

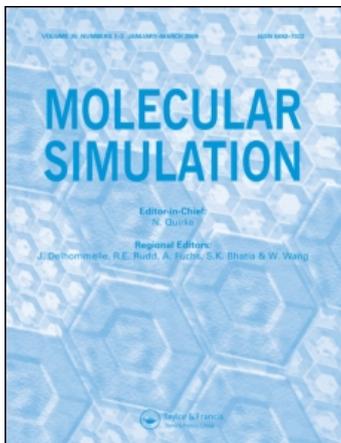
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Similarity of electroosmotic flows in nanochannels

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This paper investigates the similarity of electroosmotic flows in nanochannels numerically using the NEMD method and therefore analyzes the applicability of the embedding technique. The results indicate that the near-wall ion distribution is greatly influenced by the wall charge density, the ion arrangement and the interaction between ions and walls. If all these factors are same, the electroosmotic flows in different channel sizes are of similarity, which is to say that the ion distributions close to walls are same and the velocities across the channel are similar. The embedding method is available once the similarity holds. One can predict the ion distributions and fluid flow in larger channels using the continuum equations by introducing MD results of near-wall effective potential or transport coefficients of smaller channels. The results also suggest the similarity is preferred to the channel size larger than 10 times diameter of fluid molecules.

Keywords: Electroosmotic flow; Molecular dynamics; Similarity; Embedding method

1. Introduction

Electroosmotic transports in nanofluidic channels have recently received increasing attention due to important applications in biological and engineering systems, such as ion channels, fuel cells, and chemical analysis devices [1–6]. In the classical continuum-based modeling of electrokinetic transport, the ion transport is modeled by using the Poisson–Nernst–Planck equations and the fluid transport is generally governed by the Navier–Stokes equations [3]. However, as the surface-to-volume ratio is increasing with miniaturization, interfacial effects become more and more important, so that the continuum-based equations could no longer provide a detailed description of electrokinetic flow behavior in nanochannels exactly. Molecular dynamics is a microscopic method which can capture the particular transport characteristics at a molecular level, especially near charged walls. Recently it has been widely used in nanofluidic predictions [7–18].

However, molecular based methods are always very time-consuming or even unacceptably expensive for microscale electroosmotic flows. Qiao and Aluru [11] developed a velocity embedding technique by introducing the information near charged walls from MD simulations, such as extract effective potential or transport coefficients,

into continuum-based calculations for a microscale channel flow, which actually built a bridge from atomic descriptions to continuum equations. Good agreements have been reported when comparing the calculated velocities by the embedding technique with the results from full MD simulations for larger channel cases [11,14–17]. This embedding technique is based on the assumption that the transport properties, such as viscosity, near charged channel walls would not change appreciably when the channel width increases if the other operating conditions do not change significantly or remain the same. However in practices it is hard to insure all the operating conditions remaining the same when changing the channel width only. For a neutral system, for example, one has to increase the wall charge densities when widening the channel for a certain bulk net ionic concentration. Any change of the operating conditions may affect the near-wall transport coefficients of electrokinetic nano-flows. Therefore, it is of great interest and significance to make clear what are the most important factors influencing the near-wall information for different width channels and when the embedding technique is available.

This paper investigates the similarity of electroosmotic flows in various channels using the NEMD method. Different factors will be considered, including the channel

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width, the ionic concentration, the wall charge density, the ion type, the wall type and the external electric field strength. The applicability of the embedding technique is therefore analyzed.

2. Numerical simulation details

2.1 NEMD method

Nonequilibrium molecular dynamics (NEMD) method [18] is used to simulate the electro-osmotic flow in nanochannels in this contribution. The accuracy of this type of method 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 similarity, the simplest possible physical model is used to capture the essential physics. Use of a simplified model has precedent in several areas of condensed phase simulations, and can provide qualitative conclusions that should be applicable to real systems [7,8,17,18,20–23]. Both solvent molecules and ion particles interact with a shifted Lennard–Jones potential,

$$V^{\text{LJ}}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 - \left(\frac{\sigma_{ij}}{r_c} \right)^{12} + \left(\frac{\sigma_{ij}}{r_c} \right)^6 \right], \quad (1)$$

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 . The interaction is set to zero when molecules are separated by farther than the cut-off length $r_c = 2.5\sigma$. The molecular parameters for the solvent and ions are chosen to match those in the electrolyte solution of NaF or NaCl [19]. The walls are made up of silicon. The other values of the force field parameters are listed in table 1.

Not all interaction parameters are specified explicitly but the Lorentz–Berthelot combination rules are used:

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (2)$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (3)$$

Each ion is assigned a charge of $\pm e$ (e is the electronic charge, 1.6×10^{-19} C), while the solvent particles are

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

Species	m (g/mol)	σ (Å)	ϵ (kJ/mol)
O	18.00	3.165	0.6503
Si	28.08	3.386	2.4470
Na ⁺	22.99	2.350	0.0618
F ⁻	19.00	3.121	0.6080
Cl ⁻	35.45	4.448	0.4456

neutral. In order to approximately describe the polarity of real water, ion–ion electrostatic interactions are calculated using a screened Coulomb interaction,

$$V^{\text{C}}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r\epsilon_{ij}}, \quad (4)$$

where ϵ_0 is the dielectric permittivity of vacuum and ϵ_r the relative permittivity of the fluid, which is approximately set to 78. The electro-static interactions are computed using the direct summation over the whole domain with no truncation for the Coulomb interactions [24–26].

The equations of motion are integrated using the Verlet scheme with time step $\Delta t = 0.005\tau$, where $\tau \equiv (m\sigma^2/\epsilon)^{1/2}$ is the characteristic time of the Lennard–Jones potential [20]. A Langevin thermostat [21] with damping rate τ^{-1} is used to maintain a constant temperature of $1.1\epsilon/k_B$, where k_B is the Boltzmann constant. The thermostat is only applied in the y -direction, since it is periodic and normal to the main flow direction.

2.2 Simulation system

NEMD simulations are performed for systems consisting of a slab of electrolyte solution sandwiched by two channel walls. Figure 1 shows a schematic diagram of the system under investigation. The two channel walls are symmetrical with respect to the channel center line. Each wall is made up of five layers of atoms oriented in the $\langle 111 \rangle$ 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. In this paper, only the outermost wall layers are charged uniformly among the wall atoms. The flow is driven by an external electric field with a strength of E .

At the beginning of the simulation, the molecules are randomly positioned and assigned Maxwellian distributed velocities at the temperature of $1.1\epsilon/k_B$. Periodic boundary is performed in the x and y directions. Before the macroscopic characteristics are sampled, the NEMD simulations are run for 6×10^5 time steps to reach steady state flow. After that, the densities and velocities are computed time-averaged, over 3×10^6 times, by using

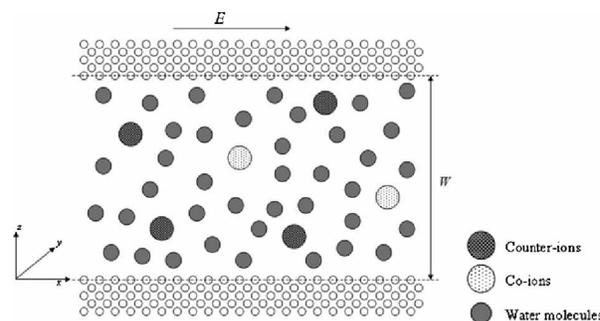


Figure 1. A schematic of the electro-osmotic flow in nanochannel. The two channel walls are symmetrical with respect to the channel center line. Each wall is made up of five layers of solid atoms. The channel width W is defined as the distance between centers in the two innermost wall layers.

Table 2. Summary of the simulated cases.

Cases#	W (nm)	σ_s (C/m ²)	Water molecules #	Counter-ions #	Co-ions #	E_{ext} ($\times 10^6$ V/m)	L (nm)
1	2.01	-0.127	480	20 Na ⁺	0 F ⁻	5.0	4.11
2	3.68	-0.127	980	20 Na ⁺	0 F ⁻	5.0	4.11
3	5.36	-0.127	1480	20 Na ⁺	0 F ⁻	5.0	4.11
4	7.04	-0.127	1980	20 Na ⁺	0 F ⁻	5.0	4.11
5	10.39	-0.127	2980	20 Na ⁺	0 F ⁻	5.0	4.11
6	5.36	-0.127	1460	30 Na ⁺	10 F ⁻	5.0	4.11
7	5.36	-0.255	1460	40 Na ⁺	0 F ⁻	5.0	4.11
8	5.36	-0.127	1480	20 Na ⁺	0 F ⁻	0.5	4.11
9	5.36	-0.127	1480	20 Na ⁺	0 F ⁻	50.0	4.11
10	5.36	+0.191	1460	35 F ⁻	5 Na ⁺	5.0	4.11
11	5.36	+0.191	1460	35 Cl ⁻	5 Na ⁺	5.0	4.11

the binning method [20]. The various simulated cases performed in this paper are summarized in table 2.

3. Results and discussion

3.1 Channel width effect

Figure 2 shows the Na⁺ concentration profiles for different channel widths with same wall charge density, channel length and ion numbers in the fluid (cases 1–5 in table 2). The results indicate that the ion concentrations have almost same distributions near walls when the channel width is larger than 2.01 nm (about 6 times diameter of fluid molecules). The ion distribution close to walls is mainly determined by interactions between wall molecules, fluid molecules and ions, but not sensitive to the channel size. This result can explain why the modified Poisson–Boltzmann equation of Qiao’s using the ion distribution information in a smaller channel from MD simulation could predict the ion distribution in a larger channel with good accuracies [14–17]. When the channel size is too small (smaller than 6 times the diameter of fluid molecule), the ions distribution is not only determined by the interaction from the near wall, but also affected by the

other wall surface. As a result, the ion concentration changes greatly from the other cases (see the dotted line in figure 2). Similar results were also observed by Travis *et al.* [22,23] in MD simulations for simple fluid channel flows.

The velocity profiles for cases 2–5 are shown in figure 3. Different channel sizes lead to different velocity profiles with a similar shape (shown as figure 3(a)). When the velocities are normalized by the maximum velocity of

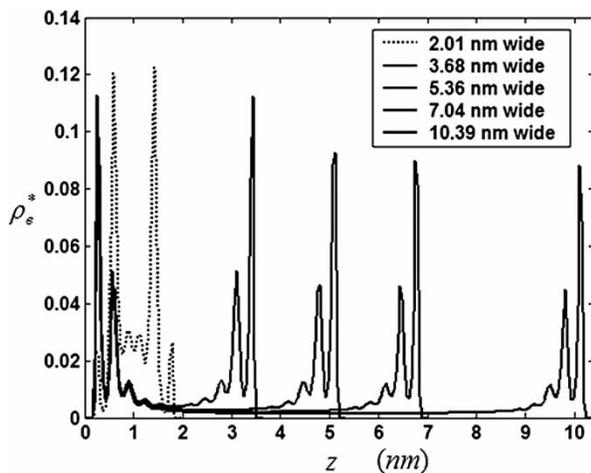


Figure 2. Counter-ion concentration across the channels for different channel widths (cases 1–5: $\sigma_s = -0.127$ C/m², 20 counter-ions). The ion density is normalized by $|e|/\sigma^3$, e.g. $\rho_e^* = \rho_e/(|e|/\sigma^3)$.

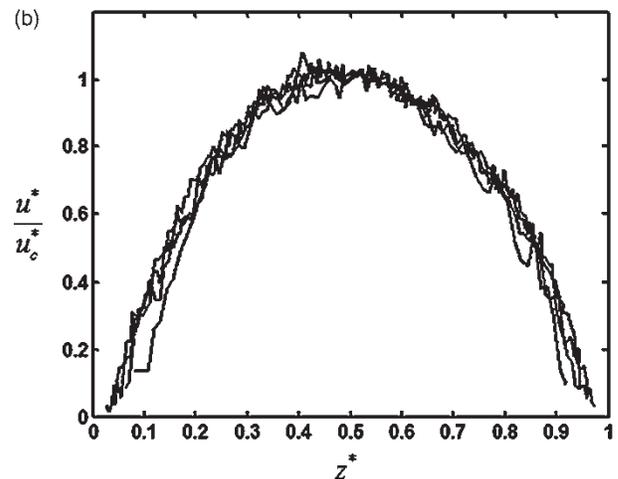
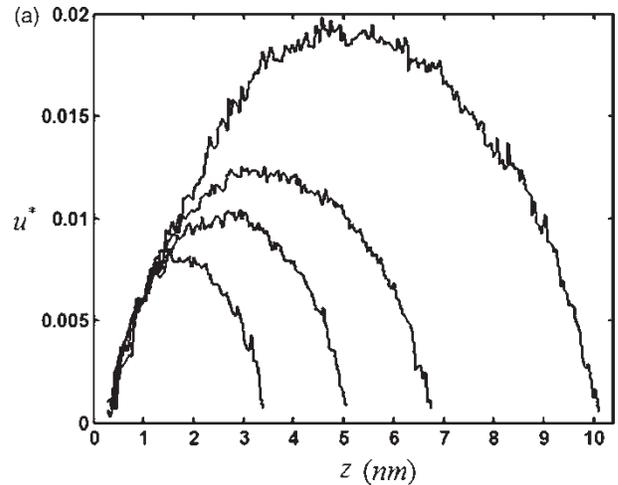


Figure 3. Velocities across the channels for different channel widths (cases 2–5). The x -velocity is normalized by the characteristic velocity, e.g. $u^* = u/(\sigma/\tau)$, u_c^* the dimensionless velocity at the central line, and the z -position normalized by the channel width, e.g. $z^* = z/W$.

each case, u_c , the results almost align (shown as figure 3(b)). That means the electro-osmotic channel flows for different sizes are of similarity. For the cases in the present investigations, figure 3 shows the similarity works well when the channel width is larger than 3.68 nm (about 10 times diameter of the fluid molecules), and seems perfect when the channel width is larger than 5.36 nm (about 15 times diameter of the fluid molecules). The similarity insures the accuracy of Qiao's embedding technique [11] so that it is suggested here the usage of the embedding technique in channels larger than 15 times (or at least 10 times) diameter of the fluid molecules.

3.2 Ion number arrangement effect

Consider two cases with different ionic arrangements for a certain net ionic concentration (see cases 3 and 6 in table 2). There are 20 counter-ions and none co-ions in case 3, while 30 counter-ions and 10 co-ions in case 6. The channel size and the wall charge density are the same for the two cases. Figure 4 shows the ion concentration profiles (a) and the velocity comparisons (b). The results indicate the net ion concentration distributions are different for the two cases though they have a similar

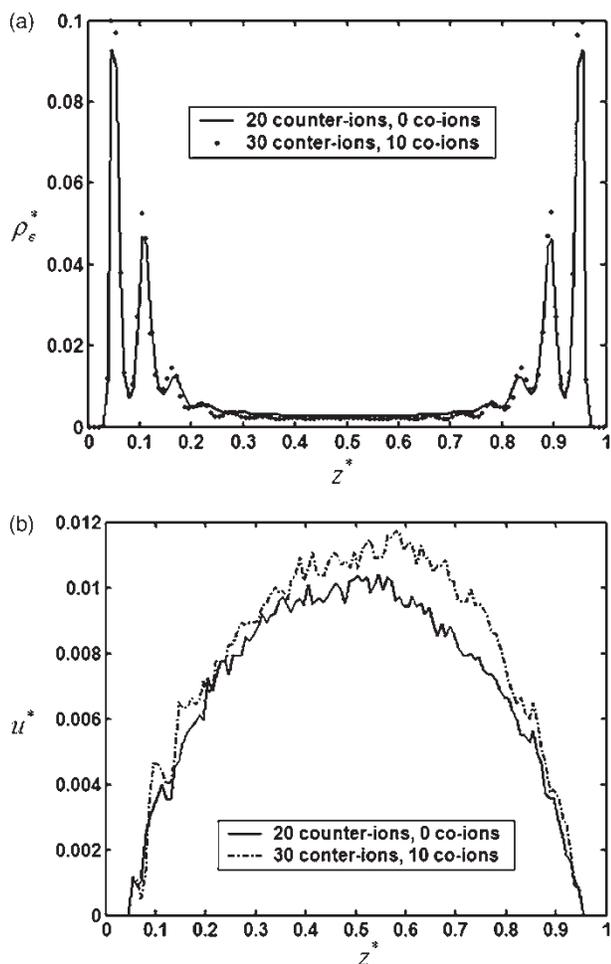


Figure 4. Ion concentration and velocities across the channels for different ionic numbers (cases 3 and 6).

profile sharp. The case with more ions (case 6) has higher values at first and second peaks and lower values in the bulk region than the case with only counter-ions (case 3). The bulk velocity with co-ions is about 10% higher than that without co-ions driven by a same external electric field. The results advise that applications of the similarity of electro-osmotic flows should be in same or close ionic arrangements.

3.3 Wall charge density effect

The wall charge density has great effects on the ionic concentration distribution near the wall. Comparison between cases 3 and 7 shows the wall charge density effects on the ion transport and fluid flow characteristics, as shown in figure 5. Although the wall charge density in case 7 is only twice that in case 3, the ionic concentration values of the first peak are over 3.5 times larger. The velocity profiles are also much different. The results indicate the ion transport and fluid flow are sensitive to the wall charge density. Different wall charge densities will lead the similarity to failure.

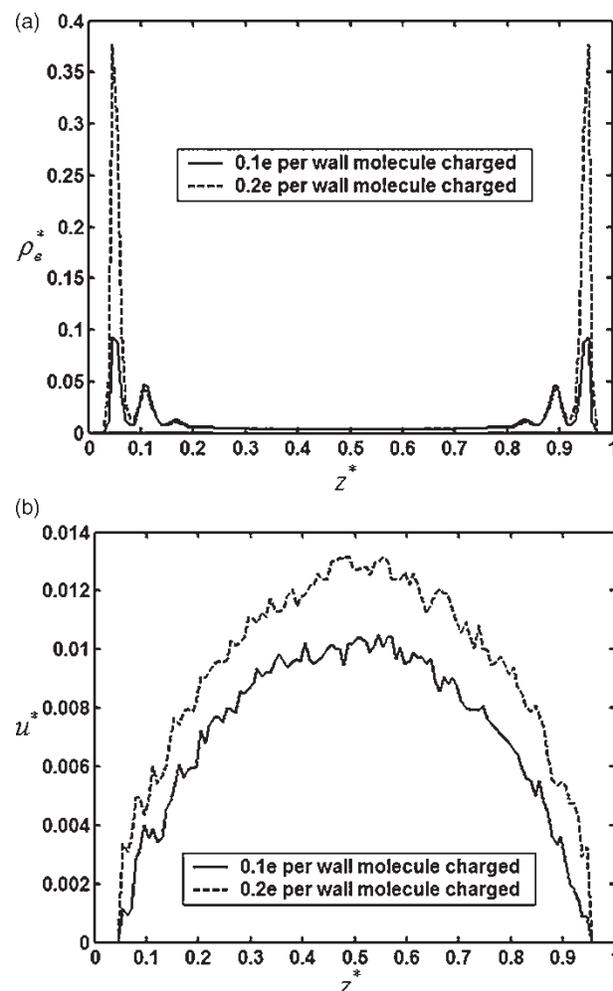


Figure 5. Ion concentration and velocities across the channels for different wall charge densities (cases 3 and 7).

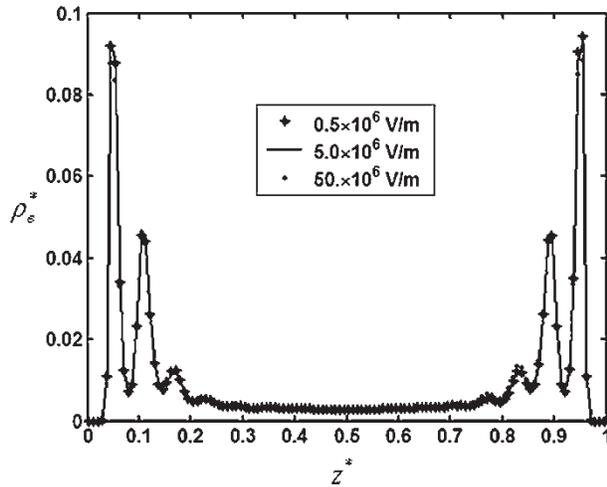


Figure 6. Ion concentrations for different external electric field strengths (cases 3, 8 and 9).

3.4 External electric field strength

It is reported that the mobility of ions changes when the external electric field strength is very large [12]. Here we would like to check the similarity in a wide electric field strength range. Comparing the cases 3, 8 and 9, we vary the electric field strength for 100 times; however, the ion concentrations for these cases are exactly the same, as shown in figure 6. This result suggests the external electric field strength not affect the similarity of the electroosmotic flows in general.

3.5 Molecular type effect

The so-called molecular type includes two aspects: ionic type and wall type. The ionic type effect on the transport characteristics in the nanochannel electroosmotic flows has been recently reported. Qiao and Aluru [15] reported the asymmetric phenomena of cation dominated flow versus anion dominated flow in confined silicon

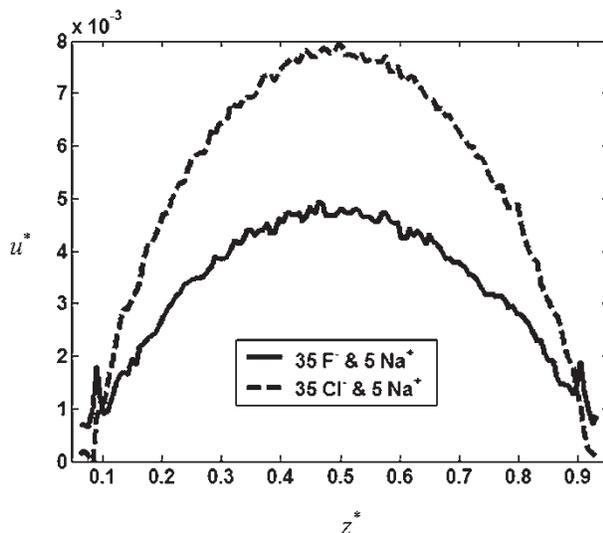


Figure 7. Velocities across the channels for different types of counterions (cases 10 and 11).

nanochannels. Figure 7 shows the velocity profiles of NaF and NaCl solutions under the same operating conditions (case 10 and 11), which indicate that even for same ion charge arrangements, different kinds of ions may induce quite different flows. We also compared the results for different wall types and the results showed the wall type also affect the transport behaviors near walls greatly. Similar results can be found in previous publications for simple fluid flow in nanochannels [18,20].

4. Conclusions

Electroosmotic flows in nanochannels have been simulated using the NEMD method and the similarity of the electrically driven flows is analyzed. The results indicate that the near-wall ion distribution is greatly influenced by the wall charge density, the ion arrangement, the ion type and the wall type. If these factors are all same, the electroosmotic flows in different channel sizes are of similarity, which leads to the near-wall ionic distributions are same and the velocities across the channel are similar. The results also suggest the similarity requires the channel size larger than 10 times diameter of fluid molecules. When the similarity holds, the embedding method is available so that one can predict ionic distribution and fluid flow in larger channels using the continuum theories by introducing near-wall information of MD results for smaller channels.

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