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Computational evidence of two driving mechanisms for overcharging in an electric double layer near the point of zero charge

Zhi-yong Wang[1,2,*] and Yu-qiang Ma[2,3,†]
[1] *School of Optoelectronic Information, Chongqing University of Technology, Chongqing 400054, China*
[2] *National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China*
[3] *Center for Soft Condensed Matter Physics and Interdisciplinary Research, Soochow University, Suzhou 215006, China*

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We have adopted an ensemble Monte Carlo simulation method to systematically verify two physical driving mechanisms responsible for overcharging which refers to the adsorption of an effective charge onto a like-charged planar surface around the point of zero charge within the primitive model of mixed electrolytes with varying salt concentrations. One is electrostatic in character dominated by dielectric images and the other is purely entropic in origin by ionic size asymmetry effects, of which the former has never been reported both theoretically and experimentally and the latter could be interpreted satisfactorily in terms of available theoretical approaches. The electrostatically driven mechanism is found to critically depend on the ionic sizes while the entropically driven mechanism occurs with almost the same efficiency in a relative wide range of surface charge density. Depending on the delicate interplay between charge and steric correlations, the two distinct driving mechanisms may cooperatively give rise to a more pronounced overcharging process.

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One of the most striking physicochemical questions is on understanding how electrolytes impact the interfacial structures and how they are distributed close to the interfaces [1]. Going through the literature, a great deal of research work in theory, experiment, and computation has been devoted to the analysis of aqueous electrolytes trapped within different shape nanopores for the purpose of gaining a fundamental understanding of the rich, yet sometimes counterintuitive events of these systems. Related examples include charge inversion and its converse, overcharging. The former means the fact that an electric double layer carries more countercharge than needed to compensate for the native surface charge, while the latter stands for the adsorption of like-charged ions onto the charged surface. The conceptual difference between these two phenomena is known in principle, but they are often used interchangeably without too much thought on the subtleties associated with them [2]. Altogether, despite the origins responsible for charge inversion being well known, the mechanisms behind overcharging remain poorly understood.

In general, protonation, deprotonation, adsorption, and other reaction equilibria define a surface charge density on the interfaces which strongly depends on the local environmental factors such as *p*H, ionic strength, and background electrolyte composition [3–7]. As is well known, the dissociation reaction equilibria are typically treated with so-called surface complexation models in many experimental systems [8–10]. Such models that consider the surface charging and ion adsorption as surface complexation reactions combine concepts of coordination chemistry with the Gouy-Chapman formalism of the double layer. Their application, however, requires a significant amount of empirical knowledge. In particular, one must assume various chemical reactions and characterize them by equilibrium constants [11]. Besides, surface complexation models invoke a mean-field approximation to deal with the double layer. It is well established that this approximation fails when the systems involve multivalent electrolytes or polarizable particles [12–20]. Therefore the commonly introduced coordination complexes of multivalent ions might actually represent an artifact due to the neglect of ion-image interactions as well as of interionic charge and steric correlations inherent to the mean-field description, or at least partially.

Although surface complexation models did include a capacitive term on "physical" interpretations, the interpretation of experiments was entirely "chemical" [8–10]. To clearly identify the physical origins, interest has grown in clarifying the driving forces that overcharge particles around the point of zero charge in the absence of dissociative processes [2,21–24]. Unfortunately, the dielectric forces are not captured in these theoretical studies. More generally, these often-overlooked image charge interactions could exert a profound effect on any system in which charges reside near an interface between two different dielectric phases [14–20,25–29]. On the other hand, definitive experimental evidence is particularly difficult to obtain because of the short length scales involved. Fortunately, computer simulations in the field of electrolyte solutions are emerging as important tools by which the results of theories that are more approximative in nature can be validated or refined and information not easily accessible by experiments can be obtained. In this Brief Report, we continue to explore the physical mechanisms operating to produce overcharging for a given weakly charged wall by extensive canonical Monte Carlo computer simulations within the primitive model that explicitly covers steric effects of finite volume of the ions in addition to electrostatic forces.

We are concerned with the predominant polarization effects due to the dielectric discontinuity between the membrane and the aqueous phases. The membrane is modeled with a hard planar surface carrying a constant native charge density σ_0, which locating at $z = 0$ extends infinitely in the x and y

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[*] wzyong@cqut.edu.cn
[†] myqiang@nju.edu.cn

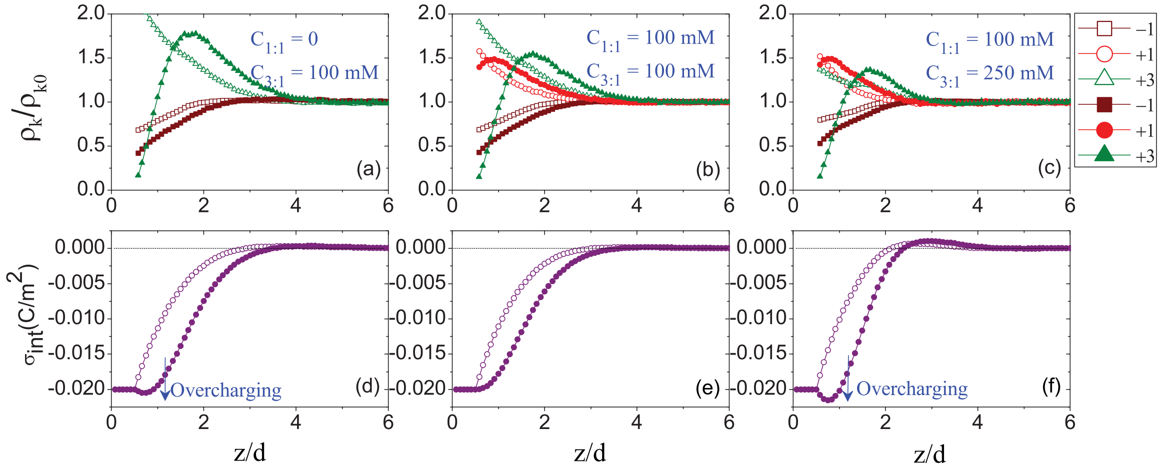

FIG. 1. (Color online) Actual density profile normalized with their bulk value and integrated charge distribution as a function of the distance from the membrane of surface charge density $\sigma_0 = -0.02$ C/m^2 for varying salt conditions. The distance is rescaled by the diameter of all ionic species $d = 4.8$ Å. Open and solid symbols correspond to the situations in the absence and presence of dielectric breakdown, respectively.

directions with periodic boundary conditions and confines the mixed solution of 1:1 and 3:1 electrolytes to the positive half space. The simulation box is closed by a neutral impenetrable wall at $z = L$. The exact length of the box in the z direction was chosen according to the requirement that we have bulk phase in its middle.

In all simulations we employ the primitive model where the solvent only enters the picture implicitly through its dielectric constant $\epsilon_> = 78.5$. The hydrocarbon substrate located symmetrically at the negative half space is characterized by a relative dielectric permittivity $\epsilon_< = 2$. All ionic species are reduced to points at the centers of excluded-volume spheres with the same dielectric constant as the solvent and cannot overlap with hard walls in the system under study. The charged hard spheres interact via the Coulomb potential $U_C = q_i q_j [1/r_{ij} + \Delta_\epsilon / \sqrt{r_{ij}^2 + 4 z_i z_j}]/4\pi\epsilon_0\epsilon_>$, where q_i, q_j are the charges and z_i, z_j the z coordinates of the ith and jth ions, respectively, r_{ij} is the distance between ions i and j and ϵ_0 is the permittivity of free space, and the dielectric jump at the interface is defined as $\Delta_\epsilon = (\epsilon_> - \epsilon_<)/(\epsilon_> + \epsilon_<)$. Note that the expression U_C involves the direct Coulomb interaction between real ions as well as the interaction between the real ion i and the image of ion j and vice versa. The electrostatic energy of interaction between an ion i and the charged membrane reads $U_E = [-2\pi q_i (1 + \Delta_\epsilon)\sigma_0 z_i + q_i^2 \Delta_\epsilon / 4 z_i]/4\pi\epsilon_0\epsilon_>$ that involves a self-energy contribution due to the interaction between the ion and its dielectric image. For the calculation of the electrostatic interaction, an efficient modified Lekner summation was employed in order to take into account the long range nature of the interaction [30], which allows the slowly convergent series to be separated into a summation that converges rapidly in real space and another that converges rapidly in reciprocal space.

The model systems were solved by performing Monte Carlo simulations in the canonical ensemble at a temperature of 298 K. Each simulation starts with a random distribution of the N ions in the primary box. The Metropolis algorithm was used to accept or reject new configurations [31]. This procedure involves attempts to make moves of the ions in a random fashion and the ions to be moved are selected randomly as well. N attempts to move an ion are referred to as one Monte Carlo circle. The first roughly 1×10^6 circles were discarded as the system equilibrated, statistics were gathered over the next typically 6×10^6 circles. It was checked that the simulation cell is large enough to circumvent system size dependencies.

The first series of our calculations were done for the restrictive primitive model with the size of all ionic species being 4.8 Å and the surface charge density being $\sigma_0 = -0.02$ C/m^2. An overview is provided in Fig. 1 for the laterally averaged density profile of ions and the integrated charge distribution at different concentrations of 1:1 and 3:1 salts in the absence and presence of dielectric discontinuity. For the ideal case of no dielectric images, it seems that counterions and coions can be diffusely distributed with a respectively decreasing and increasing concentration from the surface to reach their value of the normalized bulk density. At the same time, the integrated charge in its absolute value becomes smaller and eventually becomes zero sufficiently deep inside the bulk. Upon polarizing the interface, it is found that ion-image charge interactions that are neglected by the mean field approximation have a nontrivial effect on the structure of electric double layer. In more details, the counterions are pushed towards the aqueous phase and then their profiles exhibit a peak density away from the contact points. The trivalent counterions are depleted to a greater extent in comparison with the monovalent counterions. In particular, we noted that due to this large dielectric jump, the integrated charge distribution displays an obvious valley in the immediate proximity to the surface, implying the occurrence of overcharging. Overall, it can be observed from Figs. 1(d)–1(f) that the counterintuitive phenomenon is rather sensitive to the amount of salt composition.

To get a better insight into the underlying mechanism responsible for overcharging, we further take into account the effect of spatial correlation, we have looked at Fig. 2 where a comparison of the cumulative charge distribution within the restrictive primitive model is made for two series of parameters of ionic size based on the same condition of the surface charge

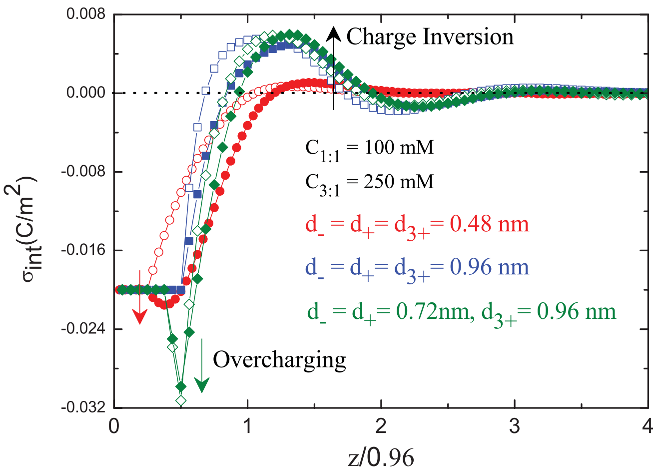

FIG. 2. (Color online) Comparison of integrated charge profile for different ionic diameters as specified in the legend at $\sigma_0 = -0.02$ C/m^2. Open and solid symbols correspond to the cases in the absence and presence of dielectric discontinuity, respectively. The solid lines serve only to guide the eyes.

density and electrolyte contents. It can be clearly seen from the comparison that doubling the size of the ions eliminates the overcharging process despite the fact that the polarization effects are still appreciable to the double layer structure. In contrast, we see another counterintuitive charge inversion phenomenon which originates from the overcrowding of counterions in the close vicinity of the surface. The underlying origin for this peculiar behavior can be definitely attributed to a more favorable entropic effects due to the relevance of ionic sizes, which have separately predicted by the integral equation method and a simple Landau-Ginzburg-type continuum theory in the previous reports [32,33]. It should be stressed that the short-range ionic correlations driving the reversal of polarity go beyond the scope of the strong-correlated liquid theory applicable only to the coupling regime involving both the value of high surface charge density and the presence of polyvalent counterions [12,13,16]. These findings show that the size effects of the ions extremely modify their surface adsorption. In particular, overcharging is electrostatically driven by dielectric images being dependent crucially not only on excluded-volume interactions but also on salt contents, for which there are no available theoretical approaches and experimental data.

We now turn to the second series of simulations that were carried out within the framework of the unrestricted primitive model of electrolytes in which the diameter of monovalent species is assumed to be 7.2 Å while the diameter of trivalent counterions takes 9.6 Å. In Fig. 3, we show the typical density profiles of the microions and the cumulative charge distribution in the normal direction to the membrane of surface charge density $\sigma_0 = -0.05$ C/m^2, from which we can observe a dissimilar tendency as before that for both cases there is almost no change at all in the ionic density profiles. Moreover, whether or not a sharp dielectric boundary occurs, the multivalent counterions are always dominantly distributed near the surface and the density peak still resides at the distance of closest approach. These findings show that the effects are considerably negligible of image charge repulsive interactions when compared with the results of surface charge density $\sigma_0 = -0.02$ C/m^2. In addition, it is remarkable that the density profiles of all ionic species exhibit a nonmonotonic behavior evolving into the bulk of the solution, which departs strongly from the mean field predictions and has been interpreted as a signature of charge inversion. Actually, charge inversion can be also appreciated clearly through the cumulative charge distribution which overshoots the neutralization line at a certain moderate distances from the surface. Also, an oscillating integrated charge appears around the neutralization line at high salt regime, which is connected to the packing effects of alternating counter- and coions layers. The anomalous behavior falls beyond the present emphasis but nevertheless deserves mentioning because it has been invoked as proofs of the interaction of ion-ion correlations.

Rather interestingly, we continue to see the appearance of surface overcharging from Fig. 3 which still depends in a nontrivial way on the concentration of electrolyte type. Repulsive image charge forces between microions and a low dielectric boundary yield no appreciable deviation in the integrated charge distribution, which differs completely from the preceding situation. The underlying mechanism here for

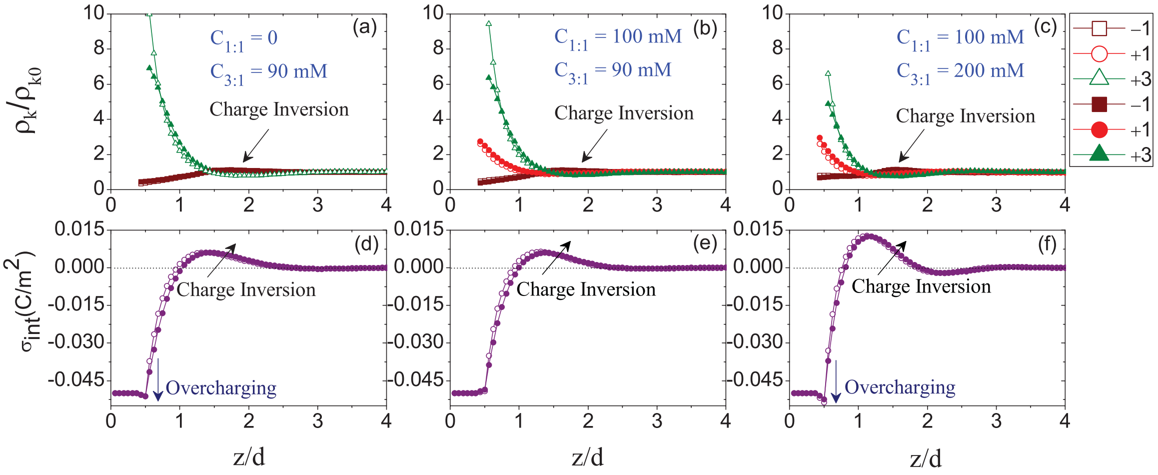

FIG. 3. (Color online) Same as Fig. 1 but with a slightly strong charged membrane of $\sigma_0 = -0.05$ C/m^2 at different electrolyte contents.

this anomaly can be unequivocally traced back to the effects of ionic size asymmetry (also see Fig. 2). The data of our simulations are satisfactorily consistent with theoretical predictions of adsorption of charged colloids onto an oppositely charged planar surface [2,21], in which the role of the small coions is crucial in capturing the nature of interfacial overcharging. Most recently, taking the single asymmetric 1:1 and 2:2 simple electrolytes as the working fluid to substitute for colloidal dispersions also witnessed the occurring of surface overcharging in high salt regime [22–24]. As a matter of fact, it comes to the conclusion that as long as the difference of ionic size is present, overcharging naturally takes place, and the larger the size difference, the more pronounced surface overcharging becomes. Our earlier research also reported the overcharging phenomenon through the addition of multivalent electrolyte under physiological conditions, but the impact of monovalent salt concentration was not taken into account [18,19]. In a complementary work, we further detected that the presence of multivalent interface functional groups could favorably promote the degree of surface overcharging in constant ionic strength [20].

To deeply appreciate the intricate interplay between dielectric discontinuity and ionic size asymmetry, we in Fig. 4 present the cumulative charge distribution respectively for the restricted and unrestricted primitive models of mixed electrolytes subject to the same ionic strength and surface charge density. Once again, it is clearly observed that the increase of ionic size reduces the degree of image repulsion. In particular, the image-driven overcharging process vanishes for the small-sized primitive model electrolytes at this large value of surface charge density. This fact along with Fig. 2 points out that the electrostatically driven mechanism arising from the dielectric images responsible for overcharging remains only valid in a relative narrow range of surface charge density value when compared to the entropically driven mechanism. Moreover, we can recognize from Fig. 2 that for the same magnitude of surface charge and salt concentrations, the degree of overcharging caused by ionic size asymmetry is much greater than that by dielectric images. Obviously, one can easily speculate that the two typical mechanisms might result jointly in an overwhelming overcharging process as long as both the surface charge density and ionic size asymmetry are matched to a moderate extent.

Additionally, Fig. 4 reveals that in both situations the electrostatic correlations between charges drastically influence the adsorption of multivalent counterions leading to a clear effect of charge overneutralization despite the fact that a direct correlation of their favorable entropic contributions is present as well. Therefore the mechanism of charge inversion here could be well interpreted in terms of the strong-correlated liquid theory [12,13] instead of the entropic arguments adaptive to weak-coupling systems [32,33]. Moreover, our data are highly consistent with the more recent predictions of the strong coupling dressed counterions theory [16]. Also, we notice that at this high surface charge value, both charge inversion and overcharging take place simultaneously for the case of nonequal radii of ions. These results have substantial implications for biological and for ordinary colloid systems at moderate salt concentrations.

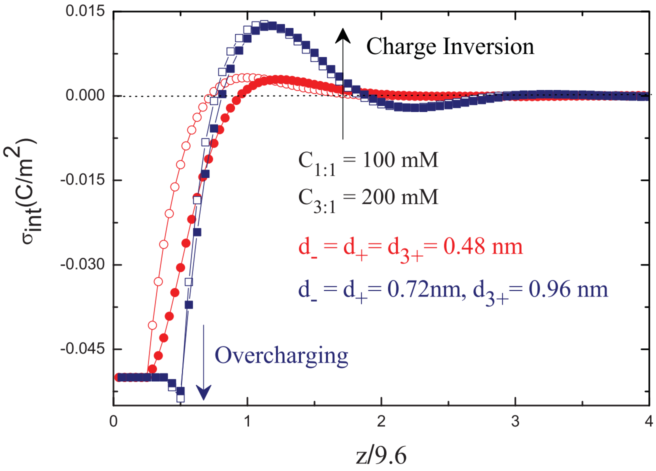

FIG. 4. (Color online) Same as Fig. 2 but with a slightly strong charged membrane of $\sigma_0 = -0.05\ \mathrm{C/m^2}$ for varying ionic diameters within the scope of restricted and unrestricted primitive models, respectively.

In conclusion, we have carried out an ensemble Monte Carlo computer simulation to evidence that the origins of overcharging have a physical nature. In our study, both the full electrostatic potential and the excluded volume interactions are taken into account explicitly within the primitive model of electrolytes. Our findings highlight the prominent roles of both ionic size asymmetry and dielectric discontinuity in determining the occurrence of overcharging close to the point of zero charge. This work will hopefully stimulate research in the development of both further discriminative experiments and more sophisticated theoretical frameworks.

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