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Negative electrostatic contribution to the bending rigidity of charged membranes and polyelectrolytes screened by multivalent counterions

T. T. Nguyen, I. Rouzina, and B. I. Shklovskii
Theoretical Physics Institute, University of Minnesota, 116 Church Street Southeast, Minneapolis, Minnesota 55455

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Bending rigidity of a charged membrane or polyelectrolyte screened by monovalent counterions is known to be enhanced by electrostatic effects. We show that in the case of screening by multivalent counterions the electrostatic effects reduce the bending rigidity. This inversion of the sign of the electrostatic contribution is related to the formation of two-dimensional strongly correlated liquids (SCL) of counterions at the charged surface due to strong lateral repulsion between them. When a membrane or a polyelectrolyte is bent, SCL is compressed on one side and stretched on the other so that thermodynamic properties of SCL contribute to the bending rigidity. Thermodynamic properties of SCL are similar to those of Wigner crystal and are anomalous in the sense that the pressure, compressibility and screening radius of SCL are negative. This brings about substantial negative correction to the bending rigidity. For the case of DNA this effect qualitatively agrees with experiment. [S1063-651X(99)16011-2]

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I. INTRODUCTION

Many polymers and membranes are strongly charged in a water solution. Among them are biopolymers such as lipid membranes, DNA, actin, and other proteins as well as numerous synthetic polyelectrolytes. In this paper, we concentrate on bending of membranes and cylindrical polyelectrolytes with fixed uniform distribution of charge at their surfaces. For a flat symmetrical membrane, the curvature free energy per unit area can be expressed in terms of the curvatures c_1 and c_2 along two orthogonal axes as [1]

$$\frac{\delta F}{S} = \frac{1}{2}\kappa(c_1+c_2)^2 + \kappa_G c_1 c_2, \tag{1}$$

where κ is the bending rigidity, κ_G is the Gaussian rigidity, and S is the membrane surface area. For cylindrical and spherical deformations with the radius of curvature R_c (see Fig. 1),

$$\frac{\delta F^{cyl}}{S} = \frac{1}{2}\kappa R_c^{-2}, \tag{2}$$

$$\frac{\delta F^{sph}}{S} = (2\kappa + \kappa_G) R_c^{-2}, \tag{3}$$

respectively. In general, $\kappa = \kappa_0 + \kappa_{el}$, where κ_0 is the ''bare'' bending rigidity related to short range forces and κ_{el} is electrostatic contribution which is determined by the magnitude of surface charge density and the condition of its screening by small ions of the water solution. Similarly, for a rodlike polymer, such as double helix DNA, the change in free energy per unit length due to bending is given by

$$\frac{\delta F}{\mathcal{L}} = \frac{1}{2} Q R_c^{-2}, \tag{4}$$

where $\mathcal{L}$ is the length of the rod, $Q = Q_0 + Q_{el}$ is the bending constant of the rod, which consists of a ''bare'' component, Q_0, and an electrostatic contribution Q_{el}. In the worm model of a linear polymer, the persistence length, L, of the polymer is related to Q,

$$L = \frac{Q}{k_B T} = \frac{Q_0}{k_B T} + \frac{Q_{el}}{k_B T} = L_0 + L_{el}, \tag{5}$$

where L_0 is the bare persistent length and L_{el} is an electrostatic contribution to it. In the absence of screening, repulsion of like charges of a membrane or a polyelectrolyte leads to infinite κ_{el} and L_{el}. Only screening makes them finite. When the surface charge density is small enough Debye-Hückel (DH) approximation can be used. For a membrane

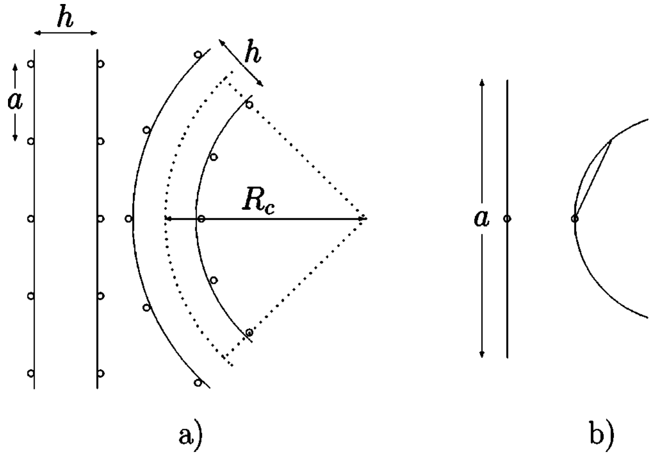

FIG. 1. Bending of membrane (the curvature has been exaggerated). For simplicity, the WC case is depicted. (a) A thick membrane. The right WC is compressed, while the left WC is stretched. For thick membranes, this is the dominant cause of the change in free energy. (b) A very thin membrane. Only one Wigner-Seitz cell is shown. Due to finite curvature of the surface, the distance from any point of the Wigner-Seitz cell to the central ion is shorter than that in the flat configuration. For thin membranes, this is the dominant cause of free energy change.

with the surface charge density $-\sigma$ on each side, κ_{el} was calculated [2–5] when DH screening length r_s is larger than membrane thickness h:

$$\kappa_{DH}=3\pi\frac{\sigma^2 r_s^3}{D}, \quad \kappa_{G,DH}=-\frac{2}{3}\kappa_{DH} \quad (h\ll r_s). \tag{6}$$

Here D is dielectric constant of water.

For cylindrical polyelectrolyte with diameter d much smaller than r_s, calculations in the DH limit lead to the well known Odijk-Skolnick-Fixman formula [6] for the persistence length,

$$L_{DH}=\frac{\eta^2 r_s^2}{4Dk_BT} \quad (d\ll r_s), \tag{7}$$

where $-\eta=\pi\sigma d$ is the charge per unit length of the polymer. Equations (6) and (7) show that, in DH approximation, κ_{el} and L_{el} vanish at $r_s=0$ so that one can measure κ_0 and L_0 in the limit of high concentration of monovalent salt. At $r_s>0$, the quantities κ_{el} and L_{el} are always positive and grow with r_s. However, in many practical situations, polyelectrolytes are so strongly charged that DH approximation does not work and the nonlinear Poisson-Boltzmann (PB) equation was used to calculate κ_{el} and L_{el}. If counterions have charge Ze, the PB equation gives, for a thin membrane [3],

$$\kappa_{PB}=\frac{k_BTr_s}{\pi l}, \quad \kappa_{G,PB}=-\frac{\pi^2}{3}\kappa_{PB} \quad (h\ll r_s) \tag{8}$$

and for the thin rod [7]

$$L_{PB}=\frac{r_s^2}{4l} \quad (d\ll r_s), \tag{9}$$

where $l=Z^2e^2/Dk_BT$ is the Bjerrum length with charge Z. Equations (6)–(9) give positive κ_{el} and L_{el} in agreement with the common expectations that electrostatic effects can only increase bending rigidity.

This paper deals with the case of a strongly charged membrane or polyelectrolyte with a uniform distribution of immobile charge on its surface. It was shown in Refs. [8–14] that screening of such surface by multivalent counterions with charge $Z\geqslant 2$ cannot be described by the PB equation. Due to strong lateral Coulomb repulsion, counterions condensed on the surface form strongly correlated two-dimensional liquid (SCL). Their correlations are so strong that a simple picture of the two-dimensional Wigner crystal (WC) of counterions on a background of uniform surface charge is a good approximation for calculation of the free energy of the SCL. The concept of SCL was used to demonstrate that two charged surfaces in the presence of multivalent counterions attract each other at small distances [10,13,14]. It was also shown that cohesive energy of SCL leads to much stronger counterion attraction to the surface than in conventional solutions of the Poisson-Boltzmann equation, so that surface charge is almost totally compensated by the SCL [14].

In this paper we calculate effect of SCL at the surface of a membrane or a polyelectrolyte on its bending rigidity. When a membrane or polyelectrolyte is bent, the density of its SCL follows the changes in the density of the surface charge, increasing on one side and decreasing on the opposite side (see Fig. 1). As a result the bending rigidities can be expressed through thermodynamic properties of the SCL, namely, two-dimensional pressure and compressibility. For two-dimensional one component plasma (on uniform background) these quantities were found by Monte Carlo simulation and other numerical methods [15–17] as functions of temperature. The inverse dimensionless temperature of SCL is usually written as the ratio of the average Coulomb interaction between ions to the thermal kinetic energy k_BT,

$$\Gamma=\frac{(\pi n)^{1/2}Z^2e^2}{Dk_BT}, \tag{10}$$

where $n=\sigma/Ze$ is concentration of SCL (e.g., for $Z=3$ and $\sigma=1.0\ e/\mathrm{nm}^{-2}$, $\Gamma=6.3$). We will show that in the range of our interest $3<\Gamma<15$ the free energy, the pressure the compressibility, and, therefore, electrostatic bending rigidities differ only by 20% from those in the low temperature limit $\Gamma\rightarrow\infty$, where SCL freezes into the WC. This difference is due to the effects of finite temperature, in particular due to long-wavelength phonons and higher anharmonic corrections. All these effects are taken into account in Secs. III and IV, where general results for the bending rigidity of membranes [Eqs. (32) and (33)] and polyelectrolytes [Eq. (39)] are given. Now we present only very simple results obtained in the WC limit,

$$\kappa_{WC}=-0.68\frac{\sigma^2}{D}h^2a=-0.74\frac{\sigma^{3/2}(Ze)^{1/2}h^2}{D},$$

$$\kappa_{G,WC}=-\frac{2}{3}\kappa_{WC}, \tag{11}$$

$$L_{WC}=-0.054\frac{\eta^2}{Dk_BT}da=-0.10\frac{\eta^{3/2}(Ze)^{1/2}d^{3/2}}{Dk_BT}. \tag{12}$$

Here $a=(2Ze/\sqrt{3}\sigma)^{1/2}$ is the lattice constant of the triangular close packed WC. The membrane and the cylinder are assumed to be reasonably thick, $2\pi h\gg a$ and $\pi d\gg a$. In contrast with results for DH and PB approximations, κ_{WC} and L_{WC} are *negative*, so that multivalent counterions make a membrane or a polyelectrolyte more flexible. For a membrane with $\sigma=1.0\ e/\mathrm{nm}^{-2}$, $h=4$ nm at $Z=3$ we find that $a=1.7$ nm, inequality $2\pi h\gg a$ is fulfilled and Eq. (11) yields $\kappa_{WC}=-14k_BT$ (at room temperature). This value should be compared with typical $\kappa_0\sim 20-100k_BT$. For a cylindrical polyelectrolyte with parameters of the double helix DNA, $d=2$ nm and $\eta=5.9\ e/\mathrm{nm}$, inequality $\pi d\gg a$ is valid and we obtain $L_{WC}=-4.9$ nm, which is much smaller than the bare persistence length $L_0=50$ nm. We should, however, note that our estimates are based on the use of the bulk dielectric constant of water $D=80$. For the lateral interactions of counterions near the surface of organic material with low dielectric constant, the effective D can be substantially smaller. (In macroscopic approach, it is close to $D/2$.) As a result, absolute values of κ_{WC} and L_{WC} can grow significantly.

Negative electrostatic contributions to the bending rigidity were also predicted in two recent papers [18,19]. The authors considered this problem in the high temperature limit where attraction between different points of a membrane or a polyelectrolyte is a result of correlations of thermal fluctuations of screening atmosphere at these points. Such theories describe negative contribution to rigidity for $Z=1$ or for larger Z but with weakly charged surfaces where $\Gamma<1$. On the other hand, at $Z\geqslant 3$ and large σ, one deals with low temperature situation when $\Gamma\gg 1$. In this case the main terms of the electrostatic contribution to the bending rigidity are given by Eqs. (11) and (12), which are based on *static* spatial correlations of ions. As we mentioned above, at $\Gamma\gg 1$, the inclusion of all the dynamic terms result in less than 20% corrections to Eqs. (11) and (12).

We would like to emphasize that, contrary to Ref. [19], this paper deals only with small deformations of a membrane or a polyelectrolyte. We are not talking about a global instability of a membrane or polyelectrolyte due to self-attraction, where, for example, a membrane rolls itself into a cylinder or a polyelectrolyte, as in the case of DNA, rolls into a toroidal particle [10]. Global instabilities can happen even when total local bending rigidities are still positive. To prevent these instabilities in experiment one can work with a small area membrane or short polyelectrolyte [20] or keep their total bend small by an external force, for example, with optical tweezers [21,22].

It is known that, in a monovalent salt, DNA has a persistence length $L>50$ nm that saturates at 50 nm at large concentration of salt. Thus, it is natural to assume that the bare persistence length $L_0=50$ nm. However, it was found in Refs. [20–22] that a relatively small concentration of counterions with $Z=2,3,4$ leads to an even smaller persistence length, which can be as low as $L=25-30$ nm. We emphasize that a strong effect was observed for multivalent counterions which are known to bind to DNA due to the nonspecific electrostatic force.

These experimental data can be interpreted as a result of replacement of monovalent counterions with multivalent ones that create SCL at the DNA surface. As we stated before, multivalent counterions should produce a negative correction to L_0, although the above calculated correction to persistence length is smaller than the experimental one.

This paper is organized as follows. In Sec. II we discuss thermodynamic properties of SCL and WC as functions of its density and temperature. In Secs. III and IV we use expressions for their pressure and compressibility to calculate κ_{SCL} and L_{SCL} and their asymptotic expressions κ_{WC} and L_{WC}. In Sec. V we calculate contributions of the tail of screening atmosphere to κ_{el} and L_{el} and show that for $Z\geqslant 2$ and strongly charged membranes and polyelectrolytes, tail contributions to the bending rigidity are small in comparison with that of SCL.

II. STRONGLY CORRELATED LIQUID AND WIGNER CRYSTAL

Let us consider a flat surface uniformly charged with surface density $-\sigma$ and covered by concentration $n=\sigma/Ze$ of counterions with charge Ze. It is well known that the minimum of Coulomb energy of counterion repulsion and their attraction to the background is provided by a triangular close packed WC of counterions. Let us write energy per unit surface area of WC as $E=n\varepsilon(n)$, where $\varepsilon(n)$ is the energy per ion. One can estimate $\varepsilon(n)$ as the interaction energy of an ion with its Wigner-Seitz cell of background charge (a hexagon of the background with charge $-Ze$). This estimate gives $\varepsilon(n)\sim -Z^2e^2/Da\sim -Z^2e^2n^{1/2}/D$. A more accurate expression for $\varepsilon(n)$ is [23]

$$\varepsilon(n)=-\alpha n^{1/2}Z^2e^2D^{-1}=-1.1\Gamma k_BT, \tag{13}$$

where $\alpha=1.96$. At room temperature, Eq. (13) can be rewritten as

$$\varepsilon(n)\simeq -1.4\ \ Z^{3/2}(\sigma/e)^{1/2}k_BT, \tag{14}$$

where σ/e is measured in units of nm^{-2}.

At $\sigma=1.0\ \ e/\mathrm{nm}^{-2}$, Eq. (14) gives $|\varepsilon(n)|\simeq 7k_BT$ or $\Gamma=6.3$ at $Z=3$, and $|\varepsilon(n)|\simeq 13k_BT$ or $\Gamma=12$ at $Z=4$. Thus, for multivalent ions at room temperature we are dealing with the low temperature regime. However, it is known [17] that due to a very small shear modulus, WC melts at even lower temperature: $\Gamma\simeq 130$. Nevertheless, the disappearance of long range order produces only a small effect on thermodynamic properties. They are determined by the short range order, which does not change significantly in the range of our interest $5<\Gamma<15$ [10,11,13,14]. This can be seen from numerical calculations [15–17] of thermodynamic properties of classical two-dimensional SCL of Coulomb particles on the neutralizing background. In the range $0.5<\Gamma<50$, the internal energy of SCL per counterion, $\varepsilon(n,T)$, was fitted by

$$\varepsilon(n,T)=k_BT(-1.1\Gamma+0.58\Gamma^{1/4}+0.74), \tag{15}$$

with an error of less than 2% [15]. The first term on the right-hand side of Eq. (15) is identical to Eq. (13) and dominates at large Γ. All other thermodynamic functions can be obtained from Eq. (15). In the next section we show that κ_{el} and L_{el} are proportional to the inverse isothermal compressibility of SCL at a given number of ions N,

$$\chi^{-1}=n(\partial P/\partial n)_T, \tag{16}$$

where

$$\begin{aligned}P&=-(\partial F/\partial S)_T=[n\varepsilon(n,T)+nk_BT]/2\\&=nk_BT(-0.55\Gamma+0.27\Gamma^{1/4}+0.87)\end{aligned} \tag{17}$$

is the two-dimensional pressure, F is the free energy of SCL and $S=N/n$ is its area. Using Eq. (17) and relation $\partial\Gamma/\partial n=\Gamma/2n$, one finds

$$\chi^{-1}=nk_BT(-0.83\Gamma+0.33\Gamma^{1/4}+0.87), \tag{18}$$

where the first term on the right-hand side follows from Eq. (13) and describes the WC limit. The last two terms describe finite temperature effects, in particular the contributions of phonons and anharmonic terms; they give a 33% correction to the WC term at $\Gamma=5$ and only a 12% correction at $\Gamma=15$. So one can use zero temperature, Eq. (13), as first approximation to calculate κ_{el} and L_{el}. This is how we obtained Eqs. (11) and (12).

Equations (17) and (18) show that, in contrast with most of liquids and solids, SCL and WC have *negative* pressure P and compressibility χ. We will see below that anomalous behavior is the reason for anomalous *negative* rigidity κ_{el} and persistence length L_{el} and *positive* Gaussian rigidity $\kappa_{G,el}$. The curious negative sign of compressibility of two-dimensional electron SCL and WC was first predicted in Ref. [24]. Later it was discovered in magnetocapacitance experiments in metal-oxide-semiconductor field-effect transistors and semiconductor heterojunctions [25,26].

According to Eq. (18) $\chi^{-1}=0$ at $\Gamma=1.48$, $P=0$ at $\Gamma=2.18$ and they become positive at smaller Γ. As one can see from Eqs. (14) and (10), at $\sigma\sim1.0\ e/\mathrm{nm}^{-2}$ such small values of Γ correspond to $Z=1$. Thus, the surface layer of monovalent ions does not produce large negative κ_{el} and L_{el} in comparison with multivalent ions. For them, the conventional results of Eqs. (6)–(9) related to counterions in the long distance tail of screening atmosphere work better. We will return to this question in Sec. V where we discuss the role of these tails.

Before ending this section, we would like to mention that Eq. (15) for the internal energy was obtained by Monte Carlo simulations of a flat two-dimensional system with a large number of particles. In reality, a membrane or a polyelectrolyte are flat only on the local scale. The accuracy of our approach is proportional to the ratio of the Wigner-Seitz cell size to the size of the local flat area. Depending on specific membranes and polyelectrolytes, this correction may vary from a fraction of one percent to 10–20 %. A Monte Carlo simulation to investigate the finite size effect would be desirable.

III. MEMBRANE

We will consider a ‘‘thick’’ membrane for which one can neglect the effects of the correlation of SCL on two surfaces of the membrane. If we approximate SCL by WC, the energy of such correlations between two surfaces of the membrane decay as $\exp(-2\pi h/a)$, so the condition of ‘‘thickness,’’ $h\gg2\pi a$, is actually easily satisfied for a strongly charged membrane.

Let us first write the free energy of each surface of the membrane as

$$F=Nf(n,T), \tag{19}$$

where $f(n,T)$ is the free energy per ion.

When a membrane is bent [see Fig. 1(a)], the surface charge on the right side is compressed to a new density $n_R>n$, while the surface charge on the left-hand side is stretched to $n_L<n$. Since the total charge on each surface is conserved, this change in density leads to a change in the free energy of each surface,

$$\delta F_{L,R}=N\left(\frac{\partial f}{\partial n}\delta n_{L,R}+\frac{1}{2}\frac{\partial^2 f}{\partial n^2}\delta n_{L,R}^2\right), \tag{20}$$

in which we kept only terms up to second order in $\delta n_{L,R}=n_{L,R}-n$.

Using the definitions (17) and (16) for the pressure and the compressibility of 2D systems

$$P=-\left(\frac{\partial F}{\partial S}\right)_{N,T}=-N\left(\frac{\partial f}{\partial S}\right)_{N,T}=n^2\frac{\partial f}{\partial n}, \tag{21}$$

$$\frac{1}{\chi}=n\left(\frac{\partial P}{\partial n}\right)_T=2n^2\frac{\partial f}{\partial n}+n^3\frac{\partial^2 f}{\partial n^2}, \tag{22}$$

Eq. (20) can be rewritten as

$$\delta F_{L,R}=\frac{SP}{n}\delta n_{L,R}+\frac{S}{n^2}\left(\frac{1}{2\chi}-P\right)\delta n_{L,R}^2. \tag{23}$$

So, the total change in the free energy of the membrane per unit area is

$$\frac{\delta F}{S}=\frac{\delta F_L+\delta F_R}{S}=\frac{P}{n}(n_L+n_R-2n)+\frac{1}{n^2}\left(\frac{1}{2\chi}-P\right)\times[(n_L-n)^2+(n_R-n)^2]. \tag{24}$$

In the case of cylindrical geometry, keeping only terms up to second order in the curvature R_c^{-1}, we have

$$n_{L,R}=\frac{R_c}{R_c\pm h/2}n\simeq\left(1\mp\frac{h}{2R_c}+\frac{h^2}{4R_c^2}\right)n. \tag{25}$$

Substituting Eq. (25) into Eq. (24), we get

$$\frac{\delta F^{\mathrm{cyl}}}{S}=\frac{1}{4\chi}h^2R_c^{-2}. \tag{26}$$

Similarly, in the case of spherical geometry we have

$$n_{L,R}=\left(\frac{R_c}{R_c\pm h/2}\right)^2n\simeq\left(1\mp\frac{h}{R_c}+\frac{3h^2}{4R_c^2}\right)n \tag{27}$$

and

$$\frac{\delta F^{\mathrm{sphere}}}{S}=\left(\frac{1}{\chi}-\frac{P}{2}\right)h^2R_c^{-2}. \tag{28}$$

Comparing Eqs. (26) and (28) with Eqs. (2) and (3), we obtain general expressions for the electrostatic contribution to the bending rigidity,

$$\kappa_{el}=\frac{h^2}{2\chi},\quad \kappa_{G,el}=-\frac{h^2P}{2}. \tag{29}$$

For example, in the case of low surface charge density, the DH approximation can be used to get [2]

$$f(n,T)=2\pi\frac{\sigma^2}{D}n^{-1}r_s, \tag{30}$$

from which we can easily get a generalization of Eq. (6) for a ‘‘thick’’ membrane ($h\gg r_s$),

$$\kappa_{DH}=2\pi\frac{\sigma^2}{D}h^2r_s,\quad \kappa_{G,DH}=-\frac{1}{2}\kappa_{DH}. \tag{31}$$

In the case of high surface charge density that we study in this paper, a SCL of multivalent counterions resides on each surface of the membrane. The expressions for the pressure and the compressibility given by Eqs. (17) and (18) can be used to calculate the bending rigidity,

$$\kappa_{SCL}=\frac{nh^2}{2}k_BT(-0.83\Gamma+0.33\Gamma^{1/4}+0.87), \tag{32}$$

$$\kappa_{G,SCL}=-\frac{nh^2}{2}k_BT(-0.55\Gamma+0.27\Gamma^{1/4}+0.87). \tag{33}$$

In the limit of a strongly charged surface ($\Gamma\gg1$), the first term in Eqs. (32) and (33) dominates, the free energy of SCL is close to that of the WC. Using Eq. (10) one arrives at Eq. (11) for the bending rigidity in the WC limit.

As already stated in Sec. I, for $\Gamma>3$, Eqs. (32) and (33) give a negative value for the bending modulus and a positive value for the Gaussian bending modulus. In other words, multivalent counterions make the membrane more flexible. This conclusion is the opposite of the standard results obtained by mean field theories [Eqs. (6), (8), and (31)] where electrostatic effects are known to enhance the bending rigidity of membranes ($\kappa_{el}>0$ and $\kappa_{G,el}<0$). Obviously, this anomaly is related to the strong correlation between multivalent counterions condensed on the surface of the membrane, which was neglected in mean field theories.

We can also look at Eqs. (31) and (11) from another interesting perspective: apart from a numerical factor, Eq. (31) is identical to Eq. (11) if we replace r_s by $-a$. So the WC of counterions has effect on bending properties of the membrane as if one replaces the normal 3D screening length of counterions gas by a *negative* screening length of the order of lattice constant. Such negative screening length of the WC or SCL was derived for the first time in Ref. [27]. It follows from the negative compressibility predicted in Ref. [24], and observed in Refs. [25] and [26].

Until now we have ignored the effects related to Poisson's ratio σ_P of the membrane material. We are talking about the bending induced increase of the thickness of the compressed (right) half of the membrane, simultaneous decrease of the thickness of its stretched (left) half, and the corresponding shift of the neutral plane of the membrane (the plane which by definition does not experience any compression or stretching) to the left from the central plane. These deformations can be found following Ref. [28] and lead to the additional term $\sigma_P h^2/(1-\sigma_P)R_c^2$ in the right-hand side of Eq. (25). It gives for the bending rigidity

$$\kappa_{el}=\frac{h^2}{2\chi}+\frac{\sigma_P}{1-\sigma_P}\frac{Ph^2}{2}. \tag{34}$$

So, for example, at $\sigma_P=1/3$, the second term of Eq. (34) gives a 33% correction to Eq. (11).

According to Eqs. (29), (32), and (33) $\kappa_{el}=0$ at $h=0$. This happens because in this limit two SCL merge into one, whose surface charge density remains unchanged after bending. Nevertheless, there is another effect directly related to the curvature of SCL. It can be explained by concentrating on one curved Wigner-Seitz cell [see Fig. 1(b)]. One can see that, due to the curvature, points of the background come closer to the central counterion of the cell in the three-dimensional space where Coulomb interaction operates. As a result, the energy of SCL goes down. In the Wigner-Seitz approximation, where energy per ion of the WC is approximated by its interaction with the Wigner-Seitz cell of the background charge, we obtain

$$\kappa_{WC}^{thin}\simeq-0.006\frac{\sigma^2a^3}{D}, \qquad \kappa_{G,WC}^{thin}=-\frac{2}{3}\kappa_{WC}^{thin}. \tag{35}$$

We see that this effect also gives anomalous signs for electrostatic contribution to rigidity in the WC limit, but with a very small numerical coefficient. Also note that, as in the thick membrane case, we can obtain Eq. (35) for a thin membrane by replacing r_s in Eq. (6) by a negative screening radius of the WC with absolute value of the order a.

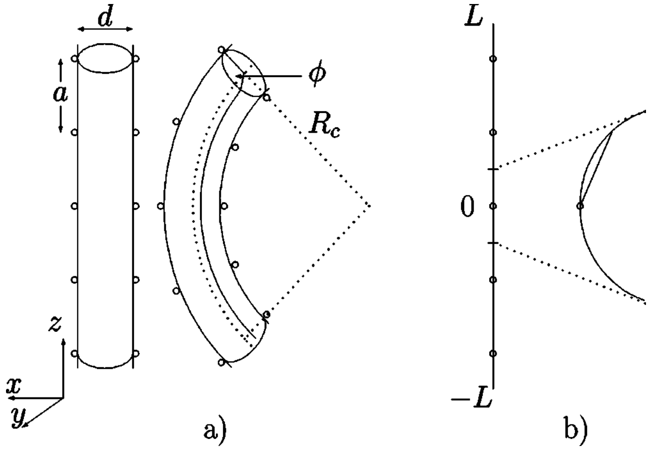

FIG. 2. Bending of cylindrical polyelectrolytes. (a) A thick cylinder. Rigidity is mostly determined by the change in density of SCL. (b) A thin cylinder. The curvature effect is the dominant cause of change in free energy.

IV. CYLINDRICAL POLYELECTROLYTES

In this section, we study the bending properties of cylindrical polyelectrolytes with diameter d and linear charge density η (see Fig. 2). As in the membrane problem, we will assume that the cylinder is thick, i.e., its circumference πd is much larger than the average distance a between counterions on it surface. The calculation is carried out exactly in the same way as in the case of thick membrane. The only difference is that, instead of summing the free energy of two surfaces of the membrane, we average over the circumference of the cylinder.

Let us denote by n_ϕ the local density at an angle ϕ on the circumference on the cylinder [see Fig. 2(a)]. Before bending $n_\phi=n=\eta/\pi dZe$, after bending it changes to a new value,

$$n_\phi=n\frac{R_c}{R_c-(d/2)\cos\phi}\simeq n\left(1+\frac{d\cos\phi}{2R_c}+\frac{d^2\cos^2\phi}{4R_c^2}\right). \tag{36}$$

Using Eq. (24) the free energy per unit length of the polymer can be written as

$$\frac{\delta F}{\mathcal{L}}=\int_0^{2\pi}\frac{d}{2}d\phi\left(\frac{P}{n}(n_\phi-n)+\frac{1}{n^2}\left(\frac{1}{2\chi}-P\right)(n_\phi-n)^2\right)$$
$$=\frac{\pi}{2\chi}\left(\frac{d}{2}\right)^3R_c^{-2},\tag{37}$$

where we keep terms up to second order in the curvature R_c^{-1}.

Comparing Eq. (37) with Eqs. (4) and (5), one can easily calculate the electrostatic contribution to the persistence length

$$L_{el}=\frac{\pi}{\chi k_BT}\left(\frac{d}{2}\right)^3.\tag{38}$$

In the case of a highly charged polymer, a SCL of counterions resides on the polymer surface. For a thick cylinder, the SCL is locally flat and we can use the numerical expression (18) for χ^{-1} to obtain

$$L_{SCL}=\frac{\pi}{8}nd^3(-0.83\Gamma+0.33\Gamma^{1/4}+0.87).\tag{39}$$

Again, we see that correlations between counterions on the surface of a polymer lead to a negative electric contribution to persistence length for $\Gamma>1.5$. In the WC limit $\Gamma\gg1$, the first term in Eq. (39) dominates, and using Eq. (10) one can easily obtain Eq. (12).

As in the membrane case, for simplicity, in writing Eqs. (36), we have ignored the effect of finite value of the Poisson's ratio of the polymer material. In membranes, this effect results in a gain in energy due to the shift of the neutral plane toward the convex (stretched) sides. For a cylinder, there is an additional expansion in the y direction (Fig. 2) that reduces the change in surface charge density, hence compensates for the above gain. These deformations can be found following Ref. [28] and lead to a correction to Eqs. (36),

$$n_\phi=n\left(1+\frac{d\cos\phi}{2R_c}(1-\sigma_P)+\frac{d^2\cos^2\phi}{4R_c^2}\left(1-\frac{\sigma_P}{2}+\sigma_P^2\right)\right.$$
$$\left.-\frac{d^2\sigma_P^2}{8R_c^2}(1-\cos^2\phi)\right).\tag{40}$$

This gives, for the persistence length,

$$L_{el}=\frac{\pi}{k_BT}\left(\frac{d}{2}\right)^3\left(\frac{1}{\chi}(1-\sigma_P)^2+P(3\sigma_P-\sigma_P^2)\right).\tag{41}$$

Obviously, due to the expansion in y direction, the correction to energy is not as strong as in the membrane case. For example, at $\sigma_P=1/3$, Eq. (41) gives only 3% correction to Eq. (12).

According to Eqs. (39) and (12), at $d=0$, κ_{el} vanishes. In this limit, we have to directly include the curvature effect on one dimensional SCL, as shown in Fig. 2(b). As already mentioned in the previous section, after bending, points on a Wigner-Seitz cell come closer to the central ion, which lowers the energy of the system. This effect can be calculated easily in the WC limit. Let us consider the electron at the origin; its energy can be written as

$$\varepsilon=\sum_i\frac{Z^2e^2}{Dr_i}-\int_{-L}^{L}ds\frac{Ze\eta}{Ds},\tag{42}$$

where $r_i=ia$ and s is the contour distance from our ion to an lattice point i and the element ds of the background charge. In the straight rod configuration the space distant is the same as the contour distance; however, after bending they change to

$$r_i'\simeq r_i(1-r_i^2/24R_c^2),\quad s'\simeq s(1-s^2/24R_c^2).\tag{43}$$

Using these new distances to calculate the energy of the bent rod and subtract Eq. (42) from it, one can easily calculate the change in energy due to curvature and the corresponding contribution to persistence length:

$$L_{WC}^{thin}=-\frac{l}{96},\tag{44}$$

which is negative and very small. For example, for $Z=3$, 4, $L_{WC}^{thin}=-0.065$ and -0.116 nm, respectively.

V. CONTRIBUTIONS OF THE TAIL OF THE SCREENING ATMOSPHERE

In preceding sections, we calculated the contribution of a SCL of counterions that is condensed on the surface of a membrane or polyelectrolyte to their bending rigidity. We assumed that charge density σ is totally compensated by the concentration $n=\sigma/Ze$. Actually, for example, for a membrane, some concentration, $N(x)$, of counterions is distributed at a distance x from the surface in the bulk of solution (we call it the tail of the screening atmosphere).

The standard solution of PB equation for concentration $N(x)$ at $N(\infty)=0$ has a form

$$N(x)=\frac{1}{2\pi l}\frac{1}{(\lambda+x)^2},\tag{45}$$

where $\lambda=Ze/(2\pi l\sigma)$ is Gouy-Chapman length. At $\Gamma\gg1$, correlations in SCL provide additional strong binding for counterions, which dramatically change the form of $N(x)$ [14]. It decays exponentially at $\lambda\ll x\ll l/4$, and at $x\gg l/4$ it behaves as

$$N(x)=\frac{1}{2\pi l}\frac{1}{(\Lambda+x)^2}.\tag{46}$$

Here $\Lambda=Ze/(2\pi l\sigma^*)$ is an exponentially large length and σ^* is the exponentially small uncompensated surface charge density at the distance $\sim l/4$. In any realistic situation when $N(\infty)$ is finite or a monovalent salt is added to the solution, Eqs. (45) and (46) should be truncated at the screening radius r_s. Then the solution of the standard PB equation gives [3] Eq. (8) at $r_s\gg\lambda$ or Eq. (6) at $r_s\ll\lambda$. In the case of SCL, for realistic values of r_s in the range $l/4<r_s\ll\Lambda$, we obtain a contribution of the tail similar to Eq. (6),

$$\kappa_t = 3\pi \frac{(\sigma^*)^2 r_s^3}{D}. \tag{47}$$

At reasonable values of r_s, this expression is much smaller than κ_{WC} due to very small values of the ratio σ^*/σ.

Now we switch to a cylindrical polyelectrolyte. In this case, the solution of the PB equation is known [29] to confirm the main features of the Onsager-Manning [30] picture of the counterion condensation. This solution depends on the relation between $|\eta|$ and $\eta_c = Ze/l$. In the case interesting for us, $|\eta| \gg \eta_c$, the counterion charge $|\eta| - \eta_c$ is localized at the cylinder surface, while the charge η_c is spread in the bulk of the solution. This means that at large distances the apparent charge density of the cylinder, η_a, equals $-\eta_c$ and does not depend on η. Equation (9) can actually be obtained from Eq. (7) by substituting η_c for η.

It is shown in Ref. [14] that at $\Gamma \gg 1$, the existence of SCL at the surface of the cylinder leads to substantial corrections to the Onsager-Manning theory. Due to additional binding of counterions by SCL $|\eta_a| < |\eta_c|$ and is given by the expression

$$\eta_a = -\eta_c \frac{\ln[N(0)/N(\infty)]}{\ln(4r_s/l)}, \tag{48}$$

where $N(0)$ is an exponentially small concentration at the distance $r \gg l/4$ from the cylinder axis, used in Ref. [14] as a boundary condition for PB equation at $x=0$. Therefore, one can obtain for the tail contribution the estimate from the above using Eq. (9). For $Z=3$ and $r_s = 5$ nm this gives $L_t < 1$ nm. For DNA, this contribution is much smaller than $L_{SCL} \simeq -5$ nm.

VI. CONCLUSION

We would like to conclude with the discussion of approximations used in this study. First, we assumed that the surface charges are immobile. This is true for rigid polyelectrolytes, such as double helical DNA or actin, as well as for frozen or tethered membranes. But if the membrane is fluid, its charged polar heads can move along the surface. In this case surface charges can accumulate near a *Z*-valent counterion and screen it. Such screening creates short dipoles oriented perpendicular to the surface. Interaction energy between these dipoles is much weaker than the correlation energy of SCL. Therefore, it produces a negligible contribution to the membrane rigidity. The mobility of the charged polar heads eliminates effects of counterion correlation only in the situation where the membrane has polar heads of two different charges, for example, neutral and negative ones. In such a membrane, the local surface charge density can grow due to the increase of local concentration of negative heads. But if all of the closely packed polar heads are equally charged their motion does not lead to redistribution of the surface charges. Then our theory is valid again.

Another approximation which we used is that the surface charge is uniformly smeared. This cannot be exactly true because localized charges are always discrete. Nevertheless our approximation makes sense if the surface charges are distributed evenly, and their absolute value is much smaller than the counterion charge. For example, when the surface charged heads have charge -*e* and the counterion charge is $Ze \gg e$, then the repulsion between counterions is much stronger than their pinning by the surface charges. At $Z \geqslant 3$ we seem to be close to this picture. On the other hand, if the surface charges were clustered, for example, they form compact triplets, the trivalent counterion would simply neutralize such cluster, creating a small dipole. Obviously our theory would overestimate electrostatic contribution to the bending rigidity in this case.

All calculations in this paper were done for pointlike counterions. Actually counterions have a finite size and one can wonder how this affects our results. Our results, of course, make sense only if the counterion diameter is smaller than the average distance between them in SCL. For a typical surface charge density, $\sigma = 1.0$ e/nm^{-2}, the average distance between trivalent ions is 1.7 nm, so that this condition is easily satisfied. The most important correction to the energy is related to the fact that due to the ion's finite size, the plane of the center of the counterion charge can be located at some distance from the plane of location of the surface charge. This creates an additional planar capacitor at each surface and results in a positive contribution to the bending rigidity similar to Eq. (31) that can compensate our negative contribution. On the other hand, if the negative ions stick out of the surface and the centers of counterions are in the same plane with centers of negative charge this effect disappears.

In the general case, one can look at this problem from another angle. Let us assume that the bare quantities κ_0 and L_0 are constructively defined as experimental values obtained in the limit of a high concentration of monovalent counterions. Let us also assume that the distances of closest approach of monovalent and *Z*-valent counterions to the surface are the same. This means that the planar capacitor effect discussed above is already included in the bare quantities κ_0 and L_0. Then the replacement of monovalent counterions by *Z*-valent will always lead to Eqs. (11) and (12).

In summary, we have shown that condensation of multivalent counterions on the surface of a charged membrane or polyelectrolyte happens in the form of a strongly correlated Coulomb liquid, which closely resembles a Wigner crystal. Anomalous properties of this liquid lead to the observable decrease of the bending rigidity of a membrane and polyelectrolyte.

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