Surface-charge-induced asymmetric electrokinetic transport in confined silicon nanochannels

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(Molecular dynamics simulations of a NaF solution transport in a confined silicon nanochannel indicated that the water flux and the ionic conductivity through two oppositely charged silicon channels, that are otherwise similar, differ by a factor of more than three, and the co-ion fluxes are in the opposite direction. Such a behavior cannot be predicted by the classical electrokinetic transport theory, and is found to originate from the asymmetric dependence of the transport properties of water near the charged silicon surface. © 2005 American Institute of Physics. [DOI: 10.1063/1.1897430]

Electrokinetic transport, referring to the transport of water and ions induced by an external electric field, is widely encountered in many biological and engineering systems, e.g., ion channels, fuel cells, and chemical analysis devices.1−4 Electrokinetic transport is widely used in nanoscale fluidic systems due to its scalability and ease-of-control.4 In the classical continuum modeling of electrokinetic transport, the ion transport is modeled by using the Poisson-Nernst-Planck equations and the fluid transport (usually referred to as electro-osmotic transport) is modeled by using the Navier-Stokes equations.5 In this letter, through detailed molecular dynamics (MD) simulations, we report on the asymmetric effect of surface charge on the electrokinetic transport of a NaF solution in silicon slit nanochannels. Classical electrokinetic theory predicts that the water flux and ionic conductivity of an electrolyte in two oppositely charged channels are the same if the magnitude of the external electric fields is identical. However, MD simulations indicate that the water flux and the ionic conductivity through a negatively charged silicon nanochannel are more than three times larger compared to those in a positively charged channel with the magnitudes of the external electric field and the surface charge density kept the same. We explain this unexpected behavior by the asymmetric dependence of the transport properties, e.g., viscosity, of the interfacial water on the surface charge.

The simulation system consists of a slab of water/ions confined between two channel walls.5 Each wall is made up of four layers of silicon atoms oriented in the (111) direction. The channel width, defined as the distance between the two innermost wall layers, is 3.49 nm. A total charge of 32e (or −32e) was distributed evenly among the atoms of the innermost layer of the channel wall, giving a surface charge density (σs) of 0.13 C/m² (or −0.13 C/m²). Water was modeled by using the SPC/E model,6 and ions were modeled as charged Lennard-Jones (LJ) particles. The number of ions in the system were chosen to maintain the electroneutrality of the system and the desired ion concentrations at the channel center. The LJ parameters for the O–O, Si–O pairs were taken from the Gromacs force field,7 and those for the ion–ion and ion–O pairs were taken from Ref. 8.

Simulations were performed with a modified Gromacs 3.0.5.7 Periodic boundary conditions were used in the channel length directions (x and y directions). Fluid temperature was maintained at 300 K by a Nose thermostat.9 The electrostatic interactions were computed by using a particle mesh Ewald method with a slab correction.10 The electrokinetic transport is obtained by applying an external electric field Ex, in the x direction. Other simulation details can be found in a prior paper.5 Starting from a random configuration, the system was simulated for 2 ns to reach steady state, followed by a production run of 10 ns.

We first consider the electrokinetic transport of NaF solution through two channels with surface charge densities of 0.13 C/m² (case 1) and −0.13 C/m² (case 2). The external electric field, Ex, is −0.25 and 0.25 V/nm in case 1 and case 2, respectively. Such strong fields are necessary to generate a velocity field that can be retrieved with reasonable accuracy from MD simulations. Figure 1(a) compares the counter-ion concentration profiles in case 1 (counter-ion: F−) and case 2 (counter-ion: Na+). As |σs| is identical, and the size of Na+ and F− ions is comparable, the counter-ion distributions are similar in both cases.11 The co-ion concentration profiles are also similar in both cases and are not shown because of the small contribution of co-ions to the fluid flow. Figure 1(b) compares the water velocity (ueo) profiles for case 1 and case 2 as obtained from continuum and MD simulations. The continuum simulation is based on the Stokes equation:

\[ \frac{d}{dz}[\mu d\varepsilon_{eo}(z)/dz] + \sum_{i=1}^{N} q_i c_i(z) E_{ex,i} = 0, \]

where z is the position across the channel width, \( \mu \) is the water viscosity, \( N \) is the number of ionic species, and \( q_i \) and \( c_i(z) \) are the charge and the concentration of ion \( i \). Here, \( c_i(z) \) is taken from the MD simulation results. The continuum theory predicts a similar velocity in both cases,12 while the MD results predict that \( u_{eo} \) in a negatively charged silicon channel is much higher compared to that in a positively charged silicon channel, and the difference in \( u_{eo} \) between the two cases is mainly due to the different velocity behavior in the region of about 5 Å from the channel wall.

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transport of the co-ions. Table I also shows that the ionic conductivity in case 2 is 3.61 times of that of case 1, even though the number of ions and the magnitude of the surface charge is identical in both cases.

Phenomenologically, the above results can be attributed to the different transport properties of water and ions near the charged silicon surfaces, i.e., the water viscosity \( \mu \) (counter-ion mobility) is much higher (lower) near a positively charged silicon surface compared to that near a negatively charged silicon surface. To evaluate this quantitatively, we computed the effective viscosity of water in the two channels. Specifically, we divided the channel into 5 bins (0–0.46, 0.46–0.76, 0.76–2.73, 2.73–3.03, and 3.03–3.49 nm), and assumed that the viscosity in each bin is represented by an effective viscosity \( \mu_{\text{eff}} \). \( \mu_{\text{eff}} \) in each bin was computed by solving Eq. (1) and requiring that the solution match with the MD velocity at the edge of each bin and at the channel center. Figure 2(b) shows the effective water viscosity in the two channels. We observe that \( \mu_{\text{eff}} \) in the bin adjacent to the positively charged channel surface is 4.90 times of that in the channel center (\( \mu_0=0.736 \text{ mPa s} \)), while the \( \mu_{\text{eff}} \) in the bin adjacent to the negatively charged channel surface is almost the same as that in the channel center. Since in both nanochannels, most of the driving force for the fluid flow exists only within a thin layer near the surface, the different viscosity of the interfacial water can lead to dramatically different water flow in the entire channel. The dependence of the water viscosity on the surface charge has been reported. However, the asymmetric effect of surface charge, to our knowledge, is not known. We also investigated the diffusion coefficient of water in the direction parallel to the surface, \( D_i \), by turning off the external electrical field in case 1 and 2, and by performing equilibrium MD simulations. Figure 3 shows that \( D_i \) is much smaller near the positively charged surface compared to that near the negatively charged silicon surface. This is consistent with the viscosity variation results shown in Fig. 2 which indicate that the water near a positively charged silicon surface is less mobile (more viscous) compared to that near a negatively charged silicon surface.

In summary, we have observed that the electrokinetic transport of water and ions through charged silicon...
nanochannels has an asymmetric dependence on the surface charge. Specifically, for the same magnitude of surface charge, the water flux and ionic conductivity is much higher in the negatively charged silicon channel compared to that in the positively charged silicon channel. Such a behavior is mainly caused by the transport properties of the interfacial water and ions. Though such an asymmetric effect may not significantly alter transport in macroscopic channels, in nanofluidic channels, where the surface-to-volume ratio is very high and a significant portion of the fluid is in contact with the surface, the interfacial properties can govern the overall transport in confined channels. As a result, to predict the electrokinetic transport in nanofluidic systems accurately, it is necessary to model the transport properties of the interfacial water and ions accurately.

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1M. H. Friedman, Principles and Models of Biological Transport (Springer, Berlin, 1986).  
12The two velocity profiles will be identical if the ion concentrations obtained by using the continuum theory are used in the Stokes equation.