

DEVELOPMENT AND APPLICATIONS OF REAL-SPACE  
ELECTROSTATIC INTERACTION METHODS FOR  
CHARGE-MULTIPOLES IN CONDENSED PHASE ENVIRONMENTS

Abstract

by

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Computing electrostatic interactions is usually the most expensive portion of a molecular dynamics simulation. Generally, traditional and modified Ewald methods are used for calculating electrostatic interactions in molecular dynamics (MD) communities. But these methods are computationally very expensive for large systems. There is a growing interest in developing real-space methods, which scale roughly linearly with the system size. The real-space method for charge-charge interaction was originally developed by Wolf and extended by Gezelter et al. In this dissertation, I present three new real-space methods: Shifted Potential (SP), Gradient-Shifted Force (GSF), and Taylor-Shifted Force (TSF), for computing electrostatic interactions between charges, dipoles, and quadrupoles. I also discuss the various static and dynamic properties evaluated using the newly developed real-space methods. Additionally, I use three methods: fluctuation, perturbation, and potentials of mean force (PMF), for computing dielectric properties for multipolar fluids.

The SP method is the multipolar version of Wolf's electrostatic method. Similarly, the GSF and TSF method are natural extensions of the original Damped

Shifted Force (DSF) method developed. The energies evaluated using the SP method shows quantitative agreement with the Ewald sum, therefore it is a good choice for Monte Carlo (MC) simulations. The energies, forces, and torques calculated from the GSF method agree with the Ewald's result and produce excellent conservation of energy in MD simulations. Both SP and GSF method with a suitable damping parameter perform remarkably well in predicting static and dynamic properties of liquid systems.

For the both dipolar and quadrupolar fluids, the dielectric properties predicted using the perturbation method agree with those from the fluctuation formula. Real-space methods need a correction factor to obtain dielectric constants and susceptibilities from the directly measurable polarizabilities extracted from the simulation. I tabulate the correction factors for both dipolar and quadrupolar fluid for all real-space methods as well as the Ewald sum. Finally, the dielectric screening from the perturbation and fluctuation method are compared with the directly measured screening factors using the PMF method.