Charge-Fluctuation-Induced Nonanalytic Bending Rigidity

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In this Letter, we consider a neutral system of mobile positive and negative charges confined on the surface of curved films. This may be an appropriate model for (i) a highly charged membrane whose counterions are confined to a sheath near its surface and (ii) a membrane composed of an equimolar mixture of anionic and cationic surfactants in aqueous solution. We find that the charge fluctuations contribute a nonanalytic term to the bending rigidity that varies logarithmically with the radius of curvature. This may lead to spontaneous vesicle formation, which is indeed observed in similar systems.
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Electrostatics of charged objects such as polyelectrolytes and membranes in aqueous solution plays an important role in many biological systems [1]. The fundamental description of these systems has been the mean-field approaches—the Poisson-Boltzmann (PB) or Debye-Hückel (DH) theory (for a review, see [2]). However, for a highly charged surface, the Manning theory of counterion condensation [3] provides an analytically tractable approximation to the PB theory. Indeed, it has been demonstrated rigorously from the solutions to the PB equation [4] that the electrostatic potential far away from the charged surface is independent of the charge density above a certain critical value, implying that the counterions are confined to a thin layer close to the charged surface. However, like the PB theory, it fails to capture the correlation effects of the counterions since it expressly assumes that the "condensed" counterions are uniformly distributed. On physical grounds, we should expect that at low enough temperatures the fluctuations of these condensed counterions about a uniform density would give rise to new phenomena. Indeed, recent simulations [5,6] show that the effective force between two like-charged rods and planar surfaces actually becomes attractive at short distances. These surprising results shed new light on the understanding of the electrostatic adhesion between cells [7] and the puzzling problem of DNA condensation [8]. In this Letter, we examine the effect of fluctuations of these condensed counterions on the bending rigidity of a charged membrane.

The elastic properties of a fluid membrane are characterized by three macroscopic parameters—a bending elastic modulus κ, a Gaussian modulus κ_G, and a spontaneous curvature H_0. The deformation free energy per unit area, expressed in terms of the mean curvature H and Gaussian curvature K may be given by the Helfrich free energy [9,10]:

$$f = \frac{\kappa}{2} (H - H_0)^2 + \kappa_G K. \tag{1}$$

Within an additive constant, the free energy of a sphere with radius R is given by $f_s = (2\kappa + \kappa_G)/R^2 - 2\kappa H_0/R$ and of a cylinder with radius R by $f_c = \kappa/2R^2 - \kappa H_0/R$. Therefore, the parameters κH_0 and $\kappa + \kappa_G$ may be determined from f_s and f_c.

The problem of the electrostatic contribution to the bending constants of layered membranes within the PB mean-field approach has been studied [11]. The electrostatic renormalization of the bending rigidity turns out to be positive; hence electrostatics augments the rigidity of charged membranes. Here we go beyond these PB approaches by assuming that the surface charge density n_0 is sufficiently high that the condensed counterions are confined to a layer of thickness $\lambda \ll L$, where λ is the Gouy-Chapman length, which scales inversely with n_0 and L is the linear size of the charged membrane. By considering the in-plane fluctuations of the condensed counterions and charges on the membranes, we model the system effectively as a 2D Coulomb gas interacting with a r^{-1} potential. Here we have assumed no salt added to the aqueous solution in which the charged membrane is embedded. Under real experimental conditions, the screening of salt might be important. However, as the present analysis focuses on the fundamental effects on the bending constants due to charge fluctuations, the issue of Debye screening will be addressed in a later publication. The present treatment therefore is valid provided that the 3D screening length is larger than the Gouy-Chapman length. Note that this model has yet another experimental realization—a neutral membrane composed of a dilute mixture of anionic $(-)$ and cationic $(+)$ surfactants in pure water.

The electrostatic free energy of the system is the sum of the entropy of the charges and the electrostatic interaction energy among them:

$$\beta F_e = \sum_{i=\pm} \int d^2\mathbf{x} \; n_i(\mathbf{x}) \{\ln[n_i(\mathbf{x}) \lambda_T^2] - 1\}$$
$$+ \frac{l_B}{2} \sum_{i=\pm} \int d^2\mathbf{x} \int d^2\mathbf{x}' \frac{n_i(\mathbf{x})n_i(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}$$
$$- l_B \int d^2\mathbf{x} \int d^2\mathbf{x}' \frac{n_+(\mathbf{x})n_-(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}, \tag{2}$$

where λ_T is the de Broglie wavelength of the charges, $l_B \equiv \frac{e^2}{\epsilon k_B T} \approx 7$ Å is the Bjerrum length for an aqueous solution of dielectric constant $\epsilon = 80$ (H$_2$O), $\beta^{-1} \equiv k_B T$, k_B is the Boltzmann constant, T is the temperature, and $n_i(\mathbf{x})$ is the coarse-grained density of the charges of species i. The domain of the integral in Eq. (2) spans the entire charged membrane. In order to calculate the change in the free energy due to fluctuations, we assume that $n_i(\mathbf{x}) = n_0 + \delta n_i(\mathbf{x})$ and expand the electrostatic free energy to second order in δn_i [13]:

$$\beta \Delta F_e = \frac{1}{2} \int d^2\mathbf{x}\, d^2\mathbf{x}' \left[\frac{l_B}{|\mathbf{x} - \mathbf{x}'|} + \frac{\delta^2(\mathbf{x} - \mathbf{x}')}{2n_0} \right] \times \delta\sigma(\mathbf{x})\delta\sigma(\mathbf{x}'), \quad (3)$$

where $\delta\sigma = \delta n_+ - \delta n_-$. The first term in the bracket is the Coulomb interaction of the charges. The second term comes from the second variation of the ideal gas entropy of the charges. The change in the free energy is obtained by summing all fluctuations weighted by the Boltzmann factor:

$$\beta G_e = -\ln\left[\int d\delta\sigma(\mathbf{x}) \exp -\beta \Delta F_e \right]. \quad (4)$$

It should be mentioned that Eq. (4) contains a divergent self-energy term which has to be subtracted out. This means that we have to discard the first two terms in the expansion for $l_B \to 0$, as can be seen easily by considering the zero temperature limit. As $T \to 0$, the free energy is reduced to the electrostatic energy which is first order in l_B. Since the self-energy is just a constant independent of temperature, it must be linear in l_B. In the following, we employ this "subtraction scheme" [12] together with Eq. (4) to calculate the free energy where charges are confined to the surfaces of three geometries: (i) a plane, (ii) a sphere, and (iii) a cylinder.

For the case of charges confined to a plane ΔF_e in Eq. (3) can be diagonalized by Fourier transform and is quadratic in $\delta\sigma$. Performing the Gaussian integrals in Eq. (4) and subtracting out the self-energy term, we obtain the free energy per unit area due to fluctuations [13,14]

$$\beta g_{\rm pl} = 1/2 \int \frac{d^2\mathbf{q}}{(2\pi)^2} \left\{ \ln\left[1 + \frac{1}{2|\mathbf{q}|\lambda_D} \right] - \frac{1}{2|\mathbf{q}|\lambda_D} \right\}, \quad (5)$$

where $\beta = 1/k_B T$ and $1/\lambda_D = 8\pi n_0 l_B$, which scales like the Gouy-Chapman length, is a length scale analogous to the Debye screening length in 3D. This result can also be obtained by solving the Debye-Hückel equation in 2D [15]. Note that Eq. (5) is ultraviolety divergent because of the infinite energy associated with the collapse of opposite charges. Thus a microscopic cutoff is necessary. In Ref. [16], the author shows by partial summation of the Mayer series that the resulting free energy is convergent and indeed equivalent to a microscopic cutoff. From Eq. (5), one can deduce that the screening of the charges is weak and the potential to the lowest order has the dis-

tance dependence of a dipolar field, where λ_D plays the role of the dipole moment.

For the case of charges confined on a sphere of radius R, after following a similar procedure to that described above we obtain

$$\beta g_{\rm sp} = \frac{1}{8\pi R^2} \sum_{l=0}^{\infty} (2l + 1) \times \left\{ \ln\left[1 + \frac{R/\lambda_D}{2l + 1} \right] - \frac{R/\lambda_D}{2l + 1} \right\}. \quad (6)$$

It is easy to show that by setting $k = l/R$ and taking the limit $R \to \infty$, we recover the planar result. Equivalently we may write Eq. (5) as

$$\beta g_{\rm pl} = \frac{1}{8\pi R^2} \int_{-1/2}^{\infty} dl\, (2l + 1) \times \left\{ \ln\left[1 + \frac{R/\lambda_D}{2l + 1} \right] - \frac{R/\lambda_D}{2l + 1} \right\}. \quad (7)$$

The difference $g_{\rm sp} - g_{\rm pl}$, can be evaluated as an asymptotic expansion in $1/R$ using the Euler-MacLaurin summation formula [17] with $f(l) = (2l + 1)\ln(2l + 1 + R/\lambda_D)$. The result is

$$\beta (g_{\rm sp} - g_{\rm pl}) = -\frac{11}{96\pi R^2} \ln(R/\lambda_D) + \dots. \quad (8)$$

In deriving the result above, we have regularized the integral in Eq. (7) and the sum in Eq. (6) by an ultraviolet cutoff Λ. However, the leading term in Eq. (8) is cutoff independent and those higher order cutoff dependent terms tend to zero as $\Lambda \to \infty$.

For the case of a cylinder, we obtain the free energy:

$$\beta g_{\rm cyl} = \frac{1}{4\pi R} \sum_{m \geq 0} \int_0^{\infty} dq \times \frac{2}{\pi} \left\{ \ln\left[1 + \frac{R}{\lambda_D} I_m(qR)K_m(qR) \right] - \frac{R}{\lambda_D} I_m(qR)K_m(qR) \right\}, \quad (9)$$

where I_m and K_m are modified Bessel functions of order m. The evaluation of the integrals here is relatively difficult. However, we argue that $g_{\rm cyl} - g_{\rm pl}$ has the following asymptotic expansion:

$$\beta (g_{\rm cyl} - g_{\rm pl}) = -\frac{1}{48\pi R^2} \ln(R/\lambda_D) + \dots, \quad (10)$$

for $R \to \infty$. First, we note that the only relevant contributions to the q integral in Eq. (9) are sharply peaked at $q \approx 0$ with width $\Delta q \approx m/R$. Hence, the Bessel functions can be approximated by $I_m(qR)K_m(qR) \sim 1/2m$, yielding

$$\beta g_{\rm cyl} = \frac{1}{4\pi R^2} \sum_{m \geq 0} m \left[\ln\left(1 + \frac{R/\lambda_D}{2m} \right) - \frac{R/\lambda_D}{2m} \right] + O(1/R^3). \quad (11)$$

Equation (10) can now be obtained by using the Euler-MacLaurin summation formula with $f(m) = m \ln(2m + R/\lambda_D)$.

The modifications to the bending constants can be obtained from Eqs. (8) and (10) to yield

$$\Delta\kappa = -\frac{k_B T}{24\pi} \ln(R/\lambda_D),$$

$$\Delta\kappa_G = -\frac{k_B T}{12\pi} \ln(R/\lambda_D). \qquad (12)$$

We thus find that the contribution to the membrane elastic constants due to charge fluctuations is nonanalytic. This kind of nonanalyticity in the bending constants exists in the literature in other situations—for example, in a system consisting of a membrane and rodlike cosurfactants [18]. In the present case, this nonanalyticity can be considered a signature of 2D charged systems. The DH theory in 3D yields an expression for the change in the free energy per unit volume [19] $\Delta f_{3D} \sim -\lambda_D^{-3} + \dots$. In contrast, Eq. (5) has a similar expansion for the free energy per unit area but contains a logarithmic term [15]: $\Delta f_{2D} \sim -\lambda_D^{-2} \ln[\lambda_D/a] + \dots$. Therefore, it is not unexpected to find logarithmic corrections to the bending constants. Typically, for $R/\lambda_D \sim 10^4$–10^6 the factor $\ln(R/\lambda_D)$ is of order 10 and thus $\Delta\kappa$ and $\Delta\kappa_G$ are of the order of $k_B T$.

Second, we remark that both $\Delta\kappa$ and $\Delta\kappa_G$ are negative, in contrast to the mean-field PB contributions, where the renormalization of the bending moduli is always positive and the Gaussian moduli may be negative in some cases. In a system in which $R/\lambda_D \gg 1$, $\Delta\kappa$ is large compared to the mean-field contribution and the membrane becomes more flexible. Therefore, charge fluctuations induce bending of a charged membrane. This conclusion can be seen physically in light of the recent works [13,14] on attractive interactions between two planar charge-fluctuating membranes. It is found that for large distance h separating the two membranes, the attractive force per unit area scales as h^{-3}. Now, a sphere or a cylinder can be approximated as two flat planar surfaces in the limit $R \to \infty$ and their interaction free energies per unit area therefore should scale like $f \sim -R^{-2}$. Hence negative contribution to the bending modulus.

The negative contribution of $\Delta\kappa_G$ from charge fluctuations has interesting experimental consequences since strongly negative values of κ_G favor the formation of many disconnected pieces with no rims, like spherical vesicles. Therefore, when the surface charge density is made sufficiently large, the membrane might spontaneously form vesicles, due to fluctuations of condensed counterions. Experiments [20] on charged surfactant systems support this conclusion.

The result presented in this Letter is particularly relevant to recent experiments [21] where the authors find the formation of vesicles by mixing anionic and cationic surfactants. In the regions of the phase diagram where vesicles form spontaneously, the composition of each of the vesicles in oppositely charged species is almost equimolar [22]. Two aspects of their experiment can be qualitatively accounted for by the present model. They find, in equilibrium, large vesicles with $R \sim 1000$ Å and substantial size polydispersity. Indeed, the vesicle free energy per unit area given by

$$f_{\text{ves}} = \kappa_b/R^2 - \frac{11 k_B T}{96\pi R^2} \ln(R/\lambda_D), \qquad (13)$$

where κ_b is the bare value of the bending rigidity, including possibly the mean-field contribution due to the small excess charges on the vesicle, has an equilibrium value $R^* \sim \lambda_D \exp(\kappa_b/k_B T)$, which can be large even for a moderate value of κ_b of the order of $(5-7)k_B T$. Furthermore, the second derivative of the free energy $f''(R^*) \sim e^{-\kappa_b/k_B T}$ is exponentially small. Hence the variance or fluctuations in R, $\langle (\Delta R)^2 \rangle \sim 1/f''(R^*)$ is large, implying size polydispersity.

In conclusion, by studying fluctuations of charges on curved films, we have deduced nonanalytic contributions to the bending energy of a membrane. Our calculation is applicable to condensed counterions on a highly charged membrane, and mixing of surfactants of opposite charges. For the latter case, we find qualitative agreements with experiments.

[1] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic Press, Inc., San Diego, 1992).

[2] J. L. Barrat and J. F. Joanny, Adv. Chem. Phys. **94**, 1 (1996).

[3] G. S. Manning, J. Chem. Phys. **51**, 924 (1969).

[4] B. Zimm and M. LeBret, J. Biomol. Struct. Dyn. **1**, 461 (1983); C. A. Tracy and H. Widom, Physica (Amsterdam) **244A**, 402 (1997).

[5] N. Grønbech-Jensen, R. J. Mashl, R. F. Bruinsma, and W. M. Gelbart, Phys. Rev. Lett. **78**, 2477 (1997).

[6] L. Guldbrand, B. Jönsson, H. Wennerström, and P. Linse, J. Chem. Phys. **80**, 2221 (1984); S. Engström, H. Wennerström, O. G. Mouritsen, and H. C. Fogedby, Chem. Scr. **25**, 92 (1985).

[7] S. Marcelja, Biophys. J. **61**, 1117 (1992).

[8] B.-Y. Ha and A. J. Liu, Phys. Rev. Lett. **79**, 1289 (1997).

[9] W. Helfrich, Z. Naturforsch. **28C**, 693 (1973).

[10] S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, Reading, MA, 1994).

[11] M. Winterhalter and W. Helfrich, J. Phys. Chem. **92**, 6865 (1988); H. N. W. Lekkerkerker, Physica (Amsterdam) **159A**, 319 (1989); D. J. Mitchell and B. W. Ninham, Langmuir **5**, 1121 (1989); P. Pincus, J. F. Joanny, and D. Andelman, Europhys. Lett. **11**, 763 (1990); P. G. Higgs and J. F. Joanny, J. Phys. (France) **51**, 2307 (1990); R. E.

Goldstein, A. I. Pesci, and V. Romero-Rochin, Phys. Rev. A **41**, 5504 (1990).

[12] Note that this subtraction scheme is independent of geometry. What is being subtracted out is the Coulomb self-energy or equivalently the diverging part of the electrostatic potential as $r \rightarrow 0$.

[13] P. Pincus and S. A. Safran, Europhys. Lett. **42**, 103 (1998).

[14] Phil Attard, Roland Kjellander, and D. John Mitchell, J. Chem. Phys. **89**, 1664 (1988); Chem. Phys. Lett. **139**, 219 (1987); Phil Attard, D. John Mitchell, and Barry W. Ninham, J. Chem. Phys. **88**, 4987 (1988).

[15] E. S. Velazquez and L. Blum, Physica (Amsterdam) **244A**, 453 (1997).

[16] H. Totsuji, J. Phys. Soc. Jpn. **40**, 857 (1976).

[17] G. Arfken, *Mathematical Methods for Physicists* (Academic Press, Inc., San Diego, 1996).

[18] J. B. Fournier, Phys. Rev. Lett. **76**, 4436 (1996); K. Yaman, P. Pincus, and C. M. Marques, Phys. Rev. Lett. **78**, 4514 (1997).

[19] L. D. Landau and E. M. Lifshitz, *Statistical Physics,* (Pergamon, New York, 1980), 3rd ed., rev. and enl. by E. M. Lifshitz and L. P. Pitaevskii.

[20] See J. Oberdisse and G. Porte, Phys. Rev. E **56**, 1965 (1997), and references therein.

[21] E. W. Kaler, A. K. Murthy, B. E. Rodriguez, and J. A. N. Zasadzinski, Science **245**, 1371 (1989); E. W. Kaler, K. L. Herrington, A. K. Murthy, and J. A. N. Zasadzinski, J. Phys. Chem. **96**, 6698 (1992).

[22] J. A. N. Zasadzinski (private communication). Note also that equimolar mixtures of anionic and cationic surfactants precipitate from solution. This is due to the residual van der Waals attractions between surfactants; thus this situation cannot be investigated by the present theory.