A New Poisson-Nernst-Planck Equation for Charge Inversion near Charged Walls

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Abstract

We introduce a mathematical model which describes the charge inversion phenomena in systems with a charged wall or boundary. The mathematical model is derived using the energy variational approach that takes into account ion diffusion, electrostatic, finite size effect, and boundary behavior. In ion dynamic theory a well-known system of equations is the Poisson-Nernst-Planck (PNP) equation that includes entropic and electrostatic energy. The PNP type of equation can also be derived by the energy variational approach. However, the PNP equations have not produced the charge inversion/layering in charged wall situations presumably because conventional PNP does not include the finite size of ions and other physical features needed to create for the charge inversion. In this present paper we investigate the key features needed to produce the charge inversion phenomena using a mathematical model, the energy variational approach. One of the key features is a finite size (finite volume) effect which is an unavoidable property of ions important for their dynamics on small scales. The other is an interfacial constraint to capture the spatial variation of electroneutrality in systems with charged walls. The interfacial constraint is established by the diffusive interface approach that approximately describes the boundary effect produced by the charged wall. The energy variational approach gives us a self-consistent way to introduce an interfacial constraint for electroneutrality. We mainly discuss those two key features in this present paper. Employing the energy variational approach, we derive a non-local partial differential equation with a total energy consisting of the entropic energy, electrostatic energy, repulsion energy representing the excluded volume effect, and the contribution of an interfacial constraint related to the electroneutrality between bulk/bath and wall. The resulting mathematical model produces the charge inversion phenomena near charged walls. We compare the computational results of the mathematical model to those of Monte-Carlo computations. and suggest that the interfacial constraint may be generally useful even in more detailed and chemically realistic descriptions of charged walls and boundaries.

Monte-Carlo Methods

• For ions of species i and j , the interaction potential is

$$u_{i,j}(r)=\begin{cases}\infty, & r\le a_{i,j},\\ \dfrac{z_i z_j q^2}{4\pi\varepsilon\varepsilon_0 r}, & r>a_{i,j}\end{cases}$$

where r is the distance between the ion centers, z_i is valence of i th ion, q is the fundamental charge, and ε is the permittivity of free space. $a_{i,j}$ is average radius of ions of species i and j .

• The interaction between an ion and the wall as infinite sheets of charge is

$$u_i(d_i)=\begin{cases}\infty, & r\le \dfrac{d_i}{2},\\ -\dfrac{z_i q\sigma}{2\varepsilon\varepsilon_0}, & r>\dfrac{d_i}{2}\end{cases}$$

where d_i is the distance to the closest point on the wall and σ is the surface charge density of the wall.

Diffusive Interface Methods for Interfacial Constraint

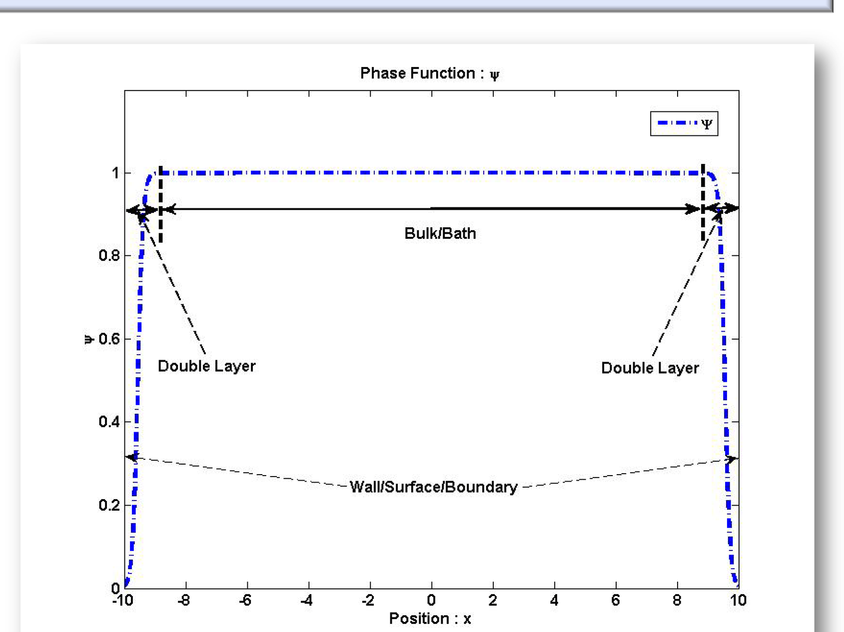
• Allow mixing/interfacial region between two different solutions (e.g., oil and water)
• The label/phase function ψ for the interfacial constraint between bulk and charged wall :

$$\psi=\begin{cases}1, & in\ bulk,\\ 0, & at\ the\ chareged\ wall.\end{cases}$$

•The explicit form of ψ in one-dimensional domain is established by

$$\psi(x)=\frac{1}{2}\tanh\left(\frac{d(x)}{\sqrt{2}\eta}\right)+\frac{1}{2}$$

where $d(x)$ is the distance function from the walls and η is the thickness of interface.



Poisson-Nernst-Planck Equation

• Total Energy for Modified PNP equation with Finite-size Effect and Interfacial Constraint

$$\widetilde{E}^{total}_{PNP}=\int\left\{k_BT\sum_{i=1}^{N}c_i\log c_i+\frac{1}{2}\left(\rho_0+\sum_{i=1}^{N}z_iqc_i\right)\phi+\lambda\psi\sum_{i=1}^{N}z_iqc_i\right.$$
$$\left.\sum_{i=1,\,j\ge i}^{N}\int\frac{\Psi_{i,j}(|\vec{x}-\vec{y}|)}{2}c_i(\vec{x})c_j(\vec{y})d\vec{y}\right\}d\vec{x}.$$

where Ψ is the repulsive part of Lennard-Jones potential, ψ is label function, and λ is a Lagrange multiplier.

• The resulting PNP-FS-IF system after taking **a** variational derivative is

$$\frac{\partial c_i}{\partial t}=\nabla\cdot\left[D_i\left\{\nabla c_i+\frac{c_i}{k_BT}\left(z_iq\nabla(\phi+\lambda\psi)+\int\frac{1}{2}\left\{\sum_{j=1}^{N}\frac{\varepsilon_{i,j}(a_i+a_j)^{12}}{|\vec{x}-\vec{y}|^{12}}c_j(\vec{y})\right.\right.\right.\right.$$
$$\left.\left.\left.\left.+\frac{\varepsilon_{i,i}(2a_i)^{12}}{|\vec{x}-\vec{y}|^{12}}c_i(\vec{y})\right\}d\vec{y}\right)\right\}\right],\quad for\ i=1,\cdots,N,$$

$$\nabla\cdot(\varepsilon\nabla\phi)=-\left(\rho_0+\sum_{i=1}^{N}z_iec_i\right).$$

Uncharged Wall Case

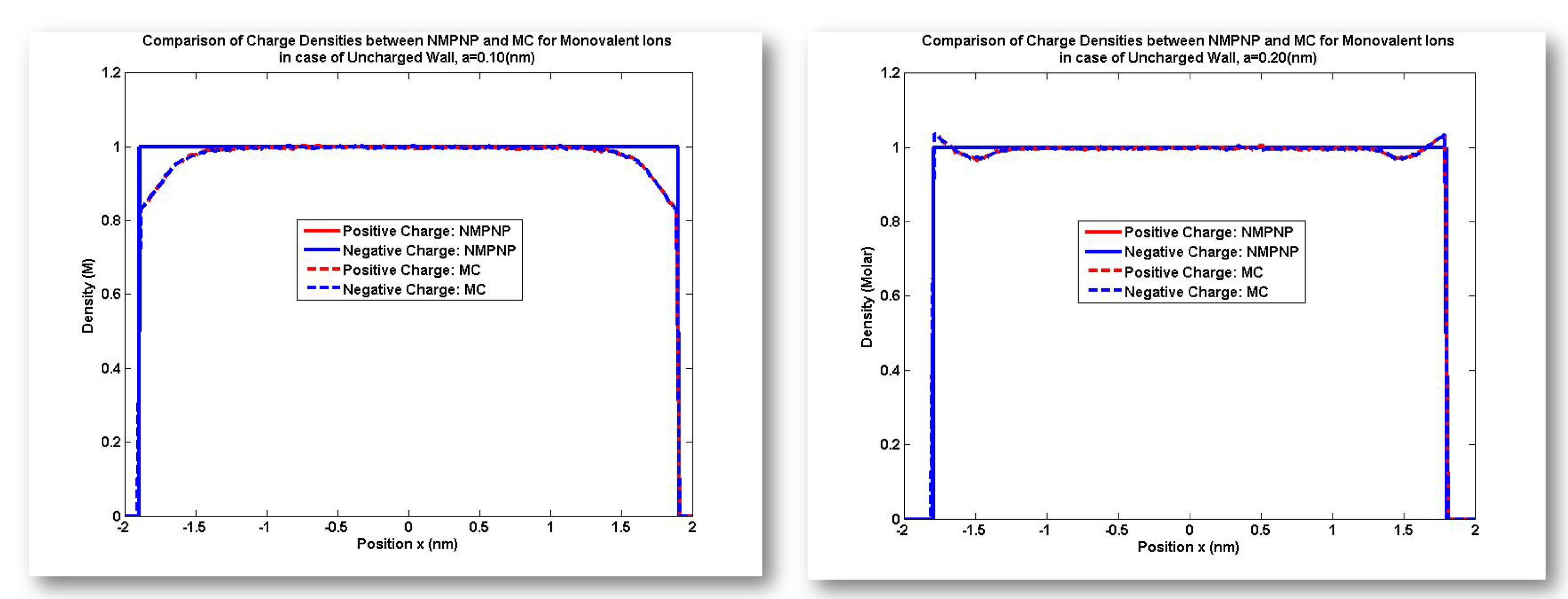


Figure 1. Uncharged wall cases, $z_p=1, z_n=-1,$ with radii, $a=1.0, 2.0\,(\dot{A})$

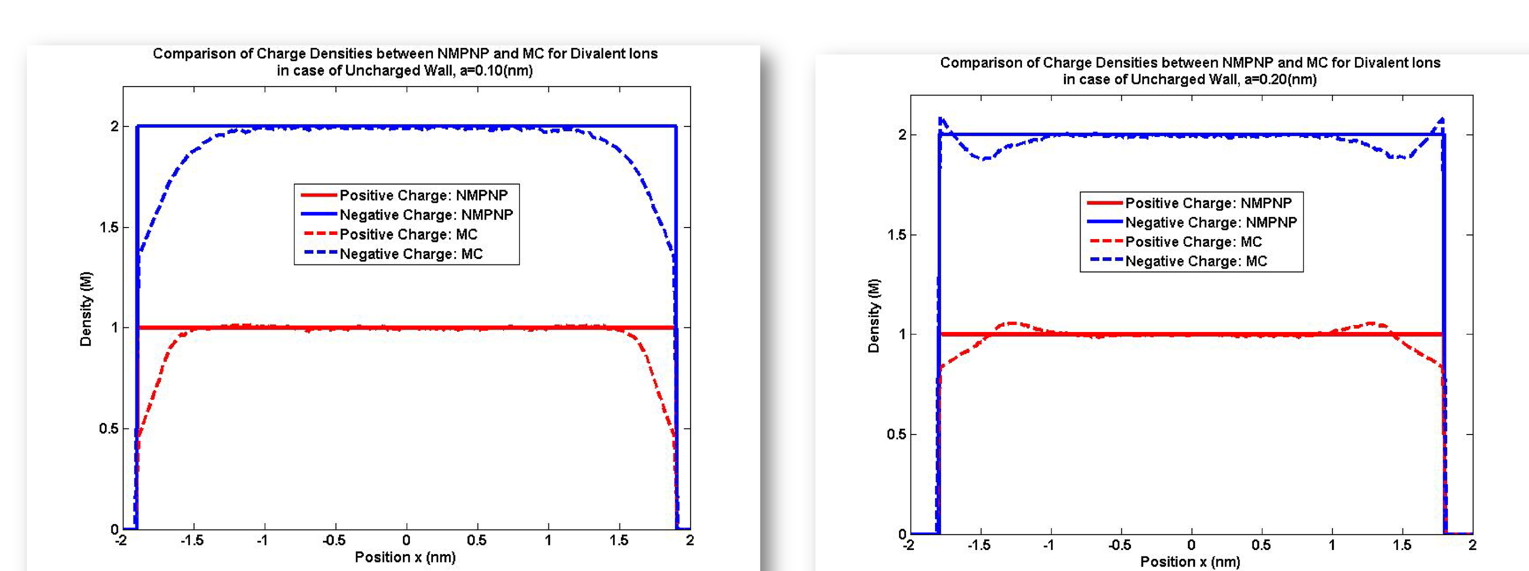


Figure 2. Uncharged wall cases, $z_p=2, z_n=-1,$ with radii, $a=1.0, 2.0\,(\dot{A})$

Charged Wall Cases

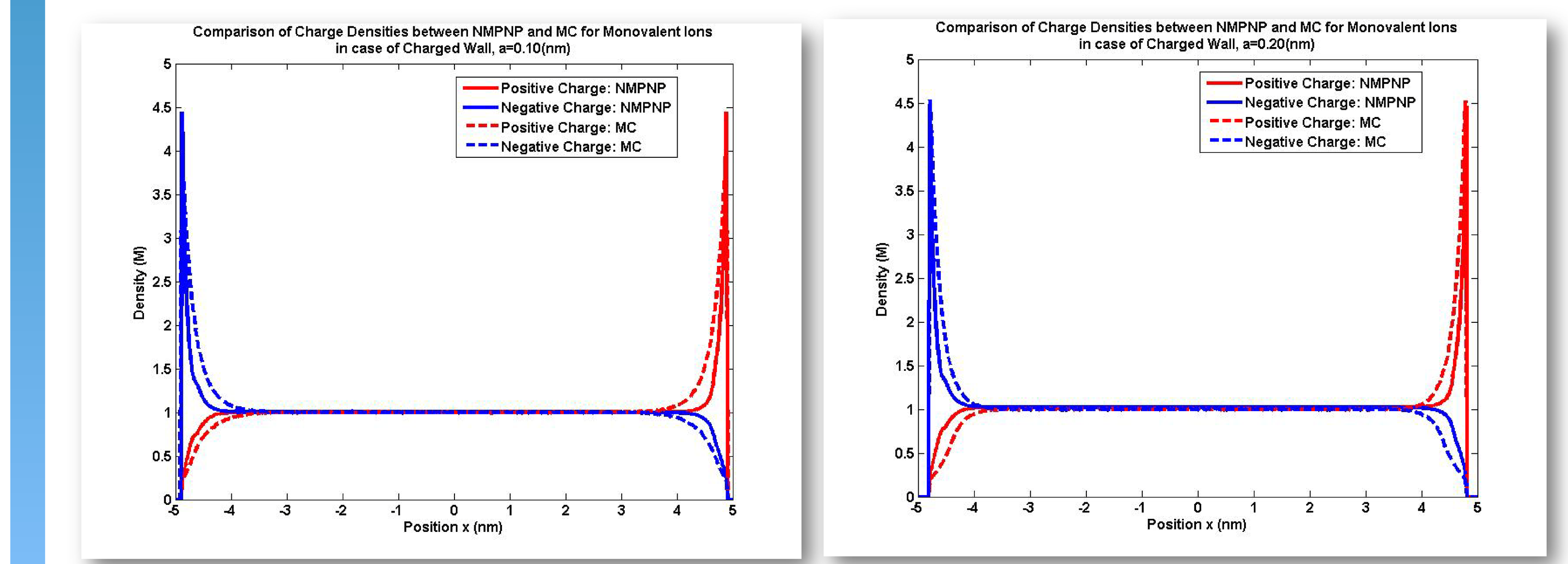


Figure 3. Charged wall cases, $z_p=1, z_n=-1,$ with radii, $a=1.0, 2.0\,(\dot{A})$

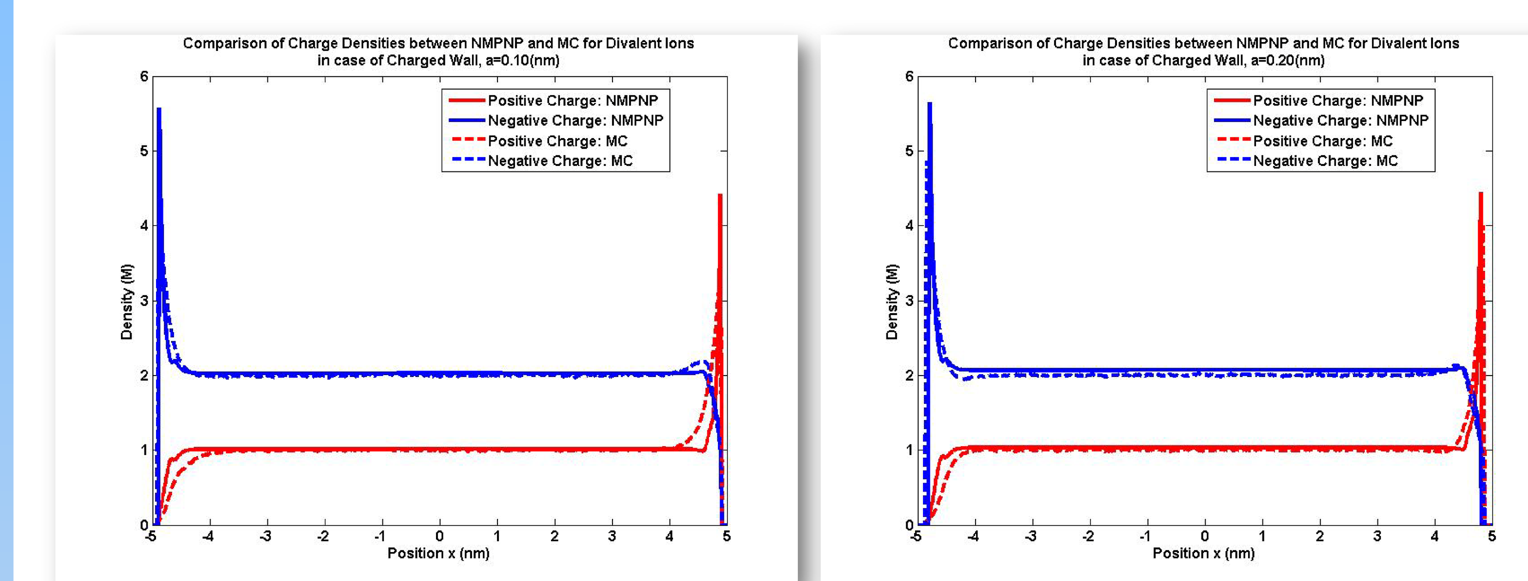


Figure 4. Charged wall cases, $z_p=2, z_n=-1,$ with radii, $a=1.0, 2.0\,(\dot{A})$

Discussion & Conclusion

• MC and PNP-FS-IF are not identical:
  - Entropic energy
  - Interaction between ion and wall.
• The PNP theory with **excluded** volume effect needs further investigation in two and three dimensional systems
• The resulting system PNP-FS-IF **was derived in a self-consist way and satisfies the energy dissipation law.**
• Energy variational approach recovers a charge inversion(layering) phenomena.

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