# Steric effects on ion dynamics near charged electrodes

Pedro H. R. Alijó[a], Frederico W. Tavares[a,b], Evaristo C. Biscaia Jr.[a], Argimiro R. Secchi[a]

[a]Programa de Engenharia Química, COPPE, Universidade Federal do Rio de Janeiro, Av. Horácio Macedo, 2030, Cidade Universitária, Rio de Janeiro/RJ, 21941-972, Brazil
[b]Departamento de Engenharia Química, Escola de Química, Universidade Federal do Rio de Janeiro, Av. Athos da Silveira Ramos, 149, Cidade Universitária, Rio de Janeiro/RJ, 21949-909, Brazil

**Abstract**

We present a modified Poisson-Nernst-Planck (mPNP) model to include steric effects on ion dynamics near charged electrodes. This contribution appears directly on chemical potential of each ion in solution as a non-electrostatic term. After spatial discretization, the model consists in a differential-algebraic equations (DAE) system, which can be dynamically solved by the well-established DASSLC code, implemented in EMSO simulator. A carefully dimensional analysis was carried out to turn the DAE system dimensionless with normalized spatial domain. Size correlation effects for equally sized ions avoid unphysical charge densities near the electrodes (especially at high voltages), and also give some insights on double layer formation. Time evolution of free charge density profiles show a diffusion controlled dynamics with a very fast response ($t \sim 10^{-8}$ s). The methodology proposed here allows the inclusion of new contributions on PNP model framework for ion dynamics, as well as to solve both stationary and dynamical ion distributions, taking advantage of the EMSO software simulator features.

Keywords: Ion dynamics; modified Poisson-Nernst-Planck model; size effects.

## 1. Introduction

Electrical double layer properties when charged surfaces are immersed in electrolyte solutions are an important task on colloid and interface science. Since the first work of Gouy **Erro! Fonte de referência não encontrada.** and Chapman **Erro! Fonte de referência não encontrada.**, theories have been widely proposed, mainly based on Poisson-Boltzmann (PB) equation and their extensions (modified versions), covered by recent reviews **Erro! Fonte de referência não encontrada.Erro! Fonte de referência não encontrada.**. Recently, with the rapidly growing interest in micro-electromechanical systems (MEMS) and the general trend of miniaturization of processes and systems, electro-kinetic flow phenomena have received much more attention. In this context, transient double layer analysis is crucial to understanding the mechanisms involved in diffusion-controlled chemical kinetics and transport properties of electrolyte solutions through membranes and micro-channels **Erro! Fonte de referência não encontrada.**.

Several works on electro-kinetic phenomena have been presented in the literature. Recent reviews **Erro! Fonte de referência não encontrada.**,**Erro! Fonte de referência não encontrada.Erro! Fonte de referência não encontrada.** show some of these applications, mainly focused on miniaturized processes and microfluidics **Erro! Fonte de referência não encontrada.Erro! Fonte de referência não encontrada.**. The fundamental difficulty in modeling electro-kinetic phenomena is associated with the complex molecular behavior of interfacial phenomena, giving rise to bulk fluid flow. The "standard model" on electro-kinetic phenomena description is based on the simultaneous solution of Navier-Stokes (NS) equation for viscous flow, associated with Poisson-Nernst-Planck (PNP) equations for ion transport, constituting the so called family of PNP/NS models [4].

Analytic results related to ion diffusion in the electrical double layer using PB equation for the mean electrostatic potential and the Smoluchowski equation [10] for the ion diffusion is developed for planar, cylindrical and spherical geometry by using certain useful integral equations [5]. Recently, there is a trend of seeking analytical and/or linearized solutions for PNP model on ion dynamics [11-18]. Some authors are concerned in decoupling Poisson and Nernst-Planck

equations [19,20] for ion transport modeling through membranes, or even to solve PB equation instead of Nernst-Planck equations in modeling complex ionic systems with multiple species [21].

It is well known that ion transport modeling through PNP model has some limitations. In addition to those who are inherent to mean-field approaches, such as the fact that the solvent is a continuum without any correlation, the ion size are neglected, as well as any type of ion-ion electrostatic correlations and non-electrostatic interactions that may appear between the ions and the electric field [22]. Baker-Jarvis *et al*. [23] present an electrodynamics analysis to account for potential fluctuations on the electric double layer. Ion dynamics near a charged electrode is modeled by transient Poisson and Nernst-Planck equations, coupled with a Maxwell equation and some constitutive relations derived from electromagnetism. Although presented a rigorous equating, the authors use some simplifications and approximations in order to achieve analytical solutions for the problem.

Although extensively applied in modeling ion transport, some open questions remain about the application of PNP model, especially concerning its extensions to include non-electrostatic effects. Some recent works attempted to include size effects on ion transport modeling through PNP model, either in case of direct current (DC) voltage electrodes [17,23], alternating current (AC) voltage electrodes [24-26], electro-kinetic flow and mobility [27-30], or in membrane and porous medium modeling [31,32].

The main purpose of this work is to analyze the effects of ion size on mobile charge dynamics. Thus, we have proposed a modified Poisson-Nernst-Planck (mPNP) model that accounts for size effects in a thermodynamically consistently way, enabling to account for ion size asymmetries. We show that the steric repulsion avoid unphysical charge distributions nearby electrodes at high voltages. Time evolution of ion distribution for a suddenly applied DC voltage is presented for the case of a single plate electrode (SPE), and for parallel-plate electrodes (PPE), both without Faradaic reactions (blocking electrodes).

## 2. Methodology

Ion dynamics is considered here in a simple picture sketched in Fig. 1: (a) single plate electrode (SPE) immersed in electrolyte solutions in a semi-infinite domain, and suddenly subjected to a DC voltage $V$; and (b) parallel-plate electrodes (PPE) separated by $L$ and immersed in electrolyte solutions suddenly subjected to a DC voltage $2V$. The solvent is represented only by the dielectric permittivity $\varepsilon$ in both cases. We consider "blocking electrodes", i.e., no Faradaic reactions occur (no ion flux through the electrodes).

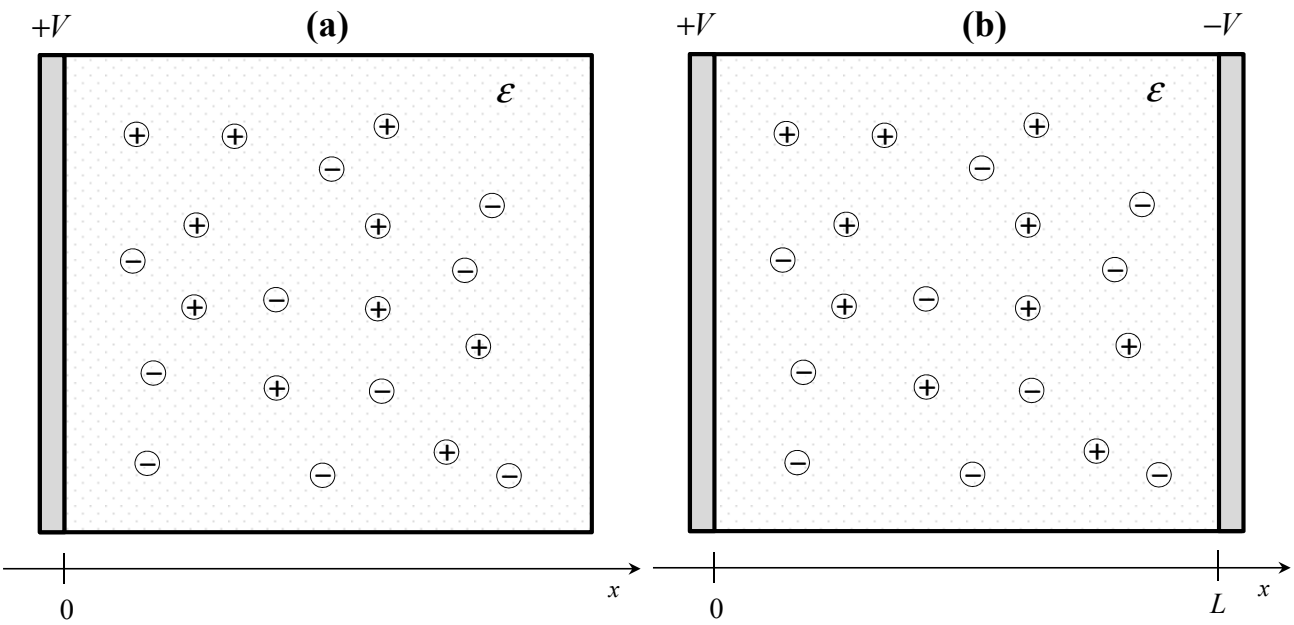

Fig 1. Sketches of the ion dynamics modeling: a DC voltage is suddenly applied to electrolyte solutions under the influence of: (a) single plate electrode (SPE); (b) parallel-plate electrodes (PPE) separated by *L*.

The choice of the configurations presented in Fig. 1 is for better understanding ion specificity and steric effects on diffuse charge dynamics, aside from test the model in confinement scenarios (as in case of PPE). In transient analysis, when one is interested in mobile charge dynamics subjected to variations in the electric field, additional equations derived from electromagnetism are required to describe the system behavior. In all analysis presented here the fluid is stationary and we focus only in the solution of ion transport equations (Poisson-Nernst-Planck equations), without considering bulk fluid flow (Navier-Stokes and continuity equations).

### *2.1 Governing equations*

The electric field vector **E** produced by a charged entity immersed in an electrolyte solution is given by [23]:

$$\mathbf{E} = -\nabla \psi - \frac{\partial \mathbf{A}}{\partial t}, \tag{1}$$

where $t$ is the time, □ and **A** are the scalar potential and the vector potential, respectively.

Deriving two non-homogeneous Maxwell equations in a dielectric medium, considering the primitive model of the system, in which the molecular nature of the solvent is ignored by treating it as a continuous medium with constant dielectric permittivity [34]:

$$\nabla \times (\nabla \times \mathbf{A}) - \varepsilon\mu \frac{\partial \mathbf{E}}{\partial t} = \hat{\mu}\mathbf{J} \tag{2}$$

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon}, \tag{3}$$

where $\rho$ is the ion mobile charge density, $\hat{\mu}$ is the magnetic permeability of the medium and **J** is the current density.

Applying the electrical potential definition (eq. 1) in eqs. (2) and (3), and using the Lorentz gauge condition (eq. 4), generally employed in the calculation of time-dependent electromagnetic fields through retarded potentials [23,34]:

$$\nabla \cdot \mathbf{A} + \varepsilon\hat{\mu} \frac{\partial \psi}{\partial t} = 0, \tag{4}$$

we obtain the pair of differential equations:

$$\varepsilon\hat{\mu} \frac{\partial^2 \psi}{\partial t^2} - \nabla^2 \psi = \frac{\rho}{\varepsilon} \tag{5}$$

$$\varepsilon\hat{\mu}\frac{\partial^2 \mathbf{A}}{\partial t^2} - \nabla^2 \mathbf{A} = \mu \mathbf{J} \tag{6}$$

where the potentials **A** and  both satisfy the tridimensional non-homogeneous wave equation, with source terms given by **J** and $\rho$, respectively [34]. These source terms are given by the following constitutive relations:

$$\mathbf{J} = e\sum_{i}^{n_c} z_i \mathbf{\Gamma}_i \tag{7}$$

$$\rho = e\sum_{i=1}^{n_c} z_i c_i, \tag{8}$$

where $e$ is the elementary charge, $z_i$ is the ion valence, $\mathbf{\Gamma}_i$ is the ion flux, and $c_i$ is the concentration of ions $i$, respectively. The ion flux $\mathbf{\Gamma}_i$ is written in terms of Fick's first law of diffusion, as follows:

$$\mathbf{\Gamma}_i = -\frac{D_i}{k_B T} c_i \nabla \mu_i, \quad \text{for } i = 1, \ldots, n_c, \tag{9}$$

where $D_i$ is the diffusion coefficient of ion $i$, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $\mu_i$ is the $i^{\text{ith}}$ ion chemical potential, given by:

$$\mu_i = \mu_i^0 + k_B T \ln c_i + z_i e\psi + \sum_{j}^{ne} \xi_{ij}, \text{ for } i = 1, \ldots, n_c, \tag{10}$$

where $\mu_i^0$ is the reference chemical potential of the ion $i$. The second and the third term in right hand side of eq. (10) accounts for the entropy and the purely electrostatic (Coulomb) contributions, respectively. The last term is the total contribution due to all $j^{\text{th}}$ non-electrostatic contributions ($j$ = 1,…, $ne$) on the chemical potential, such as steric effects, electrostatic correlations, hydration effects, image effects, etc. The term "non-electrostatic" is used in sense of grouping every contribution that is not purely electrostatic (i.e., non-Coulombic) contributions.

Expressing the chemical potential for the problem domain, one can calculate the ion flux by simple differentiation of eq. (10), according to eq. (9), giving:

$$\mathbf{\Gamma}_i = -D_i\left[\nabla c_i + \frac{c_i}{k_B T}\left(z_i e \nabla \psi + \sum_j^{ne} \nabla \xi_{ij}\right)\right], \quad \text{for } i = 1,\ldots,n_c. \tag{11}$$

Ion transport through the electrolyte solution is modeled through the Nernst-Planck equations (eq. 12), which is a diffusion equation that describes charge conservation with possible sources $g_i$ of creation or recombination of charges.

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{\Gamma}_i = g_i, \text{ for } i = 1,\ldots,n_c. \tag{12}$$

Since in this paper there is no source of creation or recombination of charges, in all analysis presented here $g_i = 0$. The Navier-Stokes equation is not included in our transient analysis, as the bulk fluid is static and only the mobile charges dynamics are considered.

As we suppose a planar shape to the electrodes (Fig. 1), the properties only vary in $x$ direction, and the equations described above should be rewritten in one-dimensional Cartesian coordinates. Therefore, the vector potential **A**, which is directly associated with the magnetic field **B** by $\mathbf{B} = \nabla \times \mathbf{A}$, can be properly neglected, since we are not interested in the electromagnetic interaction. Therefore, equations (6) and (7) are not considered in our analysis, and the model reduces to solve the transient Poisson equation for the electric potential:

$$\varepsilon\hat{\mu}\frac{\partial^2 \psi}{\partial t^2} - \frac{\partial^2 \psi}{\partial x^2} = \frac{\rho}{\varepsilon}, \tag{13}$$

associated with the Nernst-Planck equations for the ion transport:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial \Gamma_i}{\partial x}, \text{ for } i = 1,\ldots,n_c, \tag{14}$$

where the ion flux is derived from Fick's law:

$$\Gamma_i = -\frac{D_i}{k_B T} c_i \frac{\partial \mu_i}{\partial x}, \quad \text{for } i = 1,\ldots,n_c, \tag{15}$$

with $\rho$ and $\mu_i$ given by eqs. (8) and (10), respectively.

The electrical potential □ can be calculated once the free charge density $\rho$ is known. However, $\rho$ also depends on the ion concentrations. Therefore, the problem involves the simultaneous solution of eqs. (13) and (14), both subjected to the algebraic constraints given by eqs. (8), (10), and (15), and also to properly initial and boundary conditions (see the next section). This problem consists on the Poisson-Nernst-Planck (PNP) model, which, as discussed in Section 1, is the "standard model" [4] in mobile charge dynamics modeling.

### *2.2 Non-dimensional equations*

The PNP model is a system of differential-algebraic equations (DAE) involving variables and parameters in various scales. In case of the Boltzmann constant ($k_B$) and ion concentrations ($c_i$), for instance, the orders of magnitude are, in S.I., of about $10^{-23}$ and $10^{26}$, respectively. Furthermore, the independent variable $x$ ranges often in the nanometer scale, possible in a semi-infinity domain, since $x$, according to Fig. 1(a), may vary from zero (electrode surface) to "infinity" (bulk phase). These aspects encourages the use of scaled variables and parameters for non-dimensionalization and problem re-parameterization, with gain in terms of smoothly and accuracy of the numerical solution.

In terms of the independent variable $x$, we associate a new variable to normalize the domain. An important distinction between the SPE (Fig. 1a) and PPE (Fig. 1b) is imposed here, since in SPE configuration $0 \leq x < \infty$, while in PPE $0 \leq x \leq L$. Therefore, the new spatial variable $\zeta$ must also be different in both cases in order to give a normalized domain: $0 \leq \zeta \leq 1$. Table 1 list all the dimensionless variables and parameters used in this work for SPE and PPE. The gray rectangles in Fig. 1 are schematic representations of the Stern layer [35], which have to be naturally included in our model since we are not dealing with point-like ions. Since the ions are all of equal sizes, the Stern layer thickness $\lambda$ is equal to the ion radius: $\lambda = \sigma_i/2$; where $\sigma_i$ is the ion diameter.

Table 1. Dimensionless variables and parameters for SPE and PPE.

| Variable / Parameter | Symbol | Relation with original variables | |
|---|---|---|---|
| | | SPE | PPE |
| Spatial coordinate | $\zeta$ | $1-\exp[-\kappa x]$ | $x/L$ |
| Time | $\tau$ | $t\kappa^2 D_0$ | $t\kappa D_0/L$ |
| Concentration | $\chi_i$ | $c_i/c_{i,0}$ | $c_i/c_{i,0}$ |
| Electric potential | $y$ | $e\psi/k_B T$ | $e\psi/k_B T$ |
| Ion flux | $\bar{\Gamma}_i$ | $\Gamma_i/D_0 c_0 \kappa$ | $\Gamma_i/D_0 c_0 \kappa$ |
| Chemical Potential | $\bar{\mu}_i$ | $\left(\mu_i-\mu_i^0\right)/k_B T$ | $\left(\mu_i-\mu_i^0\right)/k_B T$ |
| Non-electrostatic potentials | $\bar{\xi}_{ij}$ | $\xi_{ij}/k_B T$ | $\xi_{ij}/k_B T$ |

The Debye screening length is the characteristic length used to rescale the independent variable, given by:

$$\kappa^{-1} = \left(\frac{\varepsilon k_B T}{e^2 \sum_i z_i^2 c_{i,0}}\right)^{1/2} = \left(\frac{\varepsilon k_B T}{2e^2 I}\right)^{1/2}, \tag{16}$$

where $I$ is the ionic strength, related with the ion concentrations by:

$$I = \frac{1}{2}\sum_i z_i^2 c_{i,0} \tag{17}$$

The diffusion coefficients $D_i$ is assumed to be constant and equal to $D_0$ for all ions $I$, which is consistent with the fact that mobile charges are all equally sized ($\sigma_i = \sigma$, for all $i$).

Applying the relations listed in Table 1 to equations (10, 13-15), we obtain the following DAE system for SPE:

$$\varepsilon\hat{\mu}\kappa^2 D_0^2 \frac{\partial^2 y}{\partial \tau^2} = (1-\zeta)\left[(1-\zeta)\frac{\partial^2 y}{\partial \zeta^2} - \frac{\partial y}{\partial \zeta}\right] + \frac{1}{2I}\sum_i z_i c_{i,0}\chi_i \tag{18}$$

$$\frac{\partial \chi_i}{\partial \tau} = (\zeta - 1)\cdot\frac{\partial \overline{\Gamma}_i}{\partial \zeta}, \quad \text{for } i = 1,\ldots,n_c. \tag{19}$$

$$\overline{\Gamma}_i = \frac{D_i}{D_0}\chi_i(\zeta - 1)\frac{\partial \overline{\mu}_i}{\partial \zeta}, \quad \text{para } i = 1,\ldots,n_c. \tag{20}$$

and for PPE:

$$\varepsilon\hat{\mu}\kappa^2 D_0^2 \frac{\partial^2 y}{\partial \tau^2} = \frac{\partial^2 y}{\partial \zeta^2} + \frac{L^2 e^2}{k_B T \varepsilon}\sum_i z_i c_{i,0}\chi_i \tag{21}$$

$$\frac{\partial \chi_i}{\partial \tau} = -\frac{\partial \overline{\Gamma}_i}{\partial \zeta}, \quad \text{for } i = 1,\ldots,n_c. \tag{22}$$

$$\overline{\Gamma}_i = -\frac{D_i}{D_0 \kappa L}\chi_i \frac{\partial \overline{\mu}_i}{\partial \zeta}, \quad \text{for } i = 1,\ldots,n_c. \tag{23}$$

where, in both cases, the chemical potential is given by:

$$\bar{\mu}_i = \ln c_0 + \ln \chi_i + z_i y + \sum_j \bar{\xi}_{ij}, \quad \text{for } i = 1,...,n_c. \tag{24}$$

Equations (18-20) (SPE) and (21-23) (PPE), together with equation (24), constitute the PNP model. Although originally developed for transient potential behavior, we can neglect the dynamics on potential, since the term $\left(\varepsilon\bar{\mu}\kappa^2 D_0^2\right)$ pre-multiplying $\partial^2 y/\partial\tau^2$ is very small compared to the others. Moreover, as we are neglecting electromagnetic interactions, the effects of fluctuations on electrical potential can be properly overlooked for our purposes without loss of generality. The PNP model is subjected to the following boundary conditions (BC) for SPE and PPE:

$$\text{SPE}\begin{cases} y(\zeta=0,\tau)=y_0 \\ y(\zeta=1,\tau)=0 \\ \chi_i(\zeta=1,\tau)=1, \text{ for } i=1,...,n_c \\ \left.\dfrac{\partial\chi_i}{\partial\zeta}\right|_{\zeta=1}=0, \text{ for } i=1,...,n_c \end{cases} \qquad \text{PPE}\begin{cases} y(\zeta=0,\tau)=-y_0 \\ y(\zeta=1,\tau)=y_0 \\ \bar{\Gamma}_i(\zeta=0,\tau)=0, \text{ for } i=1,...,n_c \\ \bar{\Gamma}_i(\zeta=1,\tau)=0, \text{ for } i=1,...,n_c \end{cases} \tag{25}$$

where $y_0 = eV/k_BT$ is the dimensionless voltage applied to the electrodes. Bulk initial condition (IC) is assumed for the ion concentrations, i.e., initially, the ions have all the same (bulk) concentration, for both SPE and PPE:

$$\chi_i(\zeta,\tau=0)=1, \text{ for } i=1,...,n_c. \tag{26}$$

Therefore, the problem consists on the analysis of ion dynamic response against a suddenly applied voltage $y_0 = eV/k_BT$. Because the ion dynamics is naturally associated to ion diffusion and to interaction with electric fields, ion size effects may play an important role on ion dynamics. The inclusion of this contribution gives rise to a new modified Poisson-Nernst-Planck (mPNP) model, which we derive in the next section.

### *2.3 A modified Poisson-Nernst-Planck model (mPNP)*

Following recent works [37-41] we account for the size effects through residual chemical potentials derived from the Boublik-Mansoori-Carnahan-Starling-Leland Equation of State (BMSCL EoS) [42-43] for a mixture of rigid spheres, as follows:

$$\begin{aligned} w_i = \frac{\mu_i^{\text{res,BMCSL}}}{k_BT} &= -\left(1+\frac{2\phi_2^{\,3}\sigma_i^3}{\phi_3^{\,3}}-\frac{3\phi_2^{\,2}\sigma_i^2}{\phi_3^{\,2}}\right)\ln(1-\phi_3) \\ &+\frac{3\phi_2\sigma_i+3\phi_1\sigma_i^2+\phi_0\sigma_i^3}{1-\phi_3}+\frac{3\phi_2\sigma_i^2}{(1-\phi_3)^2}\left(\frac{\phi_2}{\phi_3}+\phi_1\sigma_i\right)-\phi_2^3\sigma_i^3\,\frac{\phi_3^2-5\phi_3+2}{\phi_3^2(1-\phi_3)^3}, \end{aligned} \tag{29}$$

with:

$$\phi_k = \frac{\pi}{6} \sum_i c_{i,0} \chi_i(\zeta) \sigma_i^k, \text{ for } k = 0,...,3. \tag{30}$$

where $\mu_i^{\text{BMSCL}}$ is the residual chemical potential correspondent to the BMSCL EoS.

It should be emphasized that the main feature of the size correlation expression based on BMSCL EoS is the possibility of accounting for ion size asymmetries. Although here we limit our analysis for the symmetric case, in which all ions have the same size $\sigma$, the effect of size asymmetries may play an important role on double layer calculations, as pointed out in a previous work [37]. Therefore, the application of BMCSL EoS in a thermodynamically consistent way is encouraged.

The steric effect is directly included on the chemical potential of each ion $i$, as a non-electrostatic term in equation (24):

$$\bar{\mu}_i = \ln c_0 + \ln \chi_i + z_i y + w_i, \quad \text{for } i = 1,...,n_c. \tag{31}$$

in which $\sum_j \bar{\xi}_{ij} = w_i$ represent the non-electrostatic contribution accounted in this work. When $\sum_j \bar{\xi}_{ij} = 0$, mPNP model reduces to the (classical) PNP approach, in which the ions are point-like charges with valence $z_i$. In this case, the stationary solution of PNP model is equivalent to PB equation solution. For a SPE immersed in a continuous solvent with charge simmetrical electrolytes ($z$:$z$), an analytical solution for the PB equation was developed by Voyustky [44]:

$$y(\zeta) = \frac{2}{z} \ln \left[ \frac{1 + \gamma(1-\zeta)}{1 - \gamma(1-\zeta)} \right], \tag{32}$$

with:

$$\gamma = tgh\left( \frac{z y_0}{4} \right), \tag{33}$$

where the ion concentrations can be obtained from the electric potentials using Boltzmann distribution:

$$\chi_\pm = \exp\left(-z_\pm y(\zeta)\right) \tag{34}$$

Therefore, the steady-state solution of PNP model for a SPE under the conditions described above must be equal to PB analytical solution. The main purpose of this paper is to analyse the effects of ion size correlation on diffuse charge

dynamics. Although we neglect other important influences, mainly ion specificity effects [33,36], and electrostatic correlations [45], the mPNP model enable us to include any non-electrostatic effects as new contributions to the chemical potential in equation (24), without loss of generality and with no significative addition in terms of computational effort.

Althought ion steric effects are widely explored in double layer modeling, there are still many open questions, especially on ion dynamics analysis. Besides some recent works including steric effects on mobile charge dynamics [17,24-30,45], this is the first report on ion dynamics that include size asymmetries directly on the PNP approach to the best of our knowledge. The mPNP model described in this section is numerically integrated in time after spatial approximation via orthogonal colocation method using the Jacobi polynomial, $P_n^{(\alpha,\beta)}(\zeta)$. Mesh convergence is ensured with $n$ = 12 internal points and $\alpha = \beta = 1$. The time derivatives are then integrated using DASSLC code [46], implemented in the dynamic simulator EMSO (Environment of Modeling, Simulation and Optimization) [47].

## 3. Results and discussion

### *3.1 Numerical solution consistency*

Before presenting results for the mPNP model proposed here, we must verify our numerical scheme. A simple way to proceed with this is to compare the stationary solution of PNP model with the analytical solution available, as discussed in Section 2.3. For a single plate electrode immersed in a monovalent and symmetrical electrolyte (1:1), subjected to a suddenly applied DC voltage of $y_0 = 4$ in a continuous solvent, the PNP model should converge on stationary state to the analytical solution of Poisson-Boltzmann (PB) equation, presented by Voyutsky [44]. Table 2 list the values of some parameters used in the simulations presented here. The electric potential $y$ and anion concentration $\chi_-$ time evolution in the middle of the domain ($\zeta = 0.5$) for the PNP model and for the PB analytical solution are presented in Fig. 2. We observe a very good agreement between the numerical and the analytical solution.

Table 2. Specified parameters used in mPNP analysis.

| | | | |
|---|---|---|---|
| $e = 1.602\times10^{-19}\,\mathrm{C}$ | $\varepsilon = 6.951\times10^{-10}\,\mathrm{C^2J^{-1}m^{-1}}$ | $k_\mathrm{B} = 1.38065\times10^{-23}\,\mathrm{J\,K^{-1}}$ | $T = 298.15\,\mathrm{K}$ |
| $I = 0.5\,\mathrm{M}$ | ‡ $\hat{\mu} = 1.257\times10^{-6}\,\mathrm{J\,A^{-2}m^{-1}}$ | $L = 10\kappa^{-1}$ | $D_0 = 1.0\times10^{-9}\,\mathrm{m^2s^{-1}}$ |

‡ Vacuum magnetic permeability [34].

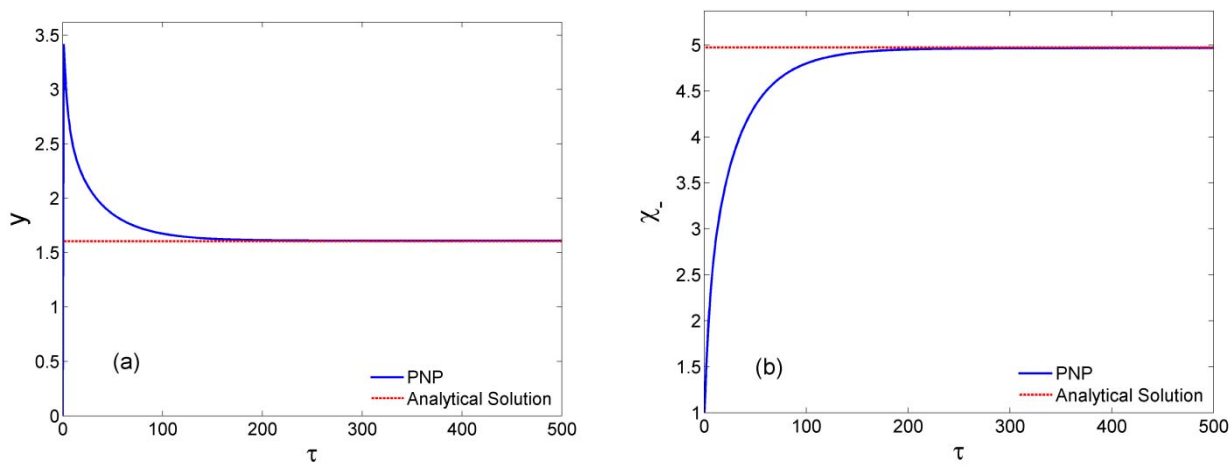


Fig 2. Dynamic evolution of PNP model results for $\zeta = 0.5$ and $y_0 = 4$, neglecting size effects (blue solid line), as compared to the analytical solution (red dashed line) available for SPE case: (a) electric potential ($y$); and (b) anion concentration ($\chi_-$).

### *3.2. mPNP model results*

In order to properly observe size correlation (SC) effects, we present dynamic profiles for the electrical potential $y$ and free charge density $\rho$ calculated by the PNP model and by the mPNP model proposed here. Although our formulation for the size correlation term enable to account for ion size asymmetries in a thermodynamically consistent way, based on BMSCL EoS expression for hard sphere mixtures, for all the simulations presented here the ions are equally sized, since model adjustment are required when ion size asymmetries are included, as pointed out by Alijó *et al*. [37]. Therefore, in this first report, ion diameters are all equal to 0.4 nm ($\sigma$ = 0.4 nm), which is a common value for ion simulations.

Fig. 3 show surface time evolution profiles for the electric potential $y$ (Figs. 3a and 3b) and free charge density $\rho$ (Figs. 3c and 3d) under the influence of a SPE with DC voltage $y_0 = 4$, and ionic strength 0.5 M. Comparing Figs. 3a and 3b, we observe an almost imperceptible influence of SC on electric potential dynamics. However, SC effects play an important role on free charge density dynamics (Figs. 3c and 3d). For PNP model results (Fig. 3c), the formation of the equilibrium ion distribution is quite slower as compared to mPNP model results (Fig. 3d), i.e., steady state (SS) is reached faster when steric effects are accounted. Because of SC, the absolute ion charge density tends to decrease nearby the electrodes, and the ion diffusion is not so intense from the bulk initial configuration ($\rho$ = 0) until SS, as compared to PNP case (without SC). Therefore, Figs. 3c and 3d show that ion dynamics for PNP-like models are controlled by the ion diffusion.

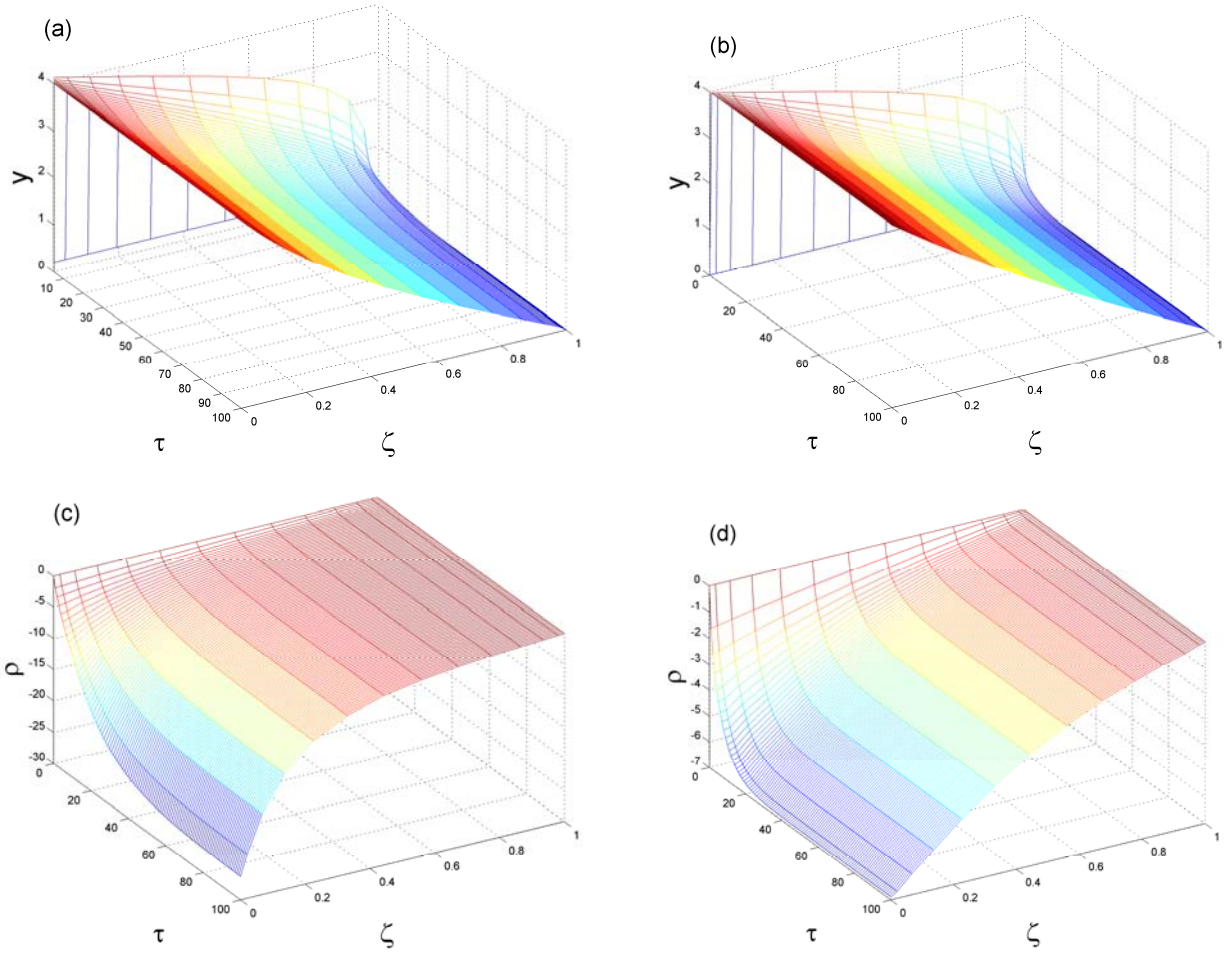


Fig 3. Surface time evolution responses for a single plate electrode with $y_0$ = 4, immersed in a 1:1 electrolyte of $I$ = 0.5M for: (a) electric potential $y$ (PNP model), (b) electric potential $y$ (mPNP model), (c) free charge density $\rho$ (PNP model), (d) free charge density $\rho$ (mPNP model).

Fig. 4 shed further light on the role of SC effects on the surface profiles of Fig. 3, by presenting sections for certain dimensionless times $\tau$ and at SS. Size effects influence tends to increase with time. From Fig. 4a, we observe that electric potential $y$ profiles are not the same for PNP and mPNP, as indicates the comparison of Figs. 3a and 3b, especially near SS. Initially the system is in bulk condition, with no steric repulsion. When the DC voltage is applied ($\tau > 0$), the mobile charges reorganize themselves and steric repulsion started to increase, until the steady state (SS) is reached. At SS, we observe the role of size correlation effects, increasing the electric potential (Fig. 4a), and decreasing the negative free charge accumulation near the positive electrode (Fig. 4b), due to steric repulsion. Moreover, we observe the normal trend of a continuous decrease in SC effects with distance to the electrode $\zeta$.

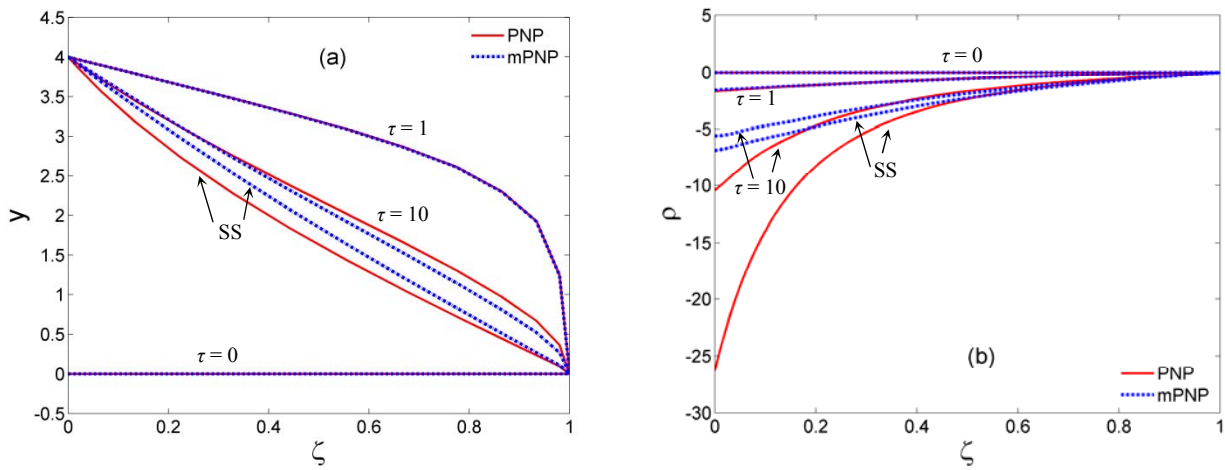


Fig 4. PNP model (red solid line) and mPNP model (blue dotted line) time evolution responses for a single plate electrode with $y_0 = 4$, immersed in a 1:1 electrolyte of $I$ =0.5M for: (a) electric potential $y$, and (b) free charge density $\rho$. SS denotes *Steady State* profile.

The same analysis is carried out in for PPE in Fig. 5. The plates are separated by a distance correspondent to 10 times the Debye screening length ($L = 10\kappa^{-1}$), and are charged with a voltage of $y_0 = \pm 4$ (i.e., $y_0|_{\zeta=0} = 4$, and $y_0|_{\zeta=1} = \square 4$). A similar behavior is observed in Figs. 5a and 5b for the PNP and mPNP electric potential responses, respectively, indicating a little influence of SC effects on electric potential dynamics, as in SPE case (Figs. 3a and 3b). Compared to SPE, SC effects play a minor role free charge density $\rho$ dynamics, despite steric repulsion tends to decrease the charge accumulation nearby electrodes, as observed from the comparison of PNP (Fig. 5a) and mPNP (Fig. 5b) responses. Diffusion effects play a minor role in PPE due to the limited domain available between the electrodes, which explain the little differences in terms of free charge density time responses between PNP and mPNP models for PPE, despite of differences observed in SPE case.

Fig. 6 details time evolution profiles presented in Fig. 5. Figs. 6a and 6b show profiles for the whole domain, while Figs. 6c and 6d are focused on the double layer near the positive electrode ($\zeta = 0$), to better observe the SC effects. A similar behavior is observed in Figs. 4 and 6, except by the fact that the SC effect is almost insignificant for the PPE case (Fig. 6a), as compared to the SPE case (Fig 4a). Fig. 6d exhibits a very similar behavior with Fig. 4b, with the SC effect playing an important role, reducing the negative excess of charges near the positive electrode because of hard sphere repulsion.

Note that the dynamics in PPE case is about one order of magnitude faster than in SPE case, due to the different dimensionless parameters used for time and space re-parameterization. According to Table 1, for $L = 10\ \kappa^{-1}$, $\tau^{SPE} = 10\ \tau^{PPE}$. We have proposed different time re-parameterizations to follow the different dimensionless space coordinates defined to give a normalized domain in both cases.

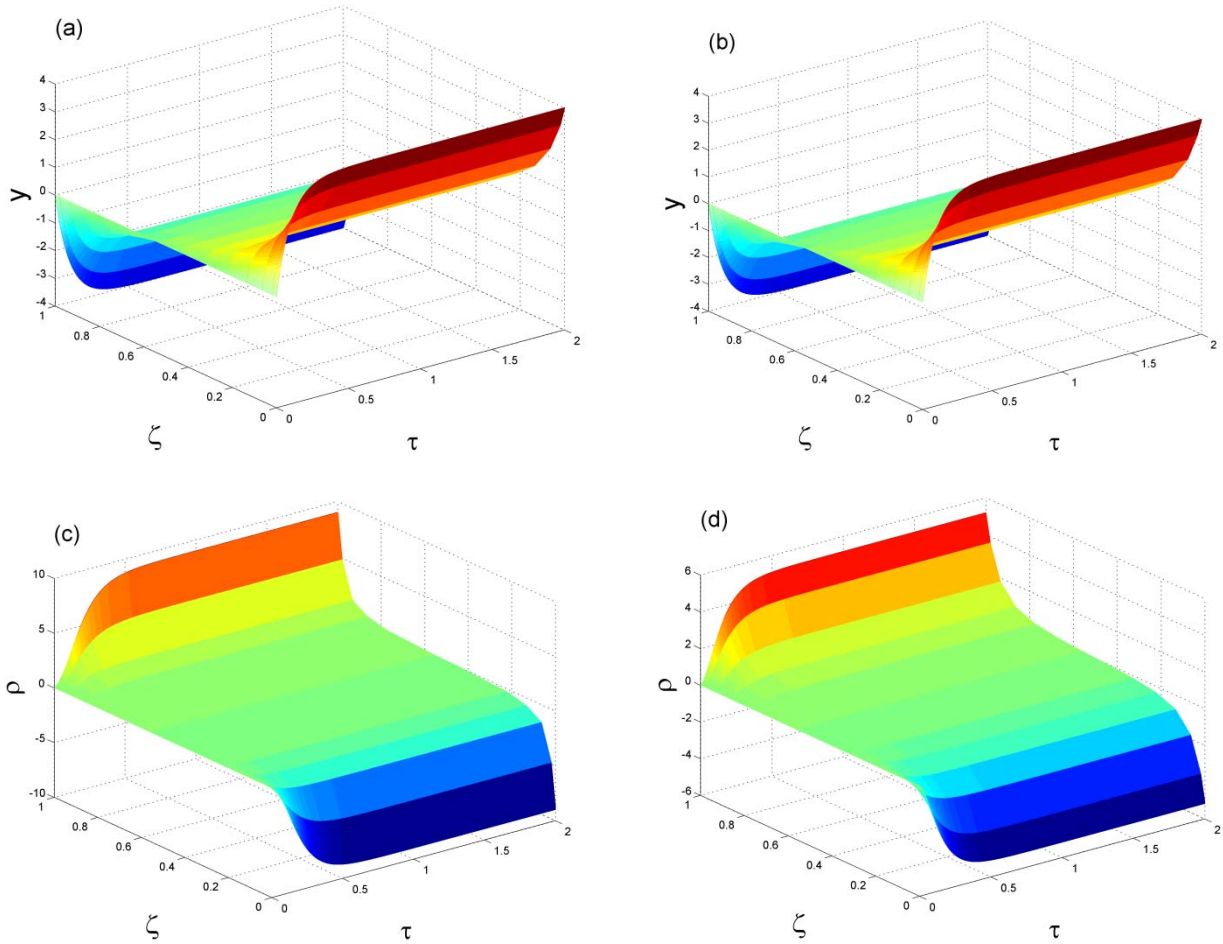


Fig 5. Surface time evolution responses for parallel-plate electrodes with $y_0 = \pm 4$, immersed in a 1:1 electrolyte of $I = 0.5$M for: (a) electric potential $y$ (PNP model), (b) electric potential $y$ (mPNP model), (c) free charge density $\rho$ (PNP model), (d) free charge density $\rho$ (mPNP model).

In order to shed further light on steric effects in ion dynamics, we show in Fig. 7 time evolution of charge density profiles for mPNP model. The electric potential applied to each PPE ($y_0 = \pm 10$) is strategically greater than these applied in previous scenarios to increase the size correlation contribution. The map of charge density time evolution are given for several instants after the application of the electric field at $\tau = 0$. Bulk salt depletion and double layer charging are clearly shown in Fig 7a for the space between the electrodes, while Fig. 7b shows details near the positive electrode. SS profiles for mPNP (solid red line) and PNP (dotted red line) are also plotted in Fig. 7. Comparing these two profiles, charge density decreases more than 50% due to steric repulsion nearby electrode walls, indicating the huge influence of SC at such high voltages.

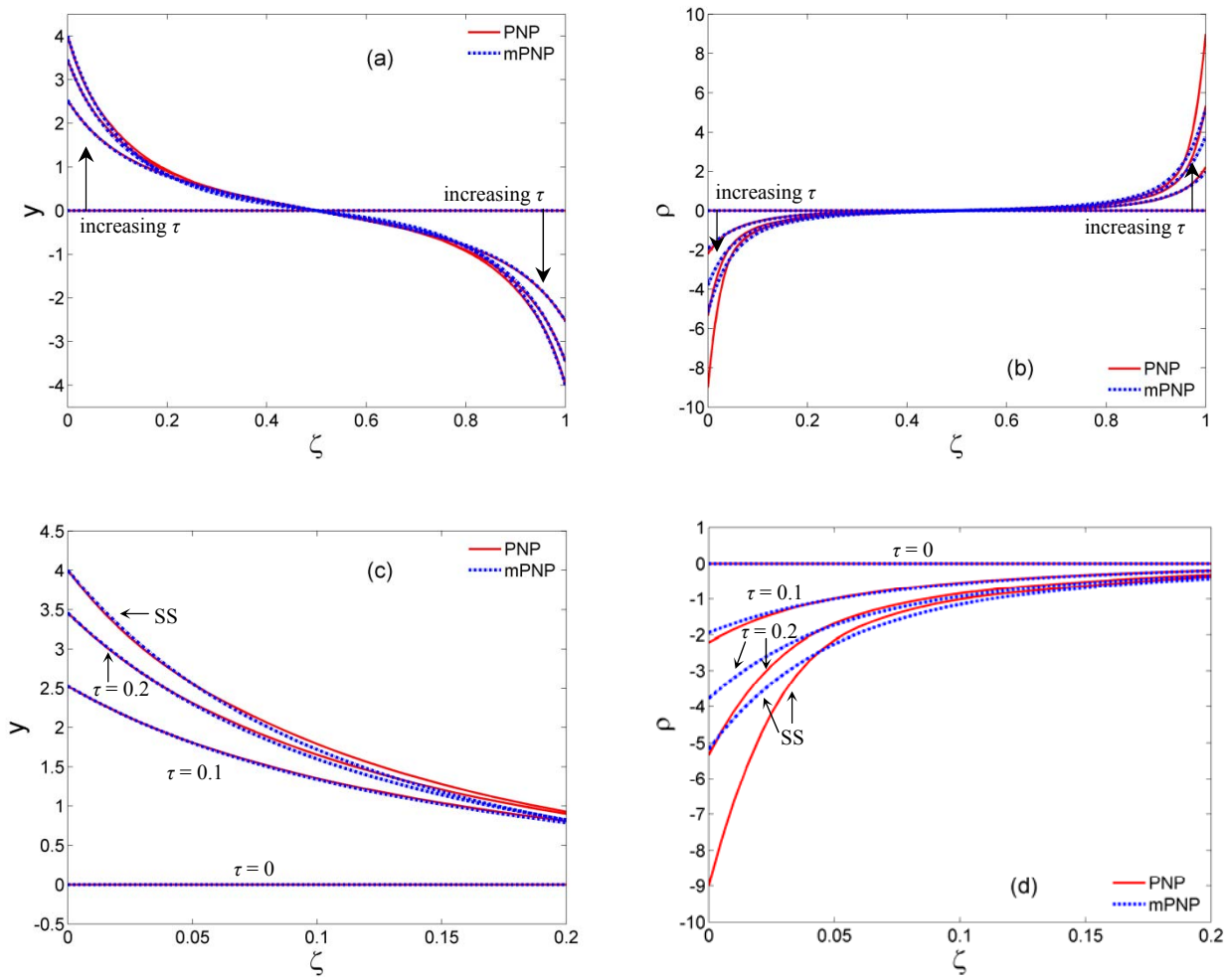


Fig 6. Profiles for PNP (solid red line) and mPNP (dotted blue line) models for $\tau = 0$, $\tau = 0.1$, $\tau = 0.2$, and SS, for (a) dimensionless electric potential and (b) free charge density $\rho$ for PPE with $y_0 = \pm 4$, immersed in a 1:1 electrolyte of $I = 0.5$M. (c) and (d) depict details of (a) and (b) near the electrode, respectively. SS denotes *Steady State* profile.

We shall emphasize that our approach to include SC in PNP model is slightly different from recent works [17,23-30] based on Bikerman [48] formulation, in which the ions must be equally sized and its concentration saturates to a maximum value. In contrast, the mPNP proposed here enables to include ion size asymmetries and do not impose ion density saturation at the electrodes under high applied voltages, since the mPNP proposed here is based on liquid state theory instead of lattice theory, as in case of Bikerman-like approaches.

Although ion dynamics is considerably fast, since SS is reached at $\tau \approx 1$ ($t \sim 10^{-8}$ s), it can give insights on how mobile charges reorganize itself when subjected to perturbations on initial configuration and/or on external electric field. Moreover, ion dynamics analysis in the context of mPNP model is an important step to properly understanding electro-kinetic flows and macroscopic transport properties originating from the interaction between electric field and fluid flow.

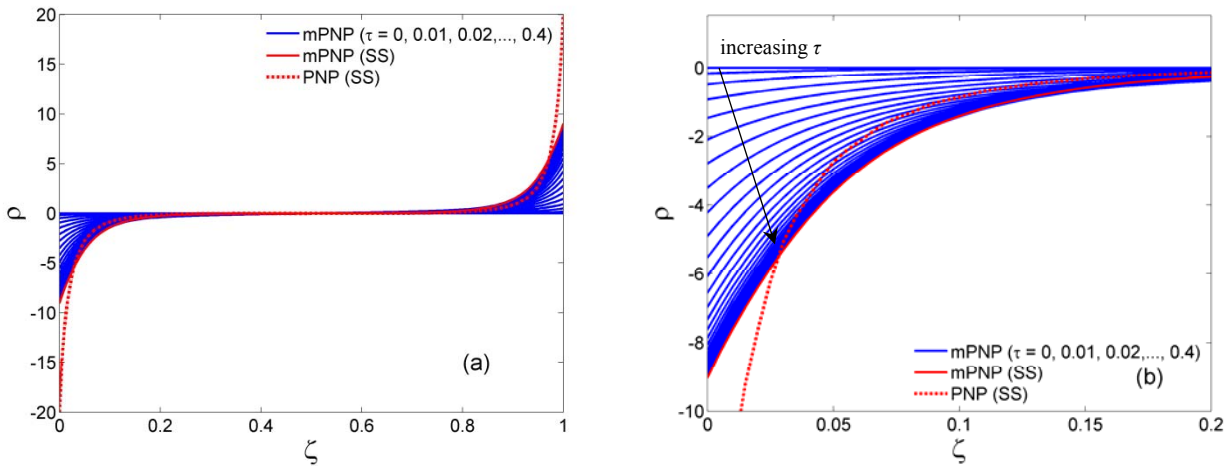


Fig 7. Mobile charge density $\rho$ profiles for PPE with $y_0 = \pm 10$, immersed in a 1:1 electrolyte of $I = 0.5$M, for (a) mPNP (solid blue line) at $\tau = 0, 0.01, 0.02, \ldots, 0.4$, mPNP (solid red line), and PNP (dotted red line) at SS, and (b) same as (a), in the region near the positive electrode. SS denotes *Steady State* profile.

We follow Kilic *et al*. [17] to state that the mPNP presented here, as well as other mean field models with different energy functionals to include non-electrostatic effects, have wide potential of application, with no more difficulties in terms of computational cost for the numerical solution. Actually, the numerical solution of mPNP is more suitable for high electric potentials, in which ion concentrations nearby electrodes is exponentially divergent. This behavior is clearly unphysical, since PNP predicts infinite concentration at sufficiently high applied voltage, while steric repulsion in mPNP model prevents exponentially divergent responses.

Therefore, future research directions include coupling mPNP model with Navier-Stokes equation (mPNP/NS model) to describe electro-kinetic flows through capillary micro-channel devices. Subsequent works should also include ion size asymmetries and different diffusion coefficients for each ion. Effects of alternating currents (AC) voltages and Faradaic reactions on mobile charge dynamics for the configurations proposed here are also important extensions to improve ion dynamics modeling. Finally, we should emphasize that the methodology presented here for derivation of mPNP model allows the exploration of new modifications, representing a possible way for future advances on the description of mobile charge dynamics via Poisson-Nernst-Planck approach.

## 4 Conclusions

Mobile charge dynamics under the influence of charged electrodes is treated in a Poisson-Nernst-Planck framework. We have proposed a new modified Poisson-Nernst-Planck (mPNP) model to account for ion size correlation effects directly on chemical potential, in a thermodynamically consistent way. A complete formalism to derive transient versions of model equations is presented, in which all the variables and parameters are non-dimensional and the system domain is normalized, viewing their numerical resolution. After spatial discretization, we convert the problem into a system of ordinary differential-algebraic equations, which can be easily solved by the DASSLC code implemented in the dynamic simulator EMSO. Results for a single plate and parallel-plate electrodes show that the ion size effects play an important role on ion dynamics, especially at high electrode surface electrical potentials and moderate ionic strengths. The ion dynamic response to an abrupt change in electric field is diffusion controlled, and considerably fast, with a response time around $10^{-8}$ s. Future works may focus on the consideration of ion size asymmetries as well as different ion diffusivity coefficients for application in electro-kinetic flow modeling. The methodology proposed here turns possible to include new contributions on PNP approach, paving the way to better understanding ion dynamics analysis in electro-kinetic and colloid transport phenomena.

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