Transient Analysis of Electroosmotic Flow in Nano-diameter Channels

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ABSTRACT

Transient analysis of electroosmotic flow in a nano-diameter channel is presented. The time for flow to reach steady state in a nano-diameter channel for various Debye lengths is investigated by solving the Navier-Stokes equations in the presence of electrical forces. The results indicate that the time for flow to reach steady state depends on the interaction of Debye layers. Preliminary results on molecular dynamics simulation of electroosmotic flow are also presented. A comparison between continuum theory results and molecular dynamics simulation results indicates that for a 5 nm channel, continuum theory based on the Poisson-Boltzmann equation can overestimate the ion density near the channel wall, but agrees fairly well in the rest of the channel region. The velocity profile obtained from the continuum model agrees qualitatively with the molecular dynamics simulation result.

Keywords: Electroosmotic flow, nano-channel, molecular dynamics simulation, transient analysis.

1   INTRODUCTION

Fluidic transport through nano-diameter channels plays an important role in many engineering applications e.g. in the design and development of nanoscale sensors for chemical and biological analysis. A straight nano-channel is a fundamental component of any nano-fluidic network, and a good understanding of the transient flow in a straight channel can help understand the transient flow in more complicated geometries. In particular, we investigate the time needed for the flow to reach steady-state in a straight channel. By solving the 2-D electroosmotic flow model, we investigate three different cases of Debye layer interactions and their effect on the flow. The three different cases are (i) the Debye layers are very small compared to the channel critical dimension and do not interact (ii) the Debye layers interact weakly and (iii) the Debye layers interact strongly.

One important question that needs to be addressed in nanoscale research is whether continuum theories can be used reliably to predict flow characteristics. In this paper, we study the electroosmotic flow in a 5nm wide channel by using molecular dynamics simulations. The continuum theory results for ion distribution and velocity profile across the channel agree qualitatively with molecular dynamics simulation results. More extensive testing and validation of the continuum theory is necessary before any conclusions can be drawn.

2   TRANSIENT ANALYSIS OF ELECTROOSMOSTIC FLOW

Electroosmotic transport can be described by the Laplace equation, the Poisson-Boltzmann equation and the incompressible Navier-Stokes equations. A detailed description of the electroosmotic transport model can be found in [1,4]. The model includes:

$$\nabla^2 \Phi = 0 \tag{1}$$

$$\nabla^2 \Psi = -\frac{\rho_E}{\varepsilon} \tag{2}$$

$$\rho_E = \sum_{i=1}^{N_{ions}} \pm z_i \frac{\varepsilon RT}{2F\lambda_D{}^2} exp\left(\mp \frac{z_i F\Psi}{RT}\right) \tag{3}$$

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}\cdot\nabla)\mathbf{u} = \upsilon\nabla^2\mathbf{u} - \frac{1}{\rho}\nabla p - \frac{1}{\rho}\rho_E\nabla\Phi \tag{4}$$

$$\nabla\cdot\mathbf{u} = 0 \tag{5}$$

The Laplace equation (1) describes the potential in the device (or in the electrokinetic geometry) because of applied potentials and the Poisson-Boltzmann equation (2) describes the potential (ψ–field) in the device because of the ζ-potential at the solution-capillary interface. Equations (4-5) describe the fluid flow in the device because of the applied and ζ-potential. Specifically, equation (4) is the Navier-Stokes equation and equation (5) is the continuity equation.

The Debye length (λ_D in equation (3)) is a crucial parameter in the model. Within a few Debye lengths from the channel wall, the solution has a net charge. These charges can move when subject to an external potential gradient. λ_D is related to the ion concentration c_0 in the solution by:

$$\lambda_D = \sqrt{\frac{\varepsilon RT}{2F^2 c_0}} \tag{6}$$

Where ε is the permittivity of the solution, R is the universal gas constant, T is the solution temperature and F is the Faraday constant.

The mathematical model stated in equations (1-6) along with the appropriate initial and boundary conditions describes the electroosmotic problem. The model was solved using the meshless finite cloud method in two-dimensions [1]. In particular, a semi-implicit multi-step (SIMS) technique was used to solve the transient Navier-Stokes equations.
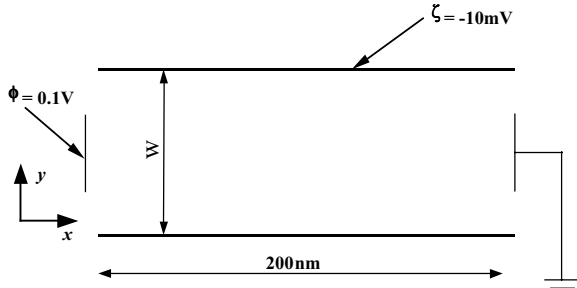

Figure 1. Nano-channel flow problem studied. W is the width of the channel and is varied in simulations.

Figure 1 shows the geometry of the nano-channel studied. An applied potential of 0.1V is applied at the left entrance and the right exit is grounded. The Debye length is
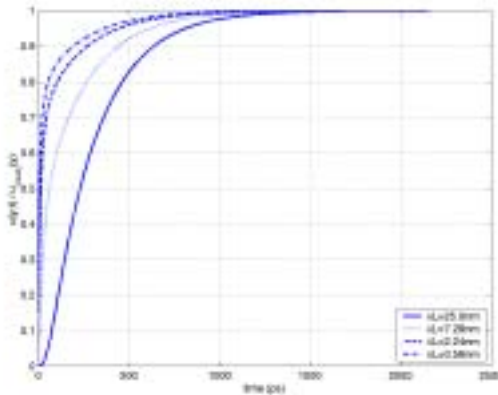

Figure 2. Evolution of velocity at different positions in the channel for the case where W=50nm, and λ_D=2.5nm.

taken to be 2.5nm (corresponds to an ion concentration of 15mM at 300K) and the ζ-potential on the channel wall is taken to be –10mV. The channel width (W) is varied in simulations.

Three cases with different channel width are considered. In the first case, the channel width is set to be 50 nm, thus the Debye layers do not interact. The evolution of velocity at different positions (along the width) in the channel is shown in Figure 2. The results indicate that the flow within a few Debye lengths from the wall reaches steady state very quickly and the flow in the central portion of the channel takes much longer to reach steady state. This is because the flow near the channel wall is dominated by electrokinetic force that acts in an instantaneous way, while the flow in the central portion of channel is driven by a viscous force that develops much more slowly. Because the flow in

central portion of the channel is driven solely by viscous force, the time needed for the flow to reach steady state (Ts) can be predicted very well by viscous flow theory i.e. $Ts = 0.491\ W^2/\nu$, where ν is the fluid viscosity.
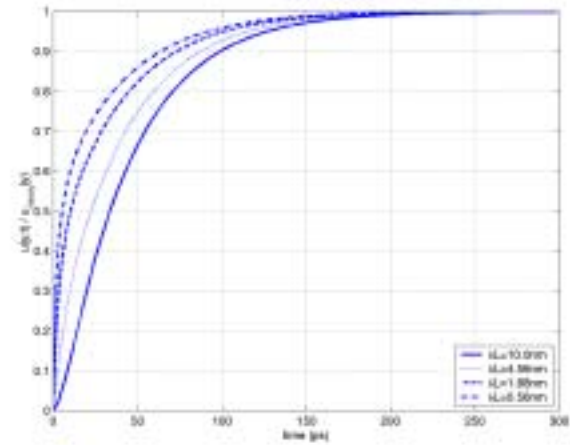

Figure 3. Evolution of velocity at different positions in the channel for the case where W=20nm, and λ_D=2.5nm.

In the second case, the channel width is chosen to be 20nm, i.e. the Debye layers near the two channel walls are interacting very weakly. The results for this case are shown in Figure 3. It can be seen that Ts varies little for the different positions compared to the case shown in Figure 2. This is because the electrokinetic force now exists in most of the channel and the flow is driven by both electrokinetic and viscous forces. However, it turns out that Ts for flow in the central portion of channel can still be predicted accurately (with in 5%) by the viscous theory. In the third case, the channel width is taken to be 5nm and the Debye layers are interacting very strongly. Figure 4 shows the evolution of velocity at different positions. It can be seen that Ts shows very weak dependence on the position in the channel. This is because the electrokinetic force is more or
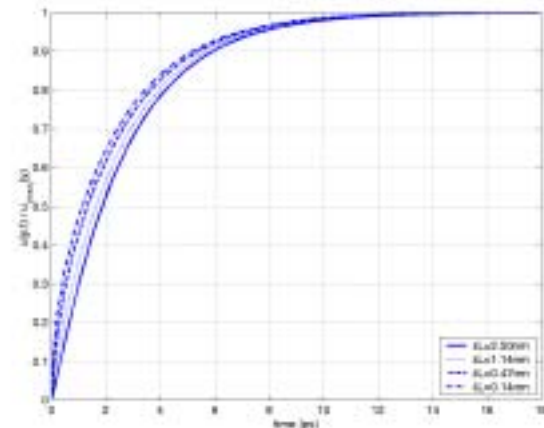

Figure 4. Evolution of velocity at different positions in the channel for the case where W=5nm, λ_D=2.5nm.

less uniform throughout the channel. This suggests that *Ts* is primarily dominated by viscous forces. In fact, *Ts* for flow in the central portion of the channel can be predicted within 7% accuracy.

In summary, *Ts* for different positions in the channel is related to both electrokinetic and viscous forces, and depends on whether the Debye layers interact or not and how strongly they interact.

3 MOLECULAR DYNAMICS SIMULATIONS

Molecular dynamics simulation of electroosmotic flow in a 5nm channel has been done using Gromacs [2]. To simplify the simulation, only negative Cl⁻ ions are considered [3]. Figure 5 shows the sketch of the electroosmotic flow simulation.
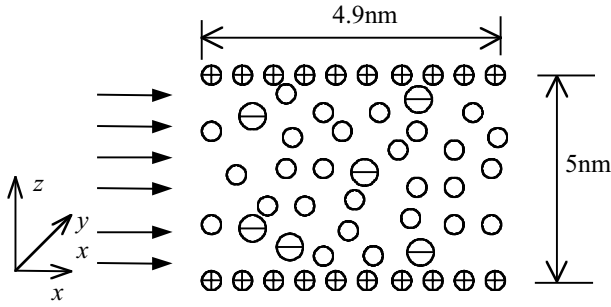

Figure 5. Sketch of electroosmotic flow in nano-channel.

The length of the simulation box is 4.9nm along *x* and *y* directions and extends periodically in both *x* and *y* directions. The distance between the upper and lower channel walls is 5nm. 3676 water molecules and 72 Cl⁻ ions are used in the channel, corresponding to a density of $1g/cm^3$ for water and 0.98M concentration for Cl⁻ ion. SPC/E model is used for water. The Cl⁻ ion is modeled as a charged Lennard-Jones atom. Each channel wall is represented as a fixed lattice of 196 Silicon atoms, which were modeled as partially charged Lennard-Jones atoms. The charge density on the wall is chosen to be $0.24C/m^2$, corresponding to a charge of $0.184e$ per silicon atom. The external electrical field strength is set to b.e 0.07V/nm in the simulation. The interaction between oxygen atom of water molecule, Cl⁻ ion and wall atom is modeled by the Lennard-Jones potential whose parameters are summarized in Table 1. In addition, the charged atoms interact with each other also by electrostatic force.

Interaction	A (KJ/mol·nm^{12})	C (KJ/mol·nm^6)
O-O	2.6331×10^{-6}	2.6171×10^{-3}
O-Cl	4.0635×10^{-5}	6.1404×10^{-3}
Si-O	3.0100×10^{-6}	3.2749×10^{-3}
Si-Cl	4.6474×10^{-5}	7.7658×10^{-3}
Cl-Cl	1.0691×10^{-4}	1.3804×10^{-2}

Table 1 Lennard-Jones potential ($U=A/r^{12}-C/r^6$) parameters.

The cut-off radius for Lennard-Jones interaction is chosen to be 0.9nm. The electrostatic interaction is calculated using the PME method [2] with a Fourier spacing of 0.12nm in *x*, *y* and *z* direction. A Berendsen thermostat is used to keep the system at a constant temperature of 300K. The time constant τ for the thermostat is chosen to be 0.1ps. The simulation starts from a random distribution of water molecules and Cl⁻ ions in the system, and the time step size is chosen to be 3fs. Then the simulation is run for 1ns to equilibrate the system. The simulation is run for another 800ps to gather statistics.

The continuum theory described in the previous section has been applied to the problem shown in Figure 5. The boundary condition for the Poisson-Boltzmann equation is given by:

$$Q_0 = \varepsilon \frac{d\Psi}{dz}\bigg|_{wall} \tag{7}$$

where Q_0 is the charge density at the wall.

Figure 6 shows the comparison of Cl⁻ density across the channel obtained from the molecular dynamics simulation and the continuum theory model. Compared to the continuum theory result, the molecular dynamics simulation result shows a higher peak for the Cl⁻ concentration near the wall. However, the concentration decreases faster compared to the continuum theory result. One possible reason for the discrepancy is that the continuum theory assumes a constant permittivity for the solution. This could be a problem as it has already been shown that the surface charge can lower the solution permittivity near the surface [5].
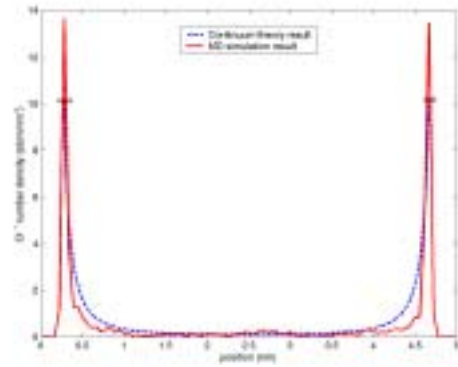

Figure 6 Comparison of Cl⁻ density profile across channel. The two short horizontal lines indicate the highest Cl⁻ density obtained from continuum theory.

Figure 7 shows the comparison of the velocity profile obtained from molecular dynamics simulation and continuum theory. There is significant scattering in the molecular dynamics result indicating that more data should be collected to obtain a more accurate velocity profile. Nevertheless, the molecular dynamics result agrees qualitatively with the continuum theory result.
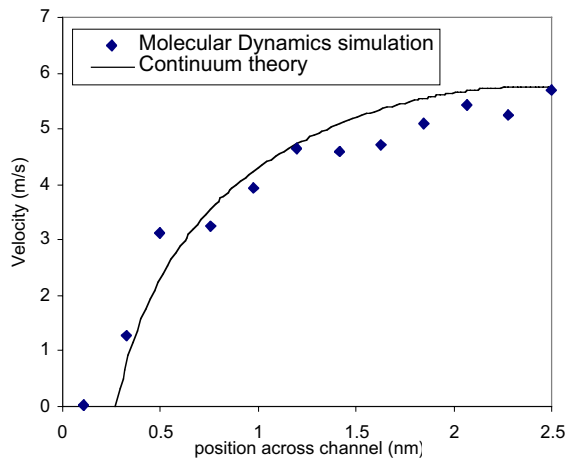
Figure 7 Comparison of velocity profile obtained by molecular dynamics simulation and continuum theory.

4   CONCLUSIONS

Transient behavior in a straight nano-channel is investigated under different conditions. Results show that:

1. When the Debye layers are not interacting ($\lambda_D \ll W$), the flow within a few Debye lengths from the channel wall will reach steady-state much faster compared to the flow in the central portion of the channel. The time for flow in the central portion of channel to reach steady state (T_s) can be predicted accurately using the classical viscous theory.

2. When the Debye layers are interacting weakly, Ts varies little for the different positions across channel.

3. When the Debye layers are interacting strongly, Ts shows very weak dependence on the position in the channel. The time for flow to reach steady-state at the central portion of the channel can be predicted to within 7% error using the classical viscous theory result.

Electroosmotic flow in a 5nm wide nano-channel is simulated using the molecular dynamics technique. The results indicate that:

1. Very close to the channel wall there is disagreement in ion concentration predicted by continuum theory and molecular dynamics. In the rest of the channel region, the continuum theory result matches well with the molecular dynamics result. The continuum theory assumes a constant permittivity and an infinitesimal ion size. Both these assumptions could be the causes for disagreement in the ion concentration near the channel wall.

2. The velocity profile obtained from molecular dynamics simulation agrees qualitatively with the continuum theory result. More extensive testing is necessary before conclusions can be drawn on the accuracy of continuum theories.

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