

Harmonic Surface Mapping Algorithm for Electrostatic Potentials in an Atomistic/Continuum Hybrid Model for Electrolyte Solutions

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Abstract. Simulating charged many-body systems has been a computational demanding task due to the long-range nature of electrostatic interaction. For the multi-scale model of electrolytes which combines the strengths of atomistic/continuum electrolyte representations, a harmonic surface mapping algorithm is developed for fast and accurate evaluation of the electrostatic *reaction potentials*. Our method reformulates the reaction potential into a sum of image charges for the near-field, and a charge density on an auxiliary spherical surface for the far-field, which can be further discretized into point charges. Fast multipole method is used to accelerate the pairwise Coulomb summation. The accuracy and efficiency of our algorithm, as well as the choice of relevant numerical parameters are demonstrated in detail. As a concrete example, for charges close to the dielectric interface, our method can improve the accuracy by two orders of magnitudes compared to the Kirkwood series expansion method.

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Key words: Multi-scale modeling, linearized Poisson-Boltzmann equation, Green's function, Harmonic surface mapping, image charges.

1 Introduction

Electrostatic effect is ubiquitous in nature, and have caught broad attention in theoretical and numerical investigations, such as the criticality in electrolytes [42, 47, 63], stability of colloid suspensions [17, 28, 38, 43], and charged biomolecular systems [30, 41, 49]. For all these studies, an accurate model of the electrolyte solvent is essential, which

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have aroused widespread concern up to the present [7, 9, 12, 16, 22, 53]. The explicit solvent model [34, 35], where the solvent is represented explicitly with discrete ions and water molecules, provides an accurate description of the solvent. However, its application becomes limited due to the expensive computational cost. The implicit solvent model [5, 18, 46, 48] replaces atomic details of the solvent with a dielectric continuum, by taking the so-called mean-field approximation of the electrolyte solvent. Such model can dramatically save the computational cost, but the detailed electrostatic interaction between water molecules/ions and the biomolecule is ignored.

An alternative that taking advantage of both models is the multi-scale hybrid model [44, 45]. The hybrid model introduces a spherical cavity within which a microscopic atomistic model is used, while outside the cavity continuum theory is used to describe the (same) electrolyte solvent. In this study, one assumes that the ionic strength lies in the weak coupling regime, where the well-known linearized Poisson–Boltzmann (LPB) equation can be used to approximate the bulk electrolyte solvent accurately [4, 13, 19, 61]. Now the whole simulation system is splitted into two coupled atomistic/continuum regions, one further needs to decide the parameters in the hybrid model, namely the inverse Debye length κ and the inside/outside dielectric constants to self-consistently couple the two regions, i.e., minimize the artificial boundary effect near the spherical cavity. For dilute electrolytes considered here, the inverse Debye length κ can be accurately determined as a function of the ionic densities, while the choice of inside/outside dielectric constants ϵ_1/ϵ_2 depends on different levels of microscopic descriptions inside the cavity. There are two types of model for the inside region: i) in the hybrid *explicit/implicit* model [44], both the ions and solvent molecules are treated explicitly, in that case the dielectric constant inside ϵ_1 should be taken as vacuum permittivity while the outside ϵ_2 takes the permittivity of the solvent; ii) by contrast, in the hybrid *primitive/implicit* model [57] the solvent inside the cavity is modeled implicitly as a dielectric continuum but the ions are treated explicitly, in which case the inside dielectric ϵ_1 should also be taken to be that of the solvent. In recent years, the multi-scale model has been applied in Monte Carlo simulations of 1 : 1 electrolytes and compared with the periodic boundary condition (PBC) using Ewald-based methods [36, 37]. The hybrid model shows its advantage in capturing the correct charge density profile with a smaller simulation domain, while the PBC was found to give artifacts [37]. However, after introducing the multi-scale hybrid model, one needs to solve for the reaction potential inside the cavity due to the implicit solvent outside. Thus it becomes very important to improve the performance in solving the LPB equation in the presence of a spherical dielectric interface.

To solve the electrostatic reaction potential for the hybrid model of electrolytes, a variety of approaches have been proposed. For water solvent, Friedman [20] developed the image charge approximation methods, and later Abagyan and Totrov [2] proposed a modified approximation based on Friedman's approach. These image methods have been extensively used in molecular dynamics or Monte Carlo simulations. The multiple image charge method has also been proposed [10], which can be further accelerated using the fast multipole method (FMM) [11, 25, 26, 58] with $\mathcal{O}(N)$ complexity. And later, the