Supplementary Material of "Local Inversion of the Mean Electrostatic Potential, Maximum Charge Reversal, and Capacitive Compactness of concentrated 1:1 salts: the crucial role of the ionic excluded volume and ion correlations"

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In this appendix, some details of the Monte Carlo (MC) simulations performed in this work are given. In the main text, several ionic radii and salt concentrations of 1:1 aqueous electrolytes are reported. The largest number of ions considered in the simulations corresponds to the highest electrolyte concentration, namely, 6.3 M. We will focus here only on equally sized ions of radius $a = 2.0$ $\mathring{A}$ around a macroion of diameter $D_M = 2R_M = 40.0$ $\mathring{A}$ placed in cubic simulation box under periodic boundary conditions. However, a similar scheme was used for the other ionic radii and salt concentrations. Notice that the Monte Carlo simulations were performed in the NVT canonical ensemble, adjusting the size of the simulation box until the desired bulk concentration was achieved. This is more efficient than perfoming grand canonical simulations of very dense particle systems.

For a fixed electrolyte concentration, the length $L^* = L/a$ of a cubic simulation box with volume L^3 is defined as follows:

$$L^* = \alpha H^* + \frac{D_M}{a}, \tag{1}$$

in order to scale the size of the simulation box regarding the ionic radius a of the salt. Here, $H^* = 30$ for a salt concentration 6.3 M. However, a larger value of H^* was used for lower salt concentrations, trying to keep an approximate constant number of particles. Let us define the nominal or desired bulk concentration of the electrolyte as ρ_{bulk}. In order to know the number of bulk ions that should be placed in the simulation box, a salt concentration $\rho'_{bulk} = \beta\rho_{bulk}$ is used. The parameter β is a number close to the unity, and its specific value is chosen in order to obtain the desired bulk concentration $\rho_{bulk} \pm \varepsilon$ in Monte Carlo simulations, where ε is a percentage error. For an specific bulk concentration, several short Monte Carlo simulations with different β values were performed until the prescribed error in bulk was achieved. Afterwards, long Monte Carlo simulations were performed with the appropriate β value. In the main text, the percentange error was lower than 1%. Once the length of the simulation box is determined, the total number of ions can be found by adding the bulk ions, that are equal to the salt concentration ρ'_{bulk} multiplied by the simulation box volume, $N_{bulk} = 2\rho'_{bulk}L^3$, plus the number of counterions of the macroion $N_c = |Z_M|$:

$$N_T = N_{bulk} + N_c, \tag{2}$$

fulfilling also the electroneutrality condition:

$$Z_M + N_+ z_+ + N_- z_- = 0. \tag{3}$$

Notice that for large values of L, $\beta \to 1.0$, that is, $\rho'_{bulk} \to \rho_{bulk}$.

On the other hand, a Monte Carlo cycle in a system of N particles corresponds to N attempts to move a particle, independently if the particle was moved or not. As it was

commented in the main text, Ewald sums with conducting boundary conditions have been used to take into account correctly the long-range behaviour of Coulomb interactions. The damping constant used in this study is $\gamma = 5/L$, with L the length of the cubic simulation box. 725 vectors in the k-space have been employed to compute the reciprocal space contribution to the Coulomb energy.[1,2] Notice that in the work performed by Terao[3] isotropic approximations to Ewald sums based on Kubic Harmonics have been used in order to take into account properly long-range electrostatic interactions, whereas full Ewald sums were performed in the main text. In table 1, a comparison of some parameters used in Monte Carlo simulations using full Ewald sums is presented, for several lengths L of the simulation box. In such a table, it is observed that the number of MC cycles decreases dramatically as a function of the total number of particles. This is because a standard Ewald sums implementation has been used in this study, which scales in the best case scenario as $N^{\frac{3}{2}}$.[4] An alternative formulation to Ewald sums, such as the Particle-Particle Particle-Mesh (3PM) method, could improve significantly the number of MC cycles that can be achieved per unit time given that the 3PM approach scales as $N \log N$.

All the serial runs reported here were performed individually in Intel Xeon Gold CPU processors, model 5222 at 3.8 GHz.

In Fig. 1, ionic profiles, $\rho(r)$, associated to the smallest and the largest simulation box reported in table 1 are portrayed. Here, it is observed that the phenomenon of charge inversion do not change significantly when the size of the simulation box is doubled. The fluctuations for the largest simulation box are more evident because the number of MC cycles is two orders of magnitude smaller regarding the MC cycles performed for the smallest simulation box for the same amount of running time. In Fig. 2, the integrated charge, $P(r)$, associated to the different values of the simulation box L^* reported in the table 1 are shown. In this instance, it is observed that the phenomenon of charge reversal, i.e, the change of sign of $P(r)$, persists and displays a very similar shape for all values of L^*. Thus, these results allow us to discard box size effects if a length of the simulation box $L^* \geq 50$ is

used for a 6.3 M concentration of monovalent ions. A value of $L^* = 50$ allow us to keep a balance between computing time and statistical accuracy in the structural properties of the electrical double layer, such as the mean electrostatic potential at the colloidal surface and at the Helmholtz plane, the capacitive compactness, the integrated charge, and the corresponding ionic profiles.

Table 1: Some typical parameters used in Monte Carlo simulations with full Ewald sums for several lengths L of a cubic simulation box. In all instances, a 1:1 electrolyte with equally sized ions of radius $a = 2.0$ $\mathring{A}$ and bulk concentration $\rho_{bulk} = 6.3$ M bathes a macroion of radius $R_M = 20.0$ $\mathring{A}$ and valence $Z_M = -20$. The whole system is immersed in a continuum solvent with dielectric constant $\epsilon = 78.0$ at a temperature $T = 300$ K. $H^* = 30$ is used in all cases.

L^*	α	β	N_T	Number of days	MC cycles
50.0	1.0	0.959	7299	60	2.8×10^6
65.0	1.5	0.980	16361	60	6.0×10^5
80.0	2.0	0.990	30795	60	1.6×10^5
95.0	2.5	0.995	51553	60	5.4×10^4

References

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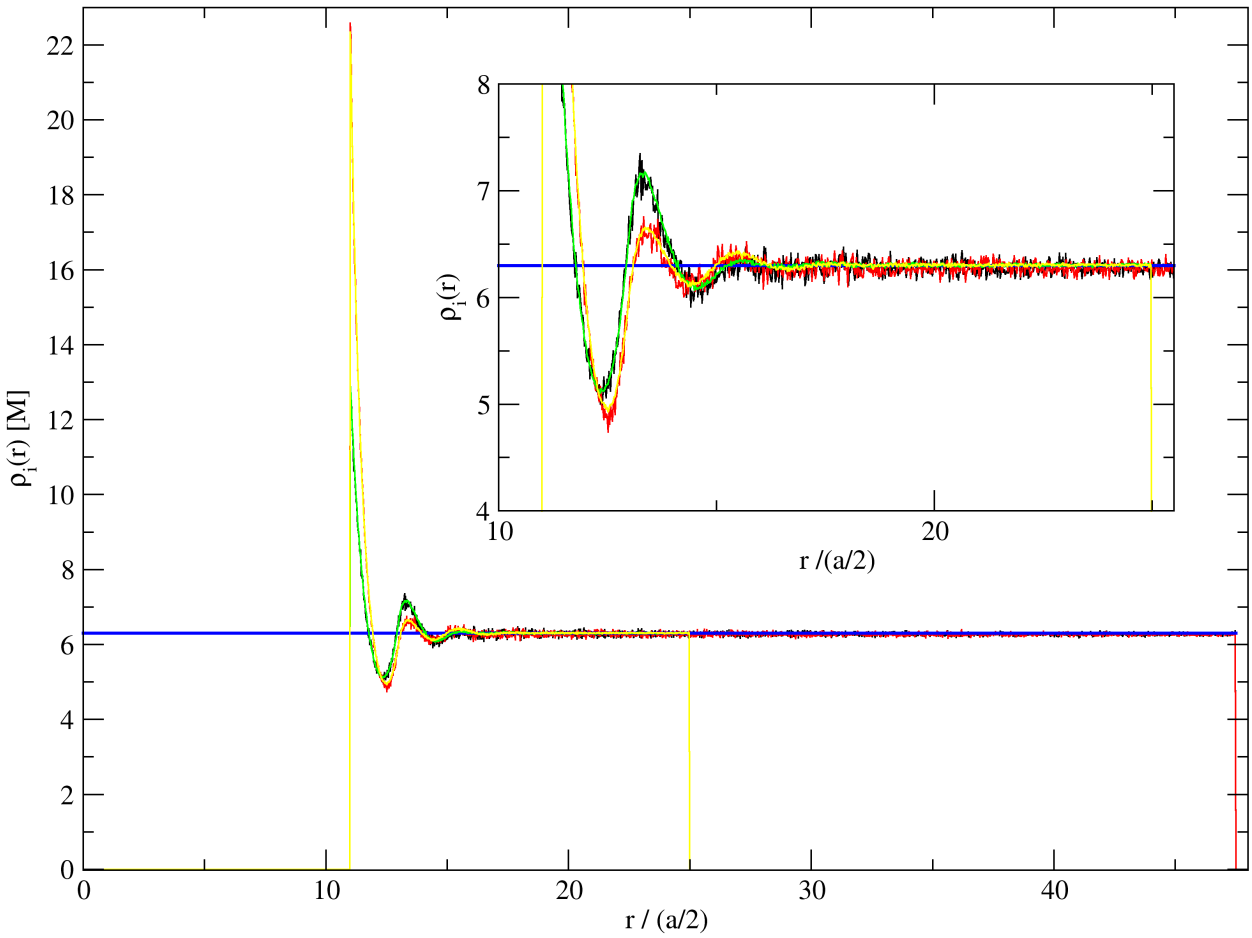

Figure 1: (Color online): Ionic profiles as a function of the distance of a 1:1 equally-sized electrolyte of radius $a = 2.0$ $\mathring{A}$, at a bulk salt concentration 6.3 M, bathing a macroion of radius $R_M = 20.0$ $\mathring{A}$ and valence $Z_M = -20$. The index $i = +, -$ corresponds to cations and anions. Green and yellow lines correspond to a simulation box of size $L^* = 50$, whereas black and red lines correspond to a simulation box of size $L^* = 95$. The blue line corresponds to 6.3 M. Some relevant parameters used in the Monte Carlo simulations are given in the table 1. The distance r is measured from the center of the macroion.

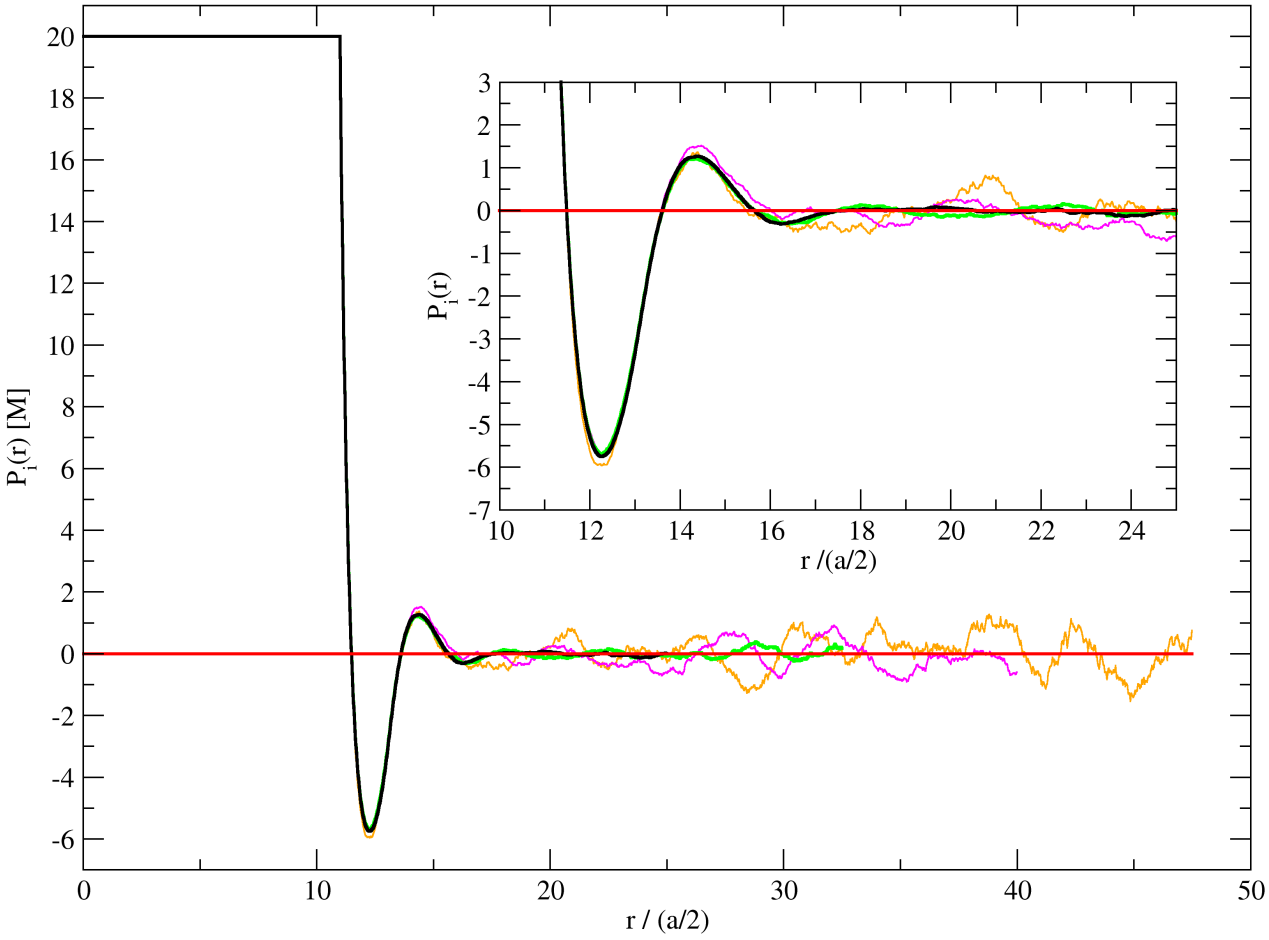

Figure 2: (Color online): Integrated charge $P_i(r)$ as a function of the distance r to the center of a macroion, under the same conditions used in Fig. 1, for i different simulation boxes. The red line corresponds to zero. Orange, pink, green, and black lines correspond to simulation boxes of size $L^* = 50, 65, 80,$ and 95, respectively. Some relevant parameters used in the Monte Carlo simulations are given in the table 1.