494b Non-Additive Force Fields for Ions: Charge Equilibration Models for Chloride, Sodium, and Potassium Ions

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In this contribution, we will discuss the parameterization of polarizable force fields for the chloride, sodium, and potassium ions to be ultimately applied for simulations of ion conductance in narrow, single-ion channels such as the bacterial Gramicidin A channel. The charge equilibration method is applied to the mentioned ionic species by introduction of virtual sites representing the spatial extent of electronic density in the vicinity of the ionic nucleus. Polarization is then effected via the redistribution of charge amongst the constituent sites in the presence of varying electric fields. The ionic polarizability is straightforwardly modeled by an appropriate choice of geometry.

The parameterization of the electrostatic and non-bond components of the force field is based on reproducing gas-phase cluster geometries and energetics of the ion with water; in particular, incremental hydration enthalpies (obtained experimentally from Van't Hoff analysis of gas-phase reaction equilibria) are targeted to obtain the proper balance of interactions. During the parameterization process, the ion force field is intimately coupled to a specific water model, in this case, the fluctuating charge TIP4P-FQ model of Rick et al.

Following discussion of the model parameterization, we will discuss results of molecular dynamics simulations of solutions of sodium and potassium chloride, with particular attention to structural and electronic properties. In the case of the ions, the current approach provides an efficient mechanism to modulate the polarizability of an ionic species by manipulation of the electrostatic model parameters. In solution, this translates to varying degrees of induced polarization of the ions as determined by the model polarizability.

Finally, we will discuss unique properties of polarizable models of ionic species at the liquid-vapor interface. Unlike fixed-charge force fields, polarizable force fields show a segregation of the more polarizable ion in the interfacial region relative to less polarizable species. In the present case, we observe that the polarizable chloride ion density is enhanced in the liquid-vapor interface relative to that of the less polar sodium and potassium ions.