Comparison of efficient techniques for the simulation of dielectric objects in electrolytes

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ABSTRACT

We review two recently developed efficient approaches for the numerical evaluation of the electrostatic polarization potential in particle-based simulations. The first is an image-charge method that can be applied to systems of spherical dielectric objects and provides a closed-form solution of Poisson's equation through multiple image-charge reflections and numerical evaluation of the resulting line integrals. The second is a boundary-element method that computes the discretized surface bound charge through a combination of the generalized minimal residual method (GMRES) and a fast Ewald solver. We compare the accuracy and efficiency of both approaches as a function of the pertinent numerical parameters. We demonstrate use of the image-charge method in a Monte Carlo simulation using the Barnes–Hut octree algorithm and the boundary-element method in a molecular dynamics simulation using the Particle–Particle Particle–Mesh (PPPM) Ewald method, and present numerical results for the ensemble-averaged induced force between two spherical colloids immersed in an electrolyte.

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1. Introduction

Electrostatic interactions are of fundamental importance for understanding the structure–function relationships of many physical and biological systems, including colloidal suspensions, membranes, biopolymers, and energy devices [1–3]. All-atom computer simulations of such systems are generally prohibitively expensive, due to the required repeated evaluation of the forces or internal energies of molecular configurations. Thus, continuum approximations and coarse-grained models are often adopted. For example, the solvent is usually treated as an implicit continuum described by a (static) dielectric permittivity. The ion distributions in this solvent can be described by mean-field approximations such as the Poisson–Boltzmann theory and its modifications [4–7]. These continuum models have been widely used, but are only accurate in limited parameter regimes, as polarization and many-body effects are often ignored.

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Alternatively, water can be treated in the continuum approximation, whereas the ions are treated as discrete particles, incorporating ionic correlations and ion-size effects. This coarse-graining strategy, the so-called primitive model for electrolytes, is commonly employed in particle-based molecular dynamics (MD) or Monte Carlo (MC) simulations (see, e.g., [8,9]). Although this is a powerful approach, a formidable computational challenge that remains is the rapid calculation of electrostatic polarization due to the dielectric mismatch at material interfaces, such as the dielectric contrast between the implicit solvent and the solutes. Polarization is relevant in a wide range of systems, including colloidal suspensions [10–12], cloud droplets [13,14], and protein folding and stabilization [15]. Determination of the polarization field through analytical solution of Poisson's equation is very difficult. Closed-form representations, in the form of harmonic series, of the Green's function are known only for specific geometries such as planar, spherical, and cylindrical interfaces [16–19,11,20,21]. Moreover, even if the closed-form Green's function is employed, the computation of the harmonic series during simulations can still be too expensive if large systems are investigated.

For these reasons, methods for the determination of electrostatic polarization at dielectric interfaces have attracted significant renewed attention [11,22–25,12]. In certain cases, it is possible to avoid the evaluation of harmonic series via an image-charge representation of the closed-form Green's functions [26–30]. Recently, this *image-charge method* (ICM) has been extended to the treatment of multiple spheres via recursive reflections [31]. This approach not only provides a fast approximation to the Green's function, but also can be easily accelerated by well-known algorithms, because the approximation is a sum of Coulomb potentials. Alternatively, various approaches to direct numerical solution of the Poisson equation using the *boundary-element method* (BEM) have been proposed [32–39,25]. The BEM offers the advantage that arbitrary geometries can be handled with relative ease. Moreover, the BEM facilitates the treatment of periodic geometries commonly employed in electrostatics problems.

Here, two recently developed adaptations of both approaches are investigated in detail. The BEM for general mobile dielectric objects was proposed and implemented in [25,12] for MD simulations. The ICM for multiple spheres was presented in [31]; here we present its first implementation within a MC simulation. For the BEM, surface bound charge is obtained from the solution of a dense linear system via the generalized minimum residual (GMRES) method [40], using a formulation that is particularly well conditioned [41,25]. Moreover, the matrix–vector product required in each GMRES iteration is accelerated by a fast Ewald solver, in our implementation the particle–particle particle–mesh (PPPM) method [42,43] (but note that the BEM is independent of the choice of the solver). This combination of techniques yields a near-linear scaling calculation in the number of discrete boundary elements. For the ICM, the single-sphere image-charge formula is applied recursively using reflections between spheres. The singular or nearly singular quadrature problem for the image line charge integral has been well approximated. The image-charge number is chosen to achieve a specified accuracy at minimal cost. Thus, a set of image charges is constructed that represents the polarization potential. The Barnes–Hut octree algorithm [44–46] is used to efficiently calculate the interaction of a source charge with other charges, in a manner tailored for the single-particle displacements employed in MC simulations [47].

The relevance of polarization problems in wide areas of science makes it pressing to perform a quantitative comparison of the BEM and ICM methods in terms of accuracy, efficiency, and performance. To illustrate these algorithm properties, we present results for a representative problem, namely the ensemble-averaged mean force between a pair of colloidal particles immersed in an electrolyte. The mean force is typically employed to investigate the effective interactions between colloids (although typically without taking into account dielectric effects), and has attracted significant interest in recent years [48–54], due to its fundamental importance in colloidal science. We demonstrate how the simulations can decompose the total mean force into contributions arising from ion–polarization interactions, interactions between bound charges, and entropic effects.

This paper is organized as follows. We first describe the formulations of the BEM and ICM in Sections 2 and 3, respectively (with an error analysis of the ICM in Appendix A). Then, their computational complexity is compared in Section 4, followed by tests of the accuracy and parameter choices of both algorithms in Section 5. In Section 6, we present a practical illustration in the form of MD and MC simulation results for the induced mean force between dielectric colloidal spheres. We conclude with a summary in Section 7.

2. Boundary-element method

Starting from the electrostatic field **E**, we provide a brief derivation of the BEM presented in [25]. At an arbitrary location in the domain $V \in \mathbb{R}^3$, **E** satisfies the differential form of Gauss's law [55],

$$\nabla \cdot \mathbf{E}(\mathbf{r}) = \frac{\rho(\mathbf{r})}{\epsilon_0} \, , \tag{1}$$

and—if no time-dependent magnetic field is present—Faraday's law,

$$\nabla \times \mathbf{E}(\mathbf{r}) = \mathbf{0} \, , \tag{2}$$

where $\rho(\mathbf{r})$ is the total charge density and ϵ_0 the vacuum permittivity. From the Helmholtz decomposition,

$$\mathbf{E}(\mathbf{r}) = -\nabla \Phi(\mathbf{r}) \, , \tag{3}$$