A Coupled 3-D PNP/ECP Model for Ion Transport in Biological Ion Channels

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Ion channels are proteins embedded in the membrane of all biological cells, folded in a manner that creates nanoscopic pores that control the flow of ions in and out of the cell. All ion channels carry a highly localized distribution of permanent charge and possess specific properties (e.g., selectivity and switching) that are interesting to the device engineering community. Molecular Dynamics (MD) is the most popular tool for simulating ion channels but computational requirements limits MD simulations to ~100ns whereas measurable current requires much longer timescales. The Poisson-Nernst-Planck (PNP) or Drift-Diffusion theory, can be used to compute macroscopic current in ion channels quickly. However, PNP theory can be problematic when applied to regions of constricted volume, such as the interior of ion channels. The reason is two-fold: firstly, PNP theory replaces discrete charges with a continuous distribution function, grossly underestimating the dielectric boundary force. Additionally, traditional PNP theory ignores the finite volume occupied by the ions and water molecules, as well as the non-singular distribution of charge on the ion. As a result, Coulombic screening can be overestimated, particularly in highly charged regions, leading to unphysically high ion densities. PNP theory also fails to explain the specific selectivity observed in certain ion channels.

The entropic effects of finite-sized ions and water molecules, and the non-singular charge distribution on the ion can be introduced into the PNP formulism by including an additional component to the electrochemical potential. The so-called excess chemical potential (ECP) represents the difference between the electrochemical potential of a "real" ionic solution and that of an idealized solution. Our goal was to incorporate in a 3-D PNP solver (realized with the computational platform PROPHET) an available model for ECP correction (Gillespie, Nonner and Eisenberg, J. Phys.: Condens. Matter, 2002). The ECP has a hard-sphere component, arising from the fact that ions are not point particles so there is an upper limit to the ion density in any given confined volume, and an electrostatic component, due to the fact that ions are not point charges. Both components of the ECP are functions of local charge carrier and water density, and are obtained using Density Functional Theory (DFT). The ECP terms are added to the electrostatic potential in the flux equations, yielding a modified set of PNP equations. To solve the 3-D system of PNP/ECP equations self-consistently we use a decoupled feedback method similar to Gummel's Iteration: The discretized PNP model is solved with Newton's method. The resulting charge carrier densities are used to update the ECP equations. The new values for the ECP are fed back into the PNP equations and the entire process is iterated until convergence.

To test the PNP/ECP model we first consider a simple "hole-in-wall" problem, consisting of a dielectric slab separating two electrolyte baths containing 1M NaCl under equilibrium conditions, i.e. no bias. When there is a fixed charge density (doping) on the "channel" walls the PNP/ECP model shows a significantly lower density of the majority carrier compared to that predicted from traditional PNP theory (Figure 1). In addition, in the absence of fixed charge, the PNP/ECP model indicates a non-negligible departure from charge neutrality inside the channel, arising from the disparity between the two ionic species radii (Figure 2). This result is not available from traditional PNP theory that ignores ion size.

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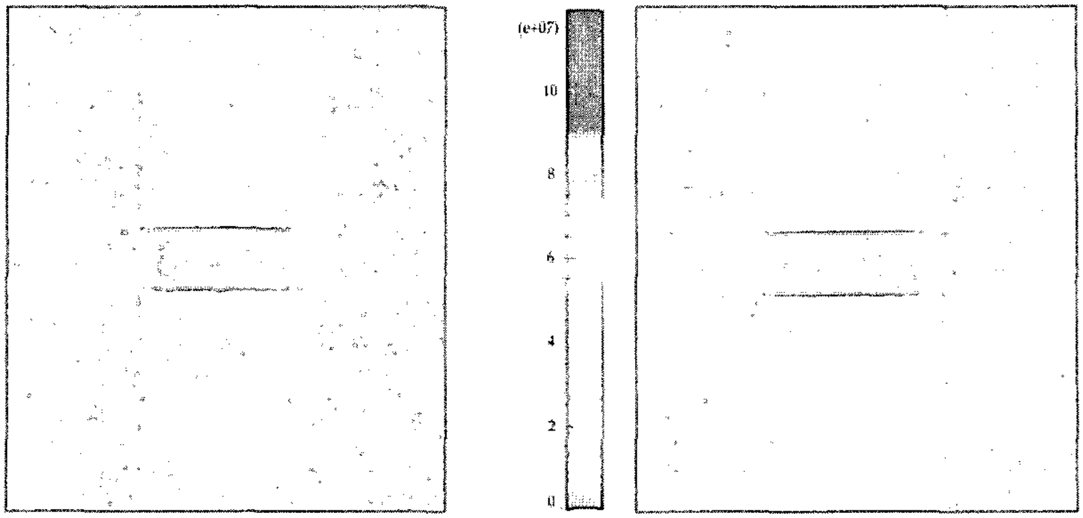

Figure 1. One cutplane along the axis of the channel of the 3-D test structure shows the anion (Cl-) density for a situation with positive fixed charge on the "channel" walls at equilibrium. Left picture shows the result from traditional PNP theory. Right side picture shows the result from modified PNP theory with ECP correction. The scale in the colorbar is: (6.022e6=1000mM/L).

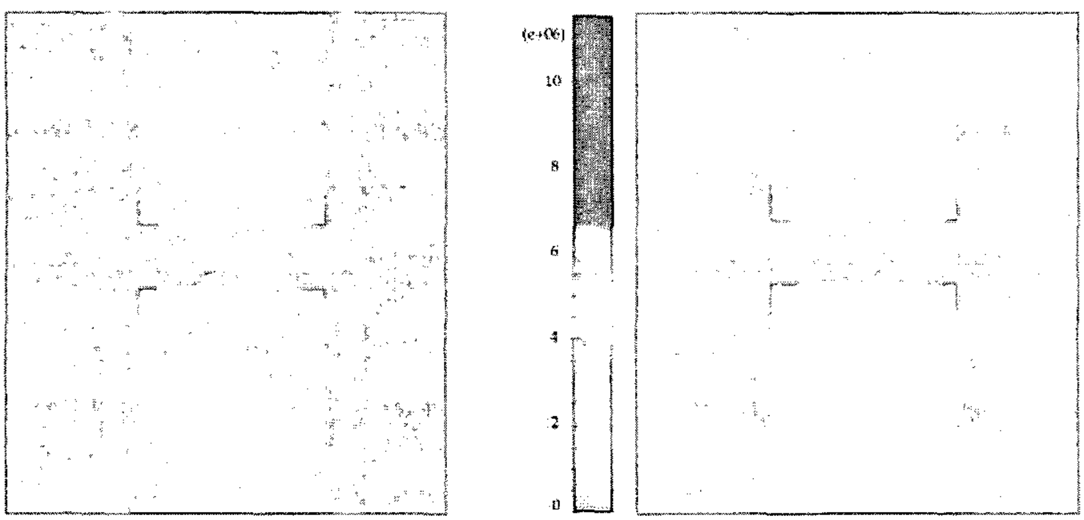

Figure 2. One cutplane along the axis of the channel of the 3-D test structure shows the ion densities at equilibrium for a situation without fixed charge on the "channel" walls from the modified PNP theory with ECP correction. Left picture shows the anion (Cl-) density. Right picture shows the cation (Na+) density. The scale in the colorbar is: (6.022e6=1000mM/L).

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