Charged surface in salty water with multivalent ions: Giant inversion of charge.

T. T. Nguyen, A. Yu. Grosberg, and B. I. Shklovskii

Department of Physics, University of Minnesota, 116 Church St. Southeast, Minneapolis, Minnesota 55455

Screening of a strongly charged macroion by oppositely charged colloidal particles, micelles, or short polyelectrolytes is considered. Due to 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 a water solution, that its net charge changes sign. As shown below the binding energy of 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 a weak field electrophoresis. Charge inversion has been observed in polyelectrolyte-micelle system 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 the living cell for the purpose of gene therapy. The problem is that both bare DNA and a cell surface is positive and as large as 3 $|Q|$. This example demonstrates the possibility of an almost 300% charge inversion. 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, description of screening of the central sphere in PB approximation smears the positive charge, as shown on Fig. 1b and does not lead to the charge inversion. Indeed, in this case charge accumulates in spherically symmetric screening atmosphere only until the point of neutrality at which electric field reverses its sign and attraction is replaced by repulsion.

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 $|Q|Ze/(a + b) - Ze^2/2(a + b)$ 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.

![FIG. 1. a) A toy model of charge inversion. b) PB approximation does not lead to charge inversion.](image-url)

In this paper we consider screening of a macroion surface with negative immobile surface charge density $-\sigma$ by finite concentration of positive $Z$-ions, neutralizing amount of monovalent coions, and a large concentration $N_1$ of a monovalent salt. This is more practical problem than one considered in Ref. [4], where monovalent salt was absent. Correspondingly, we assume that all interactions are screened with Debye-Hückel screening length $r_s = (8\pi l_B N_1)^{-1/2}$, where $l_B = e^2/(D k_B T)$ is the Bjer-
rum length, \( e \) is the charge of a proton, \( D \approx 80 \) 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 more realistic macroion which is a thick insulator charged at the surface (Fig. 2b).

Assume that the plane with the charge density \( -\sigma \) is covered by \( Z \)-ions with two-dimensional concentration \( n \). Integrating out all monovalent ions, or, equivalently, considering all interactions screened at the distance \( r_s \), we can write down the free energy per unit area in the form

\[
F = \pi \sigma^2 r_s / D - 2\pi \sigma r_s \varepsilon n / D + F_{ZZ} + F_{id},
\]

where the four terms are responsible, respectively, for the interaction between \( Z \)-ions and the plane, for the interaction between \( Z \)-ions and for the entropy of ideal two-dimensional gas \( Z \)-ions.

Our goal is to calculate the net charge density of the plane

\[
\sigma^* = -\sigma + \varepsilon n.
\]

Using Eq. (3) one can rewrite Eq. (1) as

\[
F = \pi (\sigma^*)^2 r_s / D + F_{OCP},
\]

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 \( -\varepsilon n \), which is conventionally referred to as one component plazma (OCP), and

\[
F_c = -\pi (\varepsilon n)^2 r_s / D + F_{ZZ}.
\]

is the correlation part of \( F_{OCP} \). This transformation can be simply interpreted as the addition of uniform charge densities \( -\sigma^* \) and \( \sigma^* \) to the plane. The first addition makes a neutral OCP on the plane. The second plane of charge 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. (3), the electrochemical potential of \( Z \)-ions at the plane can be written as \( \mu = Ze \psi(0) + \mu_{id} + \mu_c \), where \( \mu_{id} \) and \( \mu_c = \partial F_c / \partial n \) are the ideal and the correlation parts of the chemical potential of OCP. In equilibrium, \( \mu_c \) is equal to the chemical potential, \( \mu_b \) of the bulk solution, because in the bulk electrostatic potential \( \psi = 0 \). Using Eq. (3), we have:

\[
2\pi \sigma^* r_s Ze / D = -\mu_c + (\mu_b - \mu_{id})
\]

As we show below, in most practical cases the correlation effect is rather strong, so that \( \mu_c \) 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 \( \mu_b \) and ideal part of surface chemical potential \( \mu_{id} \) should be neglected compared to \( \mu_c \). Furthermore, strong correlations imply that at least short range order of \( Z \)-ions on the surface should be similar to that of triangular Wigner crystal (WC) since it delivers the lowest energy to OCP. Therefore,

\[
\sigma^* = \frac{D}{2\pi r_s} \left| \frac{\mu_c}{Ze} \right| \approx \frac{D}{2\pi r_s} \frac{|\mu_{WC}|}{Ze}.
\]

We see now that the net charge density \( \sigma^* \) is positive. This proves inversion of the bare charge density \( -\sigma \). Eq. (2) has a very simple meaning: \( |\mu_{WC}|/Ze \) is the "correlation" voltage which charges 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 \( |\mu_{WC}|/Ze \), 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 thermodynamic properties of WC. The energy per \( Z \)-ion \( \varepsilon(n) \) of such Coulomb WC at \( T = 0 \) can be estimated as an interaction energy of a \( Z \)-ion with its Wigner-Seitz cell, because interaction energy of neighboring neutral Wigner-Seitz cells is very small.

This gives \( \varepsilon(n) = -Z^2 e^2 / R \), where \( R = (\pi n)^{-1/2} \) is the radius of a Wigner-Seitz cell (we approximate hexagon by a disc). More accurately, \( \varepsilon(n) = -1.12 Z^2 e^2 / R D = -1.96 n^{1/2} Z^2 e^2 / D \). One can discuss the role of a finite temperature on WC in terms of the inverse dimensionless temperature \( \Gamma = Z^2 e^2 / (R D k_B T) \). We are interested in the case of large \( \Gamma \). For example, at a typical \( \varepsilon(n) = 1.0 \) e/\(nm^2 \) and at room temperature, \( \Gamma = 10 \) even for \( Z = 4 \). Wigner crystal melts at \( \Gamma = 130 \), so that for \( \Gamma < 130 \) we deal with a strongly correlated liquid. Numerical calculations, however, confirm that at \( \Gamma \gg 1 \) thermodynamic properties of strongly correlated liquid are close to that of WC. Therefore, for estimates of \( \mu_c \) we can still write that \( F_c = n \varepsilon(n) \) and use

\[
\mu_{WC} = \frac{\partial (n \varepsilon(n))}{\partial n} = -1.65 \Gamma k_B T = -1.65 Ze^2 / R D.
\]
We see now that indeed $\mu_{WC}$ is negative and $|\mu_{WC}| \gg k_B T$, so that Eq. (8) is justified. Substituting Eq. (8) into Eq. (4), we get $\sigma^* = 0.83Ze/\pi r_0 R$. At $r_s \gg R$, charge density $\sigma^* \ll \sigma$, and $\Sigma n \simeq \sigma$, one can replace $R$ by $R_0 = (\pi Ze)^{-1/2}$. This gives

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

where $\zeta = Ze/\pi\sigma r_0^2$ 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 $\sigma^*$ 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, what in turn makes it easier to pack more of them on the plane. Therefore, $\sigma^*$ 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 6 nearest neighbors in Eq. (4), we can write the correction part of free energy of screened WC per unit area as

$$F_c = -\pi r_0 (Ze)^2 D + 3n (Ze)^2 \exp(-A/r_s), \quad (9)$$

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, $\mu_{WC} = \partial F_c/\partial \Sigma n$ and substituting it into Eq. (8) one finds that $A \simeq r_s \ln(3\zeta/4)$, $R \simeq (2\pi/\sqrt{3})^{1/2} r_s \ln(3\zeta/4)$ and

$$\frac{\sigma^*}{\sigma} = \frac{2\pi \zeta}{\sqrt{3} \ln(3\zeta/4)} - 1, \quad (\zeta \gg 1). \quad (10)$$

Alternatively, one can derive Eq. (10) by direct minimization of Eq. (4) with respect of $\Sigma n$. 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 $\sigma^*$ numerically. For this purpose we calculate $\mu_{WC}$ from Eq. (4) and substitute it in Eq. (8). This gives

$$\frac{1}{\zeta} = \sum_{r_s \neq 0} \frac{3 + r_s^4 / r_s^6}{8 r_s / r_s^6} e^{-r_s / r_s}, \quad (11)$$

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 $\zeta$. The resulting ratio $\sigma^*/\sigma$ is plotted by the solid curve in Fig. 3.

![Graph](image_url)

**FIG. 3.** The ratio $\sigma^*/\sigma$ as a function of the charge $\zeta$. The solid curve is calculated for a charged plane by a numerical solution to eq. (10), the dashed curve is the large $r_s$ limit, eq. (8). The • 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.

Since the value of $\sigma^*$ represents the main result of our work, its subtle physical meaning should be clearly understood. Indeed, the entire system, macroion plus overcharging $Z$-ions, is of course neutralized by the monovalent salt. One can ask then, what is the meaning of charge inversion? The answer is simple for $r_s \gg R$, when charge $\sigma^*$ is well separated in space from the oppositely charged atmosphere of monovalent salt (which leads to the interpretation based on two capacitors, see above). When $r_s \ll R$ there is no such obvious spatial separation. Nevertheless, $\sigma^*$ can be observed, because $Z$-ions are bound with energies well above $k_B T$ while small ions are only weakly bound. First, the number of bound $Z$-ions can be counted using, e.g., the atomic force microscopy. Positive $\sigma^*$ means “over-population”: there are more bound $Z$-ions than neutrality condition implies. Second, it is $\sigma^*$ that determines the mobility of macroion in the weak field electrophoresis experiments.

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 charged plane is typically a 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 details, 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 $\sigma^*/\sigma$ is reduced by a factor very close to 2 compared to the case of 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 equation (9) suggest that the ratio $\sigma^*/\sigma$ continues to grow with growing $\zeta$. However, the possibilities to increase $\zeta$ are limited along with the assumptions of the presented theory. Indeed, there are two ways to increase $\zeta = Ze/\sigma \pi r_s^2$, namely to choose surface with small $\sigma$ and ions with large $Z$. The former way is restricted because $Z$-ions remain strongly bound to the surface only as long as $|\mu_{WC}| \simeq 2\pi r_s \sigma Ze/D \gg k_BT$ 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 sphere. Assuming $Z$-ions are spheres of the radius $a$, their effective net charge at large $Z$ can be written as $Z_{eff} = (a/l_B) 2 \ln \left( Z l_B r_s/a^2 \right)$, yielding $\zeta < 8 (a^2/l_B r_s) \ln \left( Z l_B r_s / a^2 \right)^2$. Since this estimate was derived under the assumption that $r_s > a$, the largest $a$ we can choose is $a = r_s$. For $r_s = a = 10A$ charge $\zeta$ may be as high as about 10, so that the ratio $\sigma^*/\sigma$ can exceed 100%.

Since charge inversion grows with increasing $a$ we are tempted to explore the case $a > r_s$. To address this situation, our theory needs a couple of modifications. Specifically, in the first term of Eq. (1) we must take into account the fact that only a part of $Z$-ion interacts with the surface, namely the segment which is within the distance $r_s$ from the surface. One should also take into account that strong screening increases $Z_{eff}$. Assuming $Z$-ion is a sphere, this modifies upper bound for $\zeta$ by a factor $a/r_s$ and thus it makes charge inversion even larger. We do not discuss this regime in details, because it is highly non-universal, dependent on the shape and charge distribution of the $Z$-ions, plane roughness, etc.

Meanwhile, there is much more powerful way to increase charge inversion. Suppose we take $Z$-ions with 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 1. In this case, correlation between $Z$-ions leads to parallel, nematic-like ordering of rods on the surface. In other words, WC in this case is one-dimensional, perpendicular to rods. Chemical potential $|\mu_{WC}|$ in this case is about the interaction energy of one rod with the stripe of the surface charge, which plays the role of the Wigner-Seitz cell. Importantly, this energy, along with the effective net charge, $Z_{eff}$, are proportional to the rod length $L$ and thus can be very large. Rods can be strongly bound, with chemical potential much exceeding $k_BT$, even at very small $\sigma$. This holds even in spite of the Onsager-Manning condensation 12 of monovalent ions on the rods: for instance, at $A > r_s > a$ one has $Z_{eff} = L n_k/e$, where $A$ and $a$ are, respectively, the distance between rods in WC and radius of the rod (double helix), $n_k = k_BT/e$. As a result the ratio $\sigma^*/\sigma$ grows with decreasing $r_s$ as $\sigma^*/\sigma \simeq (n_k/2r_s\sigma) \ln (n_k/2r_s\sigma)$. At $r_s \sim a$ and small enough $\sigma$ 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 (500A). 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 DNA overcharges a nucleosome by about 20%.

To conclude, we have presented simple physical arguments explaining the nature and limitations of charge inversion in the 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 $Z \gg 1$, are the powerful source of charge inversion for purely electrostatic system. We have shown that even spherical $Z$-ions adsorbed on a large plane macroion can lead to charge inversion larger than 100%, while for rod-like $Z$-ions charge inversion can reach gigantic proportions.

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1. Y. Wang, K. Kimura, Q. Huang, P. L. Dubin, W. Jaeger, Macromolecules, 32 (21), 7128 (1999).
2. P. L. Felgner, Sci. American, 276, 86 (1997).
3. J. Ennis, S. Marcelja and R. Kjellander, Electrochim. Acta, 41, 2115 (1996).
4. V. I. Perel and B. I. Shklovskii, Physica A 274, 446 (1999).
5. B. I. Shklovskii, Phys. Rev. E60, 5802 (1999).
6. E. M. Mateescu, C. Jeppersen and P. Pincus, Europhys. Lett. 46, 454 (1999); S. Y. Park, R. F. Bruinsma, and W. M. Gelbart, Europhys. Lett. 46, 493 (1999); J. F. Joanny, Europ. J. Phys. B 9, 117 (1999).
7. L. Bonsall, A. A. Maradudin, Phys. Rev. B15, 1959 (1977).
8. R. C. Gann, S. Chakravarty, and G. V. Chester, Phys. Rev. B 20, 326 (1979).
9. H. Totsuji, Phys. Rev. A 17, 399 (1978).
10. M. Guerom, G. Weisbuch, Biopolymers, 19, 353 (1980); S. Alexander, P. M. Chaikin, P. Grant, G. J. Morales, P. Pincus, and D. Hone, J. Chem. Phys. 80, 5776 (1984); S. A. Safran, P. A. Pincus, M. E. Cates, F. C. MacKintosh, J. Phys. (France) 51, 503 (1990).
11. Ye Fang, Jie Yang, J. Phys. Chem. B 101, 441 (1997).
12. G. S. Manning, J. Chem. Phys. 51, 924 (1969).