Giant Charge Inversion of a Macroion Due to Multivalent Counterions and Monovalent Coions: Molecular Dynamics Study

Motohiko Tanaka¹, and A.Yu Grosberg²

¹National Institute for Fusion Science, Toki 509-5292, Japan
²Department of Physics, University of Minnesota, Minneapolis, MN 55455

We report molecular dynamics simulation of the (overall neutral) system consisting of an immobile macroion surrounded by the electrolyte of multivalent counterions and monovalent coions. As expected theoretically, counterions adsorb on the macroion surface in the amount much exceeding neutralization requirement, thus effectively inverting the sign of the macroion charge. We find two conditions necessary for charge inversion, namely, counterions must be multivalently charged and Coulomb interactions must be strong enough compared to thermal energy. On the other hand, coion condensation on the multivalent counterions similar to Bjerrum pairing is the major factor restricting the amount of charge inversion. Depending on parameters, we observe inverted charge up to about 200% the original charge of the macroion in absolute value. The inverted charge scales as \( \sim \zeta^{1/2} \) when \( \zeta < 1 \) and crosses over to \( \sim \zeta \) for \( \zeta > 1 \), where \( \zeta = (A_0/r_s)^2 \), \( r_s \) is the Debye screening length in the electrolyte and \( A_0 \) is the distance between adsorbed counterions under neutralizing conditions. These findings are consistent with the theory of "giant charge inversion" [Phys.Rev.Lett., 85, 1568 (2000)].

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I. INTRODUCTION

Correlation effects in the systems of charged particles, such as plasma or electrolyte solution, are well known since the works by Debye and Hückel in 1923 [1]. Classical intuition suggests that correlation can be viewed as screening in which a cloud of ions around, say, positive particle is slightly dominated by negative counterions, such that for an outside observer (who measures the electric field) the shield of predominantly negative charges effectively reduces the central positive charge. Recently, a significant attention has been attracted by the notion that much more dramatic effect is possible in the system with strongly charged ions [2]. Namely, instead of charge reduction due to the shielding, it is possible to observe charge inversion due to the "over-screening". Furthermore, it was shown a year ago that the inverted charge may be quite large, even larger in absolute value than the original bare charge, giving rise to the concept of "giant" charge inversion [3].

In the present paper, we use molecular dynamics simulation technique to address the question of possible limits of charge inversion. Overall, we confirm the theoretical prediction [3] and observe "giant" charge inversion, with the ratio of inverted and bare charges reaching up to about 1.6 (in absolute value).

Although we consider here only primitive schematic model with spherical ions immersed in the medium of a constant dielectric permeability \( \epsilon \), this should be viewed as the step towards better understanding of such first magnitude scientific problems as, e.g., that of chromatin structure. Indeed, chromatin represents a complex of strongly negatively charged thread of DNA with positively charged smaller protein molecules. For instance, virtually every paper on charge inversion mentions the fact that protein core of a nucleosome particle [4] carries lesser amount of positive charge than the amount of negative charge on the wrapped around DNA. On a simpler level, complexes of polycations and polyanions were under scrutiny for a long time [5], as well as complexes of charged polymers with charged colloids [6].

In theoretical aspect, the most advanced treatment of charge inversion is due to Shklovskii and his co-workers [1, 2, 5]. In these works, the universal physical mechanism behind charge inversion is recognized as correlations between shielding ions (see also brief review article [6]). In the work [2], the idealized image of these shielding counterions forming a Wigner crystal on the surface of the shielded macroion was emphasized (see also earlier work [1]). However, it was mentioned in [2] and addressed in more details in [3] that in most real cases, correlations are not quite as strong as to produce a crystal, but sufficient to maintain short range order, and, therefore, correlation energy is similar to that of a crystal. Obviously, this mechanism is operational when shielding ions are strongly charged. Furthermore, it was realized that the best situation for charge inversion occurs when monovalent salt is present in addition to strongly charged ions [3] (see also [5]). Salt ions, as their charges are small, behave in a "traditional" way; they simply screen all interactions at the distance about Debye length \( r_s \). However trivial itself, this leads to a dramatic increase of charge inversion, because the attraction of a counterion to its Wigner-Seitz cell on the macroion surface is over a significantly shorter range than the repulsion of a counterion from the uncompensated charge of all other counterions. For completeness, we mention here also recent works developing charge inversion theory to include polyelectrolyte ions [4, 1], as well as more formal theoretical approaches [1].

Charge inversion has been seen several times in simu-
lations, starting from the pioneering work [17]. In recent works [18, 22] computer simulations were reported along with various ways to re-derive and re-examine the concept of lateral correlations between counterions as the driving force behind charge inversion. The authors of [18, 21] reported quite impressive agreement between theoretical conjectures and their computation data. However, sophisticated, these simulations concentrated on the cases of no added salt and of abundance of counterions. In other words, they only examined the very dilute extreme with respect to macromions assuming at the same time finite concentration of counterions. Our first intent in the present work is to relax this serious restriction and to simulate a realistic model in which thermodynamic cost of adsorption of counterions on the surface of a macrion is contributed by both the events on the macroion surface and in the surrounding solution.

The other closely connected goal of our present study has to do with the following delicate aspect of the "giant" charge inversion scenario. In order to make correlations and charge inversion stronger, one is tempted to choose larger ratio of Coulomb energy to thermal energy. But when it is too large, the small salt ions start to condense on the surfaces of counterions, effectively reducing their charge. Therefore, charge inversion is expected to be the strongest in the intermediate regime, when correlations between counterions are already strong, but condensation of small ions on them is still weak. Therefore, we want to check in the present work computationally how robust is this theoretical prediction.

To achieve the above stated goals, we perform in the present paper molecular dynamics study of the system consisting of a single macroion, large number of multivalent counterions, and a multitude of monovalent coions immersed in a Langevin fluid. It is worth noting that hydrodynamic effects, which may be of significant importance for interactions between colloidal particles away from thermodynamic equilibrium [18, 22], are totally ignored in the present study, because we concentrate on the equilibrium aspects only.

The paper is organized as follows. The simulation method and parameters are described in Section II. In Section I, by direct measurement of the peak height of the radial charge distribution we show that giant charge inversion takes place when the following two conditions are simultaneously met: (1) multivalent counterions with valence $Z \geq 2$ are present, and (2) Coulomb energy prevails over the thermal energy at the length scale of a single ion size, $a$: $\Gamma = Z^2 e^2 / e k_B T > 1$. We study in details the dependence of charge inversion on the radius and charge of the macroion, the valence and density of counterions and coions, and temperature. For large density and valence of counterions, the amount of inverted charge increases linearly with ionic strength, and reaches up to 200% the original macroion charge.

Extension of the present work to the case under electrophoretic environments is discussed in a separate paper [27] in which the effect of an applied electric field on the charge inversion process is investigated with the use of molecular dynamics simulation.

II. SIMULATION METHOD AND PARAMETERS

A. Equations

Specifically, we consider the following model. The system includes: a single macroion with negative charge $Q_0 < 0$, $N^+$ multivalent counterions with a positive charge $Ze$ each, and $N^-$ monovalent coions with a negative charge ($-e$) each ($e > 0$ is the elementary charge). Overall charge neutrality is strictly enforced: $Q_0 + ZeN^+ - eN^- = 0$. All ions are confined within the three-dimensional simulation domain having spherical shape with radius $R_M$. The macroion is considered immobile; it is placed at the origin (center of the domain), and all other ions are mobile. All ions are supposed to be of spherical shapes, with macroion having radius $R_0$ and all mobile ions having identical radius $a$; $a$ serves also as a unit of length.

The (classical) molecular dynamics simulation solves the Newton-Langevin equations of motion

$$m_i \frac{dv_i}{dt} = -\nabla \Phi(r_i) - \nabla \phi(r_i) - \nu a v_i + F_{th} ,$$  
$$\frac{d r_i}{dt} = v_i ,$$  

(1)  

where the potentials $\Phi$ and $\phi$ describe interactions of a given ion with other mobile ions and with the macroion, respectively:

$$\Phi(r_i) = \sum_j \left\{ \frac{Z_i Z_j e^2}{\epsilon r_{ij}} + \epsilon_{LJ} \left( \left( \frac{a}{r_{ij}} \right)^{12} - \left( \frac{a}{r_{ij}} \right)^6 \right) \right\} ;$$

$$\phi(r_i) = Z_i e \frac{Q_0}{\epsilon r_i} .$$  

(2)  

Here, $r_i$ and $v_i$ are the position and velocity vectors of the $i$-th particle, $r_{ij} = |r_i - r_j|$, $\epsilon$ the dielectric constant, $\epsilon_{LJ}$ the Lennard-Jones energy. As regards boundaries, we assume elastic reflection every time when a mobile ion hits either the domain boundary at $r = R_M$ or the macroion surface at $r = R_0$. The last two terms of Eq. (1) represent the Langevin thermostat due to surrounding neutral medium. The Stokes formula for a sphere is adopted for the friction term with $\nu$ being the friction constant, and $F_{th}$ is the random $\delta$-correlated thermal agitation.

The inertia term is retained in the momentum equation for numerical stability of the electrostatic forces, masses of all mobile ions are assumed identical, equal to $m$. This leads to the choice of $\omega_p^{-1}$ as the natural time unit, where $\omega_p = (4\pi n_0 e^2 / em)^{1/2}$ is plasma frequency and $n_0$ the average ion number density.
B. Parameters

It must be born in mind that phenomena resembling charge inversion may occur when other forces, apart from Coulomb electrostatic ones, operate in the system (including complicated helical shape of the molecules involved; see, for instance, \[25\]). In this study we are interested in the situation where pure electrostatic forces dominate. Accordingly, we choose \(\epsilon_{LJ} = (1/12)e^2/\epsilon a\); this corresponds to the depth of Lennard-Jones potential well equal to \(-\epsilon_{LJ}/4 = -(1/48)e^2/\epsilon a\), which means that Lennard-Jones attraction force is very small compared to Coulomb force even at the distance of ion size \(a\) and even for monovalent ions.

We also consider densities at which short range repulsion (excluded volume effect) between ions is not important, as volume fraction of particles in the simulation domain, \(\phi = \phi^+ + \phi^- = a^3(N^+ + N^-)/(R_m^3 - R_0^3)\), is small, about \(\phi \approx 0.05\) or less for all cases considered in this paper.

By contrast, Coulomb interactions are strong. To be more specific, there are several relevant parameters controlling different manifestations of Coulomb forces. First of all, multivalent \(Z\)-ions are attracted to the macroion and can be adsorbed on its surface. This is controlled by the parameter

\[
\Gamma_Q = \frac{ZeQ}{\epsilon R_0 T}
\]  
(3)

(for the temperature \(T\), we use energy units and omit Boltzmann constant \(k_B\)). Second, monovalent coions are attracted to the multivalent counterions (\(Z\)-ions), and can condense there, which is controlled by the parameter

\[
\Gamma_a = \frac{Ze^2}{\epsilon a T}
\]  
(4)

A little more delicate matter is the possible correlation between repelling ions, particularly those adsorbed on the macroion. This is characterized by \(\Gamma = Z^2e^2/\epsilon AT\), where \(A\) can be estimated as the distance between two adsorbed counterions in the situation when the number of adsorbed counterions is just sufficient to neutralize the macroion, that is \((Q/Ze)\pi(A/2)^2 = 4\pi R_0^2\) or \(A = 4R_0 \sqrt{Ze/Q}\). Thus,

\[
\Gamma = \frac{Z^3e^3/2Q^{1/2}}{4\epsilon R_0 T}
\]  
(5)

In principle, there is also other similar \(\Gamma\) parameters which control correlations between various ions in the bulk; in this work we do not address this aspect.

In the present study, we typically look at the \(\Gamma_a\) values in the range \(\Gamma = 6 \sim 80\). For the estimates, it is useful to keep in mind that Bjerrum length \(\ell_B = e^2/\epsilon T\) is close to 7 Å under typical conditions - at room temperature in water (\(\epsilon \approx 80\)). In particular, for the typical small ions, for which \(a \approx 4\)Å (counting attached water), we get \(\Gamma_a \approx 1.7 Z\AA\), which is roughly between 4 and 10 for \(Z\) between 2 and 7. As regards \(\Gamma = \Gamma_a (a/4R_0) \sqrt{ZQ/\epsilon}\), it may be greater than \(\Gamma_a\) if macroion is strongly charged (\(Q/\epsilon\) is large).

Note also that under typical conditions, such as \(m \approx 50m_H\) and \(n_0 \approx (1/10\AA)^3\), where \(m_H\) is proton mass, and \(n_0\) the average density of counterions, the characteristic frequency and time are about \(\omega_p \approx 6.6 \times 10^{11}s^{-1}\) and \(\omega_p^{-1} \approx 1.5ps\).

In our molecular dynamics experiment, the initial positions of co- and counterions are distributed randomly between the two spheres \(R_0 < r < R_m\), each ions having the velocity that satisfies the Maxwell distribution. The integration of the equations of motion is done with the use of the leapfrog method which is equivalent to Verlet algorithm \[29\]. The time step of integration is \(\Delta t = 0.01\omega_p^{-1}\), and simulation runs are executed up to 5000\(\omega_p^{-1}\) at which time the peak height of the inverted charge Eq.(5) has become stationary.

Below, in Section II, we report the simulation results concentrating on the general properties of the charge inversion: its dependence on the radius and charge of a macroion, the valence and density of counterions, and temperature. While changing the parameters, the electrostatic binding energy of counterions to the macroion is kept constant by fixing \(\Gamma_Q\) Eq.(3).

In the present study, the following values of parameters are considered "standard" and used unless otherwise specified: radius of the macroion \(R_0 = 3a\), its charge \(Q_0 = -28e\) (assumed negative), valence of the counterions \(Z = 7\), and the number of the counterions and coions \(N^+ = 52\) and \(N^- = 336\), respectively. The radius of the outer boundary sphere is \(R_m = 20a\). The temperature is chosen such that \(\Gamma_a = 4.2Z\).

To support physical intuition, it is useful to estimate the Debye screening length. Naive application of standard formula yields

\[
r_s = \left[\frac{4\pi e^2}{3\pi(R_m^3 - R_0^3)\epsilon T}\right]^{-1/2} = a\left\{\frac{(R_M/a)^3 - (R_0/a)^3}{3^1/3 a} (ZN^+ + Z^{-1}N^-)\right\}^{1/2}
\]  
(6)

which is about 0.5\(a\) under the "standard" conditions. This result may seem surprising, as physically screening length cannot be smaller than the size of smallest ions \[30\]. Of course, such a small value of screening length indicates very strong Coulomb interactions in the bulk solution. This fact can be also seen differently, by noting that the parameters controlling validity of the linearized Debye-Hückel theory for the plasma away from macroion are \(Z \phi_{a}^{1/3}\Gamma_a\) and \(\phi_{a}^{1/3}\Gamma_a/Z\), and they are both large compared to unity, about 10–200 (\(Z = 3–7\)) and 1–4,
cause there are no pairs in which counterions are close to
tions are present between counterions, particularly be-
the macroion surface. It is clear that lateral correla-
while coions (dark blue) stay some distance away from
on the surface of the macroion with a lateral spacing,
where $\lambda = \frac{eT}{2Z\pi\epsilon\sigma} = a \frac{2(R_0/a)^2}{\Gamma_a [Q_0/e]}$ (7)
(were $\sigma = |Q_0|/4\pi R_0^2$) turns out to be about $0.15a/Z$.
(Strictly speaking, $\lambda$ is defined for the plane, not spherical
surface; however, since $\lambda/R_0 \approx 0.05 \ll 1$, defining $\lambda$
based on plane geometry is reasonable.)
For the standard run, it takes about $2.5 \times 10^3 \omega_p^{-1}$ be-
fore a state is reached which can be assumed equilibrated,
at least in terms of the inverted charge being stationary.

III. SIMULATION RESULTS

A. Observing charge inversion

1. Standard regime

The results of our simulations are presented in the
Figures 1-10. Figures 1 and 2 present typical results
of runs performed under what we call "standard" con-
ditions. Specifically, Fig. 1 shows a snapshot of the
spatial distribution of counterions and coions around the
macroion after charge distribution has become station-
ary. Since our simulation includes hundreds of particles,
it is impossible to "see" them in any meaningful way;
what we can see, however, is the configuration of ions in
the immediate vicinity of the macroion surface. This is
shown in Fig. 1 in which only the ions residing in the
thin layer $R_0 \leq r \leq R_0 + 3a$ are depicted.
As seen in Fig. 1, counterions (light blue) attach right
on the surface of the macroion with a lateral spacing,
while coions (dark blue) stay some distance away from the
macroion surface. It is clear that lateral correlations
are present between counterions, particularly be-
cause there are no pairs in which counterions are close to
each other. Not surprisingly, however, this correlations
are much weaker than in the case without coions exam-
ine in [21]; although counterions are correlated in Fig.
their spacings are not regular and cannot be identified
as Wigner crystal. As regards coions, they are seen to
condense on the top side of the counterions, presumably
because of strong repulsion of the coions from macroion
surface. We note here that this condensation of coions
on the counterions is responsible for limiting the amount
of charge inversion. In the configuration shown in Fig.
the numbers of counterions and coions within the dis-
ance $a$ from the macroion surface are $N^+ = 11$ and
$N^- = 5$, respectively. This means that the net charge
of the entire complex, i.e. "macroion + attached counte-
ion + attached coions", is $+44e$. This is to be compared
with the bare macroion charge of $-28e$, which amounts
to charge inversion of about 160% the original macroion
charge.

FIG. 1. The bird's-eye view of the screening atmosphere
within $3a$ from the macroion under "standard" conditions.
Macroion is the red ball in the middle. Multivalent coun-
terions of valence $Z = 7$ and monovalent coions are shown
in dark blue and light blue, respectively. Macroion radius
$R_0 = 3a$, charge $Q_0 = -28e$. Temperature is chosen such
that $\Gamma_a = 29.4$. Note that significant condensation of coions
on the counterions is observed. For this reason, correlations
between adsorbed multivalent counterions are nowhere near
ideal Wigner crystal while $\Gamma_a = 137$ (Eq. 5) is very large.

Figure 2 (a) shows the radial distributions of co- and
counter-ions charges
$$\rho_s(r) = eZ_s \int \frac{\delta(r - r_{si})}{4\pi r_{si}^2} d\Omega_r , (8)$$
where $s$ means either co- or counter-ions, $Z_s$ is, accord-
ingly, either $-1$ or $Z$; summation runs over all ions of
the given sort $s$, $r_{si}$ is the position vector of ion $i$ of
the sort $s$, and $\Omega_r$ is the solid angle of directions of vector $r$. 
These results are consistent with the conclusion of 160% charge inversion. Indeed, the distribution of the counterions, denoted by open bars, is sharply peaked at \( r \approx R_0 \), while that of the coions (shaded bars) is broad and detached from the macroion surface. Although at this stage we do not formulate any rigorous algorithmic definition as to which counterions are close enough to the macroion to be called "bound," we note that the peak in the radial density distribution of counterions is sharp enough to provide for quite clear distinction between bound and unbound ions. We therefore rely on this sharp peak, and in what follows we describe as bound those counterions which belong to this peak.

**FIG. 2.** Charge inversion under "standard conditions", as in Figure 1 (a) The radial distribution function of the charge \( \rho_s(r) \) (Eq. (8)) of counterions (open bars) and that of coions (shaded bars) as a function of the distance \( r \) from the macroion center. (b) The integrated charge distribution \( Q(r)/|Q_0| > 1 \) corresponds to charge inversion.

Figure 2 (b) depicts the integrated charge of the movable ion species (counterions and coions) of Fig. 2 (a), starting at the surface of the macroion,

\[
Q(r) = \sum_s \int_{r_0}^r \rho_s(r') 4\pi r'^2 dr'.
\]  

The portion above the baseline \( Q/|Q_0| = 1 \) corresponds to the charge inversion (this applies to all the following figures). The net amount of inverted charge reaches 160% for this run, as stated above, and the \( Q(r) \) profile relaxes to neutrality in a distance of approximately a few \( a \), thus suggesting once again that a significant population of coions reside on the outer sides of condensed counterions. Fluctuations of \( Q(r) \) for \( r \gg R_0 \) reflect density fluctuations which are much amplified because of the volume factor \( 4\pi r^2 \). On the other hand, we observe a nearly neutral region \( Q/|Q_0| \approx 1 \) extending for the distance comparable to the Bjerrum length \( \ell_B \) outside the charge inversion layer. Few ions exist in this region. This shows establishment of enhanced order due to strong Coulomb interactions.

The electrostatic potential drop across the charge distribution peak corresponds to energy change \( e\Delta \varphi \approx 1.2e^2/\epsilon a \), which is five times the thermal energy \( k_B T \). This implies strong binding of counterions to the macroion and coions to the counterions. In other words, this manifests very strongly non-linear screening compared with Debye-Hückel screening of weakly coupled cases. Of course, this is by no means surprising given the small value of \( \lambda \) Eq.(7), as mentioned above.

**FIG. 3.** The bird’s-eye view of the screening atmosphere within \( 3a \) from the "large" macroion: macroion radius \( R_0 = 8a \), charge \( Q_0 = -28e \). Temperature is adjusted such that \( e^2/\epsilon R_0 T = const \) is the same as in Fig. 1. This means that \( \Gamma \) Eq.(5) is the same here and in Fig. 1, while \( \Gamma_a \) is greater here than in Fig. 1 by a factor of \( 8/3 \). Accordingly, stronger binding of monovalent coions (dark blue) to multivalent counterions (light blue) is observed, and adsorbed counterions are less strongly correlated.

Speaking about the dynamics of equilibration, it is interesting to note that the buildup of counterions on the macroion occurs fairly quickly, in about \( 100\omega_p^{-1} \), which is of the order of 100 picosec for the typical numerical values of parameters, as suggested in Section 11. This time is much shorter than overall relaxation time of the system, suggesting that equilibration of plasma further away from macroion occurs fairly slowly. It is appealing to guess that this fast buildup of screening (and even over-charging) layer is connected with the fact of strongly non-linear correlated screening.
The charge inversion for the macroion with a large radius $R_0 = 8a$ is depicted in Figs. 3 and 4. Other parameters are the same as those of Fig. 5, except for the lower temperature ($\Gamma_a = 78.4$) to keep $\Gamma_Q = \text{const}$ Eq. 3. We again observe sparsely distributed counterions on the macroion surface. In this case, however, binding of the counterions to the macroion is loose, and their radial distribution in Fig. 4(a) is almost as broad as that of the coions. The counterion charge is better canceled on each site by the condensed coions than in Fig. 3.

We note that the number of condensed ions to the macroion surface in Fig. 5 is $N^+ \sim 13$ and $N^- \sim 66$, where the number of $N^+$ is comparable to that in Fig. 3. This is consistent with the fact that each counterion occupies, roughly, a neutralizing region on the macroion surface, similar to the Wigner-Seitz cell of Wigner crystal. With charge density of the macroion surface $\sigma = Q_0/4\pi R_0^2$, the size of such neutralizing region, or cell, is proportional to the size of the macroion: $eZ = \pi \sigma R_{ws}^2$, or $R_{ws} = 2R_0(Ze/|Q_0|)^{1/2}$. In other words, the neutralizing number of counterions $(R_0/R_{ws})^2$ stays unchanged as long as the macroion charge $Q_0$ is fixed. The inverted charge in Fig. 4(b) is about 40% the original charge of the macroion, which is less than that in Fig. 3. The electrostatic potential drop across the macroion surface is consistently less than the thermal energy, $e\Delta \varphi \sim 0.05e^2/\varepsilon a < k_B T \sim 0.09e^2/\varepsilon a$. The linear Debye-Hückel theory nearly applies in this case.

We found similar features, based on identification of bound ions in the peak of their radial distribution, also for the parameters further away from our standard conditions. For instance, we mention here in passing the case of the counterions with smaller valence $Z = 3$. For them, it takes somewhat less than $1 \times 10^3 \omega_p^{-1}$ to reach the stationary state, and the attained peak height is lower, about 70% the macroion charge, as shown in Fig. 7. This will be discussed in greater details in one of the sections below.

FIG. 4. Charge inversion of a "large macroion" - the system shown in Fig. 3. Plot format and notations are the same as in Fig. 5. Simulation parameters are also the same as those of Fig. 6, except that the temperature is adjusted to keep constant the quantity $\Gamma_Q = \text{const}$ Eq. (3). Each data point is an average of three runs, and a vertical bar shows the range of time variations.

B. Changing macroion properties and temperature

In the following figures, Figs. 5, 6, the ordinate $Q_{\text{peak}}$ is the maximum of the integrated charge of the counterions plus coions, Eq. (16). Each data point is an average of three runs, and a vertical bar shows the range of time variations and deviations among the runs.

The dependence of charge inversion on the radius of macroion $R_0$ shown for the counterions with the valence $Z = 3$ and 7. The charge of the macroion is $Q_0 = -28e$, and the number of coions $N^- = 335$ (or 336) corresponds to the density $n^- \sim 1 \times 10^{-2}a^{-3}$. The ordinate is the maximum of the integrated charge $Q(r)$ (Eq. (16)), i.e. $Q_{\text{peak}} = \max(Q(r))$, normalized by the macroion charge $|Q_0|$. Each data point is an average of three runs, and a vertical bar shows the range of time variations.

FIG. 5. Dependence of inverted charge on the radius of macroion $R_0$ shown for the counterions with the valence $Z = 3$ and 7. The charge of the macroion is $Q_0 = -28e$, and the number of coions $N^- = 335$ (or 336) corresponds to the density $n^- \sim 1 \times 10^{-2}a^{-3}$. The ordinate is the maximum of the integrated charge $Q(r)$ (Eq. (16)), i.e. $Q_{\text{peak}} = \max(Q(r))$, normalized by the macroion charge $|Q_0|$. Each data point is an average of three runs, and a vertical bar shows the range of time variations.

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We found similar features, based on identification of bound ions in the peak of their radial distribution, also for the parameters further away from our standard conditions. For instance, we mention here in passing the case of the counterions with smaller valence $Z = 3$. For them, it takes somewhat less than $1 \times 10^3 \omega_p^{-1}$ to reach the stationary state, and the attained peak height is lower, about 70% the macroion charge, as shown in Fig. 7. This will be discussed in greater details in one of the sections below.
Eq. (8) moderately changing between 0.3a \sim 0.8a, and λ Eq. (9) changing between 0.02a \sim 2.8a.

In Fig. 6, the inverted charge reaches its maximum for the radius $R_0 \approx 3a$ irrespectively of the valence $Z$. It falls off rapidly both for smaller and larger radii, and becomes insensitive to the radius of the macroion for $R_0/a \gg 1$. The net amount of the inverted charge is about 70% of the bare macroion charge for $Z = 3$; it increases up to 150% of $Q_0$ for $Z = 7$. We find that the charge inversion reaches maximum also at virtually the same radius $R_0 \approx 3a$ even for the smaller number of counterions $N^+ = 15$ ($Z = 7$), or for larger macroion charge $Q_0 = \pm 42e$.

It is not difficult to understand qualitatively why the charge inversion decreases at both small and large values of macroion radius $R_0$, reaching a maximum in between. When $R_0$ gets very large, the lateral spacings between bound counterions become too long to maintain correlations between them; on the other hand, when $R_0$ gets too small, the increased repulsion of the inverted charge from the macroion becomes dominant.

The net amount of the inverted charge is about 70% of the bare macroion charge $Q_0$ for $Z = 3$; it increases up to 150% of $Q_0$ for $Z = 7$. We find that the charge inversion reaches maximum also at virtually the same radius $R_0 \approx 3a$ even for the smaller number of counterions $N^+ = 15$ ($Z = 7$), or for larger macroion charge $Q_0 = \pm 42e$.

It is not difficult to understand qualitatively why the charge inversion decreases at both small and large values of macroion radius $R_0$, reaching a maximum in between. When $R_0$ gets very large, the lateral spacings between bound counterions become too long to maintain correlations between them; on the other hand, when $R_0$ gets too small, the increased repulsion of the inverted charge from the macroion becomes dominant.

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The dependence of inverted charge on the valence of the counterions $Z_{eff}$, which is the charge of the counterion minus that of the condensed ions, increases with the charge of the macroion; it is $Z_{eff} \sim 0.25Z$ for $Q_0 = -14e$ and is $Z_{eff} \sim 0.4Z$ for $Q_0 = -42e$.

C. Changing counterion properties

The dependence of inverted charge on the valence of the counterions is depicted in Fig. 6. Here, the macroion charge and radius are $Q_0 = \pm 28e$ and $R_0 = 3a$, respectively, and temperature is fixed such that $\Gamma_a/Z = e^2/\epsilon aT = 4.2$. It is emphasized that no charge inversion is observed for monovalent counterions. The amount of the inverted charge $Q_{peak}$ increases with the valence, which is well scaled by $Q_{peak} \sim Z^{1/2}$ for $Z \leq 5$. The $Z \geq 5$ part can be fit by $Q_{peak} \sim Z$. The inverted charge is also an increasing function of the number of counterions and coions, as seen by the difference of the two curves for two densities in the figure.
The dependence of inverted charge on the ionic strength, \( n_I = (Z^2N^+ + N^-)/V \), is shown in Fig. 8, where \( V = 4\pi(R_M^3 - R_0^3)/3 \) is the domain volume. The amount of inverted charge \( Q_{\text{peak}}/|Q_0| \) increases monotonically with the ionic strength. The functional form of the scaling changes at \( n_I \sim 0.05/a^3 \), as shown by fitting curves. The ionic strength of a Ca\(^{2+}\) ion and neutralizing coions in every 10\( \AA \) cube yields \( 0.048/a^3 \) for \( a = 2\AA \). The scaling \( Q_{\text{peak}} \sim n_I^{1/2} \) for the low ionic strength \( n_I < 0.02/a^3 \) smoothly joins a linear scaling \( Q_{\text{peak}} \sim n_I \) for high ionic strength \( n_I > 0.05/a^3 \). The non-dimensional parameter of the theory \( \zeta = (R_{ws}/r_a)^2 = 12a\Gamma_0 N_{ca}(e/|Q_0|)(R_0^3/R_M^3) \), is calculated to be \( 0.7 \) for \( n_I \sim 0.01/a^3 \) and \( Z = 7 \). The theory expects \( Q^{(th)} \sim (N_{ca}Z)^{1/2} \) for \( \zeta \ll 1 \), and \( Q^{(th)} \sim N_{ca}Z \) for \( \zeta \gg 1 \). The present simulation results agree with this theoretical prediction.

The potential energy presented in Fig. 10 is in line with the tendency of charge inversion dependence on variations of the Coulomb coupling parameter (cf. Fig. 6). The potential energy for the interactions between counterions and the macroion (solid circles) is negative (attractive) and is minimized at the intermediate value of \( \Gamma_a = Ze^2/eaT \sim 50 \) where largest charge inversion is obtained. The potential energy of interactions between the counterions and coions, depicted by triangles, decreases remarkably with the increase in \( \Gamma_a \). This corresponds to massive condensation of coions onto the counterions (similar to Manning-Onsager condensation) at low temperatures. This reduces the effective valence of the counterions, and the binding of counterions on the macroion surface is weakened, which tends to suppress the charge inversion. Thus, charge inversion becomes largest at the intermediate value of \( Ze^2/eaT \), as stated above. The potential energy of interaction between coions and the macroion (open circles) is positive (repulsive), and is maximized where the coions are closely located with the macroion by condensation to the counterions, namely at \( \Gamma_a \sim 50 \). On the other hand, the total potential energy
(squares) decreases with the increase in the coupling parameter \( \Gamma_a \).

IV. CONCLUSION

In this paper, we showed the occurrence of giant charge inversion and examined its parameter dependences with the use of molecular dynamics simulations. The charge inversion was found to be based on the strong correlations of the multivalent counterions and coions, particularly on the surface of the macroion. Specifically, charge inversion was observed under the conditions for which the Coulomb coupling parameter was significantly larger than unity, \( \Gamma \gg 1 \). At the same time, charge inversion occurred only in the presence of multivalent counterions with \( Z \geq 2 \). The counterions were attached to the surface of the macroion, while monovalent coions tended to condense on the counterions. This condensation, similar to Bjerrum pairing, is therefore identified as the factor limiting the amount of charge inversion. The amount of the inverted charge \( Q_{\text{peak}} \) was maximal at rather small radius of the macroion, and leveled off when radius becomes larger. It scaled linearly with the charge of the macroion \( Q_0 \), and the ratio \( Q_{\text{peak}}/|Q_0| \) was independent of the macroion charge.

With respect to the valence \( Z \) and the ionic strength \( n_I = (Z^2 N^+ + N^-)/V \), the amount of inverted charge scaled as \( Q \sim (Z n_I)^{1/2} \) for the valence \( Z \leq 5 \) or \( n_I \leq 0.02/a^3 \). As noted in Sec.III C, this ionic strength corresponds to a Ca\(^{2+}\) ion in every 10 A cube. The inverted charge scaled as \( Q \sim Z n_I \) for \( Z > 5 \) or \( n_I > 0.05/a^3 \). This agreed with the theory of giant charge inversion \( [5] \). The net inverted charge of nearly up to 160% the bare charge of the macroion was achieved at the medium temperature \( Z e^2/\epsilon R_0 T \sim 15 \), due to the competition of multivalent counterion attachment to the macroion and monovalent coion condensation on the counterions; the former was stronger at lower temperatures, and the latter was suppressed at higher temperatures.

In the present study, the macroion was assumed to be immobile. From the application points of view, it might be informative to study the distribution of counterions and coions around a moving macroion and also the effect of an applied electric field. The study of such cases is reported in a separate paper. The results indicate that a formed complex of a macroion and counterions drifts along the electric field in the direction implied by the inverted charge, and that charge inversion is not altered until the electric field exceeds a critical value \( [27] \).

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[30] To make a bridge to the theoretical work [5], we note that screening radius smaller than $a$ was indeed considered there, but that was because multivalent counterions were considered to have the size $a$, while monovalent coions were considered to have much smaller size. Therefore, Debye screening length remained much longer than the size of smallest ions.

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