Effect of the Reaction Field on Molecular Forces and Torques Revealed by an Image-Charge Solvation Model

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Abstract. We recently developed the Image-Charge Solvation Model (ICSM), which is an explicit/implicit hybrid model to accurately account for long-range electrostatic forces in molecular dynamics simulations [Lin et al., J. Chem. Phys., 131, 154103, 2009]. The ICSM has a productive spherical volume within the simulation cell for which key physical properties of bulk water are reproduced, such as density, radial distribution function, diffusion constants and dielectric properties. Although the reaction field (RF) is essential, it typically accounts for less than 2% of the total electrostatic force on a water molecule. This observation motivates investigating further the role of the RF within the ICSM. In this report we focus on distributions of forces and torques on water molecules as a function of distance from the origin and make extensive tests over a range of model parameters where Coulomb forces are decomposed into direct interactions from waters modeled explicitly and the RF. Molecular torques due to the RF typically account for 20% of the total torque, revealing why the RF plays an important role in the dielectric properties of simulated water. Moreover, it becomes clear that the buffer layer in the ICSM is essential to mitigate artifacts caused by the discontinuous change in dielectric constants at the explicit/implicit interface.

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1   Introduction

Over the last forty years, better algorithms, faster computers, distributed parallel computing and user-friendly software all contributed [1, 2] to molecular dynamics (MD) becoming an indispensable tool in detailed studies of biopolymers, aimed at gaining insight into mechanisms responsible for biological function [3]. Due to the long-range nature of electrostatic forces, they constitute the key component of MD simulations, affecting the overall speed and accuracy of the method. High accuracy is often needed because electrostatic interactions between molecules are important in biological processes, including signal transmission, ion-transport, molecular recognition, stability and function of biopolymers such as DNA, RNA and proteins. On the other hand, computational cost must be reduced to robustly reach biologically relevant time scales.

The latter consideration motivates the development of implicit solvent models that treat the solute in atomic detail and the solvent as a dielectric continuum to eliminate the molecular degrees of freedom associated with the solvent. A common approach is to solve the linearized Poisson-Boltzmann (LPB) equations to model the effects of the solvent on the solute [4–7]. However, it suffers from two main drawbacks: 1) atomic details of solvent near the surface of solute molecules are neglected where atomic details could be critically important [8], and, 2) the discontinuous change in the dielectric constants at the implicit solvent boundary is a mathematical idealization that leads to artifacts in the electric field within the solute [9]. The alternative approach is the explicit solvent model with full atomic detail for both solute and solvent, which typically employs periodic boundary conditions. A range of explicit solvent methods exist that calculate the electrostatic forces using simple cutoff [10], Ewald summation [11, 12], particle-mesh Ewald (PME) [13, 14], particle-particle particle-mesh [15, 16] and the fast multipole method (FMM) [17–19]. However, for a small simulation box the electrostatic interactions between particles in different periodic image boxes can introduce artifacts [20]. The simple solution to this problem is to increase the box size, but this will incur more computational cost, perhaps to a point of being impractical.

Combining the implicit and explicit approaches, many hybrid models have been [7, 21–23] introduced going back to Kirkwood [24]. However, much care is needed to maintain the homogeneous properties of bulk water while using a hybrid approach because many subtle problems arise due to boundary conditions. We devised the Image-Charge Solvation Model (ICSM) [25] to address these concerns. The ICSM faithfully reproduces the properties of bulk TIP3P waters [26], and solvation free energies, and other key physical properties such as radial distribution functions for the sodium and chlorine ions compared to accurate explicit models [27]. Using more image charges systematically increases the accuracy of the RF within the ICSM. We found that one image charge is sufficient to reproduce bulk water properties at temperatures near 300 K. Interestingly, the relative contribution of the forces from the RF are typically less than 2%. Nevertheless, when the RF is turned off (no image charges used), the dielectric response deviates far from that of bulk water, while structural properties are only marginally affected. These