Investigation of transport phenomena in nanochannels and its applications in energy conversion using COMSOL Multiphysics

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Outline

- Nanaofluidics: fluid/ion transport
- Electrokinetics: electrical double layer
- Modeling using COMSOL Multiphysics
- Physical problems
- Conclusions
What is “Nanofluidics”?

**Aquaporins (AQP)**

- Slippage
- Electrostatic gate

**Kidney**

Electrostatic repulsion of proteins
Glomerular proteinuria
Engineered Nanofluidics

New nanofluidics (engineered nanofluidics):

1. **Well-designed and controlled nanochannels** are ideal physical modeling systems to study fluidics in a precise manner.

2. Learning **new science** using **controlled regular nanospaces**.


![Diagram showing space size comparison](image)

Silica  |  PET  |  AAO
Electrokinetics

Electrokinetics refers to transport phenomena related to the non-electroneutral EDL, which is created to neutralize the surface charges produced on surface.

Surface charges are produced by the dissociation of surface functional groups:

\[ \text{AH} \leftrightarrow \text{A}^- + \text{H}^+ \]
\[ \text{AH}_2^+ \leftrightarrow \text{AH} + \text{H}^+ \]

EDL thickness (i.e., Debye length) is dependent on salt concentration \( c_0 \):

\[ \lambda_D = \sqrt{\frac{\varepsilon_f \varepsilon_0 RT}{2z^2F^2c_0}} \propto \frac{1}{\sqrt{c_0}} \]

<table>
<thead>
<tr>
<th>KCl solution (mM)</th>
<th>( \lambda_D ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>1.0</td>
<td>10</td>
</tr>
<tr>
<td>0.1</td>
<td>30</td>
</tr>
</tbody>
</table>

DI water: 300nm
**Electro-osmosis** refers to the movement of liquid relative to a stationary charged surface under an external electric field.

- Electrical body force (Coulomb force) is produced within EDL:
  \[
  \mathbf{F}_e = \rho_e \mathbf{E}
  \]

- Liquid motion outside of EDL is driven by **viscous diffusion**

- Plug-like flow

- Net charge density:
  \[
  \rho_e = Fz(c_+ - c_-)
  \]

**Electro-osmotic flow (EOF)** in a thin EDL microchannel
Nanochannel: ion selectivity

Microscale: $a > 1 \mu m >> \lambda_D$

Nanoscale: $a < 1 \mu m \sim \lambda_D$

\[ K_n = \frac{2wh}{l} c_\infty (\Lambda_+ + \Lambda_-) + \frac{2w|\sigma|}{zF} \Lambda_+ \]

- (1) bulk conductance
- (2) Surface conductance

- ion-transport/ion-current control
- electrical sensing
- separators: energy conversion

Silica nanochannels

$K_n (nS)$

$C_\infty$ (molar concentration)
Nanofluidic transistor

\[ \Delta V_g = V_g - V_D/2 > 0 \]

\[ \Delta V_g < 0 \]

Its function looks like a metal-oxide-semiconductor field-effect transistor (MOSFET).

Negatively charged dye: exclusion effect

R. Karnik et al., *Nano Lett.* 5, 943 (2005)
Flow field: incompressible Navier-Stokes equation (continuum theory)

\[ \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \mu \nabla^2 \mathbf{u} + \mathbf{F}_e \]

\[ \nabla \cdot \mathbf{u} = 0 \]

where \[ \mathbf{F}_e = -\rho_e \nabla \phi \]

Poisson-Nernst-Planck model

Electric field: Poisson equation (electrostatics)

\[ \nabla^2 \phi = -\frac{\rho_e}{\varepsilon_f \varepsilon_0} \]

where \[ \rho_e = F \sum_i z_i C_i \]

Ionic concentration field:

\[ \mathbf{j}_i = -\nu_i z_i F c_i \nabla \phi - D_i \nabla c_i + c_i \mathbf{u} \quad : \text{Nernst-Planck equation} \]

\[ \nabla \cdot \mathbf{j}_i = 0 \quad : \text{Species transport equation} \]
**Mathematical Model**

**Geometry:**

- Reservoir
- Nanochannel
- Reservoir

**Boundary condition:**

- Reservoir 1:
  - \( n \cdot \nabla u = 0 \)
  - \( n \cdot \nabla \phi = 0 \)
  - \( n \cdot \nabla c_z = 0 \)

- Nanochannel:
  - \( u = 0 \)
  - \( \nabla \phi = -\frac{\sigma_s}{\varepsilon_f \varepsilon_0} \)
  - \( n \cdot j_z = 0 \)

- Reservoir 2:
  - \( n \cdot \nabla u = 0 \)
  - \( n \cdot \nabla \phi = 0 \)
  - \( n \cdot \nabla c_z = 0 \)

**Symmetric boundary condition:**

- \( p = p_L \)
- \( \phi = \phi_L \) or \( n \cdot \nabla \phi = 0 \)
- \( c_z = c_0 \)
COMSOL Modeling using PDE Mode

- Navier-Stokes eq.
- Poisson eq.
- Nernst-Planck eq.
Validation with PB model

**MESH:** 28000-32000 quadrilateral elements

**Results:** compared with analytical solution of PB model

\[
\sigma_s = -1\text{mC/m}^2
\]

\[
\sigma_s = -3\text{mC/m}^2
\]

\[
\sigma_s = -5\text{mC/m}^2
\]
Streaming current

Under a hydrostatic pressure (\(\Delta p\)), the pressure-driven liquid flow carries the charges within EDL towards the downstream end and results in an electrical convection current, namely the streaming current.

\[
\Delta p = p_2 - p_1
\]

Streaming current: 
\[
I_{str} = S_{str} (-\Delta p) = \int_A \rho_e u_p \, dA
\]
Streaming current in silica nanochannels

140 nm silica nanochannel

\[ I/\Delta P \text{ (pA/bar)} \]

\[
\begin{array}{c}
\text{van der Heyden et al. [2]} \\
\text{self-consistent PB model [1]} \\
\text{present model (} b_{\text{Stern}} = 0 \text{)} \\
\text{present model (} b_{\text{Stern}} = 0.8 b_{K^+} \text{)} \\
\text{self-consistent PNP model [1](} b_{\text{Stern}} = 0.8 b_{K^+} \text{)}
\end{array}
\]

\[ C_0 \text{ (M)} \]

Streaming potential

At open-circuit condition (i.e., zero-current condition), the charges accumulate at the downstream end and then an electrical potential difference called the **streaming potential** (i.e., open-circuit voltage, OCV) is produced.

\[ E_{str} = \frac{\Delta \phi_{str}}{l} \]

**Streaming potential:** \[ I = I_{str} + I_c = 0 \Rightarrow \Delta \phi_{str} = \frac{S_{str}(-\Delta p)}{K_c} \]
**Electro-kinetic battery** refers to the external electronic load driven by the electric power from **streaming current/potential**.
Open circuit voltage versus Short-circuit current

Open-circuit voltage

Short-circuit current
Short-circuit condition: Concentration polarization

\[ \phi = 0 \]

\( \Delta p = 0.01 \text{MPa} \)
\( \Delta p = 0.05 \text{MPa} \)
\( \Delta p = 0.1 \text{MPa} \)
\( \Delta p = 0.2 \text{MPa} \)
\( \Delta p = 0.5 \text{MPa} \)
Numerical results: I-P curve

- Ohmic current region
- Limiting current region
- Over-limiting current region

$I (\mu A/m)\backslash\Delta p (MPa)$

- $C_0$
  - $10^{-5} M$
  - $10^{-4} M$
  - $10^{-3} M$
Numerical results: I-V curve

\( \Delta p = 0.05 \text{MPa} \)

\( \Delta p = 0.1 \text{MPa} \)
Numerical results: I-V curve

\( \Delta p = 0.5 \text{MPa} \)

\( \Delta p = 1.0 \text{MPa} \)
Conversion efficiency

30 nm

60 nm

\( \eta_{\text{max power}} (\%) \)

\( C_0 (M) \)

\( \sigma_s \)

- 1mC/m²
- 3mC/m²
- 5mC/m²
- 10mC/m²

- \( \Delta P \)
- 0.05MPa
- 0.1MPa
- 0.2MPa
- 0.5MPa
- 1.0MPa

- 0.1MPa
- 0.2MPa
- 0.5MPa
Navier slip velocity:

\[ u_s = b \frac{\partial u}{\partial y} \]

where \( b \) is the slip length.
Ion concentration polarization (ICP) - nonequilibrium phenomenon at interface

- **Electromigration flux**
- **Ion depletion**
- **Concentration gradient**
  - $c_n^+ >> c_\infty$
  - $c_n^- << c_\infty$
- **Diffusion flux**
- **Ion enrichment**
Ion depletion and enrichment

~ 60 nm nanochannel

Simulation using COMSOL
Nanofluidic sample preconcentration/desalination

1. bio-sample preconcentration
2. species separation
3. sea water desalination

Applications: Simulation using COMSOL
Electroosmotic pump using a conical-nanopore membrane (cont.)

Electro-osmosis

Electric power ➔ hydraulic power

Track-etched PET membrane

A single conical-shaped nanopore

Load

EO pump cell (membrane)

Liquid reservoir
Electro-osmotic pump using a conical-nanopore membrane

forward bias $\rightarrow$ resistance is decreased.
$\rightarrow$ decreased electric field.
$\rightarrow$ lower pumping efficiency.

Reverse bias: ion-depletion
$\rightarrow$ resistance is increased.
$\rightarrow$ increased electric field.
$\rightarrow$ amplified EK flow.
$\rightarrow$ better pumping efficiency.

Current rectification

|V bias| 0 2 4 6 8 10 |
|---|---|---|---|---|---|---|
|I (pA)| 0 100 150 200 250 |

Flow rectification

|V bias| 0 2 4 6 8 10 |
|---|---|---|---|---|---|---|
|Q (fL/s)| 0 2 4 6 8 |

• Forward bias: ion-enrichment
  $\rightarrow$ resistance is decreased.
  $\rightarrow$ decreased electric field.
  $\rightarrow$ lower pumping efficiency.

• Reverse bias: ion-depletion
  $\rightarrow$ resistance is increased.
  $\rightarrow$ increased electric field.
  $\rightarrow$ amplified EK flow.
  $\rightarrow$ better pumping efficiency.

\( c_0 = 10^{-3} M \)
\( \sigma = 3 \text{mC/m}^2 \)
Reverse electro-dialysis (RED)

Electrodialysis

Electricity ➔ Gibbs free energy of mixing

RED

Gibbs free energy of mixing ➔ Electricity

Diffusion current/potential
RED in a conical-shaped nanopore

\[ a_t = 5\text{nm} \]

\[ a_b = 55\text{nm} \quad a_b = 110\text{nm} \]

\[ l = 5\mu m \]

![Diagram of nanopore](image)
Conclusions

COMSOL Multiphysics

- User friendly
- Flexibility: PDE mode
- A quick simulation tool for continuum nanofluidics and multiphysics
- A very good tool for researchers and graduated students to speed up their research works.