

## Effects of the ionic size-asymmetry around a charged nanoparticle: unequal charge neutralization and electrostatic screening

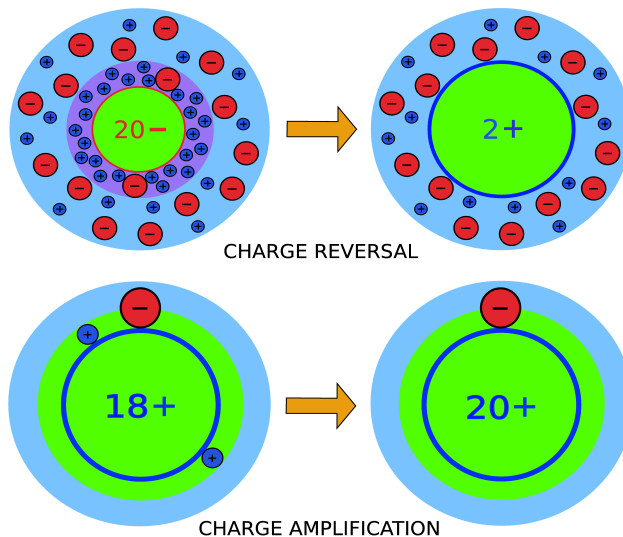
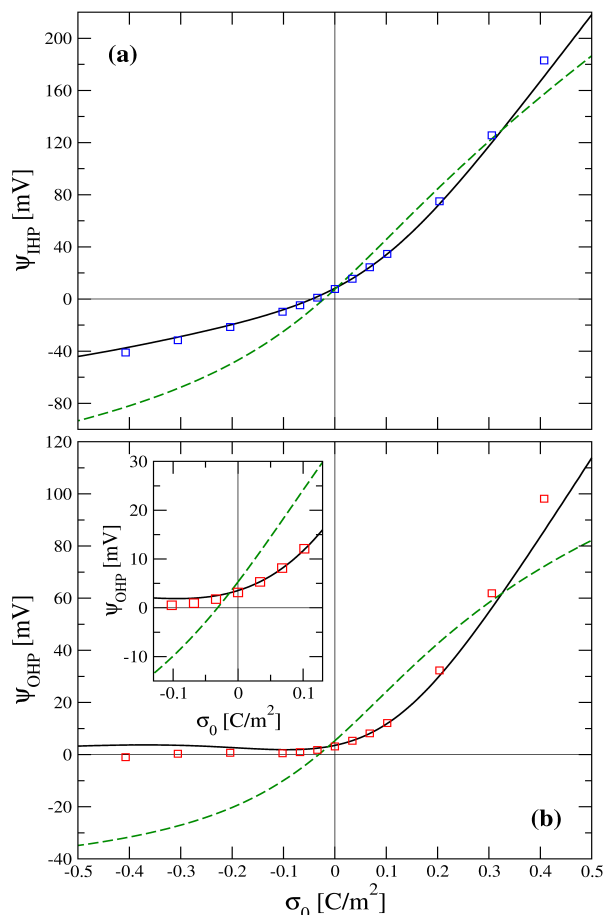
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G. I. Guerrero Garcia, E. Gonzalez Tovar, and M. Olvera de la Cruz

The study of charged colloidal solutions is of great relevance due to the enormous potential of possible technological applications in both industry and biological sciences. For diluted colloidal dispersions, the microscopic and thermodynamical properties of the system will depend mainly on the ionic distribution of ions (or electrical double layer) around a single macroion.

One of the most simple models proposed to study the electrical double layer is based in the classical Poisson-Boltzmann theory of point ions in a continuum solvent, which is incorrect at moderate/high charged colloidal dispersions, and is unable to predict interesting phenomena as local charge reversal (or the overcompensation of the macroion's bare charge by counterions at a certain distance from the macroion's surface), or the non-dominance of counterions, i.e., that the properties of coions matter at high ionic concentrations even far from the point of zero charge (*Eur. Phys. J. E* **4**, 143 (2001); *JCP* **117**, 9009 (2002); *JCP* **123**, 034703 (2005); *PRE* **80**, 021501 (2009)). On the other hand, the solvent (water for example) taken into account explicitly can lead to unexpected behavior, as an asymmetric renormalization of charge depending on the sign of the macroparticle (i.e., positive or negative) (*PRE* **79**, 031901 (2009)). Nevertheless, although the explicit inclusion of water gives a more accurate description, is at the same time very expensive computationally.

Thus, in this work we study theoretical (HNC/MSA integral equations) and simulationally (Monte Carlo simulations) the electrical double layer of a monovalent salt around a macroion in a less expensive coarse-graining model by using an unrestricted primitive model. This approach allows to predict charge reversal and layering (because takes into account consistently ionic size correlations), but at the same time considers the natural size differences in solvated ions, by assigning different effective hydrated radii to each ionic species.



Some interesting phenomena observed in our simulations are the appearance of surface charge amplification, or the attraction of like-charged ions to the first layer of ions in the surface of the colloid, and the observation of an unequal colloidal charge neutralization and electrostatic screening depending on the sign of the macroion, analogous to that observed theoretically when water is included explicitly.

Figure Caption. Mean electrostatic potential at the inner (a) and outer (b) Helmholtz planes as a function of the surface charge density of the macroion. Squares, solid lines and dashed lines correspond to Monte Carlo simulations, HNC/MSA integral equations results and URMGC theory, respectively.