribution

$$\Psi_{\mathrm{R}}(y) = \int_0^\infty (\Psi(y+x) + \Psi(y-x))\, f(x)\, \mathrm{d}x = 4\pi\Sigma_{\mathrm{eff}} \exp(-\kappa y + {}^1/_4\kappa^2 d^2) \tag{6}$$

Here, y is the distance from the respective membrane in the reference configuration. If we now consider a test membrane surrounded by two fluctuating membranes—but no more in view of the electrostatic screening—it experiences on average the sum of two potentials given by eq 6.

$$\Psi_{\mathrm{tot}}(y) = \Psi_{\mathrm{R}}(D+y) + \Psi_{\mathrm{R}}(D-y) \tag{7}$$

Again, because the fluctuating platelets of the test membrane are highly ordered, the electrostatic free energy per unit area is simply

$$F_{\mathrm{el}}/k_{\mathrm{B}}T = \sigma_{\mathrm{eff}} \int_{-\infty}^{\infty} \Psi_{\mathrm{tot}} f\, \mathrm{d}x = 8\pi\Sigma^2_{\mathrm{eff}}\kappa Q^{-1} \exp(-\kappa D + {}^1/_2\kappa^2 d^2) \tag{8}$$

As expected this increases with d and indeed very rapidly when $\kappa d \gg 1$ because of the renormalization. On the other hand there is also an opposing Helfrich free energy[12] of entropic origin which arises because the test membrane is confined owing to the restriction (eq 4)

$$F_{\mathrm{H}}/k_{\mathrm{B}}T = c/Kd^2 \tag{9}$$

The constant c is close to ${}^1/_{32}$. As we decrease d, more and more configurations are frozen out so that F_{H} increases. On minimizing the total free energy $F_{\mathrm{el}} + F_{\mathrm{H}}$, we get

$$A^4 e^{A^2/2} = \frac{cQ\kappa e^{\kappa D}}{4\pi K \Sigma^2_{\mathrm{eff}}} \tag{10}$$

$$A \equiv \kappa d$$

For a highly charged membrane the effective charge density Σ_{eff} reduces to a constant π^{-1} and the bending modulus K to $1/\pi Q\kappa$ according to recent work.[2,3] Equation 10 simplifies to

$$A^4 e^{A^2/2} \simeq \pi^2 (Q\kappa)^2 e^{\kappa D}/128 \tag{11}$$

In this case, $A = \kappa d$ is a function of two dimensionless variables $Q\kappa$ and κD, which is tabulated in Table I (recall that the Bjerrum length $Q = 0.71$ nm and the Debye radius $\kappa^{-1} = 0.30 n_{\mathrm{s}}^{-1/2}$ nm for an aqueous monovalent electrolyte of concentration n_{s} (in M) at room temperature). It is remarked that A is generally substantially greater than unity; i.e. the amplitude of the undulations $d/2^{1/2}$ is greater than the Debye radius. In other words the renormalizing factor $\exp({}^1/_2 A^2)$ in eq 8 is very influential. Hence, the undulations of the surrounding layers exert a considerable effect on the fluctuations of a test membrane. If we were to set A much smaller than unity in eq 10, we would recover an expression first derived by Pincus et al.[11] This is what one expects since in this limit the surrounding surfaces are effectively flat on the scale of the Debye length. However, this regime occurs at small separations D.

Table I. Dimensionless Quantity $A \equiv \kappa d$ as a Function of $Q\kappa$ and κD

	κD		
$Q\kappa$	10	30	100
0.3	2.1	6.0	13.0
0.1	1.5	5.6	12.9
0.03	1.0	5.3	12.7
0.01	0.6	4.9	12.5

It is possible to obtain a convenient expression for the osmotic pressure P needed to keep the membranes together, from eqs 8, 9, and 10

$$P = -\frac{\partial(F_{\mathrm{el}} + F_{\mathrm{H}})}{\partial D} = +\frac{2ck_{\mathrm{B}}T}{K\kappa d^4} \tag{12}$$

Accordingly, the pressure scales essentially as d^{-4} but there is no simple power law in terms of the separation D as can be seen from Table I.

The idea that the potential exerted on a test membrane is renormalized by the fluctuations of the surrounding layers is not new. Evans and Parsegian[16] and Sornette and Ostrowsky[17] added a compression term to the bending Hamiltonian parametrized by a modulus. The modulus was eliminated at the end of the analysis (but not by a variational method). A discussion of these works is deferred to a forthcoming publication. It is of considerable interest to investigate the salt-free case, but then one has to come to terms with the coupling of the counterion distribution to the undulations. One way of tackling this nontrivial problem may be to suppose the counterions within the inner double layer condense nonuniformly for each membrane configuration in a manner analogous to the one introduced in ref 18 for linear micelles. It would also be useful to examine the effect of the undulations of all the membranes by renormalization theory. So far most renormalization analyses start from a Hamiltonian describing one membrane fluctuating in a bare or unrenormalized field exerted by one nearby flat plane.[19]

Acknowledgment. I thank Henk Lekkerkerker for continued discussions on surfaces.

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