

Self-Consistent Particle-Based Simulations of Three-Dimensional Ionic Solutions

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ABSTRACT

In this work, the ionic motion in an aqueous electrolyte solution is studied within the framework of a fully self-consistent Langevin-Poisson solver in order to verify the accuracy of the approach. The primitive model is used to describe the individual ions as charged spheres moving in a continuum solvent. The P³M method is used to self-consistently resolve the electrostatic behavior of both the long-range forces of the collective plasma and the boundary conditions, and the short-range inter-particle interactions resulting from the Coulombic force between close ions.

A small test volume representing a portion of the large aqueous electrolyte solution is simulated to calibrate the simulation tool under nonequilibrium conditions. Results of the conductivity of NaCl and KCl solutions are presented for several concentrations and the radial distribution functions in these liquids is discussed.

Keywords: Electrolyte solutions, Brownian dynamics, nonequilibrium.

1 INTRODUCTION

Ion channels are an important class of proteins responsible for controlling the ion flux into and out of cells. These channels are also interesting for their possible application in bio-electronics, more specifically for a new class of bio-sensors. It is therefore important to develop realistic modeling techniques to accurately describe the permeation of charge carriers through these pores. The first step toward a reliable simulation model is to properly represent the ionic solution surrounding the channel.

The goal of this work is to further develop the self-consistent particle-based simulation tool described in [1], and verify the accuracy of the approach by modeling nonequilibrium transport in bulk electrolyte solutions.

In the following sections the self-consistent solver will be presented, including the coupling of the Brownian dynamics with electrostatic interactions. Computational aspects related to boundary conditions and ion injection are also discussed. Finally, the results are presented for a small test volume of dissociate NaCl and KCl solutions at different molar concentrations.

2 SELF-CONSISTENT LANGEVIN-POISSON SOLVER

Particle-based methods are a powerful class of simulation techniques which have long been used to successfully model complex charge transport characteristics in semiconductors [2] [3] and aqueous ionic solutions [2] [4]. These approaches are based on a stochastic representation of the particle motion through phase space governed by interactions with their environment. Particle-based methods are particularly useful for investigating the mesoscopic characteristics of systems because all the spatial and temporal carrier data is stored and easily accessible. Bulk properties are calculated by averaging over the ensemble of individual particles.

An important aspect of these methods is the self-consistent coupling of the particle dynamics with the electrostatic forces. These forces result from external boundary conditions as well as internal particle-particle interactions. The self-consistency is realized by allowing the dynamic properties to evolve with time governed by the electrostatic forces, and periodically updating the forces using the spatial distribution of charge. This alternating approach in calculating the force and charge distribution allows the accurate simulation of transient highly nonequilibrium charge transport [5].

2.1 Brownian Dynamics

The simulation tool in this work is based on the repeated solution of the Langevin equation [6] coupled self-consistently to the Poisson equation. The primitive model [7] is used to describe the ionic transport. Each ion is treated as a Brownian particle in a continuum dielectric and is tracked through phase space governed by the Langevin dynamics. The ions interact with the solvent through the macroscopic properties of water which include the dielectric constant and friction constant [8] [7].

The full Langevin equation is discretized with the first order Euler scheme,

$$\vec{v}(t+\delta t) = \vec{v}(t) - \delta t \left[\gamma \vec{v}(t) - \frac{\vec{F}}{m} - \sqrt{\frac{2\gamma k_B T}{m}} N(0, \delta t) \right], \quad (1)$$

where \vec{v} is the ion velocity, \vec{F} is the total force on the ion, δt is the time step, γ is the friction constant divided

by the ion mass, m is the ion mass, k_B is Boltzmann's constant, T is the absolute temperature and $N(0, \delta t)$ is a random variable, with zero mean and variance δt , that represents the fluctuating force due to bombardment from water molecules.

2.2 Electrostatics

The electrostatics interactions within the ionic solution are accounted for using the P^3M method [2] [9]. Within this approach, the inter-particle force is divided into a smoothly varying long-range component and a short-range part that is only defined for a finite radius.

The long range force is defined on a mesh which includes the external boundary conditions and is calculated from the solution of Poisson's equation. The iterative multigrid method is chosen to resolve the mesh force since the time between consecutive solutions is very short and the change in solution is small. This method is one of the fastest available [10] and is based on a hierarchy of grids with different mesh sizes that are used to simultaneously reduce different error components [11]. The nearest-grid point method is used for the charge assignment and field interpolation schemes.

The short range force due to the Coulombic interaction and the finite-size effect of the ions is calculated using an inverse power equation described in detail in [2] [1]. This expression is dependent on the ionic radius and on the strength of the repulsion between ions. Since neither of these parameters are easily defined, various quantities exist in literature [12] [2] [13]. Simulations using different values will be discussed and compared in the next section.

3 RESULTS

The simulation regime consists of a $20 \times 20 \times 20$ tensor product grid discretized with a homogeneous mesh in 3D with side length 0.5 nm, where the grid size is chosen to be smaller than the Debye length. The number of Brownian particles used in the simulation is determined by the molar concentration being simulated, and is in the range 100-1000. The input parameters are the ion diameter, the hardness (the strength of the short range repulsive force due to the electron cloud overlap), and the friction constant in the Langevin equation. The friction constant is calculated with the Einstein relation [7],

$$\gamma = \frac{k_B T}{mD}, \quad (2)$$

where D is the diffusion coefficient. The parameters used in this work are given in Table 1, where the hardness parameter is equal to 8. Two values are given for Cl ions since the diffusion constant is different in the two electrolyte solutions.

3.1 Ion Injection

A crucial component of this modeling approach is the ion injection applied at the boundaries. Simulation results are sensitive to the velocity distribution of the ions as well as the time evolution of the particle flux across the boundaries. In this work, electrostatic contacts with Dirichlet conditions are located on opposite planes of the 3D volume boundary, while Neumann conditions are imposed on the other four planes. Ions are allowed to pass freely through the Dirichlet contacts and are perfectly reflected from the Neumann boundaries.

At each timestep the correct ion flux needs to be imposed at the contacts. Since the simulated volume represents a portion of a larger electrolyte bath the contact cells are assumed to maintain a constant ion concentration. Therefore the particle flux is determined by the integral of the charge density along the plane perpendicular to the direction of current flow. The velocity of the injected ions is calculated with a Maxwellian distribution. In the direction normal to the contact cells the distribution is a half-Maxwellian directed into the volume and in the other two directions the distribution is a full Maxwellian. This injection technique results in a stable ionic concentration within the simulation volume.

3.2 Current-Voltage Characteristics

To properly calibrate the simulation tool, the conductivity of several dissociated electrolyte solutions are calculated using the current-voltage characteristics. The equivalent conductivity is calculated with the equation [14],

$$\Lambda = \frac{E_y}{zcj_y}, \quad (3)$$

where j_y is the current density in the direction of the electric field, E_y . The molar concentration is given by c and the charge number, z , is unity for the electrolyte solutions in this work.

Simulations were run at a temperature of 298 K and an applied bias of 1 V across the structure. The results of the calculated equivalent conductivity for NaCl for a concentration of 0.1 M is $107.3 \text{ Scm}^2 \text{ mol}^{-1}$, which is in excellent agreement with published data which is $106 \text{ Scm}^2 \text{ mol}^{-1}$ [15]. This value is very sensitive to the diffusion coefficient and the same simulations with the diffusion constant equal to $2 \times 10^{-5} \text{ cm}^2/\text{s}$ (compared with $1.48 \times 10^{-5} \text{ cm}^2/\text{s}$) results in an equivalent conductivity 40 percent higher.

The equivalent conductivity calculated for aqueous solutions of KCl are approximately 20 percent higher than published values for a range of concentrations from 0.1 M to 1 M. The diffusion coefficient used in these simulations are $2 \times 10^{-5} \text{ cm}^2/\text{s}$ which is only slightly higher than experimental values [15] and may be partially responsible for the high conductivity.

Table 1: Ion parameters used in simulations for 298 K.

Ion	mass [amu]	diameter [Angstroms]	friction constant [s ⁻¹]
Cl	35.4527	3.10	3.73×10 ¹³ (KCl) 4.71×10 ¹³ (NaCl)
Na	22.9898	1.54	7.278×10 ¹³
K	39.0983	2.26	3.383×10 ¹³

3.3 Radial Distribution Function

Another important test of the simulation method is the calculation of the radial distribution function (RDF), which relates the probability of finding a pair of ions a specific distance apart, relative to the probability in a homogeneous distribution at the same density [16],

$$g(r) = \frac{1}{\rho N} \left\langle \sum_i \sum_{j \neq i} \delta(\vec{r} - \vec{r}_{ij}) \right\rangle, \quad (4)$$

where $g(r)$ is the RDF for an inter-particle distance r , ρ is the ion density, and N is the number of ions.

This function provides important insight into the liquid structure and can be used to calculate the ensemble average of any pair function, including the free energy, pressure and chemical potential [16]. The knowledge of these three quantities then allows for the calculation of all other thermodynamic functions, resulting in a complete description of the liquid state [7].

The simulated RDF for NaCl and KCl is shown in Fig. 1 and is calculated for a molar concentration of 0.5 M at 300 K. The total simulation time is 10 ns and the RDF is averaged over the last 2 ns with the timestep is equal to 2×10^{-14} s. Since the simulation approach in this work does not include the structure of the water molecules the RDF decays smoothly to unity after approximately 1.5 nm, in this limit the particles are homogeneously distributed. The peak value is higher and sharper for the Na-Cl versus K-Cl because of the smaller radius of the Na ions (see Table 1) so that the particles are able to pack more tightly together. The function goes to zero when the inter-ionic distance is less than the sum of the individual ionic radii. The slope at which the function goes to zero is determined by the hardness parameter which controls the strength of the repulsive force. In these simulations the hardness parameter is equal to 8 [2]. The behavior of like ions is different in that there is no peak in the RDF because there is no attractive interaction.

The volume of the simulation regime is 10 nm cubed and corresponds to approximately 300 anions and 300 cations. The total CPU time for each of these simulations is approximately 20 hours.

4 CONCLUSION

The self-consistent Langevin-Poisson solver has been shown to be applicable for modeling nonequilibrium charge transport behavior in aqueous electrolyte solutions. This test is an important first step toward the development of a simulation tool for modeling ion flow through membrane channels.

The simulations reproduce satisfactory values for the equivalent conductivity for NaCl, but more work needs to be done to determine the correct parameters used in the KCl

The RDF demonstrates the appropriate behavior for the continuum water model used in this work. The RDF does not show the oscillatory behavior that is associated with ion hydration shells and the discrete structure of the water molecules. The implementation of an effective potential (from molecular dynamics or experimental measurements) to correct for this structure would be one approach to reproduce more physical bulk-behavior. Since the primary goal for this simulation tool is to model channels, it may be more useful to interface the Langevin component with an explicit model for the water molecules in a small region around the mouth of the channel [17].

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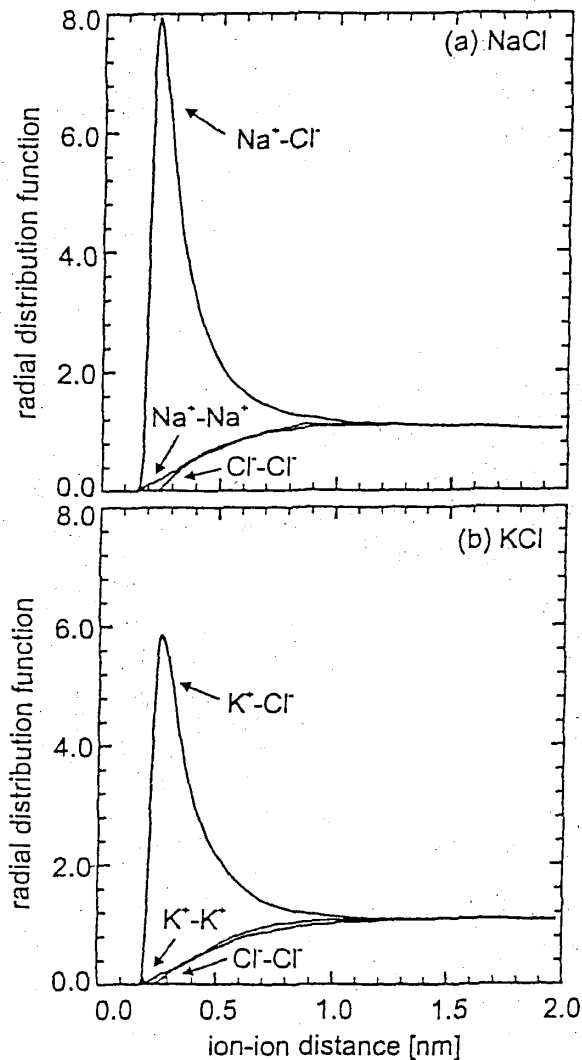


Figure 1: Radial distribution function in NaCl and KCl aqueous solutions at 300K.