TEMPERATURE, VISCOSITY, AND CHARGE DENSITY EFFECTS ON THE VELOCITY PROFILE OF A NANOCHANNEL ELECTRO-OsmOTIC FLOW

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Electrokinetic process - definitions

**Electrokinetic phenomena**: electric field related effects occurring in heterogeneous fluids in porous materials

**Electroosmosis**: motion of fluid under the influence of electric field

**Electrophoresis**: motion of particles under the influence of electric field

**Streaming potential**: electric potential generated by moving fluid

**Cause**: **Double layer** of charges on solid-liquid interface

**Applications**: dewatering of concrete structures, decontamination, nanoscale devices, even source of electric energy?
Atomic system configuration

**Na\(^+\)** and **Cl\(^-\)** ions solvated in *water*,
confined between two negatively charged Si walls

Applied **electric field** parallel to the walls

Measured **velocity profiles** and **ionic concentrations**

Final goal: obtain effective diffusion coefficients and ionic mobilities to supplement continuum level model

References:


Construction of simulation cell

Channel walls of silicon crystal surface in (111) direction
Dimensions 4.66x4.22x3.49 nm
Uniform negative charge on inner surface layers
Walls: 924 uncharged Si atoms
308 neg. charged Si atoms
Construction of simulation cell

Periodic boundary conditions in x and y directions $\Rightarrow$ slab with infinite surface area

Studied variation along z direction

Solvation:
Randomly inserted 2290 water molecules
Avoided overlap, even across PBC boundaries
Construction of simulation cell

Insertion of ions:
- Replaced random water molecules with Na\(^+\) and Cl\(^-\) ions

Ionic solution:
- 2144 water molecules
- 108 Na\(^+\) ions
- 38 Cl\(^-\) ions
Energy minimization

Molecules reorient and settle to local minimum of energy position.

H from H$_2$O molecules points to the negative surface.

Na$^+$ ions move slightly closer to the negatively charged surface.

Cl$^-$ ions move slightly away from the negatively charged surface.
Pressure adjustment

- Bottom wall is fixed
- External force is applied on the top wall atoms in the downward direction
- Magnitude of the external force is calculated so that the total force on each atom corresponds to the desired pressure
- External force is balanced by the fluid pressure
Equilibration of atomic system

Equilibration:
- MD simulation, $t = 2 \text{ ns}$
- Without ext. electric field
- $T = 300 \text{ K}$

Result:
- Ionic concentration profile is formed along the $z$ direction
Simulation with applied electric field

Electric field applied in the +x direction (to the right)

\[ \mathbf{E}_{\text{ext}} \]

\( \text{Na}^+ \) ions (dark blue):
move in the direction of \( \mathbf{E}_{\text{ext}} \)
or adsorb at the negatively charged surface

\( \text{Cl}^- \) ions (light blue):
move opposite to \( \mathbf{E}_{\text{ext}} \)
Simulation with applied electric field

Na\(^+\) adsorb at the negatively charged surface or move in the direction of \(\vec{E}_{\text{ext}}\)
Cl\(^-\) move opposite to \(\vec{E}_{\text{ext}}\)
Velocity profiles

- H$_2$O, center of mass
- Na$^+$
- Cl$^-$

Velocity [m s$^{-1}$]

z [nm]

5 5.5 6 6.5 7 7.5 8

-20 -15 -10 -5 0 5 10 15 20
Selective thermostat

Themostating of velocity component in the field direction (x) slightly influences velocity profile – we chose to apply selective (yz) thermostat
Mass flux areal density profiles

Flux \([10^3 \text{ kg m}^{-2}\text{s}^{-1}]\)

- \(\text{H}_2\text{O}, \text{center of mass} \)
- \(\text{Na}^+ \)
- \(\text{Cl}^- \)
Concentration profiles
Temperature dependence

**Flux**

- T = 280K
- T = 300K
- T = 320K

**Velocity**

- T = 280K
- T = 300K
- T = 320K

Graphs showing the temperature dependence of flux and velocity for different temperatures and ions.
Temperature effects on concentrations
Temperature effects on driving force

$$\vec{F}_d(z) = e \left[ c_{Na^+}(z) - c_{Cl^-}(z) \right] \vec{E}_{ext}$$
Viscosity

Stokes equation:

\[
\frac{d}{dz} \left[ \eta(z) \frac{du_x(z)}{dz} \right] = -F_d(z)
\]

Integrated:

\[
\eta(z)\big|_{z=z_0} = \frac{-\int_{0}^{z_0} F_d(z) \, dz}{\left. \frac{du_x(z)}{dz} \right|_{z=z_0}}
\]

Velocity approximation:

\[
u_{\text{fit}}(z) = \sum_{n=0}^{7} a_n \cos \left( \frac{n\pi z}{h} \right)
\]
Velocity predicted from charge density

Stokes equation:

\[
\frac{d}{dz} \left( \eta(z) \frac{du_x(z)}{dz} \right) = -F_d(z)
\]

- **Black:** Molecular Dynamics
- **Red:** constant viscosity
- **Blue:** inverse power viscosity

\[
\eta(z) = \left[ 1 - \frac{z}{h} \right]^{-p} \eta_{\text{exp}}
\]
Lennard-Jones and Coulomb interaction

**Lennard-Jones**

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

\(\sigma_{ij}\) values:
- O-O: 3.17
- O-Si: 3.27
- O-Cl: 2.86
- Si-Si: 3.75
- Si-Na: 3.39
- Si-Cl: 2.95
- Na-Na: 3.88
- Na-Cl: 2.58
- Cl-Cl: 3.38
- Na+1: 4.45

\(\epsilon_{ij}\) values:
- O-O: 155
- O-Si: 301
- O-Cl: 47.9
- Si-Si: 129
- Si-Na: 584
- Si-Cl: 92.9
- Na-Na: 249
- Na-Cl: 14.8
- Na+1: 39.6

**Electrostatic (Coulomb)**

\[
V_C(r) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r}
\]
Concentration profiles

![Graph showing concentration profiles for different ions (H₂O, Na⁺, Cl⁻) as a function of distance from the channel wall (nm). The graph includes a zoomed-in inset for a smaller scale.]
Lennard-Jones and Coulomb interaction

**Lennard-Jones**

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

**Coulomb**

\[ V_C(r) = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r} \]

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The nearest-to-wall peak of high Na⁺ concentration corresponds to the favorable adsorption sites on the silicon surface.
Potential energy profile of an ions was measured along the line perpendicular to the surface. The line passed through different adsorption sites.
Effects of ionic concentrations

Surface charge: -70 e

Na\(^+\): 108

Cl\(^-\): 38
Effects of ionic concentrations

Surface charge: -70 e

Na\(^{+}\): 100

Cl\(^{-}\): 30
Effects of ionic concentrations

Surface charge: 
-70 e

$\text{Na}^+$: 93

$\text{Cl}^-$: 23
Effects of ionic concentrations

Surface charge: -70 e

Na\(^+\): 78

Cl\(^-\): 8
Effects of surface charge density

Surface charge: -70 e

Na⁺: 100

Cl⁻: 30
Effects of surface charge density

Surface charge: -60 e

\( \text{Na}^+ : 100 \)

\( \text{Cl}^- : 40 \)
Effects of surface charge density

Surface charge: -50 e

$\text{Na}^+: 100$

$\text{Cl}^-: 50$
Effects of surface charge density

Surface charge: $-40 \text{ e}$

$\text{Na}^+$: 100

$\text{Cl}^-$: 60
Low surface charge density flow

Surface charge: 
-4 e

Na\(^+\): 108
Cl\(^-\): 104
Low surface charge density flow

Surface charge: -4 e

$\text{Na}^+: 44$

$\text{Cl}^-: 40$
Low surface charge density flow

Surface charge: -4 e

$\text{Na}^+$: 28

$\text{Cl}^-$: 24
Low surface charge density flow

Surface charge: -4 e

Na⁺: 12

Cl⁻: 8
Conclusions

- Studied temperature, viscosity, and charge density effects on a nanochannel electroosmotic flow by MD simulations
- Obtained velocity, mass flux, ionic concentration, and viscosity profiles
- Justified temperature dependence of water flow direction by thermal release of adsorbed Na\(^+\) ions and spatial variation of viscosity
- Demonstrated an improved prediction of velocity profile from charge density using non-constant viscosity
- Revealed the dependence of the flow on surface charge density and ionic concentrations