Atomic Scale Design and Three-Dimensional Simulation of Ionic Diffusive Nanofluidic Channels

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Nanofluidics

Nanofluidics refers to the study of the transport of ions and/or molecules in confined solutions as well as fluid through or past structures with one or more characteristic nanometer dimensions. A variety of nanofluidic devices have been extensively developed for molecular separation, detection, crystallization and biosynthesis.

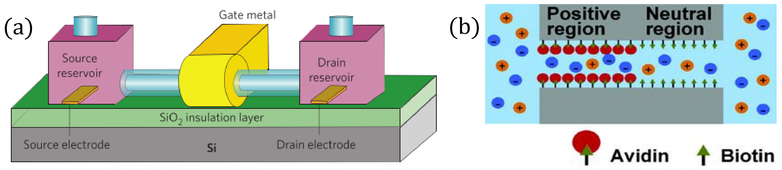

Figure 1: (a) Schematic of a nanofluidic field-effect transistor; (b) Schematic of a nanofluidic diode.

The present work introduces atomic scale design and three-dimensional simulation of ionic diffusive nanofluidic systems.
We propose a variational multiscale framework for ion transport modeling. We derive a generalized Poisson-Nernst-Planck for nanofluidic systems and develop novel mathematical algorithms to attain the second-order accuracy in three dimensional realistic setting.

Reference

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Three Types Of Nanofluidic Channels

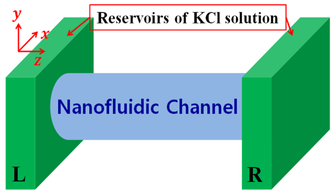

Figure 2: Schematic of a nanofluidic system.

A cylindrical nanochannel, whose radius is 5Å and length is 49Å, is placed at the center of the system.

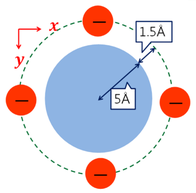

Figure 3: Schematic of an atomic charge distribution.

A number of properly charged atoms are equally positioned around the channel.

Conclusion

Three ionic diffusive nanofluidic systems, including a negatively charged channel, a bipolar channel and a double-well channel, are designed to investigate the impact of atomic charges to channel current, density distribution and electrostatic potential. Numerical findings, such as gating, ion depletion and inversion, are in good agreements with those from the literature.

Acknowledgement

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A Variational Multiscale Framework: Total Free Energy

$$G^{PNP}_{Total}[\chi, \Phi, \{C_\alpha\}] \quad (1)$$

$$= \int \left\{ \chi \left[-\frac{\varepsilon_m}{2}|\nabla\Phi|^2 + \Phi \sum_{k=1}^{N_m} Q_k \delta(\mathbf{r}-\mathbf{r}_k) \right] + (1-\chi)\left[-\frac{\varepsilon_s}{2}|\nabla\Phi|^2 + \Phi \sum_{\alpha=1}^{N_s} C_\alpha q_\alpha \right] \right.$$

$$+(1-\chi)\left[\sum_{k=1}^{N_m} C_\alpha U_{\alpha k} + \sum_{\beta=1}^{N_s} C_\alpha U_{\alpha\beta} \right]$$

$$\left. +(1-\chi)\sum_{\alpha=1}^{N_s}\left[(\mu_\alpha^0 - \mu_{\alpha 0})C_\alpha + k_B T C_\alpha \ln\left(\frac{C_\alpha}{C_{\alpha 0}}\right) - k_B T(C_\alpha - C_{\alpha 0}) + \lambda_\alpha C_\alpha \alpha \right] \right\} d\mathbf{r}$$

Electrostatic interactions:
Fixed charges +Mobile charges

Non-electrostatic interactions:
Channel-solution + Ion-ion or ion-water

Chemical potential of αth ion species:
Reference term + Entropy of mixing + Relative osmotic term

χ is the domain characteristic function, Φ is the electrostatic potential and C_α is the concentration of αth ion species

Coupled Governing Equations

Poisson Equation

$$-\nabla\cdot(\varepsilon(\chi)\nabla\Phi) = \chi\sum_{k=1}^{N_m} Q_k\delta(\mathbf{r}-\mathbf{r}_k) + (1-\chi)\sum_{\alpha=1}^{N_s} q_\alpha C_\alpha \quad (2)$$

Nernst-Planck Equation

$$\frac{\partial C_\alpha}{\partial t} = -\nabla\cdot\mathbf{J}_\alpha \qquad \mathbf{J}_\alpha = -D_\alpha\left[\nabla C_\alpha + \frac{C_\alpha}{k_B T}\nabla(q_\alpha\Phi + U_\alpha)\right] \quad (3)$$

Computational Algorithms

- **Dirichlet to Neumann Mapping** is a computational technique using Green's function to remove charge singularities in the Poisson equation.
- **Matched Interface and Boundary (MIB)** is a numerical scheme to deal with discontinuous coefficients and irregular complex geometries.
- **Successive over relaxation (SOR)-like iterative procedure** is a self-consistent manner to solve the coupled PNP equations simultaneously.

Second-Order Convergence Numerical Test

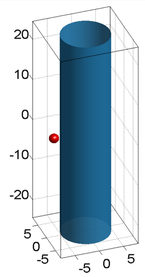

Figure 4: With a single atomic charge

	Mesh size	L_∞ Error	L_∞ Order	L_2 Error	L_2 Order
Φ	$h=0.4$	1.3742E-2	–	3.1647E-3	–
	$h=0.32$	8.7238E-3	2.0362	2.0215E-3	2.0088
	$h=0.2$	3.5614E-3	1.9062	8.7926E-4	1.7712
	$h=0.16$	2.2282E-3	2.1016	5.3548E-4	2.2224
C_1	$h=0.4$	3.8661E-3	–	1.0406E-3	–
	$h=0.32$	2.5648E-3	1.8390	6.4972E-4	2.1106
	$h=0.2$	8.4896E-4	2.3524	2.5014E-4	2.0309
	$h=0.16$	5.4286E-4	2.0039	1.5920E-4	2.0250
C_2	$h=0.4$	2.0352E-3	–	5.3493E-4	–
	$h=0.32$	1.3130E-3	1.9642	3.2772E-4	2.1958
	$h=0.2$	4.7824E-4	2.1488	1.3661E-4	1.8617
	$h=0.16$	2.7990E-4	2.4327	8.0089E-5	2.3930

Table 1: Numerical errors and orders

The computational result attains a good second-order convergence.

A Negatively Charged Channel

The negative atomic charges generate a unipolar current, which can be controlled by modifying the bulk ion concentration and charge.

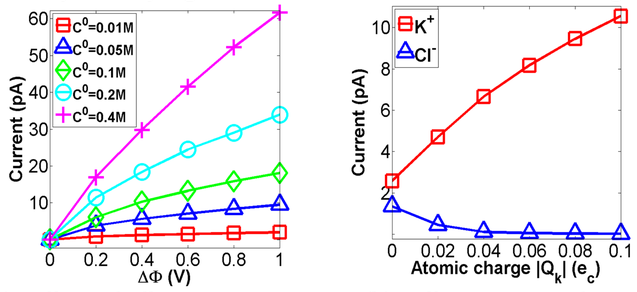

Figure 5: (a) Different bulk ion concentration (b) Different atomic charges

A Bipolar Channel

The bipolar distribution of atomic charges can create accumulation of depletion of both ions in response to the current direction.

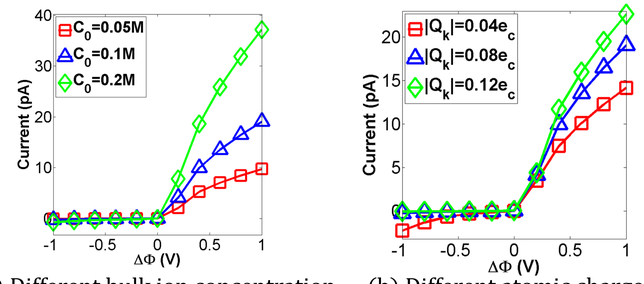

Figure 6: (a) Different bulk ion concentration (b) Different atomic charges

A Double-Well Channel

The special atomic charge distribution of the double-well channel produces two potential wells.

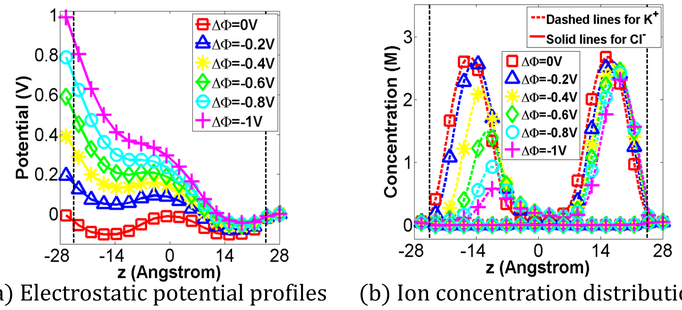

Figure 7: (a) Electrostatic potential profiles (b) Ion concentration distributions