Hierarchical Multiscale Computations of Ion Transport in Synthetic Nanopores

Sony Joseph, A. N. Chatterjee and N. R. Aluru
Beckman Institute of Advanced Science and Technology,
University of Illinois at Urbana Champaign, IL-61801
Email: aluru@uiuc.edu Phone : 217-333-1180

There is a growing interest in investigating transport and electrochemical phenomena in synthetic membrane nanopores because of the possibility of mimicking selective ion transport found in protein channels in cell membranes of living systems and also towards development of single molecule detection systems. Several experimental [1, 3, 4] approaches such as the track etch method and the ion beam method have been used with increasing success in recent years to characterize the ionic transport through nanopores of varying diameters.

However, fundamental questions regarding the effects of confinement on diffusion and mobility of ions need to be resolved for better design of these nanopore based devices and to propose novel sensing mechanisms based on chemical functionalization [2]. The traditional Poisson Nernst Planck (PNP) continuum theory typically used in the analysis of electrochemical phenomena in micro-fluidic devices cannot take into account the effects caused by the finite size of the ions and water and the water accessible volume of the nanopore. This requires atomic scale simulations where finite size of ions and water is explicitly treated. However, order of the time scales and the length scales possible in atomistic molecular dynamics (MD) simulations is far less than realistic design calculations. Further, it is known that in small diameter nanopores (~ 2nm and less) the wall partial charges and the polarization effects can influence the transport coefficients. These can be computed from Density functional theory (DFT) or by semiempirical methods to solve the Schrödinger equation. Therefore, a hierarchical multiscale approach is employed that takes into account the quantum effects, by first calculating the atomic partial charges using DFT, and then using these as inputs for the MD simulations to calculate the diffusion coefficient and mobility, and finally using those in the PNP equations to calculate the IV characteristics.

We first performed two level multiscale simulations combining the continuum Poisson Nernst Planck theory and the Molecular dynamics simulations (Figure 2) to obtain Current-Voltage characteristics of nanopores in a silicon dioxide membrane and to investigate the effects of the complex phenomena of conductivity and self diffusion of ions due to the confinement in nanopores. Statistical analysis from molecular dynamics simulations were used to obtain mobility and diffusion coefficient in SiO_2 nanopores 5nm in length and diameters of 3 nm, 2nm and 1.2 nm in 1M KCl and NaCl solutions. The data from these simulations showed that the mobility and diffusion coefficient decreases with decrease in diameter and is significantly different from the bulk especially for diameters less than 2 nm. The transport coefficients obtained were used in a continuum based Poisson-Nernst-Planck solver in a multiscale framework to obtain the I-V curves (Figure 3). Figure 4 demonstrates the partial charges obtained using DFT and semiempirical AM1, which closely matches the data for silica clusters in literature [6]. Preliminary results indicate that the presence of partial charges on the pore walls alter the transport coefficient because the counter ions stick to the walls for pores of small diameters.

[1]   Gu L-Q, Cheley S and Bayley H, 2001, Capture of a single molecule in a nanocavity, Science, 291, p636
[2]   Joseph S., Mashl R., Jakobsson E., and Aluru N. R., 2003, Electrolytic transport in modified carbon nanotubes, Nano Lett., 3, p1399
[3]   Jirage K B, Hulteen J C and Martin C R, 1997, Nanotubule-based molecular-filtration membranes, Science, 278, p655
[4]   Kuo T. C. and Sloan L. A. and Sweedler J. and Bohn P. W., 2001, Manipulating molecular transport through nanoporous membranes by control of electrokinetic flow: Effect of surface charge density and Debye length, Langmuir, 17, p6298
[5]   Murashov, V., 2003, Ab initio cluster calculations of silica surface sites, Journal of molecular structure, 650, p141
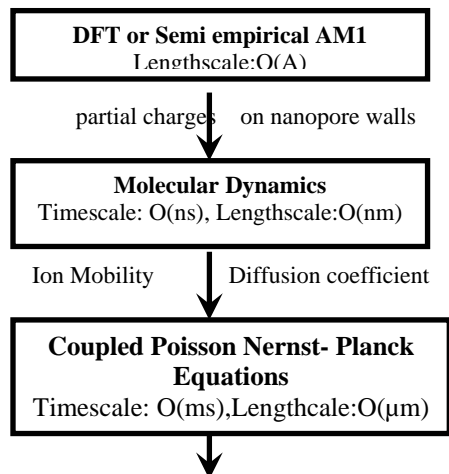
Figure 1: Multiscale Simulation Hierarchy. Partial charges of pore wall atoms obtained from DFT/AM1 are fed into the MD which generates mobility and diffusion coefficients needed for the PNP equation.
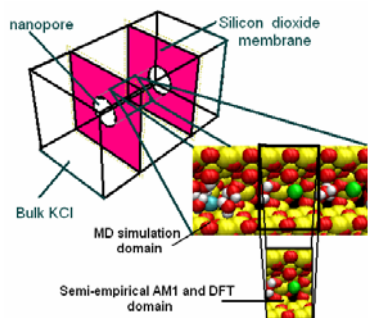

Figure 2: Continuum simulation domain (box), MD, and the semi-empirical AM1 domains with the silicon dioxide wall, water and ions.
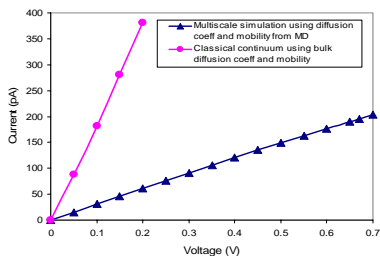

Figure 3: I-V curves obtained by a 2 level multiscale methodology: solving PNP for a 2nm diameter nanopore using bulk diffusion coefficient and bulk ionic mobility, and by using the diffusion coefficient and ionic mobility obtained from MD simulations.

PARTIAL CHARGE	AM1	DFT	CHELPG
Silicon	1.71e	1.61e	1.509e
Oxygen	-0.76e	-0.93e	-0.844e
Hydrogen	0.341e	0.45e	0.466e

Figure 4: Partial charge computations for the wall silanol atoms in the silicon dioxide membrane.
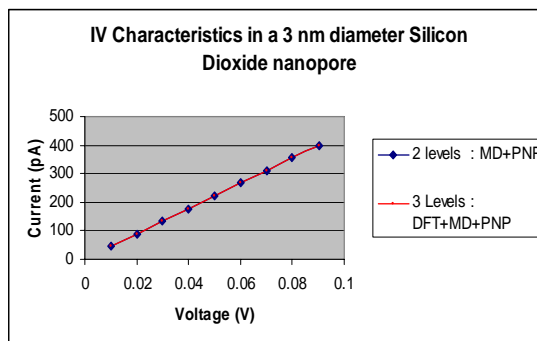

Figure 5: I-V curves obtained by a 3 level multiscale methodology: solving PNP for a 3 nm diameter nanopore using the diffusion coefficient and ionic mobility obtained from the MD simulations with and without surface charge (which is computed from DFT calculations).