On Applicability of Poisson-Boltzmann Equation for Micro- and Nanoscale Electroosmotic Flows

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Abstract. The applicability of the Poisson-Boltzmann model for micro- and nanoscale electroosmotic flows is a very important theoretical and engineering problem. In this contribution we investigate this problem at two aspects: first the high ionic concentration effect on the Boltzmann distribution assumption in the diffusion layer is studied by comparisons with the molecular dynamics (MD) simulation results; then the electrical double layer (EDL) interaction effect caused by low ionic concentrations in small channels is discussed by comparing with the dynamic model described by the coupled Poisson-Nernst-Planck (PNP) and Navier-Stokes (NS) equations. The results show that the Poisson-Boltzmann (PB) model is applicable in a very wide range: (i) the PB model can still provide good predictions of the ions density profiles up to a very high ionic concentration ($\sim$ 1 M) in the diffusion layer; (ii) the PB model predicts the net charge density accurately as long as the EDL thickness is smaller than the channel width and then overrates the net charge density profile as the EDL thickness increasing, and the predicted electric potential profile is still very accurate up to a very strong EDL interaction ($\lambda/W \sim 10$).

1 Introduction

Electroosmotic flow plays a fundamental role in many biochemical and biophysical processes [1, 2], such as ion transports in cells [3, 4] and electroosmosis in random porous

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structures [5]. Similar applications can also be found in NEMS/MEMS devices [6, 7]. A complete understanding of these physical and chemical processes need correct mathematical descriptions and accurate solutions of the electrostatic potential distributions. One of the most widespread models for the electrostatic interactions is the Poisson-Boltzmann equation (PBE) [2]. The linearized PBE (LPBE) and non-linearized PBE (NLPBE) have been applied successfully in predictions and modeling of the microscale electroosmotic flows [8–10]. However, the accuracy of the PBE depends on whether the Boltzmann distributions of ions densities can hold on within the EDL. There are several factors that could make the PBE failure, especially for micro- and nanoscale electroosmotic flows: (i) molecular nature and interactions of ions; (ii) ionic concentration effect; (iii) EDL interaction and overlap.

Concerning the molecular effects upon the applicability of the Poisson-Boltzmann equation for micro- and nanoscale electroosmotic flows, much work has been done using the atomistic simulations and comparing with the continuum theory in the last decade [11–21]. Most of them reported deviations of the Poisson-Boltzmann theory from the MD results for nanoscale electroosmotic flows [14–19]. For example, much higher ionic concentration distributions near wall surfaces predicted by MD were reported than those predicted by the Poisson-Boltzmann theory [14,15]. Qiao and Aluru [15] modified the Poisson-Boltzmann equation by introducing an electric potential correction extracted from the ion distribution in a smaller channel using MD simulations, which could be used for predicting the electric potential distribution in larger channels [15,19], however, with some rigorous conditions for similarity [20]. Cui and Cochran [17] found that the Poisson-Boltzmann equation agreed well with the MD results quantitatively at moderate ionic concentrations around 20 mM and failed at low ionic concentration and higher zeta potential over 50 mV. Dufreche *et al.* [18] simulated the electroosmosis in clays and declared that the Poisson-Boltzmann theory and MD simulation only agreed when the interlayer spacing was large enough, and a slipping modification must be considered for the hydrodynamics. Zhu *et al.* [19] also reported the failure of Poisson-Boltzmann theory in nanochannel electroosmotic flows and traced the reason to the exclusion of ions near the channel walls. Recently, Wang *et al.* [21] summarized all these previous researches and figured out that the base must be the same when the Poisson-Boltzmann theory was compared with the atomistic simulation results. Once the MD simulation results were calculated by the binning technique in which the bin size was no smaller than one molecular diameter and the focusing region was limited to the diffusion layer, the ion distributions from the MD simulations agreed well with the predictions based on the Poisson-Boltzmann theory for their cases. The Stern layer caused by the ions size and the non-Coulombic interactions between ions and walls should be excluded for the comparisons. Such a conclusion provides virtually a guide line for future comparisons between atomistic simulations and continuum predictions of electrokinetic transports.

To examine the Boltzmann distribution approximation of ions in the diffusion layer, an alternative method is to solve the basic coupled electrodynamic, hydrodynamic and ions transport equations and to compare the results with the Poisson-Boltzmann predic-

tions. Such a method is suitable for very dilute electrolytes so that the EDL interactions caused by non-fully-developed EDLs can be studied. Qu and Li [22] first built up a model based on the Debye-Huckel approximation to investigate the overlapped EDL fields and found that the Boltzmann equation lead to inaccurate predictions for small channels. Yang *et al.* [23] solved the Poisson-Nernst-Planck equations for electroosmotic entry flow in a microchannel and compared with the Poisson-Boltzmann model. The edge effect was therefore found which lead the Poisson-Boltzmann model failure for such flows. Similar analysis could be found for electroosmotic flows in "step-charged" channels [24]. Usually the strongly non-linear PNP equations coupled with the Navier-Stokes equation can be solved by the finite difference method or finite element method [25]. Recently, a new algorithm has been developed to solve the equations using multiple lattice Boltzmann models which own a high efficiency for such a multi-physical transport process, especially for complex boundary conditions [26].

The objective of this research is to clarify the applicability of the Poisson-Boltzmann model for micro- and nanoscale electroosmotic flows. First, considering the molecular nature and the existence of the Stern layer we compare the atomics simulation results with the PB model to check the high ionic concentration effect on the applicability of PB model for nanoelectroosmotic flows. Then, the relatively lower ionic concentration effect on the applicability of PB model is investigated by comparing the predictions of the dynamics theories (coupling PNP with NS equations) with those of PB model for electroosmotic flows in micro- and nanochannels. The paper is organized as follows. In Section 2, we introduce the mathematical models and their numerical solution methods, including the Poisson-Boltzmann model, the molecular dynamics (MD) modeling system and the multiple lattice Boltzmann models for solving the coupled PNP and NS equations. The analysis results and discussion on the applicability of the Poisson-Boltzmann model in micro- and nanoscale electroosmotic flows are presented in Section 3 by comparisons between different models. Finally we conclude by summarizing the previous work and the present contributions.

2　Mathematical model and numerical methods

2.1　Poisson-Boltzmann model

Consider an electroosmotic process in an infinite long straight channel. The walls are fixed and homogeneously charged. The steady electrostatic interaction can therefore be described by a Poisson equation [27, 28],

$$\nabla \cdot (\varepsilon_r \nabla \psi) = -\frac{\rho_e}{\varepsilon_0} = -\frac{1}{\varepsilon_0} \sum_{i=1}^{N} e n_i z_i, \tag{2.1}$$

where ψ is the electrical potential, ε_r the relative dielectric constant of the solution, ε_0 the permittivity of a vacuum, and ρ_e the net charge density. According to classical EDL

theory, the equilibrium Boltzmann distribution function can be assumed to describe the distributions of small ions in the dilute solution. Therefore, the net charge density distribution can be expressed as the sum of all the ions in the solution

$$\rho_e = \sum_i z_i e n_{i,\infty} \exp\left(-\frac{z_i e}{k_b T}\psi\right),$$
(2.2)

where the subscript i represents the ith species, n_∞ is the bulk ionic number concentration, z the valence of the ions (including the sign), e the absolute value of one proton charge, k_b the Boltzmann constant, and T the absolute temperature. For 1:1 electrolyte solutions, such NaF or NaCl solution in the present work, Eqs. (2.1)-(2.2) can be simplified as

$$\nabla \cdot (\varepsilon_r \nabla \psi) = -\frac{2zen_\infty}{\varepsilon_0}\sinh\left(\frac{ze\psi}{k_b T}\right).$$
(2.3)

There are two ways to present the boundary conditions for the Poisson equation (2.1), Dirichlet and Neumann boundaries. In some atomistic methods for electroosmotic flows [14, 15], the Neumann boundary condition is mostly used because the electric potential gradient is relative to the wall surface charge density. Electric charge conversation can be considered as an additional restrict for certain solution under the Neumann boundary condition, which brings a big additional computational cost as well. Recent investigations show a lattice evolution method can deal with this problem easily [29]. In this contribution we still use the Dirichlet boundary condition to solve the Poisson equation. To compare with the MD simulation results, we obtain the zeta potentials, ζ, from MD, and then use the values as the Dirichlet boundaries to solve Eq. (2.3).

2.2   Molecular dynamics method

Non-equilibrium molecular dynamics (NEMD) method [30] can be used to simulate the electroosmotic flow in a channel directly. The accuracy of this type of model is limited only by the force fields used to describe interactions between solvent molecules, ions, and the channel walls, and the simulation size and duration, which are determined by computer resources and the computational efficiency of the simulation code. In order to provide a clear picture of how the various conditions affect the applicability of continuum theory, a simplified model was used to capture the essential physics [13, 19]. Both solvent and ions are simplified as spherical, non-polar particles interacting with a shifted Lennard-Jones potential,

$$V^{LJ}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 - \left(\frac{\sigma_{ij}}{r_c}\right)^{12} + \left(\frac{\sigma_{ij}}{r_c}\right)^6\right],$$
(2.4)

where r_{ij}, ε_{ij}, and σ_{ij} are the separation, Lennard-Jones well depth and Lennard-Jones diameter, respectively, for the pair of atoms i and j . With this simplification, the simulations become more tractable while still retaining a model with discrete solvent particles. In

deed, replacing such a model for solvent with a more realistic model, such as SPC/E [15] will improve the accuracy of the simulations; however the simplified model can still provide qualitative conclusions applicable to real systems, which has been proved in many previous researches for various areas [19]. The L-J interaction is set to zero when molecules are separated by farther than the cut-off length $r_c = 2.5\sigma$. The molecular parameters are chosen to match those in a NaF electrolyte solution in a silicon channel which are listed in Table 1 [31]. The Lorentz-Berthelot combination rules were used for the interaction parameters that are not specified explicitly [31].

Table 1: Parameters for Lennard-Jones interactions between same species particles.

Species	m (g/mol)	σ (10^{-10}m)	ε (kJ/mol)
O (Water)	18.00	3.165	0.6503
Si	28.08	3.386	2.4770
Na$^+$	22.99	2.350	0.0618
F$^-$	19.00	3.121	0.6080

Each ion was assigned a charge ($+e$ or $-e$), while the solvent particles were neutral. The ion-ion electrostatic interactions were calculated using a screened Coulomb interaction,

$$V^C(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0\varepsilon_r r_{ij}}, \tag{2.5}$$

where the relative dielectric constant of fluid, ε_r, is approximately set to 78 in our simulations. The electro-static interactions were computed using the direct summation over the whole domain with no truncation for the Coulomb interactions [32].

The equations of motion are integrated using the Verlet scheme [33] with time step $\Delta t = 0.005\tau$, where $\tau \equiv (m\sigma^2/\varepsilon)^{1/2}$ is the characteristic time of the Lennard-Jones potential. A Langevin thermostat [34] with damping rate τ^{-1} is used to maintain a constant temperature of $1.1\varepsilon/k_b$. The thermostat is only applied in the y-direction, since it is periodic and normal to the main flow direction.

NEMD simulations were performed for systems consisting of a slab of electrolyte solution sandwiched by two plane walls as shown in Fig. 1. The two walls are symmetrical with respect to the channel center line. Each wall is made up of five layers of atoms oriented in the <111> direction. The channel is L in length and W in width. The wall atoms are fixed to their original positions, all of which have van der Waals interactions with the fluid molecules. Only the outermost wall layers are charged, uniformly among the wall atoms. In cases of this contribution, we use a channel with $L = 3.3$ nm, $W = 4.98$ nm and 1500 molecules flowing in it.

At the beginning of the simulation, the molecules were randomly positioned and assigned Maxwellian distributed velocities at the temperature of $1.1\varepsilon/k_b$. Periodic boundary was performed in the x and y directions. Before the macroscopic characteristics were sampled, the NEMD simulations were run for 5×10^5 time steps to reach steady state flow.

After that, the densities and velocities were computed time-averaged, over 3×10^6 times, by using the binning method [33].
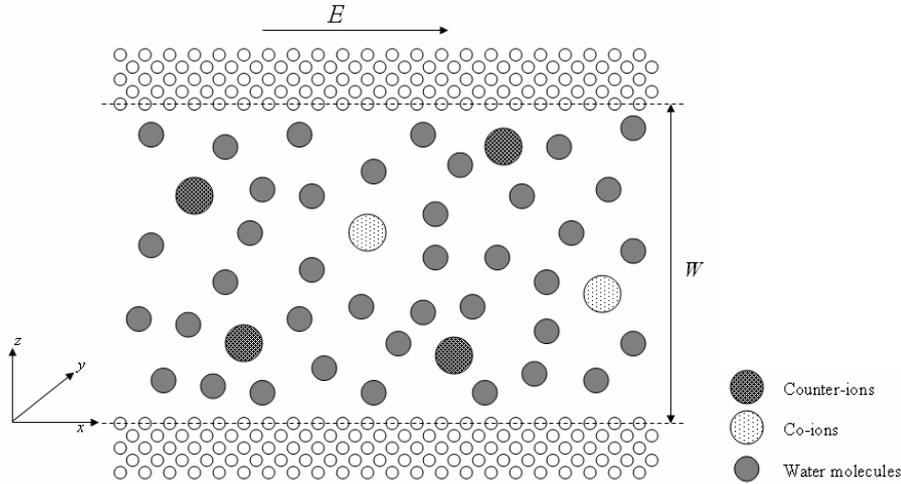

Figure 1: A schematic of the electro-osmotic flow in nanochannel. The two channel walls are symmetrical with respect to the channel center line. Each wall is made up of five layers of still solid atoms. The channel width W is defined as the distance between centers in the two innermost wall layers.

2.3 Poisson-Nernst-Planck model

When the Boltzmann distribution of ions in the diffusion layer is not preconcerted, the electric potential profile has to be determined by solving a series of coupled electrodynamic, hydrodynamic and ions transport equations. Consider an N-component Newtonian electrolyte flowing with velocity $\mathbf{u}(\mathbf{r},t)$ in a channel with no polarization and chemical reactions. The flux $\mathbf{j}_i$ of each ith ion species, composing the solute, is given by the following constitutive equation [35]

$$\mathbf{j}_i = -D_i \nabla n_i - ez_i b_i n_i \nabla \psi + n_i \mathbf{u} \tag{2.6}$$

where n_i is the number density of the ith ion species, D_i and b_i are the ion's diffusivity and electric mobility, related by the Stokes-Einstein equation

$$D_i = b_i k_b T. \tag{2.7}$$

The ionic flux $\mathbf{j}_i$ and the concentration n_i obey the continuity equation

$$\frac{\partial n_i}{\partial t} + \nabla \cdot \mathbf{j}_i = 0. \tag{2.8}$$

For an incompressible laminar electroosmotic flow, the movement of electrolyte is

governed by the continuity and momentum equations:

$$\nabla \cdot \mathbf{u} = 0, \tag{2.9}$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = \mu \nabla^2 \mathbf{u} + \mathbf{F}_E, \tag{2.10}$$

where ρ the solution density, μ the dynamic fluid viscosity and $\mathbf{F}_E$ the electric force density vector.

Eqs. (2.6)-(2.10) together with Eq. (2.1) compose the Poisson-Nernst-Planck model which govern the electroosmotic transports and are solvable subject to the following boundary conditions on the liquid-solid interface Ω

$$(\mathbf{v} \cdot \mathbf{j}_i)_\Omega = 0, \tag{2.11}$$

$$\mathbf{u}_\Omega = 0, \tag{2.12}$$

$$\psi_\Omega = \zeta, \tag{2.13}$$

where $\mathbf{v}$ is the outer normal to Ω.

The non-linear coupled Poisson-Nernst-Planck and Navier-Stokes equations can be solved using the traditional PDE solvers [25]. He and Li [36] proposed a lattice Boltzmann scheme to solve the electrochemical process; however their assumption of locally electrically neutral is too critical and may not be true for many cases [37] and their evolution equations might be unstable. Hlushkou *et al.* [38] developed a coupled numerical method between a lattice Boltzmann method for PNP equations and a finite difference method for NS equations. Unfortunately, there is a half cell/grid difference between the lattice Boltzmann simulation with a bounce-back boundary treatment and the finite difference method on the same set of grid which leads to the coupling failure [39]. Recently Wang [26] presented a new algorithm to solve the equations using multiple lattice Boltzmann models. Different from the decouple process of the lattice Poisson-Boltzmann method [7, 10, 40], the new algorithm uses a coupling evolution process. The evolution equations were proved stable and the boundary treatments were consistent. The algorithm details and efficiency discussion can be found in [26].

3 Results and discussion

In this section, we compare the Poisson-Boltzmann model with the more fundamental models to clarify the applicability of the PB model for micro- and nanoscale electroosmotic flows. First, to check the high ionic concentration effect on the applicability of PB model for nanoelectroosmosis we compare the PB model with the MD simulation results. Then, the PB model is compared with the predictions of the dynamics theories (coupling PNP with NS equations) for relatively lower ionic concentrations to make clear the EDL interaction effect on the applicability of PB model for electroosmotic flows in micro- and nanochannels.

3.1 High concentration effect

Based on the classical electrostatics theory, the solute ions have a Boltzmann distribution in the diffusion layer when the solution is dilute enough. If the ionic concentration is high, the molecular interactions will make the Boltzmann distribution assumption break down. However the classical theory did not give a quantitative description what a high ionic concentration would make this happen. Few researches have been found on this topic for two reasons: (i) it is hard through any continuum way; (ii) most of atomic researches believed that the Boltzmann distribution assumption broke down already even for dilute electrolyte solutions. Our recent research has figured out that there are two critical points when the atomic simulation results are compared with the continuum models: (i) the bin (or grid) size should be no smaller than the diameter of the dominating molecules; (ii) since the Boltzmann distribution are only assumed within the diffusion layer in the classical theory, the atomic simulation results should exclude the part of Stern layer [21]. After considering these two aspects, we have obtained good agreements between the atomic simulation results and the Poisson-Boltzmann model for dilute cases.

Thus, we use this NEMD simulation to study the critical high ionic concentration that would make the Poisson-Boltzmann model fail. The NEMD process and general parameters are described in the Section 2.2. The bin size in this work equals to one diameter of the water molecule. We obtain the outer electric potential of the diffusion layer of the MD result as the zeta potential and the averaged ionic concentrations at the middle of channel as the bulk ionic concentration for the numerical solution of the Poisson-Boltzmann equation by a lattice Poisson method [29]. We fix the wall surface charge density and change the ions numbers to vary the ionic concentrations. The various simulated cases performed in this work are summarized in Table 2. The resulted bulk ionic concentration therefore varies from 0.15 to 5.23 M.

Table 2: Summary of the simulated cases.

Case #	σ_s (C/m^2)	Counter-ion # (Na$^+$)	Co-ion # (F$^-$)
1	0.191	30	0
2	0.191	40	10
3	0.191	55	25
4	0.191	100	70
5	0.191	200	170

Fig. 2 shows the comparisons of the calculated ions density profiles between the MD simulations and the PB predictions. For a clear picture, we divide the comparisons into two parts: relatively lower concentrations and higher concentrations. The results indicate that the Poisson-Boltzmann model works well for relatively lower concentrations but fails to agree with the MD results for high concentration any more. The critical ionic bulk concentration from this research is around 1 M (Case 3). The higher than this critical concentration, the larger is the deviation. For very high ionic concentrations, the Poisson-Boltzmann model underrates the ion density near the wall surfaces.
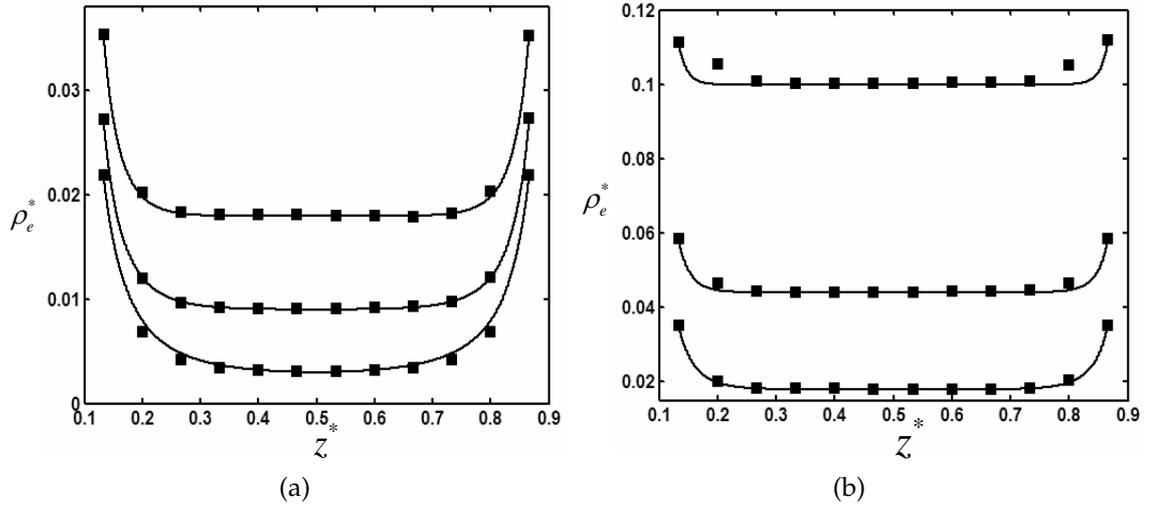
Figure 2: Ions density profiles for different ionic concentrations. (a) Cases at moderate and low ionic concentrations. The cases from bottom to top are Cases 1, 2, 3; (b) Cases at high ionic concentrations. The cases from bottom to top are Cases 3, 4, 5. The bulk ionic concentration of Case 3 is around 1 M. The solid symbols are MD results, and the solid lines are the PB model predictions. The ion density is normalized by $|e|/\sigma^3$, i.e., $\rho_e^* = \rho_e \sigma^3/|e|$, and the z-position is normalized by the channel width, e. g. $z^* = z/W$.

3.2 EDL interaction effect

On the other side of the high ionic concentrations, a too dilute solution may lead to the electric double layers interaction with each other within a very small channel. For such dilute cases, the MD simulation is not available due to its huge computational costs. Therefore we consult the dynamic models here without the Boltzmann distribution assumption. Several simplified models have been established for the overlapped EDL fields in microchannels. Differences were reported between predictions by these models and by the PB model for the electric potential distribution and the flow velocity profile across the channel, which were ascribed to the EDL interactions. For instance, Qu and Li [22] ever investigated the EDL fields overlap effect on the potential distribution for inorganic oxide-aqueous solution systems using a model based on the Debye-Huckel approximation. In this contribution, we solve the strongly non-linear coupled dynamic equations (PNP and NS equations) by the multiple lattice Boltzmann models without any linearization approximations [26] for comparisons to clarify the effect of EDL interaction on the applicability of PB equation. We are focusing on the physical transports while ignoring the chemical actions, such as the water molecules dissociation, during the electroosmotic process.

Consider an electroosmotic flow of a NaCl solution in a two-dimensional straight homogenously charged channel. The channel width (W) is fixed at 1 μm and the bulk ionic concentration is changed to vary the thickness of the EDL. Supposing the thickness
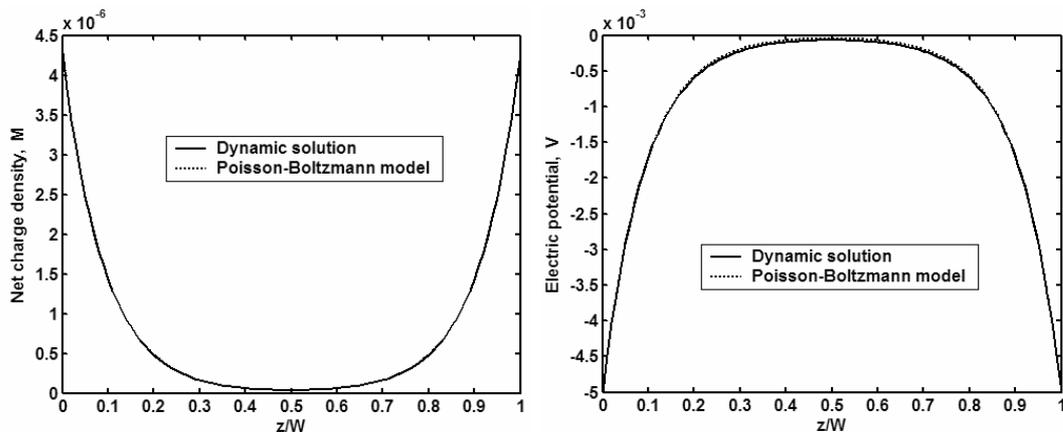
(a) $\lambda/W = 0.09$ at $n_\infty = 10^{-5}$ M
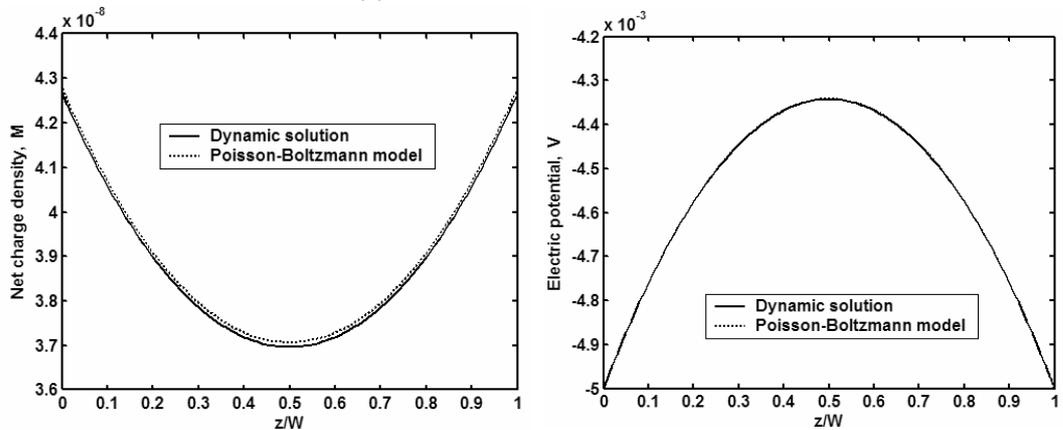
(b) $\lambda/W = 0.92$ a
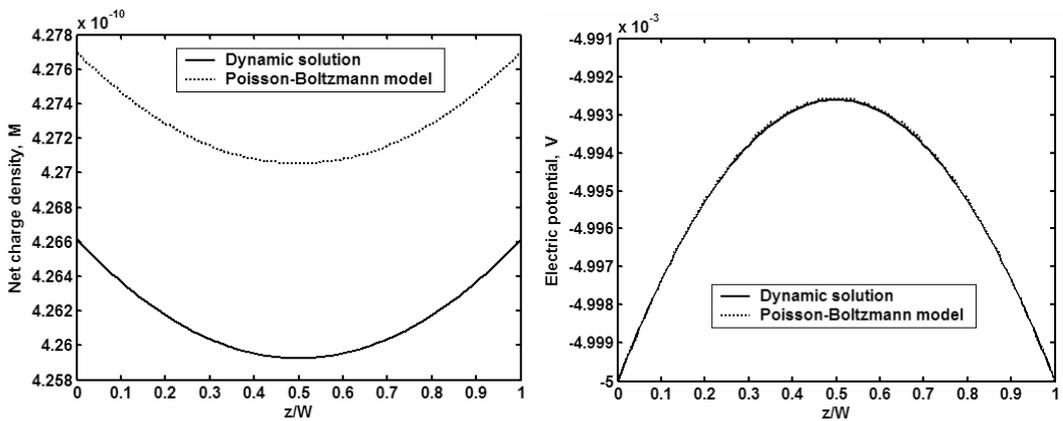
(c) $\lambda/W = 9.22$ at $n_\infty = 10^{-9}$ M

Figure 3: Net charge density and electric potential profiles for different bulk ionic concentrations.

of the EDL defined as

$$\lambda = \sqrt{\varepsilon_0 \varepsilon_r k_b T / (2 e^2 z^2 n_\infty)},$$

we vary the bulk ionic concentration from 10^{-4} M to 10^{-9} M so that the ratio of the EDL thickness to the channel width (λ/W) coves a wide range from 0.03 to 9.22. Though the real solution is not possible to have a dominating bulk ionic concentration lower than 10^{-7} M, yet these dimensionless results will be very helpful for nanoscale applications. In our present simulations, we use $\zeta = -5$ mV, $D_i = 1 \times 10^{-8}$ m^2/s, $E_x = 10^3$ V/m and the other parameters used can be found in Ref. [26].

Fig. 3 compares the net charge density and the electric potential profiles resulted from the dynamic model and the Poisson-Boltzmann model for different bulk ionic concentrations. The results indicate that as long as the EDL thickness is much smaller than the channel width both the net charge density and the electric potential profiles resulted from the PB model agree pretty well with the dynamic model predictions. Once the EDL thickness is larger than the channel width, the predicted net charge density profile by the PB model will be higher than that by the dynamic model. It is also surprising to find that the PB model can still provide very good predictions of electric potential distribution for very thick EDL ($\lambda/W = 9.22$) which means very strong EDL interactions. This result differs much from the previous researches by others, such as those in Ref. [22], which indicates that the EDL interaction effect on the applicability of the PB model was overrated and the chemical actions, such as the water molecules polarization and dissociation, and the associated effects on the boundary conditions at interfaces play a more significant role especially in the dilute solutions.

4　Conclusions

The applicability of the Poisson-Boltzmann model for micro- and nanoscale electroosmotic flows has been investigated in this contribution. First the high ionic concentration effect on the Boltzmann distribution assumption in the diffusion layer was studied by comparisons with the MD simulation results. It was found that the high bulk ionic concentration would make the Poisson-Boltzmann model fail to agree with the atomistic simulations; however the PB model can still provide good predictions up to a very high ionic concentration (~ 1 M). On the other side, the low ionic concentration for very small channels leads to the electric double layers interacting with each other within the channel. The EDL interaction effect was then discussed by comparing with the dynamic model described by the coupled Poisson-Nernst-Planck and Navier-Stokes equations. The results showed that the PB model accurately predicted the net charge density as long as the EDL thickness is smaller than the channel width and then overrated the net charge density profile as the EDL thickness increased. The PB prediction of electric potential profile was still very good up to very strong EDL interaction ($\lambda/W \sim 10$). As a summary, the Poisson-Boltzmann model is applicable in a very wide range.

Acknowledgments

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