

MOLECULAR DYNAMICS SIMULATION OF NANOCHANNEL ELECTROSMOTIC FLOWS

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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. One important question that needs to be addressed in nanofluidic research is whether continuum theories (e.g., Poisson-Boltzmann equation and Navier-Stokes equations) can be used reliably to predict flow characteristics. In this paper, we study the electroosmotic flow in straight channel of various widths ranging from 0.95 nm to 10.0 nm by using molecular dynamics simulations.

For the various channel widths studied in this paper, the ion distribution near the channel wall is strongly influenced by the finite size of the ions and the discreteness of the solvent molecules. The classical Poisson-Boltzmann equation fails to predict the ion distribution near the channel wall as it does not account for the molecular aspects of the ion-wall and ion-solvent interactions. A modified Poisson-Boltzmann equation based on electrochemical potential correction is introduced to account for ion-wall and ion-solvent interactions. The electrochemical potential correction term is extracted from the ion distribution in a smaller channel using molecular dynamics. Using the electrochemical potential correction term extracted from MD simulation of electroosmotic flow in a 2.22 nm channel, the modified Poisson-Boltzmann equation predicts the ion distribution in larger channel widths (e.g., 3.49 nm and 10.00 nm) with good accuracy.

Detailed studies on the velocity profile in electroosmotic flow indicate that the continuum flow theory can be used to predict bulk fluid flow in channels as small as 2.22 nm provided that the viscosity variation near the channel wall is taken into account. We propose a technique to embed the velocity near the channel wall obtained from MD simulation of electroosmotic flow in a narrow channel (e.g., 2.22 nm wide channel) into simulation of electroosmotic flow in larger channels. Simulation results indicate that such an approach can predict the velocity profile in larger channels (e.g., 3.49 nm and 10.00 nm) very well. Finally, simulation of electroosmotic flow in a 0.95 nm channel indicates that viscosity can not be described by a local, linear constitutive relationship that the continuum flow theory is built upon and thus the continuum flow theory is not applicable for electroosmotic flow in such small channels.

References

[1] R. Qiao and N.R. Aluru, "Ion Concentrations and Velocity Profiles in Nanochannel Electroosmotic Flows," *Journal of Chemical Physics*, 118:10, 4692-4701, 2003.