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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 ($\lambda/W \sim 10$).

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Key words: Poisson-Boltzmann model, electroosmotic flow, EDL interaction, Poisson-Nernst-Planck equation.

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-