Temperature dependence of electrokinetic flux in Si nanochannel

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Significant temperature effects on the electrokinetic transport in a nanochannel with a slab geometry are demonstrated using a molecular dynamics (MD) model. A system consisting of Na\(^+\) and Cl\(^-\) ions dissolved in water and confined between fixed crystalline silicon walls with negatively charged inner surfaces in an external electric field was investigated. Lennard-Jones (LJ) force fields and Coulomb electrostatic interactions with Simple Point Charge Extended (SPC/E) model were used to represent the interactions between ions, water molecules, and channel wall atoms. Dependence of the flow of water and ions on the temperature was examined. The magnitude of the water flux and even its direction are shown to be significantly affected by temperature. In particular, the previously reported flow reversal phenomenon does not occur at higher temperature. Temperature dependence of the flux was attributed to the charge redistribution and to the changes in viscosity of water.

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I. INTRODUCTION

Nanoscale numerical models of electro-osmosis [1-6] provide insight into the important transport mechanism, help improve current technological devices, and guide the design of new technology based on the principles of electrokinetic transport. They also improve understanding of transport processes in biology [7] and their temperature dependence [8].

The present study examines the fluid flow and ion species transport under an electric field in nanochannels typically found in heterogeneous porous media. Although the continuum conservation equations can be applied to microscale channels, the main driving force of electrokinetic transport occurs in an electric double layer (EDL) at the solid liquid interface with dimensions that can be comparable to intermolecular distances. Therefore, molecular dynamics (MD) simulations were applied to analyze the interaction between ions, water molecules, and wall atoms in the EDL region. Time averaged velocity and concentration profiles of water molecules and ionic species at different temperatures were obtained from these MD simulations. Water viscosity profile across the channel was estimated at different temperatures and its impact on the transport of water and ionic species will be discussed.

Video 1. (Color online) Simulation box without water molecules. Si wall atoms are gray, Na\(^+\) ions red, and Cl\(^-\) ions green. Water molecules are not shown. Accompanying animation shows movement of ions when electric field is applied in the positive x direction.

II. MD POTENTIALS

Models based on classical Lennard-Jones (LJ) force fields and Coulomb electrostatic interactions with Simple Point Charge Extended (SPC/E) [9] model were used to represent the interactions between ions, water molecules, and channel wall atoms. LJ contribution of atoms \(i\) and \(j\) to the total potential energy is

\[
V_{LJ}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right] .
\]  

The parameters \(\epsilon_{ij}\) (the depth of the potential well) and \(\sigma_{ij}\) (\(\sqrt{2}\sigma_{ij}\) is the minimum energy distance) depend on atomic species of \(i\)th and \(j\)th atoms (Table I). The
TABLE I. Parameters of Lennard-Jones potentials (from the gromacs force field), $\sigma_{ij}$ in Å, $\epsilon_{ij}$ in cal/mol.

| ij  | O  | O   | Na  | O   | Na  | Cl  | Na  | Cl  | Cl  |
|-----|----|-----|-----|-----|-----|-----|-----|-----|-----|
| $\sigma_{ij}$ | 3.17 | 3.27 | 2.86 | 3.75 | 3.39 | 2.95 | 3.88 | 2.58 | 3.38 | 4.45 |
| $\epsilon_{ij}$ | 155 | 301 | 47.9 | 129 | 584 | 92.9 | 249 | 14.8 | 39.6 | 106 |

Coulomb electrostatic potential energy contribution is

$$V_C(r) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r}.$$  \hspace{1cm} (2)

The $\varepsilon_0$ is vacuum permittivity, $q_i$ and $q_j$ are charges of $i$th and $j$th atoms, and $r$ is the distance between $i$th and $j$th atoms. The Particle-Particle Particle-Mesh (PPPM) method was used for long range electrostatics.

III. SIMULATION SETUP

In order to study the temperature effects, the authors first reproduced the system studied previously, a summary of which is given next. The dimensions of the solution region were 4.66x4.22x3.49 nm. Channel walls, perpendicular to the z axis, were formed by four oriented layers of Si atoms in a diamond crystal structure, each wall being 0.39 nm thick. Periodic boundary conditions were applied in the x and y directions. The size of the simulation cell in the z direction was extended to three times outermost-to-outermost wall layer distance (3x4.37 nm) to mitigate electrostatic interactions of periodic images in the z direction. The electric field of 0.55 V/nm was applied in the positive x direction.

The crystalline channel walls consisted of 1232 fixed Si atoms. A charge of $-70 \ e$ was distributed uniformly on atoms of the innermost surface layers of both Si walls (total 308 Si atoms were charged negatively and 924 were uncharged). Therefore, the innermost wall surface atoms had $-0.227273 \ e$/atom charge. That corresponds to a surface charge density of $-0.285 \ C/m^2$, which is close to typical value for a fully ionized surface 0.2 C/m$^2$ or the charge density of $-0.1 \ C/m^2$ measured at silica surface. Then 2290 water molecules were inserted avoiding close contacts, and randomly selected 146 water molecules were replaced by 108 Na$^+$ and 38 Cl$^-$ ions. Thus the whole system was electrically neutral and resulting NaCl concentration in the channel center at the temperature of 300 K was $\approx 1.2 \ M$.

First, the energy minimization of the system was performed using the conjugate gradient method. Then, the system was equilibrated by 2 ns of MD simulation without an electric field. A timestep of $2 \times 10^{-15} \ s$ was used for the leapfrog integration of Newton’s equations of motion. The resulting configuration, excluding water molecules, is shown in Video 1. Finally, a 22 ns MD run was performed with external electric field. The SHAKE algorithm was used to constrain bonds of water molecules. The solution temperature was controlled by the Nosé-Hoover selective thermostat (Sec. IV).

IV. THERMOSTAT

The thermostat in MD simulations adjusts the velocity to maintain the desired temperature and its proper fluctuations. To check how much the velocity component in the field direction is affected by thermostat, the velocity profiles from simulation with selective thermostat (adjusting y and z velocity components only) were compared to results with full thermostat (adjusting x, y, and z components of velocity). The number of thermal degrees of freedom was adjusted accordingly. Figure 1 shows that selective thermostat produces slightly more negative velocity.

Velocity profiles with profile-unbiased thermostat (PUT) that “preserves” the velocity profile (i.e. its x component) across the channel were also generated. Averages did not differ significantly from those obtained by selective thermostat (adjusting only y and z velocity components), but PUT error bars were larger, therefore the selective thermostat (adjusting y and z components of velocity only) was used.

The authors then verified that velocity profiles with full thermostat obtained from GROMACS were statistically identical to those from LAMMPS when thermostating all velocity components, even though GROMACS used the PME (Particle-Mesh-Ewald) method with a slab correction in the z direction for long range electrostatics and SETTLE algorithm to constrain bonds of water molecules.

![FIG. 1. Comparison of water velocity profiles using full thermostat (adjusting x, y, and z velocity components) and selective thermostat (adjusting y and z components only). Error bars are only shown on one side of the values to avoid overlap. The values shown (on all figures) are averages over 80.026 nm wide bins parallel to the xy plane that are then symmetrically averaged about the channel center.](image-url)
V. CONCENTRATION PROFILES

The calculated atomic concentration profiles shown in Fig. 2, which agree well with reported results [2], manifest formation of alternatively charged layers of atoms parallel to the channel walls. The negatively charged Si wall attracts both positively charged Na\(^+\) ions and slightly positively charged H atoms (0.4238 e/atom for SPC/E water) from \(\text{H}_2\text{O}\) molecules, forming the first near-wall concentration peak. The adjacent layer is formed of slightly negatively charged O atoms (−0.8476 e/atom for SPC/E water) from water molecules. Five noticeable layers with alternating charge signs are formed—four ionic layers can be seen in Fig. 3 and the fifth is a negatively charged layer of O atoms 0.25 nm from the channel wall (Fig. 2). Layering of particles near a flat surface is characteristic for polar liquids [22], LJ fluids [23], and charged surfaces [24]. Further towards the channel center, the concentrations of ions are more balanced (≈1.2 M).

![Concentration Profiles](image)

FIG. 2. Concentrations of Na\(^+\) and Cl\(^-\) ions, and H and O atoms from \(\text{H}_2\text{O}\) molecules symmetrically averaged across half of the channel. The inside plot is a magnified version of a larger plot. Concentration of Na\(^+\) ions in the channel center increases as the temperature increases.

VI. DRIVING FORCE

Since the net charge of a standalone water molecule is zero, its center of mass will not move in the presence of external electric field. The driving force for the electro-osmotic flow comes from the electric field causing the movement of a fluid region with non-zero net charge. Regions of fluid with positive net charge will drive the flow in the direction of an external electric field, while the regions with negative net charge will drive the flow in the direction opposite to an external electric field. The driving force is defined as

\[
F_d(z) = e \left[ c_{\text{Na}^+}(z) - c_{\text{Cl}^-}(z) \right] E_{\text{ext}},
\]

where \(e\) is the elementary charge, \(c_{\text{Na}^+}(z)\) and \(c_{\text{Cl}^-}(z)\) are ionic number densities across the channel, and \(E_{\text{ext}}\) is an external electric field. Figure 3 shows a dependence of the driving force on temperature.

When the temperature is increased, the driving force in the region further than 0.42 nm from the channel wall becomes more positive (because of increased Na\(^+\) concentration in that region), and water starts to flow in the positive x direction. The driving force from Cl\(^-\) ions, on the contrary, will increase only in the near-wall region, as some of the Cl\(^-\) ions will redistribute closer than 0.5 nm within the channel wall. In the following section it will be argued that this charge redistribution at increased temperature drives the flow in the positive x direction.

![Driving Force](image)

FIG. 3. Driving force for the fluid flow given by Eq. (3). Values are symmetrically averaged across half of the channel. Inside plot magnifies values in the central region of the channel—where driving force becomes more positive at higher temperature. The temperature changes in concentration profiles, resulting in changes of driving force, are the main factor contributing to the temperature dependence of the flow.
FIG. 4. Velocity profiles from MD at T=280 K (top), 300 K, and 320 K (bottom). Negative flow means movement in the direction opposite to the applied electric field. Velocity of H$_2$O is a velocity of oxygen atoms from H$_2$O molecules. Note that the temperature increase changes the water flow direction along the channel. Error bars (for Na$^+$ and H$_2$O they are represented by rectangles) were obtained by analysis of ten simulations with different seeds of initial Gaussian random velocity distribution. Large error bars near the wall are due to low concentrations (Fig. 2). Details of water velocity profiles are shown in Fig. 5.

VII. TEMPERATURE DEPENDENCE OF VELOCITY PROFILES

A significant dependence of the flow on temperature was observed. Figure 4 shows the dependence of the velocity profile of ions and water on the temperature. It demonstrates that the water flow and even its direction are directly affected by the temperature. At lower temperatures, flow reversal of water was observed, in agreement with previous results [2]. However, at higher temperatures, the water flows in the direction expected by a standard EDL model.

Note that even though Cl$^-$ ions in water move faster than Na$^+$ ions (Fig. 4), that does not affect water velocity profile. Water movement is not governed by the ionic velocities, but by the profile of the driving force. Velocity of ions relative to water is given by their respective mobilities $\mu_i$ according to the definition of mobility $v_i = \mu_i E$. The LJ potential properly reflects the experimental mobility of Cl$^-$ ions being higher than the mobility of Na$^+$ ions. Mobility of ions will affect the rate of ion accumulation on electrodes in an experiment, but not the velocity profile of water in the present model.

The temperature dependence of the electro-osmotic flow was attributed to (a) charge redistribution and to (b) changes of water viscosity with temperature.

As mentioned in Sec. VI, the positive ions will redistribute towards the channel center at higher temperatures (Fig. 4). At T=320 K, Na$^+$ ions dominate Cl$^-$ ions in the region 0.61 to 0.76 nm from the wall. The increased Na$^+$ concentration in the channel center comes from lowering two near-wall concentration peaks of Na$^+$ ions (at 0.14 and 0.38 nm from the wall in Fig. 2), that redistribute further than 0.42 nm from the channel wall at higher temperature. This increased Na$^+$ concentration in the channel center (where the water viscosity is lower than at the surface—see Sec. IX) stimulates the movement of water in the positive x direction. Even though Na$^+$ ions dominate only in regions less than 0.52 nm and 0.61 to 0.76 nm from the wall, hydrogen bonding and collisions will also drag adjacent layers of water in the channel center, outperforming the competing mechanism of water dragged in the negative x direction by Cl$^-$ ions that have higher concentration than the Na$^+$ in the channel center.

On the contrary, at lower temperatures Cl$^-$ ions are more dominant over Na$^+$ ions in the channel center, causing a flow in the negative x direction.
VIII. RELATION OF VELOCITY PROFILES AND CHARGE DISTRIBUTION

Velocity profile is related to charge density profile by the Stokes equation [25]
\[
\frac{d}{dz} \left[ \eta(z) \frac{du_x(z)}{dz} \right] = -F_d(z).
\] (4)
The magnitude of the driving force, \(F_d(z)\), given by Eq. (3), as well as the velocity profile, \(u_x(z)\), can be calculated as averages from MD simulations. The \(\eta(z)\), viscosity profile of water across the channel, can then be estimated from MD as follows.

IX. ESTIMATION OF WATER VISCOSITY

The water viscosity profile across the channel was estimated following the method of [1]. The same method (except smoothing of velocity profile) was used by [26]. To simplify equations, the coordinate system with \(z=0\) at the channel center will be used. Integration of Stokes Eq. (4) leads to viscosity estimate
\[
\eta(z)|_{z=z_0} = \int_{z=0}^{z_0} F_d(z) \, dz \frac{du_x(z)}{dz} \bigg|_{z=z_0}. \] (5)
The fit diverges near the points where the derivative of velocity is zero. This is appropriate, since the viscosity can not be estimated in the region with zero shear strain—which is the term in denominator. The numerator term represents the shear stress [26].

To obtain smooth derivative of \(u_x(z)\), the velocity profile was approximated by the sum of harmonic components
\[
u_{x,fit}(z) = \sum_{n=0}^{7} a_n \cos \left( n \pi \frac{z}{h} \right). \] (6)
The \(h\) is the distance of the furthest oxygen atom from the channel center. In contrast to the original approximation of [1], the exponential term is excluded. Also, to exploit the symmetry of the system, the origin of cosine components is set to the channel center.

The velocity, its approximation, the viscosity profile estimated by Eq. (5), and the experimental viscosity of water [27] at the simulated temperatures are shown in Fig. 5. Note that the estimated viscosity (the line made of + symbols on the upper plots in Fig. 5) at its minimum reproduces the experimental viscosity (solid horizontal line).

At lower temperatures, the viscosity of near-wall water layers increases drastically. That means the near-wall Na\(^+\) ions can not drive much water flow. Conversely, at higher temperatures, the near-wall water will become more mobile, exhibiting a partial slip at \(T=320\) K.

FIG. 5. Velocity profile fit to the sum of harmonics (lower plots) and viscosity estimate from Eq. (5) (upper plots) at \(T=280\) K, 300 K and 320 K. The inside plots are magnified versions of larger plots.
X. CONCLUSIONS

Many technological processes and phenomena in live organisms exhibit a strong dependence on temperature. It is important to understand how the temperature affects technological and natural processes. This work indicates that a variation of temperature can have deterministic effects on an electrokinetic flow.

This paper revisited the phenomenon of flow reversal during electrokinetic flow in a slit nanochannel. It was found, using a molecular dynamics analysis, that both the magnitude and direction of the electro-osmotic flow are significantly affected by temperature. Even though the results reported in [2] could be replicated, it was found that the flow reversal of water molecules no longer occurs if the temperature is increased slightly above the 300 K used in [2]. The mechanisms that lead to such a significant temperature dependence of the nanochannel flow were then investigated. In particular, it was shown that the temperature dependence of the flux can be explained by the charge redistribution and the decrease of near-wall water viscosity at higher temperatures.

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Computational packages LAMMPS [18] and GROMACS [14] versions 4.0.4 were used to perform MD simulations. Video [1] was made using Visual Molecular Dynamics [28] package. Part of this work was disclosed in [29]. Permission to publish this material was granted by the Director of the Geotechnical and Structures Laboratory of the Engineer Research and Development Center, U.S. Army Corps of Engineers.