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Screening of a macroion by multivalent ions: Correlation-induced inversion of charge

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Screening of a strongly charged macroion by multivalent counterions is considered. It is shown that counterions form a strongly correlated liquid at the surface of the macroion. Cohesive energy of this liquid leads to additional attraction of counterions to the surface, which is absent in conventional solutions of the Poisson-Boltzmann equation. Away from the surface this attraction can be taken into account by a new boundary condition for the concentration of counterions near the surface. The Poisson-Boltzmann equation is solved with this boundary condition for a charged flat surface, a cylinder, and a sphere. In all three cases, screening is much stronger than in the conventional approach. At some critical exponentially small concentration of multivalent counterions in the solution, they totally neutralize the surface charge at small distances from the surface. At larger concentrations they invert the sign of the net macroion charge. The absolute value of the inverted charge density can be as large as 20% of the bare one. In particular, for a cylindrical macroion it is shown that for screening by multivalent counterions, predictions of the Onsager-Manning theory are quantitatively incorrect. The net charge density of the cylinder is smaller than their theory predicts and inverts the sign with a growing concentration of counterions. Moreover, the condensation loses its universality and the net charge linear density depends on the bare one. [S1063-651X(99)11311-4]

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I. INTRODUCTION

Many objects with a much larger size than atomic are strongly charged in a water solution and are called macroions. One can think about a rigid polyelectrolyte which, in a water solution, dissociates into cylindrical macroion and monovalent small ions. DNA and actin are the best known examples of such biological polyelectrolytes. Other important types of macroions are charged lipid membranes and charged spherical colloidal particles. Macroions are screened by smaller ions of the solution. A correct description of the screening of macroions is tremendously important for a calculation of properties of individual macroions, for example the effective charge or the bending rigidity. Screening also determines forces acting between macroions and both thermodynamic and transport properties of their solutions.

This paper examines the screening of a rigid macroion with a fixed and uniform distribution of charge on its surface. Three standard geometries are considered below—an infinite flat surface, an infinite cylinder, and a small sphere—each uniformly charged with the surface density $-\sigma<0$. The standard approach for a description of such problems is the Poisson-Boltzmann equation (PBE) for the self-consistent electrostatic potential $\psi(\mathbf{r})$,

$$\nabla^2\psi=-\frac{4\pi e}{D}\sum Z_iN_{0i}\exp\left(-\frac{Z_ie\psi}{k_BT}\right). \tag{1}$$

Here e is the charge of a proton, $D\simeq 80$ is the dielectric constant of water, Z_ie is the charge of a small ion of sort i, and N_{0i} is their concentration at the point where $\psi=0$. The number of papers using the analytical and numerical solutions of Eq. (1) is extremely large [1]. On the other hand, there is an understanding that Eq. (1) neglects ion-ion correlations and is not exact. Deviations from the distribution of charge predicted by PBE were demonstrated numerically [2,3] for the following problem. Consider screening of a charged surface, $x=0$, of a membrane or a film by a water solution occupying half-space $x>0$. Assume that there is only one sort of counterions with the charge $Ze>0$ and their concentration $N(x)=N_0\exp(-Ze\psi/k_BT)\rightarrow 0$ at $x\rightarrow\infty$. In this case the solution of Eq. (1) is very simple and has the Gouy-Chapman form

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

where $\lambda=Ze/(2\pi l\sigma)$ is the Gouy-Chapman length, $l=Z^2l_B$, and $l_B=e^2/(Dk_BT)\simeq 0.7$ nm is the Bjerrum length. At large Z and σ, the length λ can become of the order of the size of the water molecule or even smaller. For example, at $Z=3$ and $\sigma=1.0$ e/nm^2, $\lambda=0.08$ nm. This means that almost all ions are located in the first molecular layer at the surface or, in other words, they condense at the very surface of a macroion. This raises questions about the role of their lateral correlations and the validity of the solution Eq. (2).

It was found by numerical methods [3] that for a typical charge density σ, deviations from Eq. (2) are not large for monovalent counterions, but they strongly increase with the charge of counterions Z. It was suggested in Refs. [4–7] that at $Z\geqslant 2$, repulsion between multivalent counterions condensed at the surface is so strong that they form a two-dimensional strongly correlated liquid (SCL) in which the short order of counterions is similar to that of a Wigner crystal (WC). This idea was used to demonstrate that two charged surfaces in the presence of multivalent counterions can attract each other at small distances.

A theory of the influence of SCL of multivalent counterions on the density of screening atmosphere of a macroion has been suggested recently by Perel and Shklovskii [8] (PS). Their main idea is to treat separately two subsystems:

two-dimensional SCL of multivalent counterions at the very surface and their gaslike dilute phase at some distance to the right of the surface. In the SCL, PS explicitly take into account strong correlations using the energy of WC as a simple approximation for the free energy of SCL. On the other hand, the gaslike phase is treated in the PBE approximation, while the effect of SCL is taken into account with the help of a new bounadary condition for PBE.

In this paper PS theory is developed in several directions. First, the phenomenon of charge inversion is studied in greater detail and the inverted charge as a function of the counterion concentration is found. In particular, the maximum possible value of the inverted charge is estimated. Second, the PS approach is generalized to a spherical macroion. Third, I add the comprehensive discussion of approximations made in this theory.

The next section starts with a review of the thermodynamic properties of a two-dimensional SCL, which were obtained by Monte Carlo and other numerical methods. It is shown that for $Z \gg 2$ and typical charge density σ, SCL is characterized by a large negative chemical potential of ions. In other words, due to their lateral two-dimensional correlations, ions are more strongly bound to the surface than in the PBE approximation. This phenomenon can be understood as the attraction of a Z-valent counterion to its correlation hole in SCL. While PBE fails to describe this surface correlation effect, it works well at a distance from the surface, where the energy of attraction to the correlation hole is smaller than k_BT and also $N(x)$ is small enough that three-dimensional correlations are very weak. It is found below that PBE becomes valid at $x \gg l/4 \gg \lambda$ and that the characteristic scale of the PBE solution $\Lambda \gg l/4$. Thus SCL together with the intermediate boundary layer, $\lambda < x < l/4$, from the point of view of PBE, provide only a new boundary condition $N(x) = N(0)$ at $x = 0$ for the concentration $N(x)$ of multivalent counterions. It is derived in Sec. III from the condition of equilibrium of the gaslike phase with SCL. Due to the large negative chemical potential of SCL, the new boundary condition requires that $N(0)$ is exponentially small in the dilute phase. Section III also discusses the structure of the intermediate layer $\lambda < x < l/4$ between SCL and the dilute phase, where exponential decay of $N(x)$ actually takes place.

In Secs. IV–VI, PBE is solved with the boundary condition for $N(0)$ for the standard problems of screening of a charged flat surface, a cylinder, and a sphere for different salt compositions of the bulk solution. In planar geometry and for the bulk concentration of Z:1 salt $N(\infty) = 0$, I found that at $x > l/4$ the concentration of counterions, $N(x)$, obeys Eq. (2), in which λ is replaced by an exponentially large length Λ. At finite $N(\infty)$, consequences of correlation-induced binding of counterions to the surface become even stronger. Even at exponentially small $N(\infty) = N(0)$, the positive charge density of SCL completely compensates $-\sigma$. At $N(\infty) > N(0)$, it becomes even larger than σ, so that the total charge of the surface becomes positive. This phenomenon is called charge inversion. First, it was noticed in numerical calculations [3]. This paper presents an analytical theory of charge inversion for the case of screening by small size ions. It is totally based on correlation effects. Recently a number of publications discussed similar phenomena for screening of macroions by charged polymers [9–13].

In the case of a cylinder, the conventional picture of nonlinear screening called the Onsager-Manning condensation should be strongly modified when dealing with multivalent ions. Consider a cylinder with a negative linear charge density $-\eta$ and assume that $\eta > \eta_c$, where $\eta_c = Ze/l$. Onsager-Manning theory [14], confirmed by the solution of the PB equation [15], shows that such a strongly charged cylinder is partially screened by counterions residing at its surface, so that net (total) linear charge density of the cylinder, η^*, is equal to the negative universal value $-\eta_c$. The rest of the charge is screened at much larger distances according to the linear Debye-Hückel theory.

The Onsager-Manning condensation does not take into account lateral correlations of counterions. In Sec. V, the role of these correlations is considered and an analytical expression for η^* as a function of η and the concentration $N(\infty)$ of Z:1 salt is derived [see Eq. (34)]. It is shown that due to additional binding of multivalent counterions provided by their SCL on the surface of the cylinder, the absolute value of the negative net charge density, η^*, is smaller than in the Onsager-Manning theory. Moreover, it strongly depends on a bare linear density, $-\eta$, so that attractive universality of the Onsager-Manning theory is destroyed. When concentration of counterions in the bulk $N(\infty)$ grows, the net charge density, η^*, changes sign from negative to positive at the point where $N(\infty) = N(0)$. Thus, the charge inversion takes place for a cylindrical geometry, too. Positive η^* continues to grow with $N(\infty)$ until it reaches a critical value, e/l_B, for the Onsager-Manning condensation of monovalent negative ions.

Finally, this paper studies screening of a uniformly charged small sphere with a negative charge $-Q$ and radius a. For a strongly charged sphere, the solution of PBE is well known [16–18] and is approximately valid for monovalent counterions. It shows that, in contrast with a charged plane or cylinder, a sphere has no condensed counterions, if $N(\infty) = 0$. This happens because the potential energy of a counterion on the surface of a totally ionized sphere, $-QZe/Da$, is finite. At $N(\infty) > N_c$, where $N_c \propto \exp(-QZl_B/ae)$ is an extremely small concentration, a fraction of positive screening charge condenses at the surface of the sphere and partially compensates its charge, so that the net charge of the sphere, Q^*, changes in the range $0 > Q^* > -Q$. In this regime, Q^* does not depend on Q. This universality is similar to that of the Onsager-Manning theory. The rest of the screening atmosphere can be described in the Debye-Hückel approximation. When $N(\infty)$ grows, Q^* becomes smaller in absolute value but remains negative.

It is shown in Sec. VI that in the case of screening by multivalent counterions due to additional binding by SCL, the net charge, Q^*, behaves differently. When $N(\infty) < N_c$, all counterions are still lost. But at $N(0) > N(\infty) > N_c$, a larger amount of counterions condense at the sphere than PBE predicts. As a result, at $N(\infty) = N(0)$ the net charge, Q^*, changes sign. At $N(\infty) \gg N(0)$, positive Q^* continues to grow and saturates at the value $Q^* \simeq \sqrt{QZe}$. It should be emphasized that when correlations are taken into account, the above-mentioned universality disappears and Q^* becomes a function of the bare charge, Q.

Note that the net linear charge density η^* of a cylinder and the net charge Q^* of a sphere are measurable quantities.

In both cases they include only counterions whose binding energy exceeds k_BT. These counterions move together with a cylinder or sphere, for example in the electric field. Therefore, η^* and Q^* can be studied in an electrophoresis experiment. In the case of charge inversion, a cylinder, sphere, and any other macroion should drift in an anomalous direction.

In Sec. VII, approximations of this theory are discussed. In the Conclusion, Sec. VIII, several possible extensions of this theory are mentioned.

II. WIGNER CRYSTAL AND STRONGLY CORRELATED LIQUID

It is shown below that for $\sigma \geqslant 1 \ e \ \mathrm{nm}^{-2}$ and $Z \geqslant 2$, almost all charge of the plane is compensated by SCL of counterions at its surface, which has a two-dimensional concentration $n = \sigma/Ze$. In this section, I discuss thermodynamic properties of this two-dimensional system. The minimum of the Coulomb energy of counterion mutial 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 at $T=0$ 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 the background charge [a hexagon of background with charge $-Ze$ and counterion in the center, which can be approximately viewed as a disk with radius $R = (\pi n)^{-1/2}$]. This estimate gives $\varepsilon(n) \sim -Z^2e^2/DR$. A more accurate expression for $\varepsilon(n)$ is [22]

$$\varepsilon(n) = -\alpha n^{1/2} Z^2 e^2 D^{-1}, \tag{3}$$

where $\alpha = 1.96$. Equation (3) can be rewritten in units of the room-temperature thermal energy, k_BT, as

$$\varepsilon(n) \simeq -1.4 \ Z^{3/2} (\sigma \ \mathrm{nm}^2/e)^{1/2} k_BT. \tag{4}$$

The inverse dimensionless temperature of SCL is usually written in units

$$\Gamma = \frac{Z^2e^2}{RDk_BT} = 0.9 \frac{|\varepsilon(n)|}{k_BT}. \tag{5}$$

For example, at $\sigma = 1.0 \ e/\mathrm{nm}^2$ and room temperature, Eq. (5) gives $\Gamma = 1.2$, 3.5, 6.4, and 9.9 at $Z = 1$, 2, 3, and 4. Thus, for multivalent counterions one deals with a low-temperature situation. Γ is the large parameter of this theory. In its terms, $R/\lambda \simeq 2\Gamma \gg 1$ and $l/R \simeq \Gamma \gg 1$. For example, at $Z=3$ and $\sigma = 1.0 \ e/\mathrm{nm}^2$ lengths λ, R, and l are equal to 0.08, 1.0, and 6.3 nm, respectively. The small value of λ means that almost all counterions are located in the first molecular layer at the surface and literally form a two-dimensional system.

It is known, however, that due to the small shear modulus, WC melts at a very low temperature near $\Gamma \simeq 130$ [21]. Nevertheless, the disappearance of the long-range order only slightly changes thermodynamic properties of the system. They are determined by the short-range order, which, in the range $5 < \Gamma < 15$, should not be significantly different from that of the WC [4,5,7,8]. This statement is confirmed by numerical calculations [19–21] of thermodynamic properties of the two-dimensional SCL of Coulomb particles on the neutralizing background or so-called one-component plasma. In the large range, $0.05 < \Gamma < 5000$, the excess internal energy of SCL per counterion (the difference between internal energy and energy of the ideal gas with the same concentration), $\varepsilon(n,T) = k_BTf(\Gamma)$, was fitted by the expression [19]

$$f(\Gamma) = -1.1\Gamma + 0.58\Gamma^{1/4} - 0.26 \tag{6}$$

with an error less than 8% (less than 2% in the range $0.5 < \Gamma < 5000$). The first term on the right side of Eq. (6) dominates at large Γ and leads to Eq. (3). The other two terms provide a relatively small correction to the energy of WC. It is equal to 11% at $\Gamma = 5$ and to 5% at $\Gamma = 15$. The reason for a such small correction is that short-range order in SCL is similar to that of WC. For the free energy of unit area, F, one can write

$$F = F(\Gamma = 0.05) + nk_BT \int_{0.05}^{\Gamma} f(\Gamma') d\Gamma'/\Gamma', \tag{7}$$

so that for the chemical potential which is used below to describe the equilibrium of SCL with the gaslike phase, one obtains

$$\mu(n,T) = -k_BT \ln(n_w/n) + \mu_s + \mu_c(n,T), \tag{8}$$

$$\mu_c(n,T) = -k_BT(1.65\Gamma - 2.61\Gamma^{1/4} + 0.26 \ln \Gamma + 1.95). \tag{9}$$

Here μ_c is a contribution of correlations to the chemical potential. The high-temperature chemical potential, $\mu(\Gamma = 0.05)$, with sufficient accuracy is replaced by the chemical potential $-k_BT \ln(n_w/n) + \mu_s$ of an ideal two-dimensional solution of ions in the surface layer of water with a two-dimensional concentration n_w. The term μ_s is the hydration free energy per ion at the surface, and at $n \ll n_w$ it does not depend on the concentration of ions n [23].

The first term of Eq. (9) corresponds to the WC picture. Indeed, one can find directly from Eq. (3) and Eq. (5) that

$$\mu_{\mathrm{WC}} = \frac{d[n\varepsilon(n)]}{dn} = \frac{3}{2}\varepsilon(n) = -1.65 \ \Gamma k_BT. \tag{10}$$

At large Γ, the chemical potential μ_{WC} dominates in Eq. (9). The last three terms of μ_c give 20% correction to the WC term at $\Gamma = 5$ and only 10% correction at $\Gamma = 15$. Thus, if necessary, at $5 < \Gamma < 15$ one can use μ_{WC} as a first approximation. Below μ_c is always calculated using the full Eq. (9).

All necessary information about two-dimensional SCL has been presented. It is time now to study its equilibrium with the rest of the screening atmosphere.

III. A NEW BOUNDARY CONDITION FOR THE POISSON-BOLTZMANN EQUATION

When an ion moves away from SCL, it leaves behind its negatively charged correlation hole. If $U(x)$ is the correlation energy of attraction to the hole, the condition of equilibrium between SCL at $x=0$ and the gaslike phase at a distance x can be written as

$$\mu(n) + Ze\psi(0) = \mu(N) + Ze\psi(x) + U(x). \tag{11}$$

Here $\mu(n)$ is given by Eq. (8), $Ze\psi(x)$ is the counterion energy in the self-consistent potential,

$$\mu(N)=-k_BT\ln N_w/N+\mu_b \tag{12}$$

is the chemical potential of the bulk gas-like phase, N_w is the bulk concentration of water, and μ_b is the bulk hydration free energy [23], which does not depend on N. According to the terminology of Ref. [23], Eq. (11) means that the electrochemical potential of counterions is constant.

It will be shown below that $U(x)$ becomes less than k_BT at $x>l/4$. On the other hand, in many important cases the surface is screened so strongly that the self-consistent potential changes by k_BT only at exponentially large length, Λ, which is defined below. Therefore, the condition of equilibrium between SCL and the layer $l/4\ll x\ll\Lambda$ is

$$\mu(n)=\mu(N). \tag{13}$$

Using Eq. (8) and Eq. (12) and solving Eq. (13) for $N(x)$, one obtains that at $l/4\ll x\ll\Lambda$ concentration $N(x)$ does not depend on x and equals

$$N(0)=\frac{n}{w}\exp\left(-\frac{|\mu_c(n,T)|}{k_BT}\right), \tag{14}$$

where $w=(n_w/N_w)\exp[(\mu_b-\mu_s)/k_BT)]$. Below it is assumed for simplicity that $\mu_b=\mu_s$, i. e., surface and bulk hydration free energies are equal. In this case w is the length of the order of size of the water molecule (for estimates, $w=0.3$ nm is used below).

The notation $N(0)$ reflects the fact that this value plays the role of a new boundary condition at $x\ll\Lambda$ for important solutions of PBE which have large characteristic length $\Lambda\gg l/4$. In such a class of solutions, $N(0)$ provides a universal description of the role of SCL. This paper deals only with this class of problems. Situations when one has to go beyond the universal boundary condition (14) and start directly from Eq. (11) will be studied in the next paper.

Due to the large value of $|\mu_c(n,T)|$, the concentration $N(0)$ can be very small. For example, at $\sigma=1.0$ e/nm^{-2} and $Z=2$, 3, and 4, at which $\Gamma=3.5$, 6.4, and 9.9, according to Eq. (9) one gets $|\mu_c(n,T)|/k_BT=4.5$, 8.8, and 14.3, respectively. This gives $N(0)=30$ mM, 0.3 mM, and 0.8 μM for $Z=2$, 3, and 4 ($1\ \mathrm{M}=6\times10^{26}\ \mathrm{m}^{-3}$). It is clear now that $|\mu_c(n,T)|$ plays a role similar to the work function for thermal emission, to the free energy of chemosorption, or to the evaporation energy for the cases of equilibrium gas-liquid or gas-solid interfaces. The concentration $N(0)$ is similar to the density of the saturated vapor.

Thus, correlation effects in SCL provide additional strong binding of counterions to the macroion surface. We would like to stress that such binding does not happen at $Z=1$. Indeed, at $\sigma=1.0$ e/nm^{-2} one obtains from Eq. (5) and Eq. (9) that $\Gamma=1.2$ and $\mu_c(n,T)/k_BT=1.3$. Therefore, the boundary condition Eq. (14) does not produce nontrivial effects and standard solutions of PBE remain approximately valid.

Below, I justify the role of the distance $l/4$ and give an idea how $N(x)$ evolves from n/λ at $x\sim\lambda$ to $N(0)$ at $x=l/4$. Let us move one ion of SCL along the x axis. As is mentioned above, it leaves behind its correlation hole. In the range of distances $\lambda\ll x\ll R$, the correlation hole is approximately a disk of the surface charge with radius R (the Wigner-Seitz cell) and the ion is attracted to the surface by its uniform electric field $E=2\pi\sigma/D$. Therefore, if λ were larger than w, one would get $N(x)=(n/\lambda)\exp(-x/\lambda)$ at $x\ll R$. In the cases of our interest, $\lambda<w$ and at $x<w$ one can define $N=n/w$, while at $w\ll x\ll R$

$$N(x)=\frac{n}{w}\exp(-x/\lambda). \tag{15}$$

At $x\gg R$, the correlation hole radius grows and becomes of the order of x. Indeed, SCL on the uniform background can be considered as a good conductor in the plane (y,z). It is known that a charge at a distance, x, from a metallic plane attracts an opposite charge into a disk with the radius $\sim x$ or, in other words, creates its pointlike image on the other side of the plane at the distance $2x$ from the original charge. The same thing happens to SCL. The removed counterion still repels other ions of SCL and creates a correlation hole in the form of a negative disk with the charge $-Ze$ and the radius x [24]. It is interesting to note that the correlation hole attracts the counterion and decreases its potential energy by the Coulomb term

$$U(x)=-Z^2e^2/4Dx. \tag{16}$$

This effect provides the correction to the activation energy of $N(x)$:

$$N(x)=\frac{n}{w}\exp\left(-\frac{|\mu(n)|-Z^2e^2/4Dx}{k_BT}\right)\quad(x\gg R). \tag{17}$$

The similar ‘‘image’’ correction to the work function of a metal is well-known in the theory of thermal emission. The correction decreases with x, and at $x=l/4$ it becomes equal to k_BT, so that $N(x)$ saturates at the value $N(0)$. The dramatic difference between the exponential decay of Eqs. (15) and (17) and the $1/x^2$ law of Eq. (2) is obviously related to the correlation effects neglected in PBE. Recall that it was assumed in the beginning of this paper that the charge of the surface is almost totally compensated by SCL. Exponential decay of $N(x)$ with x confirms this assumption and at $\Gamma\gg1$ makes this theory self-consistent.

Consider now what happens with $N(x)$ at distances $x\gg l/4$. At such distances, correlations of the removed ion with its correlation hole in SCL are not important and the correlation between ions of the gas phase are even weaker because $N(x)$ is exponentially small. Therefore, one can return to PBE. In the next section, solutions of PBE for the planar geometry for a different concentration of salt are discussed.

IV. PLANAR GEOMETRY

The solution of PBE with the boundary condition (14) and $N(\infty)=0$ is similar to Eq. (2):

$$N(x)=\frac{1}{2\pi l}\frac{1}{(\Lambda+x)^2}\quad(x\gg l/4). \tag{18}$$

where the new renormalized Gouy-Chapman length, Λ, is exponentially large,

$$\Lambda=[2\pi l N(0)]^{-1/2}=\sqrt{\frac{w}{2\pi n l}}\exp\left(\frac{|\mu_c(n,T)|}{2k_BT}\right). \quad (19)$$

For example, at $\sigma=1.0\ e/\mathrm{nm}^{-2}$, Eq. (19) gives $\Lambda\simeq1.8$, 12.3, 166 nm at $Z=2$, 3, 4. These lengths should be compared with $l/4=0.7$, 1.6, 2.8 nm, respectively. We see that $\Lambda\gg l/4$ for $Z\geqslant2$. This justifies the use of Eq. (14) as the boundary condition for the large distance solution of PBE.

Using Eq. (18), one finds that the total surface charge density located at distances $x<l/4$ is

$$\sigma^*=-\sqrt{N(0)/(2\pi l_B)}=-\sigma(\lambda/\Lambda). \quad (20)$$

For $\sigma=1.0\ e/\mathrm{nm}^{-2}$, one obtains that $\sigma^*=7\times10^{-2}\sigma$ at $Z=2$, $\sigma^*=7\times10^{-3}\sigma$ at $Z=3$, and $\sigma^*=4\times10^{-4}\sigma$ at $Z=4$. Corrections to $\mu_c(n,T)$ and $N(0)$ related to such small σ^* can be, of course, neglected.

One can compare these results with predictions of Eq. (2). Integrating Eq. (2) from $l/4$ to ∞, one finds $\sigma^*=2Ze/\pi l^2$, i.e., $\sigma^*=5\times10^{-2}\ e/\mathrm{nm}^{-2}$ at $Z=3$ and $\sigma^*=2\times10^{-2}\ e/\mathrm{nm}^{-2}$ at $Z=4$. These values of σ^* are much larger than Eq. (20). Thus, binding to the surface is strongly enhanced by correlation effects.

Until now, this paper has addressed the case of extremely dilute solution, when $N(\infty)=0$. Consider the case of a finite concentration, $N(\infty)$, of a Z:1 salt in the bulk of solution, or, in other words, of a concentration $N(\infty)$ of Z-valent counterions and concentration $N_-(\infty)=ZN(\infty)$ of neutralizing ions with the charge $-e$. This adds the Debye-Hückel screening radius

$$r_s=[4\pi l N(\infty)(1+1/Z)]^{-1/2} \quad (21)$$

to the problem. If $N(\infty)\ll N(0)$, the screening radius $r_s\gg\Lambda$, and the fact that $N(\infty)$ is finite changes only the very tail of Eq. (18), making the decay of $N(x)$ at $x\gg r_s$ exponential. At $x\ll r_s$, still $N(x)\gg ZN_-(x)$ and all previous results are valid. However, when $N(\infty)$ approaches $N(0)$, the solution changes dramatically and σ^* vanishes. Indeed, when $N(\infty)=N(0)$ concentration, $N(x)=N(\infty)\exp(-Ze\psi/k_BT)$ stays constant and potential $\psi(x)=0$ at $x>l/4$. This means that the surface is completely neutralized at distances $0<x<l/4$.

If $N(\infty)\gg N(0)$, negative charges dominate at $x\ll r_s$. Indeed, in the PBE approach,

$$N(x)=N(\infty)\exp(-Ze\psi/k_BT), \quad (22)$$

$$N_-(x)=N_-(\infty)\exp(e\psi/k_BT), \quad (23)$$

and when concentration $N(x)$ decreases with decreasing x, the electrostatic potential, $\psi(x)$, grows and $N_-(x)$ increases. One can derive a boundary condition for $N_-(x)$ at $x=0$ from Eqs. (22) and (23). For this purpose, one should first express $\psi(0)$ through $N(0)$ with the help of Eq. (22), and then find $N_-(0)$ from Eq. (23). This gives

$$N_-(0)=ZN(\infty)[N(\infty)/N(0)]^{1/Z}, \quad (24)$$

where $N(0)$ is given by Eq. (14). Then the solution of PBE for $N_-(x)$ at $x\ll r_s$ has a form similar to Eq. (18),

$$N_-(x)=\frac{1}{2\pi l_B}\frac{1}{(\Lambda_-+x)^2}, \quad (25)$$

where

$$\Lambda_-=[2\pi l_B N_-(0)]^{-1/2} \quad (26)$$

and $l_B=e^2/(Dk_BT)$ is the Bjerrum length. To compensate for the bulk negative charge, the positive surface charge density of SCL becomes larger than σ, so that the net surface charge density, σ^*, becomes positive. Similarly to Eq. (20), it is

$$\sigma^*=e\sqrt{\frac{N_-(0)}{2\pi l_B}}=\frac{e}{2\pi l_B\Lambda_-}. \quad (27)$$

This phenomenon is called charge inversion and is, of course, impossible in the framework of the standard PBE. Technically, charge inversion follows from the small value of $N(0)$ in Eq. (14). Its physics is related to the strong binding of counterions at the charged surface due to the formation of SCL. Remarkably, when $\Gamma\gg1$, this phenomenon happens under the influence of a very small concentration of salt.

According to Eqs. (27) and (24), the net density σ^* continues to grow with $N(\infty)$ at $N(\infty)\gg N(0)$. It is interesting to study how far it can grow and how strong the charge inversion can be.

The use of PBE with the boundary conditions Eqs. (14) and (24) is valid if $\Lambda_->l/4$. To estimate the maximum value of σ^*, which can be reached within the range of validity of this theory, one can substitute $\Lambda_-=l/4$ into Eq. (27). This gives

$$\sigma^*\simeq\frac{2e}{\pi l_B l}=\sigma\frac{2R^2}{Zl_B^2}. \quad (28)$$

For example, at $Z=3$ and $\sigma=1.0\ e/\mathrm{nm}^{-2}$ one obtains $\sigma^*\simeq0.15\ \sigma$. To find σ^* as a function of $N(\infty)$ in the whole range where $\Lambda_-\gg l/4$, one should solve Eq. (27) self-consistently substituting $n=(\sigma+\sigma^*)/Ze$ into Eqs. (14), (24), and (26).

One can show that at $R<\Lambda_-<l/4$, when our theory based on the universal boundary condition Eq. (14) is not valid, σ^* continues to grow. If Λ_- becomes smaller than the radius of a Wigner-Seitz cell R, negative ions screen each counterion separately. The effective charge of counterions becomes smaller than Z. This weakens their lateral interactions and makes $N(0)$ larger. Therefore, σ^* starts to decrease. The maximum value of the net surface charge density, $\sigma^*_{\max}$, is reached at $\Lambda_-\simeq R$ and is close to $e/(2\pi l_B R)$. For $Z=3$ and $\sigma=1.0\ e/\mathrm{nm}^{-2}$, this gives $\sigma^*_{\max}\simeq0.24\ \sigma$.

I will not try here to make the above estimates of $\sigma^*_{\max}$ more accurate because of sensitivity of this estimate to the ion size for the following reason. It was assumed above that when $\sigma^*_{\max}$ is reached, all salt molecules are still fully dissociated in water, so that the concentration, $N(\infty)$, of ions with charge Z is equal to the concentration of the salt, $N_s(\infty)$. In reality, at very large $N_s(\infty)$, the concentration of fully ionized counterions, $N(x)$, saturates at the level

$$N_{\max}(\infty)\sim b^{-3}\exp(-Ze^2/bDk_BT), \qquad (29)$$

where $-Ze^2/bD$ is the Coulomb interaction energy of the positive Z-valent ion with the negative monovalent one at the minimum distance between them, b. In this case, the majority of counterions keep a negative ion. One can refer to such a complex as a $(Z-1)$ ion. The transition to such a regime happens when the concentration of salt, $N_s(\infty)$, reaches $N_{\max}(\infty)$.

Substituting $N_{\max}(\infty)$ into Eq. (25) and then Eq. (25) into Eq. (27), one finds that at $Z=3$, $\sigma=1.0\ e/\mathrm{nm}^{-2}$, and $b\geqslant 0.4$ nm, this limitation of dissociation is not important. For smaller b, charge density, σ^*, saturates at the value $N_{\max}(\infty)$, which is smaller than Eq. (29), and stays at this level until the concentration of $(Z-1)$ ions becomes so large that they replace fully ionized ions at the surface. This leads to the drop of σ^*.

Note once more that dramatic changes of the screening atmosphere described above do not happen at $Z=1$ when $\Gamma\sim 1$ and $|\mu_c(n,T)|/k_BT\sim 1$. The standard Gouy-Chapman solution of the PBE, Eq. (2), remains valid in this case.

V. SCREENING OF UNIFORMLY CHARGED CYLINDER

Consider screening of an infinite rigid cylinder with a radius a, a negative surface charge density $-\sigma$, or, in other words, with a negative linear charge density $-\eta=-2\pi a\sigma$. Assume that σ is large enough so that the surface of the cylinder is covered by a two-dimensional SCL with $R\ll 2\pi a$ and with $\Gamma\gg 1$. Such a cylinder can be a first-order approximation for the double-helix DNA, where $a=1$ nm, $\eta=5.9\ e/\mathrm{nm}$, $\sigma=0.94\ e/\mathrm{nm}^2$, and for $Z=3$ the radius of the Wigner-Seitz cell $R\simeq 1$ nm and $l=6.3$ nm.

A screening atmosphere of a cylinder is described by the concentration $N(r)$, where r is the distance from the cylinder axis. The solution of PBE is known [15,1] to confirm the main features of the famous Onsager-Manning [14] picture of the counterion condensation. This solution depends on the relation between η and $\eta_c=Ze/l=k_BT/eZD$. For a weakly charged cylinder with $\eta\ll\eta_c$, the screening is linear and can be described by the Debye-Hückel approximation. For $\eta>\eta_c$, screening becomes nonlinear and most of the screening charge, $\eta-\eta_c$, is located at the cylinder surface, while at $N(\infty)=0$ the rest of the screening charge, η_c, is spread in the bulk of the solution. This means that at large distances, the net charge density of the cylinder, η^*, equals $-\eta_c$ and does not depend on η. Note that this is different from the planar geometry where all the charge is bound to the surface, so that far enough from the surface, the net surface density vanishes (the finite σ^* was defined at $x<l/4$). At a finite $N(\infty)$, the charge density η^* is screened only at linear screening radius r_s.

Here I deal with a strongly charged cylinder, for which $\eta\gg\eta_c$. It is easy to check that this inequality follows from our assumptions that $R<2\pi a$ and $\Gamma\gg 1$. It is also fulfilled for the case of DNA, for which $\eta/\eta_c\simeq 4Z$. The goal in this case is to verify whether in the case of multivalent counterions elegant statements of the Onsager-Manning theory [14] should be changed due to SCL at the surface of a strongly charged cylinder.

As in the preceding section, the boundary condition Eq. (14) is used below to allow for additional binding of counterions by SCL. One can introduce a radius r_T, at which energy of interaction between a counterion and its correlation hole, $U(r)$, becomes of the order of k_BT, so that the boundary condition $N(r)=N(0)$ can be used. For a cylindrical geometry, r_T, strictly speaking, differs from its analog for a planar problem $l/4$. Indeed, at $r\gg R$, energy $U(r)$ can be calculated as the energy of attraction of the charge Ze to an infinite metallic wire with the radius a:

$$\begin{aligned} U(r)&=-Z^2e^2/4D(r-a) \qquad (R<r-a<a),\\ U(r)&=-\pi Z^2e^2/4Dr\ln(r/a) \qquad (r\gg a). \end{aligned} \qquad (30)$$

One can find r_T from the equation $|U(r_T)|=k_BT$:

$$\begin{aligned} r_T&=a+l/4 \qquad (l/4<a),\\ r_T&=\frac{\pi l}{4\ln(l/4a)} \qquad (l/4\gg a). \end{aligned} \qquad (31)$$

At distances $r_T<r<r_s$, the electrostatic potential of the linear charge density η^* is not screened and the boundary condition of Eq. (14) can be used to write

$$\begin{aligned} N(r)&=N(0)\exp\left(-\frac{Ze[\psi(r)-\psi(r_T)]}{k_BT}\right)\\ &\simeq N(0)\exp\left(\frac{2\eta^*}{\eta_c}\ln(r/r_T)\right). \end{aligned} \qquad (32)$$

At $r=r_s$ concentration, $N(r_s)\simeq N(\infty)$. The solution of this equation for η^* is

$$\eta^*=-\eta_c\frac{\ln[N(0)/N(\infty)]}{\ln(r_s/r_T)^2}. \qquad (33)$$

According to Eq. (31), at a not very large $l/4a$ one can use the estimate $r_T\sim l/4$. Substituting Eq. (21) into Eq. (33), one arrives at

$$\eta^*=-\eta_c\frac{\ln[N(0)/N(\infty)]}{\ln(4/[\pi N(\infty)l^3])}. \qquad (34)$$

It is clear from Eq. (34) that if two logarithms are close to each other, i.e., if

$$\ln\frac{N(0)^2l^3}{N(\infty)}\gg 1, \qquad (35)$$

the Onsager-Manning theory is approximately correct and η^* approaches $-\eta_c$. If $\Gamma\sim 1$ and $\mu_c(n,T)\sim k_BT$, concentration $N(0)\sim n/w$ is large and inequality (35) is fulfilled at any reasonable $N(\infty)$. Thus, for a typical charge density σ and $Z=1$ the Onsager-Manning result is rederived. However, for screening by multivalent ions $\Gamma\gg 1$, $|\mu_c(n,T)|\gg k_BT$, and concentration $N(0)$ is exponentially small. Therefore, values of $N(\infty)$ at which η^* is close to $-\eta_c$ are extremely small. For example, to get $\eta^*=-0.75\eta_c$ one needs $N(\infty)=N_{0.75}=0.02N(0)^2l^3$. At $\sigma=1.0\ e/\text{nm}^{-2}$ and $Z=3$, it is shown above that $N(0)=1.7\times10^{23}\ \text{m}^{-3}=0.3$ mM and, therefore, $N_{0.75}=2\times10^{20}\ \text{m}^{-3}=0.3\ \mu$M. Switching to $Z=4$, one has $N(0)=5\times10^{20}\ \text{m}^{-3}=0.8\ \mu$M, which results in an unrealistically small $N_{0.75}=2.5\times10^{15}\ \text{m}^{-3}$.

On the other hand, in disagreement with the Onsager-Manning theory, one obtains from Eq. (34) that $|\eta^*|\ll\eta_c$ when a concentration $N(\infty)$ of the salt is still exponentially small, namely $N(0)^2l^3\ll N(\infty)\ll N(0)$. Moreover, according to Eq. (34), η^* vanishes at $N(\infty)=N(0)$. This result is easy to understand without calculations. Indeed, in this case $N(r)=N(\infty)\exp[-Ze\psi(r)/k_BT]=N(0)$ stays constant and $\psi(r)=0$ at all $r>l/4$, so that all of the charge of the polyelectrolyte is compensated inside cylinder with $r=l/4$.

The difference from the Onsager-Manning theory becomes even more apparent at $N(\infty)>N(0)$ when the density η^* becomes positive. Note that this charge inversion takes place still at exponentially small $N(\infty)$. A positive η^* continues to grow with $N(\infty)$ until it reaches critical density

$$\eta^*_{\max}=e/l_B \tag{36}$$

and the standard Onsager-Manning condensation of monovalent negative ions starts. According to Eq. (34) this happens at $N(\infty)=N_{\text{sat}}$, where

$$N_{\text{sat}}\sim l^{-3}[N(0)l^3]^{1/(Z+1)}. \tag{37}$$

At $N(\infty)>N_{\text{sat}}$, charge density η^* remains fixed at the level e/l_B. Condensed negative ions eventually screen lateral interaction of counterions in SCL, $|\mu_c(n,T)|$ decreases, and η^* drops. Comparing Eq. (37) with Eq. (29) for the maximum concentration, $N_{\max}(\infty)$, of fully dissociated Z:1 salt, one sees that they are quite close, if ion size b is not too small. For a very small distance of the closest approach b, the growth of η^* is limited earlier by the condition $N(\infty)<N_{\max}(\infty)$.

To summarize, the net charge η^* as a function of salt concentration $N(\infty)$ is given by Eq. (34). It changes in the range $e/l_B>\eta^*>-\eta_c$ when $N(\infty)$ grows. Strictly speaking, to quantitatively describe η as a function of $N(\infty)$, one should use the self-consistent concentration, $n=(\eta+\eta^*)/2\pi a$, in Eq. (34) for $N(0)$.

Finally, it should be emphasized that this result does not demonstrate the attractive universality of the Onsager-Manning theory. According to Eq. (34), η^* depends on η through $\mu(n)$ in Eq. (14). Thus, for the screening by multivalent ions at $\Gamma\gg1$, and at any reasonable $N(\infty)$, the predictions of Refs. [14,15] are qualitatively incorrect.

Return now to the case of a small concentration of a Z:1 salt, $N(\infty)\ll N(0)$, and consider what happens to η^* when a 1:1 salt with a larger concentration, $N_1\gg N(\infty)$, is added to the solution. This is a realistic experimental situation. Such a problem can be solved with the help of Eq. (33), if one substitutes $r_s=(8\pi l_BN_1)^{-1/2}$ instead of Eq. (21). The result is

$$\eta^*=-\eta_c\frac{\ln[N(0)/N(\infty)]}{\ln[2Z^2/(\pi N_1l^3)]}. \tag{38}$$

Equation (38) shows how at a given $N(\infty)\ll N(0)$, the absolute value of the net negative charge density increases with N_1. At large enough N_1, monovalent counterions replace counterions with charge Ze at the surface of the macroion. This replacement happens when the corresponding change of free energy vanishes, i.e., at

$$\begin{aligned}\mu_c(n,T)-k_BT\ln(n_w/n)-Zk_BT\ln(N_w/N_1)\\ =Z\mu_1-Zk_BT\ln(n_w/Zn)-k_BT\ln(N_w/N(\infty)).\end{aligned} \tag{39}$$

Here the left side is the free energy of a Z-valent counterion at the surface and Z monovalent ones in the bulk, while the right side is the free energy of Z monovalent ions at the surface and a Z-valent ion in the bulk. μ_1 is the correlation part of the chemical potential of a monovalent ion. At $Z\gg1$ one can neglect $Z\mu_1$ in comparison with $\mu_c(n,T)$ because, as was mentioned above, μ_1 is numerically small and the latter quantity is proportional to $Z^{3/2}$. Solving Eq. (39) for N_1, one finds

$$N_1=\frac{n}{w}\left(\frac{N(\infty)}{N(0)}\right)^{1/Z}. \tag{40}$$

Substituting this N_1 into Eq. (38), one sees that at the moment of replacement $\eta^*\simeq-\eta_cZ=-k_BT/e$, providing a natural crossover to the case of screening by exclusively monovalent counterions.

Concluding this section, I would like to note that quantitative use of Eq. (9) obtained for a two-dimensional system may be subjected to some limitations when considering a cylinder with a small enough radius, such as, for example, DNA. Even if the circumference of the cylinder $2\pi a$ is much larger than the radius of the Wigner-Seitz cell, R, thermal fluctuations can play a larger role for a cylinder than for the real two-dimensional system. This can happen because, strictly speaking, at large distances a cylinder is a one-dimensional system. However, the role of long-range fluctuations in thermodynamic properties of this system is small and these effects do not change my estimates beyond their uncertainty and, definitely, do not change my qualitative conclusions.

VI. SCREENING OF A UNIFORMLY CHARGED SPHERE

Consider application of this theory to a sphere with a small radius $a=2-5$ nm and with a charge $-Q$ screened by Z:1 salt with concentration $N(\infty)$ in the bulk. At large enough surface charge density $\sigma=-Zen_0=-Q/4\pi a^2$, the surface is covered by SCL of Z-valent counterions. The goal is to find a concentration n of this SCL and the net charge of the sphere,

$$Q^*=4\pi a^2nZe-Q, \tag{41}$$

as a function of a, Q, Z, T, and $N(\infty)$. In the case of a sphere, the screening atmosphere is characterized by a concentration of Z-valent ions, $N(r)$, as a function of distance r from the sphere center. For simplicity, assume that $a>l/4$ so that the boundary condition Eq. (14) is valid at $r=a+l/4$, where the curvature of the sphere can be neglected. At distances from the surface $r-a \ll r_s$, one can neglect screening and find the concentration, $N(r)$, similarly to Eq. (32) as

$$N(r)=N(0)\exp\left(-\frac{Ze[\psi(r)-\psi(a+l/4)]}{k_BT}\right)$$

$$\simeq N(0)\exp\left(\frac{Q^*Ze(a^{-1}-r^{-1})}{Dk_BT}\right). \tag{42}$$

At the distance $r=a+r_s$, where the linear Debye-Hückel theory starts to work, one has

$$N(a+r_s)\simeq N(\infty). \tag{43}$$

Solving this equation in the case $r_s \gg a$, one obtains

$$Q^*=-\frac{ae}{l_BZ}\ln\frac{N(0)}{N(\infty)}=-\frac{a}{l_BZ}\left(\ln\frac{n/w}{N(\infty)}+\frac{|\mu_c(n,T)|}{k_BT}\right). \tag{44}$$

This equation is similar to Eq. (34). It is to be solved for Q^*, n, and $|\mu_c(n,T)|$ together with Eq. (41) and Eq. (9) [or its low-temperature version Eq. (10)].

In the case of monovalent counterions, when $\Gamma \sim 1$, $\mu_c(n,T)/k_BT \sim 1$, so that correlations do not play any role in Eq. (44) and the solution does not differ from the solution of PBE. In this case, the concentration $N(0)\simeq n/w \sim n_0/w$ is much larger than any reasonable $N(\infty)$ so that $\ln(N(0)/N(\infty))>0$ and $Q^*<0$. Thus, Eq. (44) describes the partial compensation of charge $-Q$ by positive charge $Q+Q^*=4\pi a^2 Zen$ of counterions condensed at the very surface of the sphere. The rest of the screening charge, $-Q^*$, is situated at the distance r_s from the sphere in Debye-Hückel atmosphere. It is clear now that nonlinear screening of a sphere is similar to Onsager-Manning condensation in the case of a cylinder [16–18]. In both cases there are two separate groups of counterions: condensed and free. Moreover, for a sphere there is a similar universality of the net charge Q^*. Indeed, when $N(\infty)\ll n_0/w$ the dependence of Q^* on Q is negligible. [One can evaluate this dependence substituting n_0 for n in Eq. (44).] The only qualitative difference between the screening of a sphere and a cylinder is that at unrealistically small $N(\infty)\leqslant N_c$, where

$$N_c=\frac{1}{4\pi a^2 w}\exp\left(-\frac{Ql_BZ}{ae}\right), \tag{45}$$

the last counterion leaves the surface [15] and $Q^*=-Q$.

On the other hand, in the case of screening by multivalent ions, correlations significantly change the above-described mean-field dependence of Q^* on $N(\infty)$. These changes start, however, only at $N(\infty)>N_c$, because without condensed counterions correlations cannot play any role. At $N(\infty) \gg N_c$, when n grows and becomes comparable with n_0, one obtains that $\Gamma \gg 1$, $\mu_c(n,T)\gg k_BT$, and, according to Eq. (14), $N(0)$ is exponentially small. Therefore, it follows from Eq. (44) that the negative net charge, Q^*, grows (decreases in the absolute value) faster than it does in the case of monovalent counterions. Eventually, Q^*, vanishes at exponentially small $N(\infty)=N(0)$.

At $N(\infty)>N(0)$, the net charge, Q^*, becomes positive and continues to grow. As in other geometries, this charge inversion happens because of strong binding of counterions by SCL. At large enough $N(\infty)$, one can neglect the first term in parentheses of Eq. (44). Then using a low-temperature expression Eq. (10) for $\mu_c(n)$, one finds that Q^* saturates at the positive value

$$Q^*_{\max}=\beta\sqrt{QZe}, \tag{46}$$

where $\beta=3\alpha/4\sqrt{\pi}\simeq 0.84$. For example, at $Z=3$ for a sphere with bare charge $-50e$ $(Q=50e)$ one arrives at the net charge $Q^*_{\max}\simeq +10e$. Equation (46) is remarkably simple and universal: $Q^*_{\max}$ does not depend on a sphere radius a.

Equation (46) for $Q^*_{\max}$ is valid until one of the two following events happens. First, a concentration $N(\infty)$ can reach maximum concentration $N_{\max}(\infty)$ of fully dissociated Z:1 salt [see Eq. (37)]. Second, a condensation of monovalent negative ions on the positive sphere can start. Condensed counterions eventually screen the lateral interaction of counterions in SCL and effectively change their charge from Z to $Z-1$. As a result, $|\mu_c(n,T)|$ decreases and Q^* starts to drop. Similarly to Eq. (37), condensation starts at $N(\infty)\propto \exp(-\mu_c/(Z+1)k_BT)$. This concentrations is close to $N_{\max}(\infty)$ if ion size, b, is not too small. For a very small b condition, $N(\infty)\ll N_{\max}(\infty)$ is more restrictive. For a small sphere with radius $a=2-5$ nm, both restrictions start to work while $r_s \gg a$. Therefore, I do not consider here the case $r_s<a$. For larger spheres, r_s can become smaller than a at the point at which the above-mentioned other limits on $N(\infty)$ start to work. In this case, the sphere effectively works as a flat surface and one can use the results of Sec. IV.

VII. DISCUSSION OF APPROXIMATIONS

In this section, approximations used in this paper are discussed. First, it was assumed that charges at the surface of a macroion are fixed and cannot move. In the case of a solid or glassy surface, for example colloidal particles and rigid polyelectrolytes, such as double-helix DNA, this approximation seems to work well. On the other hand, for charged lipid membranes it can be violated. If the surface charges are mobile, they can accumulate near Z-valent counterions, forming short dipoles directed perpendicular to the surface. These dipoles interact weakly with each other so that the energy of their lateral correlations is smaller than in SCL on the uniform background. On the other hand, such a concentration of the surface charge under the counterion by itself creates an additional binding of counterions to the surface. As a result, the negative chemical potential, $\mu(n,T)$, becomes larger in the absolute value and the boundary concentration $N(0)$ becomes smaller. The theory of this paper expresses everything through $N(0)$. Therefore, the unusual effects of complete compensation of macroion charge and of the charge inversion become stronger.

The second approximation made above is the assumption that fixed charge is uniformly distributed at the surface. Localized charges are actually discrete. Therefore, it makes sense to discuss whether $-e$ charges, for example randomly distributed on the surface, work as a uniform background. In the limit $Z \gg 1$, the repulsion between Z-valent counterions is much stronger than their pinning by the surface charges, so that the concept of a uniform background works exactly. At $Z \geqslant 3$, the uniform background is still a good approximation for realistic values of the radius of closest approach, b_s, of counterions and discrete surface negative charges. On the other hand, this approximation fails at $Z=1$ because all counterions and discrete negative surface charges have a tendency to form neutral Bjerrum pairs instead of SCL if $b_s \ll R$. In this case, $N(0)$ can be small even for $Z=1$. When negative charges are clustered, for example form compact triplets, even at $Z=3$ interaction with such a cluster can be as important as interaction with the neighboring counterions. Each counterion tends to neutralize one cluster forming a neutral dipole. Again, this leads to stronger binding to the surface and smaller $N(0)$.

This discussion naturally leads us to the third approximation used above in the calculation of the chemical potential of SCL. Equation (9) was obtained for pointlike counterions. Actually, counterions have a finite size and one wonders how this affects these results. Our results, of course, make sense only if the counterion radius b_c is smaller than the radius of a Wigner-Seitz cell, R, so that counterions occupy a small fraction of the surface. In other words, the idea of SCL or WC works only when objects of large charge density arrange themselves on a background with much smaller charge density. For trivalent ions on the surface with the charge density $\sigma = 1.0\ e/\text{nm}^{-2}$, the radius of the Wigner-Seitz cell $R = 1$ nm, so that for a counterion with $b_c = 0.5$ nm this condition is easily satisfied. Positive corrections to the energy per ion of WC are proportional $(b_c/R)^2$ and appear due to the fact that the charge finite-size counterion cannot be situated exactly in the potential minimum created by its nearest neighbors.

Finally, all estimates in this paper are based on the use of dielectric constant of a water $D \simeq 80$. For the lateral interactions of counterions near the surface of an organic material with a low dielectric constant, the effective dielectric constant D can be substantially smaller. (In a macroscopic approach it is close to $D/2$.) As a result, absolute values of $|\mu(n,T)|$ can grow significantly and $N(0)$ may become even smaller.

VIII. CONCLUSION

In conclusion, the role of strong lateral correlations of Z-valent counterions condensed on a charged surface is studied. It is argued that a strongly correlated liquid (SCL), or, in other words, a two-dimensional one-component plasma, is a good model for these correlations. It is shown that, due to the additional binding provided by SCL, the concentration of counterions close to SCL is exponentially small [see Eq. (14)]. This concentration depends only on Z and the surface charge density of the macroion σ and serves as a boundary condition for the Poisson-Boltzmann equation (PBE), which is still valid far from the surface. PBE is solved with the boundary condition (14) for all three standard geometries. For a charged cylinder, it is shown that in the presence of SCL the Onsager-Manning condensation is strongly modified. The increasing bulk concentration of Z-valent counterions, $N(\infty)$, makes the net negative charge of the cylinder smaller than in the Onsager-Manning theory, drives it through zero, and makes it positive. Similar changes are predicted for a charged sphere with charge $-Q$. In this case, charge inversion can result in a positive net charge $0.84\sqrt{QZe}$. All these phenomena happen while the concentration of $Z{:}1$ salt is still exponentially small. Technically they follow from the boundary condition (14), which in turn is a result of a strong correlation of counterions of the surface layer.

This theory can be applied to a variety of other problems. First, one can study more complicated solutions where a substantial concentration of 1:1 salt is added to $Z{:}1$ salt. We gave only one example of such a problem in the end of Sec. V. Second, this theory should be extended to a finite concentration of macroions. In this case, problems of a global instability of such a solution should be addressed, too. Third, one can use a similar theory for counterions of a larger size and nonspherical shape [7], provided they have larger charge density than the macroion's surface. For example, a positively charged rigid flat surface can be screened by a solution of a rodlike polymer such as double-helix DNA [25]. If projected to the plane the negative surface density of DNA is larger by absolute value than the charge density of the plane, then DNA rods form strongly correlated nematic liquid, which provides strong binding of DNA to the surface. A net charge density of the plane can experience correlation-induced charge inversion. These and other problems will be addressed in future publications.

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[24] Note that this metal-like behavior is characteristic not only of SCL but also of a Wigner crystal on a uniform background. Ions of such a crystal slide on the uniform background and adjust their positions to the change of the electrostatic potential of the removed ion via small elastic deformation of the Wigner crystal. This adjusment does not create topological defects, dislocations, or disclinations. Therefore, SCL can react in this way not only at a distance larger than its correlation length, but also at smaller distances where it has a crystalline short-range order. The situation changes when background charge is strongly nonuniform (see the discussion of the role of such disorder in the Conclusion). In this case, effects of pinning can modify screening by the Wigner crystal and even by SCL. We plan to study this question in a future publication.

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