

# Scaling of Electroosmotic Flow and Ionic Conductivity in Nanochannels

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## ABSTRACT

Electrokinetic transport is a popular transport mechanism used in nanofluidic systems, and understanding its scaling behavior is important for the design and optimization of nanofluidic devices. In this paper, we report on the scaling of electroosmotic flow and ionic conductivity in positively charged slit nanochannels by using continuum and atomistic simulations. The effect of confinement and surface charge are discussed in detail. In particular, we found that the viscosity of the interfacial water increases substantially as the surface charge density increases and the electrophoretic mobility of the interfacial ions decreases. We show that such effects can influence the scaling of the electrokinetic transport in narrow nanochannels significantly.

**Keywords:** Electrokinetic transport, ionic conductivity, nanochannel, molecular dynamics, scaling

## 1 INTRODUCTION

Electrokinetic transport of water and ions in nanometer channels and pores plays a crucial role in many engineering and biological systems, e.g., fuel cells, ion channels, and chemical analysis devices. Understanding the scaling of electrokinetic transport as a function of various parameters, e.g., channel size, bath concentration, surface charge density, etc, is important for establishing design rules and for exploring the design space. Continuum simulations can provide useful insights on the electrokinetic transport in micro- and nano-fluidic systems, and the scaling of electrokinetic transport using continuum simulations has already been investigated [1]–[3]. However, the accuracy of continuum theories in nanometer channels can be an issue [4]. In nanochannels, the critical dimension of the channel can be comparable to the size of the fluid molecule and a significant amount of the fluid in the channel is in contact with the channel surface. Thus, the molecular nature of the fluid/ion and surface effects, which are neglected in the continuum modeling of electrokinetic transport, can become important factors influencing the fluid/ion transport inside the channel.

In this paper, we report on the scaling of electrokinetic transport in slit nanochannels. Specifically, we

investigated the scaling of electroosmotic flow as a function of surface charge density, and the scaling of ionic conductivity of the nanochannel as a function of surface charge density, bath concentration and channel width. We compare the scaling of electrokinetic transport by using molecular dynamics (MD) and continuum theories. We will limit our discussion to positively charged nanochannels since recent studies indicated that the electrokinetic transport can be more sensitive to a positive surface charge than for a negative surface charge [5].

## 2 SIMULATION METHODS

For electrokinetic transport in a straight flat channel with a uniform charge density on the channel walls (see Figure 1), the Poisson-Boltzmann (PB) equation and the Stokes equations are used to compute water and ionic transport in the channel [6]. Details of the continuum calculations can be found in a prior paper [4]. The ionic flux  $J_i$  has two components in the present system, namely, an electrical migration component given by  $J_i^{mig} = \int_{\delta_1}^{W-\delta_1} \tilde{z}_i \mu_i^e(z) c_i(z) E_{ext} dz$  and a convection component given by  $J_i^{eo} = \int_{\delta_1}^{W-\delta_1} u_{eo}(z) c_i(z) dz$  where  $\tilde{z}_i$ ,  $\mu_i^e(z)$  and  $c_i(z)$  are the valency, electrophoretic mobility, and concentration of ion  $i$ .  $E_{ext}$  is the external electrical field applied along the channel length direction, and  $u_{eo}$  is the electroosmotic velocity.  $W$  is the channel width, and  $\delta_1$  and  $\delta_2$  are the closest approach of ion and water to the channel wall, respectively.  $\delta_1$  and  $\delta_2$  are typically not known and need to be obtained from molecular theory or simulations. For the system we investigated here,  $\delta_1$  and  $\delta_2$  are found to be approximately 0.33 nm and 0.16 nm, respectively. The conductivity of the channel is given by  $\kappa = 1/(W - 2\delta_1) E_{ext} \sum_{i=1}^N \tilde{z}_i F J_i$  where  $F$  is the Faraday constant, and  $J_i = J_i^{mig} + J_i^{eo}$ .

Figure 1 shows the schematic diagram of the channel system used in the MD simulations. The system consists of a slab of KCl solution sandwiched between two walls. Each wall is made up of four layers of silicon atoms. The silicon atoms in the innermost layer of the channel wall were assigned small partial charges to produce the desired surface charge density,  $\sigma_s$  [4]. The water is modeled by using the SPC/E model and ions are modeled as charged Lennard-Jones (LJ) atoms. Force field parameters are taken from [7] and [8]. MD

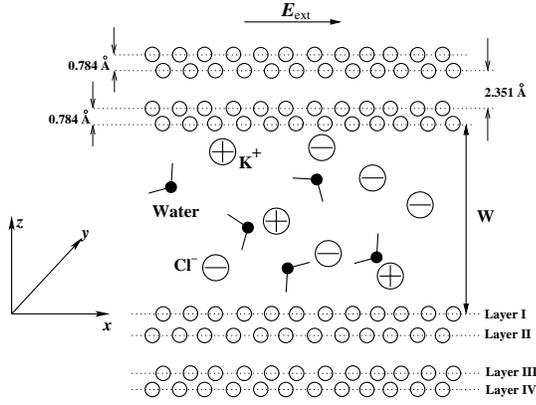


Figure 1: A schematic of the channel system under investigation. The two channel walls are symmetrical with respect to the channel center line.

simulations were performed with a modified Gromacs 3.0.5 [7]. The temperature of the fluid was maintained at 300 K by coupling the fluid atoms to a Nose thermostat. Other simulation details can be found in [4]. To study the scaling of the electrokinetic transport, we performed simulations with different surface charge densities and bath concentrations. Note that in the present MD simulations, where the channel system is not explicitly connected to an external bath, the corresponding bath concentration ( $c_\infty$ ) of the channel system need to be computed indirectly. Following [9],  $c_\infty$  is computed by using  $c_\infty = \sqrt{c_{K^+,cent} c_{Cl^-,cent}}$  where  $c_{K^+,cent}$  and  $c_{Cl^-,cent}$  are the concentration of  $K^+$  and  $Cl^-$  ion at the channel center, respectively. The electrokinetic transport was driven by an external electrical field,  $E_{ext}$ , applied along the channel in the  $x$ -direction. A strong electrical field ( $|E_{ext}| = 0.2$  V/nm) was used in our simulations so that the fluid/ion velocity can be retrieved with reasonable accuracy.

### 3 SCALING OF ELECTROSMOTIC FLOW

To quantify electroosmotic flow in a nanochannel, following [1], we define an average electroosmotic mobility  $\bar{\mu}_{eo} = \frac{1}{W-2\delta_2} \int_{\delta_2}^{W-\delta_2} u_{eo}(z)/E_{ext} dz$ . Figure 2 shows the scaling of  $\bar{\mu}_{eo}$  versus  $\sigma_s$  in a 3.49 nm channel when  $c_\infty = 0.6$  M. We observe that (1) continuum theory overestimates  $\bar{\mu}_{eo}$  for all  $\sigma_s$  investigated, and the deviation is especially significant for high surface charge densities, and (2) for the range of  $\sigma_s$  studied, the continuum theory predicts an almost linear increase in  $\bar{\mu}_{eo}$  as  $\sigma_s$  increases, while the MD simulation indicates that, at low  $\sigma_s$  (e.g.,  $\sigma_s < 0.04$  C/m<sup>2</sup>),  $\bar{\mu}_{eo}$  increases with increasing  $\sigma_s$ , and at high  $\sigma_s$  (e.g.,  $\sigma_s > 0.08$  C/m<sup>2</sup>),  $\bar{\mu}_{eo}$  decreases with increasing  $\sigma_s$ . To understand the deviation, we computed the ion distribution and velocity

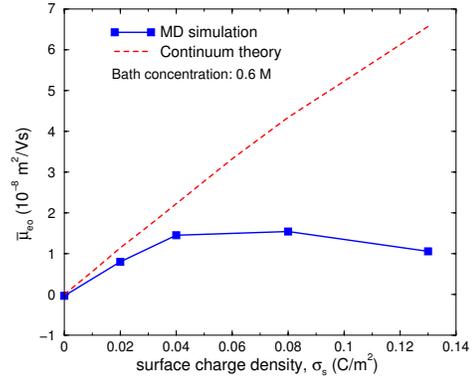


Figure 2: Scaling of the average electroosmotic mobility in a 3.49 nm wide channel with  $\sigma_s$  obtained from MD and continuum simulations.

profile in the channel when  $\sigma_s = 0.08$  C/m<sup>2</sup>. Figure 3 shows the counter-ion ( $Cl^-$ ) concentration obtained from the PB equation and the MD simulation. The co-ion concentration is not shown as its contribution is small to the electroosmotic flow. We observe that the MD simulation predicts a much higher first concentration peak compared to the PB equation, and there is an additional second peak at a position of 0.61 nm from the surface. These observations are similar to what were reported earlier [4], and the deviation originates mainly from the molecular nature of the ion and the discreteness of the water molecules, which are not accounted for in the PB equation. Figure 4 (a) compares the elec-

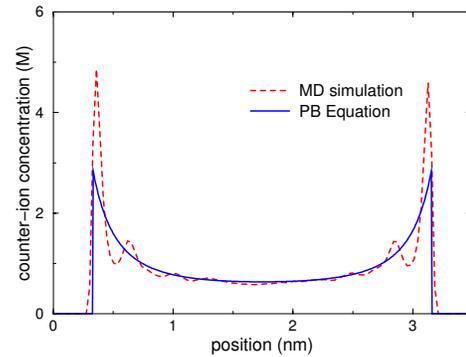


Figure 3: Counter-ion ( $Cl^-$ ) concentration profile in a 3.49 nm wide channel ( $\sigma_s = 0.08$  C/m<sup>2</sup>,  $c_\infty = 0.6$  M) obtained from the PB equation and the MD simulation.

troosmotic velocity profile in the channel obtained from (i) the Stokes equation with ion concentration from the PB equation as input, (ii) the Stokes equation with MD ion concentration as input, and (iii) MD simulation. A constant viscosity,  $\eta = 0.743$  mPa·s, was used in the Stokes equation. We observe that the Stokes equation solution using the ion concentration from the MD sim-

ulation is lower compared to the velocity obtained from the Stokes equation using the ion concentration from the PB equation. This indicates that the overestimation of the electroosmotic mobility by the continuum theory is partly caused by the inaccuracy of the PB equation in predicting the ion distribution. However, we note that the velocity obtained from the Stokes equation using the ion concentration from MD as input still overestimates the electroosmotic velocity predicted by the MD simulation. This can be attributed to the higher water viscosity near the channel surface. To quantify this, we divide the channel into five bins and compute the effective viscosity in each bin (here we assume that the viscosity in each bin is constant). Specifically, we substitute the ion concentration from the MD simulation into the Stokes equation, and require that the solution of the Stokes equation match the MD velocity at the edge of each bin and at the channel center ( $z = 1.745$  nm). Figure 4 (b) shows the effective viscosity distribution in the channel. We observe that the water viscosity near the channel surface is much higher compared to that of near the channel center. This is consistent with earlier reports [4], and may be attributed to the strong electrical field near the charged surface [6]. Calculation

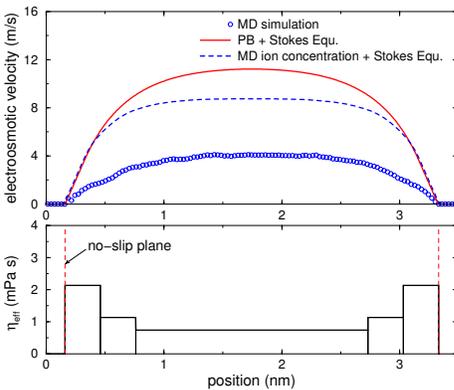


Figure 4: (a) Water velocity profiles in a 3.49 nm wide channel ( $\sigma_s = 0.08$  C/m<sup>2</sup>,  $c_\infty = 0.6$  M) obtained from the Stokes equation with the ion concentration from the PB equation as input (solid line), Stokes equation with MD ion concentration as input (dash line), and MD simulation (circle). (b) Effective water viscosity across the channel for the case studied in panel (a).

of the effective viscosity of the interfacial water in other channels indicated that, as  $\sigma_s$  increases, the viscosity of the interfacial water increases dramatically, and attains a value much larger compared to the bulk viscosity. Since the viscosity variation is not accounted for in the continuum theory, it overestimates the electroosmotic velocity, particularly at high  $\sigma_s$ , as stated in observation (1). Another consequence of the viscosity increase

in the interfacial layer with  $\sigma_s$  is that, as stated in observation (2), though the net driving force for the flow increases as  $\sigma_s$  increases, the electroosmotic velocity will increase much slower compared to the continuum prediction, and could even decrease because of the higher viscosity near the channel wall.

## 4 SCALING OF IONIC CONDUCTIVITY

In this section, we investigate the scaling of ionic conductivity in nanochannels as a function of the channel width,  $c_\infty$  and  $\sigma_s$  using both continuum and MD simulations. To account for the effect of confinement on the ionic conductivity of a nanochannel, we introduce a non-dimensional number,  $\alpha_{conf}$ , which is defined as  $\alpha_{conf} = \frac{\kappa_0}{\kappa_\infty}$ , where  $\kappa_0$  is the conductivity of a nanochannel with zero surface charge density connected to an external bath of concentration  $c_\infty$ , and  $\kappa_\infty$  is the conductivity of the bulk electrolyte at a concentration of  $c_\infty$ . As the continuum theory neglects confinement effects, it can be easily shown that  $\alpha_{conf}$  is equal to 1.0. Figure 5 shows the variation of  $\alpha_{conf}$  with bath concentration in two nanochannels with widths of 3.49 nm and 2.4 nm. We observe that, over the range of  $c_\infty$  and channel widths investigated here,  $\alpha_{conf}$  shows a weak dependence on the bath concentration. We also observe that for a larger channel width (e.g., 3.49 nm), the effect of confinement on the ionic conductivity is small and as the channel width decreases (e.g., 2.4 nm), the confinement effect becomes more important.

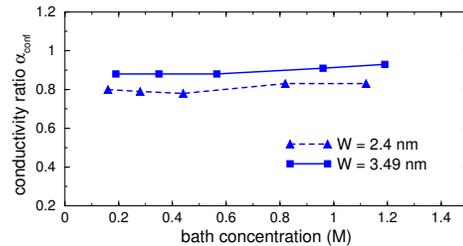


Figure 5: Scaling of the conductivity ratio,  $\alpha_{conf}$ , with  $c_\infty$  and channel width as predicted by the MD simulations.  $\alpha_{conf}$  is a measure of the effect of confinement on the channel conductivity.

To account for the effect of surface charge on the ionic conductivity of a nanochannel, we introduce another non-dimensional number,  $\beta_{sc}$ , which is defined as  $\beta_{sc} = \frac{\kappa_{sc}}{\kappa_0}$ , where  $\kappa_{sc}$  is the conductivity of the nanochannel when the surface charge is not zero, and  $\kappa_0$  is the conductivity of the same channel when the surface charge density is zero. We will first examine how  $\beta_{sc}$  scales with the continuum theory. Figure 6 shows the scaling of  $\beta_{sc}$  for a 3.49 nm wide channel as a function of  $\beta_{sc}$  and  $c_\infty$ .

We observe that  $\beta_{sc}$  increases with decreasing  $c_\infty$  and increasing  $\beta_{sc}$ , and at low  $c_\infty$  ( $c_\infty < 10^{-2}$  M) and high  $\beta_{sc}$  ( $\sigma_s > 0.08$  C/m<sup>2</sup>),  $\beta_{sc}$  is of the order of 100 or higher, indicating that the conductivity is entirely dominated by the surface charge. This is mainly caused by the fact that, at high  $\sigma_s$  and low  $c_\infty$ , the average ion concentration inside the channel is much larger compared to that of the bath electrolyte due to the attraction of counterions toward the charged channel surface (concentration enrichment). As  $c_\infty$  increases, though the average ion concentration inside the channel is high when compared to the ion concentration inside the channel when the surface charge is zero, the conductivity ratio becomes smaller. As a result,  $\beta_{sc}$  decays towards its asymptotic value of 1.0.

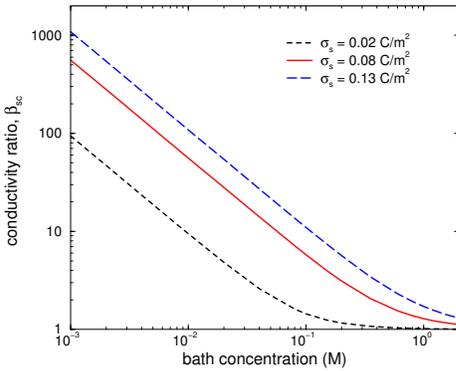


Figure 6: Scaling of the conductivity ratio,  $\beta_{sc}$ , obtained from continuum calculations, for a 3.49 nm wide channel with  $c_\infty$  and  $\sigma_s$ .  $\beta_{sc}$  is a measure of the change in conductivity of the channel in the presence of a surface charge.

We also calculated the conductivity ratio,  $\beta_{sc}$ , by using MD simulations. Figure 7 shows the scaling of  $\beta_{sc}$  for a 3.49 nm wide channel with  $\sigma_s$  and  $c_\infty$ . Comparing Figure 7 with Figure 6, we observe that, though the scaling of  $\beta_{sc}$  follows a similar trend, there exists important difference. Specifically, MD simulations indicate that  $\beta_{sc}$  can be less than 1.0 at high bath concentrations ( $c_\infty > 1.1$  M) while  $\beta_{sc}$  is never less than 1.0 in the continuum simulations. This is mainly caused by the fact that, at high positive surface charge densities, the electrophoretic mobility of the counter-ions in the nanochannel can be much smaller compared to its value when the nanochannel has zero surface charge density. In such a scenario, the decrease in the electrophoretic mobility of the counter-ions due to the presence of surface charge can be more important than the surface charge induced ion concentration enrichment in the channel. Since the concentration enhancement is less significant for high  $c_\infty$ ,  $\beta_{sc} < 1.0$  occurs mainly at high  $c_\infty$ .

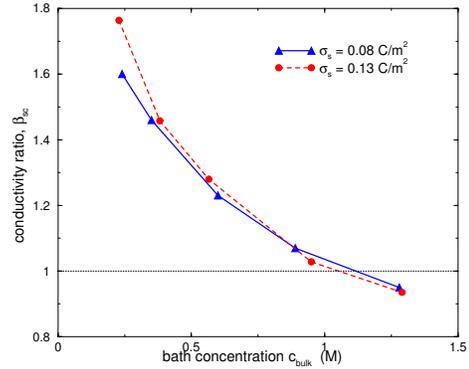


Figure 7: Scaling of the conductivity ratio,  $\beta_{sc}$ , obtained from the MD simulation for a 3.49 nm wide channel, with  $c_\infty$  and  $\sigma_s$ .

## 5 CONCLUSIONS

In this paper, we reported on the scaling of electrokinetic transport in nanometer slit channels using continuum and MD simulations. MD simulations indicated that the water viscosity and the electrophoretic mobility of ions can change substantially as the surface charge density and the channel dimension changes. Because these factors are not accounted for in the continuum theory, the continuum simulation fails to predict the scaling of electrokinetic transport in nanochannels accurately.

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