

Macroions in Salty Water with Multivalent Ions: Giant Inversion of Charge

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Screening of a strongly charged macroion by oppositely charged colloidal particles, micelles, or short polyelectrolytes is considered. Because of strong lateral repulsion such multivalent counterions form a strongly correlated liquid at the surface of the macroion. This liquid provides correlation-induced attraction of multivalent counterions to the macroion surface. As a result even a moderate concentration of multivalent counterions in the solution inverts the sign of the net macroion charge. We show that at high concentration of monovalent salt the absolute value of inverted charge can be larger than the bare one. This giant inversion of charge can be observed in electrophoresis.

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Charge inversion is a phenomenon in which a charged particle (a macroion) strongly binds so many counterions in aqueous solution that its net charge changes sign. As shown below the binding energy of a counterion with large charge Z is larger than $k_B T$, so that this net charge is easily observable; for instance, it is the net charge that determines linear transport properties, such as particle drift in weak field electrophoresis. Charge inversion has been observed [1] in polyelectrolyte-micelle systems and is possible for a variety of other systems, ranging from solid surface of mica or lipid membranes to DNA or actin. Charge inversion is of special interest for delivery of genes to living cells for the purpose of gene therapy. The problem is that both bare DNA and a cell surface are negatively charged and repel each other. The goal is to screen DNA in such a way that the resulting complex is positive [2].

Theoretically, charge inversion can also be thought of as an overscreening. Indeed, the simplest screening atmosphere, familiar from linear Debye-Hückel theory, compensates at any finite distance only a part of the macroion charge. It can be proven that this property holds also in nonlinear Poisson-Boltzmann (PB) theory. The statement that the net charge preserves the sign of the bare charge agrees with common sense, and one might think that this statement is even more universal than results of the PB equation. It was shown [3–5], however, that this presumption of common sense fails for screening by Z -valent counterions (Z -ions), such as charged colloidal particles, micelles, or short polyelectrolytes, because there are strong lateral correlations between them when they are bound to the surface of a macroion. These correlations are beyond the mean field PB theory, and charge inversion is their most spectacular manifestation.

Charge inversion has attracted significant attention in the last couple of years [6]. Our goal in the present paper is to provide a simple physical explanation of charge inversion and to show that in the most practical case, when both Z -ions and monovalent salt (such as NaCl) are present, not only can the charge change sign, but the inverted charge can become even larger in absolute value than the bare charge, thus giving rise to *giant charge inversion*.

Let us demonstrate the role of lateral correlations between Z -ions for a primitive toy model. Imagine a hard-core sphere with radius b and with negative charge Q screened by two spherical positive Z -ions with radius a . One can see that if Coulomb repulsion between Z -ions is much larger than $k_B T$ they are situated on opposite sides of the negative sphere (Fig. 1a). If $Ze < 2|Q|$ each Z -ion is bound, because the energy required to remove it to infinity, $|Q|Ze/(a+b) - Z^2e^2/2(a+b)$, is positive. Thus, the charge of the whole complex $Q + 2Ze$ can be positive and as large as $3|Q|$. This example demonstrates the possibility of an almost 300% charge inversion. (At small concentration of salt this charge will be eventually screened at a large distance, but this screening does not affect what happens at smaller distances.) It is obvious that this charge inversion is a result of the correlation between Z -ions which avoid each other and reside on opposite sides of the negative charge. On the other hand, a description of screening of the central sphere in PB approximation smears the positive charge, as shown in Fig. 1b, and does not lead to charge inversion. Indeed, in this case charge accumulates in the spherically symmetric screening atmosphere only until the point of neutrality where the electric field reverses its sign and attraction is replaced by repulsion.

In this paper we consider screening of a macroion surface with negative immobile surface charge density $-\sigma$ by a finite concentration of positive Z -ions, a neutralizing amount of monovalent cations, and a large concentration N_1 of a monovalent salt. This is a more practical

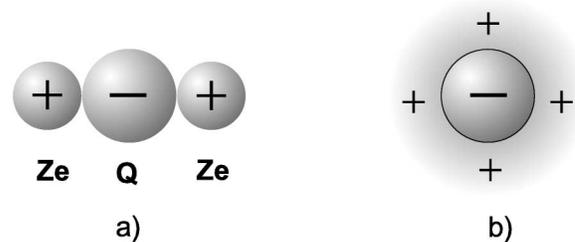


FIG. 1. (a) A toy model of charge inversion. (b) PB approximation does not lead to charge inversion.

problem than the salt-free one considered in Refs. [4,5]. Correspondingly, we assume that all interactions are screened with Debye-Hückel screening length $r_s = (8\pi l_B N_1)^{-1/2}$, where $l_B = e^2/(Dk_B T)$ is the Bjerrum length, e is the charge of a proton, and $D \approx 80$ is the dielectric constant of water.

We begin with the simplest macroion which is a thin charged sheet immersed in water solution (Fig. 2a). Later we examine a more realistic macroion, a thick insulator charged at the surface (Fig. 2b).

It should be stressed from the very beginning that Z -ions and monovalent ions contribute to the screening very differently. Indeed, under realistic conditions (which we specify in more detail below), every Z -ion, when on the plane, is adsorbed to the macroion with energy well in excess of $k_B T$. At the same time, monovalent ions, maintaining electroneutrality over the distances of order r_s , interact with the macroion with energies less than $k_B T$ each. This distinction leads us to define the net charge of the macroion including adsorbed Z -ions and excluding monovalent ions:

$$\sigma^* = -\sigma + Zen, \quad (1)$$

where n is the two-dimensional concentration of Z -ions on the plane. Calculation of σ^* represents the main task of this work, as it has direct experimental relevance. First, the number of strongly bound Z -ions can be counted using, e.g., atomic force microscopy. Positive σ^* means ‘‘overpopulation,’’ i.e., charge inversion: there are more bound Z -ions than the neutrality condition implies. Second, it is σ^* that determines mobility of the macroion in weak field electrophoresis experiments, because Z -ions are bound to the surface with binding energy larger than $k_B T$. In general, due to the condensation of monovalent ions on Z -ion, one should replace Z in Eq. (1) with an effective charge of the Z -ion. This effective charge will be considered in more detail at the end of the paper where we discuss the maximal charge inversion.

Integrating out all monovalent ions degrees of freedom, or, equivalently, considering all interactions screened at the

distance r_s , we can write down the free energy per unit area in the form

$$F = \pi\sigma^2 r_s/D - 2\pi\sigma r_s Zen/D + F_{ZZ} + F_{id}, \quad (2)$$

where the four terms are responsible, respectively, for the self-interaction of the charged plane, for the interaction between Z -ions and the plane, for the interaction between Z -ions, and for the entropy of an ideal two-dimensional gas of Z -ions.

Using Eq. (1) one can rewrite Eq. (2) as

$$F = \pi(\sigma^*)^2 r_s/D + F_{OCP}, \quad (3)$$

where $F_{OCP} = F_c + F_{id}$ is the free energy of the same system of Z -ions residing on a neutralizing background with surface charge density $-Zen$, which is conventionally referred to as one component plasma (OCP), and

$$F_c = -\pi(Zen)^2 r_s/D + F_{ZZ} \quad (4)$$

is the correlation part of F_{OCP} . This transformation can be simply interpreted as the addition of uniform charge densities $-\sigma^*$ and σ^* to the plane. The first addition makes a neutral OCP on the plane. The second addition creates two plane capacitors with negative charges on both sides of the plane which screen inverted charge of the plane at the distance r_s . The first term of Eq. (3) is nothing but the energy of these two capacitors. There is no cross term in energy between the OCP and the capacitors because each plane capacitor creates a constant potential, $\psi(0) = 2\pi\sigma^* r_s/D$, at the neutral OCP.

Using Eq. (4), the electrochemical potential of Z -ions at the plane can be written as $\mu = Ze\psi(0) + \mu_{id} + \mu_c$, where μ_{id} and $\mu_c = \partial F_c/\partial n$ are, respectively, the ideal and the correlation parts of the chemical potential of OCP. In equilibrium, μ is equal to the chemical potential, μ_b , of Z -ions in the bulk solution, because the electrostatic potential $\psi = 0$ in the bulk. Using Eq. (3), we have

$$2\pi\sigma^* r_s Ze/D = -\mu_c + (\mu_b - \mu_{id}). \quad (5)$$

As we show below, in most practical cases the correlation effect is rather strong, so that μ_c is negative and $|\mu_c| \gg k_B T$. This means that for large enough concentration of Z -ions in the bulk and at the surface, n , both bulk chemical potential μ_b and ideal part of surface chemical potential μ_{id} should be neglected compared to μ_c . Furthermore, strong correlations imply that at least short-range order of Z -ions on the surface should be similar to that of the triangular Wigner crystal (WC) since it delivers the lowest energy to OCP. Therefore,

$$\sigma^* = \frac{D}{2\pi r_s} \frac{|\mu_c|}{Ze} \approx \frac{D}{2\pi r_s} \frac{|\mu_{WC}|}{Ze}. \quad (6)$$

We see now that the net charge density σ^* is positive. This proves inversion of the bare charge density $-\sigma$. Equation (6) has a very simple meaning: $|\mu_{WC}|/Ze$ is the

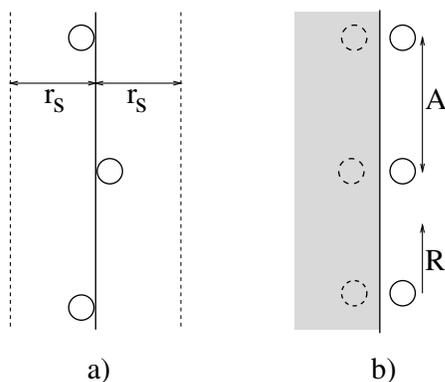


FIG. 2. Models studied in this paper. Z -ions are shown by full circles. (a) Charged plane immersed in water. (b) Surface of a large macroion. Image charges are shown by broken circles.

“correlation” voltage which charges the two above mentioned parallel capacitors with thickness r_s and total capacitance per unit area $D/(2\pi r_s)$.

To calculate the correlation voltage $|\mu_{\text{WC}}|/Ze$, we start from the case of weak screening when r_s is larger than the average distance between Z -ions. In this case, screening does not affect the thermodynamic properties of WC. The energy per Z -ion $\varepsilon(n)$ of such Coulomb WC at $T = 0$ can be estimated as the interaction energy of a Z -ion with its Wigner-Seitz cell, because the quadrupole-quadrupole interaction energy of neighboring neutral Wigner-Seitz cells is very small. This gives $\varepsilon(n) = -Z^2 e^2 / RD$, where $R = (\pi n)^{-1/2}$ is the radius of a Wigner-Seitz cell (we approximate the hexagon by a disk). More accurately [7] $\varepsilon(n) = -1.1Z^2 e^2 / RD = -1.96n^{1/2} Z^2 e^2 / D$. One can discuss the role of a finite temperature on WC in terms of the inverse dimensionless temperature $\Gamma = Z^2 e^2 / (RDk_B T)$. We are interested in the case of large Γ . For example, at a typical $Zen = \sigma = 1.0e/\text{nm}^2$ and at room temperature, $\Gamma = 10$ even for $Z = 4$. Since the Wigner crystal melts [8] at $\Gamma = 130$, we are dealing with a strongly correlated liquid for $\Gamma < 130$. Numerical calculations, however, confirm that at $\Gamma \gg 1$ thermodynamic properties of the strongly correlated liquid are close to those of WC [9]. Therefore, for our estimates of μ_c we can still write that $F_c = n\varepsilon(n)$ and use

$$\mu_{\text{WC}} = \frac{\partial[n\varepsilon(n)]}{\partial n} = -1.65\Gamma k_B T = -1.65 \frac{Z^2 e^2}{RD}. \quad (7)$$

We see now that indeed μ_{WC} is negative and $|\mu_{\text{WC}}| \gg k_B T$, so that Eq. (6) is justified. Substituting Eq. (7) into Eq. (6), we get $\sigma^* = 0.83Ze/(\pi r_s R)$. At $r_s \gg R$, charge density $\sigma^* \ll \sigma$, $Zen \approx \sigma$, and one can replace R by $R_0 = (\sigma\pi/Ze)^{-1/2}$. This gives

$$\sigma^*/\sigma = 0.83(R_0/r_s) = 0.83\zeta^{1/2}, \quad (\zeta \ll 1), \quad (8)$$

where $\zeta = Ze/\pi\sigma r_s^2$ is a dimensionless charge of a Z -ion. Thus, at $r_s \gg R$ or $\zeta \ll 1$, inverted charge density grows with decreasing r_s . Extrapolating to $r_s = 2R_0$, where screening starts to substantially modify the interaction between Z -ions, we obtain $\sigma^* = 0.4\sigma$.

Now we switch to the case of strong screening, $r_s \ll R$, or $\zeta \gg 1$. It seems that in this case σ^* should decrease with decreasing r_s , because screening reduces the energy of WC and leads to its melting. In fact, this is what eventually happens. However, there is a range of $r_s \ll R$ where the energy of WC is still large. In this range, as r_s decreases, the repulsion between Z -ions becomes weaker, which in turn makes it easier to pack more of them on the plane. Therefore, σ^* continues to grow with decreasing r_s .

At $r_s \ll R$ one is still able to estimate thermodynamic properties of OCP from the model of a triangular WC. Keeping only interactions with the six nearest neighbors

in Eq. (4), we can write the correlation part of the free energy of the screened WC per unit area as

$$F_c = -\frac{\pi r_s (Zen)^2}{D} + 3n \frac{(Ze)^2}{DA} \exp(-A/r_s), \quad (9)$$

where $A = (2/\sqrt{3})^{1/2} n^{-1/2}$ is the lattice constant of this WC. Calculating the chemical potential of Z -ions at the plane, $\mu_{\text{WC}} = \partial F_c / \partial n$, and substituting it into Eq. (6) one finds that $A \approx r_s \ln \zeta$, $R \approx (2\pi/\sqrt{3})^{1/2} r_s \ln \zeta$ and

$$\frac{\sigma^*}{\sigma} \approx \frac{2\pi\zeta}{\sqrt{3} \ln^2 \zeta}, \quad (\zeta \gg 1). \quad (10)$$

Alternatively, one can derive Eq. (10) by direct minimization of Eq. (2) with respect to n . In this way, one does not need a capacitor interpretation which is not as transparent in this case as for $r_s \gg R$.

Thus, at $r_s \ll R$, or $\zeta \gg 1$ the distance R decreases and inverted charge continues to grow with decreasing r_s . This result could be anticipated for the toy model of Fig. 1a if Coulomb interaction between the spheres is replaced by a strongly screened one. Screening obviously affects repulsion between positive spheres stronger than their attraction to the negative one and, therefore, makes maximum allowed charges Ze larger.

Above we studied analytically two extremes, $r_s \gg R$ and $r_s \ll R$. In the case of arbitrary r_s we can find σ^* numerically. For this purpose we calculate μ_{WC} from Eq. (4) and substitute it in Eq. (6). This gives

$$\frac{1}{\zeta} = \sum_{r_i \neq 0} \frac{3 + r_i/r_s}{8r_i/r_s} e^{-r_i/r_s}, \quad (11)$$

where the sum is taken over all vectors of WC lattice and can be evaluated numerically. Then one can find the equilibrium n for any given values of $\zeta = Ze/\pi\sigma r_s^2$. The resulting ratio σ^*/σ is plotted by the solid curve in Fig. 3.

The results discussed so far were derived for the charged plane which is immersed in water and screened on both sides by Z -ions and monovalent salt (Fig. 2a). In reality the charged plane is typically the surface of a rather thick membrane whose (organic, fatty) material is a dielectric with permeability much less than that of water. In this case, image charges which have the same sign as Z -ions must be taken into account (Fig. 2b). We have analyzed this situation in detail, which will be reported elsewhere. The main result turns out to be very simple: while image charges repel Z -ions and drive the entire Wigner crystal somewhat away from the surface, their major effect is that in this case only one capacitor must be charged (on the water side of the surface). Accordingly, the ratio σ^*/σ is reduced by a factor very close to 2 compared to the case of the two-sided plane (Fig. 3).

We are prepared to address now the question of maximal possible charge inversion. How far can a macroion be overcharged, and what should one do to achieve that? Figure 3 and Eq. (9) suggest that the ratio σ^*/σ continues to grow with growing ζ . However, the possibilities to increase ζ are limited along with the assumptions of

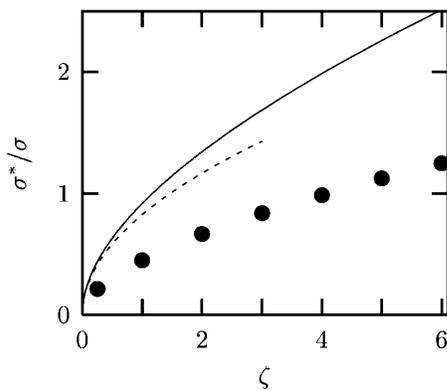


FIG. 3. The ratio σ^*/σ as a function of the charge ζ . The solid curve is calculated for a charged plane by a numerical solution to Eq. (11); the dashed curve is the large r_s limit, Eq. (8). The \bullet points are calculated for the screening of the surface of the semispace with dielectric constant much smaller than 80. In this case image charges (Fig. 2b) are taken into account.

the theory presented here. Indeed, there are two ways to increase $\zeta = Ze/\sigma\pi r_s^2$, namely, to choose a surface with small σ or to choose ions with large Z . The former way is restricted because Z -ions remain strongly bound to the surface only as long as $|\mu_{WC}| \approx 2\pi r_s \sigma Ze/D \gg k_B T$ or $\zeta < 2Z^2 l_B/r_s$. Therefore, the latter way, which is to increase Z , is really the most important. It is, however, also restricted, because at large Z , monovalent ions start to condense on the Z -ion [10]. Assuming Z -ions are spheres of radius a , their effective net charge at large Z can be written as $Z_{\text{eff}} = (2a/l_B) \ln(r_s/a)$, yielding $\zeta < 8(a^2/l_B r_s) [\ln(r_s/a)]^2$. Since this estimate was derived under the assumption that $r_s > a$, the largest a we can choose is $a = r_s$. For $r_s = a = 10 \text{ \AA}$, the charge ζ may be as high as about 10, so that the ratio σ^*/σ can exceed 100%.

Meanwhile, there is a much more powerful way to increase charge inversion. Suppose we consider Z -ions to have the shape of long rigid rods. Such a situation is very practical, since it corresponds to the screening of charged surface by rigid polyelectrolytes, such as DNA double helix [11]. In this case, correlation between Z -ions leads to parallel, nematiclike ordering of rods on the surface. In other words, WC in this case is one dimensional, perpendicular to the rods. The chemical potential μ_{WC} in this case is about the interaction energy of one rod with its corresponding stripe of surface charge, which plays the role of the Wigner-Seitz cell. Importantly, this energy, along with the effective net charge, Z_{eff} , is proportional to the rod length L and thus can be very large. Rods can be strongly bound, with chemical potential much exceeding $k_B T$, even at very small σ . This holds even in spite of the Onsager-Manning condensation [12] of monovalent ions on the rods: for instance, for $A > r_s > a$ one has $Z_{\text{eff}} = L\eta_c/e = L/l_B$, where A and a are, respectively, the distance between rods in

WC and the radius of the rod (double helix); $\eta_c = e/l_B$. As a result the ratio σ^*/σ grows with decreasing r_s as $\sigma^*/\sigma \approx (\eta_c/2r_s\sigma) \ln(\eta_c/2\pi r_s\sigma)$. At $r_s \sim a$ and small enough σ this ratio can be much larger than one. This phenomenon can be called *giant charge inversion*.

Giant charge inversion can be also achieved if DNA screens a positively charged wide cylinder with the radius greater or about the DNA double helix persistence length (500 \AA). In this case DNA spirals around the cylinder, once again with WC-type strong correlations between subsequent turns. We leave open the possibility to speculate on the relevance of this model system to the fact that bare charge of DNA overcharges a nucleosome by about 15% [6].

To conclude, we have presented simple physical arguments explaining the nature and limitations of charge inversion in a system where no interactions are operational except for Coulomb and short-range hard core repulsion. Correlations between bound ions, which are strong for multivalent counterions with $Z \gg 1$, provide the powerful mechanism for charge inversion in purely electrostatic systems. We have shown that even spherical Z -ions adsorbed on a large plane macroion can lead to charge inversion larger than 100%, while for rodlike Z -ions charge inversion can be even larger.

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