Computer Simulations of Ions in Inhomogeneous Dielectric Materials

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Abstract

In the past, chemical physics computer simulations of ions in an inhomogeneous dielectric material have been performed only for specialized geometries where Poisson's equation can be solved by the use of electrostatic images. Here we report a simulation method that is suitable for general dielectric inhomogeneities.

1. Introduction

With few exceptions, in chemical physics computer simulations of charged particles in a solvent are performed either with the solvent represented by a homogeneous dielectric medium or, less frequently, by a molecular solvent model. Both representations have their drawbacks. In a nanoscale level, dielectric materials are inhomogeneous. An explicit molecular model of the solvent eliminates this problem, but at considerable computational cost so that the simulation is restricted to fairly short runs. In addition, it is difficult to study low ionic concentrations with a molecular solvent since prohibitive numbers of solvent molecules are required.

In many situations, the representation of the solvent by an inhomogeneous dielectric is an attractive compromise. The solution of Poisson's equation at a dielectric interface predicts induced charges. In principle, in a simulation these induced charges can be calculated by solving Poisson's equation anew at each step in the simulation. This is very time-consuming and unattractive. As a result, in chemical physics, at least, simulations of systems with dielectric interfaces has been restricted to a single planar dielectric discontinuity where an explicit solution of Poisson's equation in terms of electrostatic images can be used [1]. Recently, we [2] have proposed what we call the induced charge computation (ICC) method that can be applied to a wide variety of situations. Here, we outline our method and report a few results.

2. Simulation method

In chemical physics, simulations are performed by moving particles, in our case charged particles. If the motion is time ordered and governed by Newton's equations, the simulation is called a molecular dynamics simulation. If the simulation is time independent and generates the members of an ensemble, the method is called a Monte Carlo simulation. The ICC method that we discuss briefly can be applied to either type of simulation. Here we consider the Monte Carlo method with a NVT ensemble, specified by the number of particles, volume, and temperature. Periodic boundary conditions are employed to simulate a macroscopic system.

Our ICC method is a boundary element method derived from a variational formulation of Poisson's equation, given by Allen *et al.* [3], that includes curvature corrections found to be important for correct results. After additional algebraic manipulation and discretization, the vector specifying the induced charge **h** at a dielectric interface can be computed from the matrix equation

$$\mathbf{h} = A^{-1}\mathbf{c}, \tag{1}$$

where A is a matrix that is determined by the geometry of the dielectric inhomogeneity. If, as we assume here, the dielectric inhomogeneity does not change during the simulation, the matrix A need be computed and inverted just once. Only the change in the vector **c**, that is determined by the source charges, and the resulting change in **h** need be computed at each simulation step. Once **h** is known, the simulation proceeds, using the source and induced charges, in a standard manner.

3. Some results

We consider two systems. The first has a single planar dielectric boundary. For this system, the simulation based on the ICC method may be compared with a simulation based on the standard method of electrostatic images. In Fig. 1, we consider ions whose diameter is 0.3 nm in a simulation cell in which the dielectric coefficient is 40 in the left half space and 80 in the right half space. The dielectric coefficient is discontinuous. The boundary is

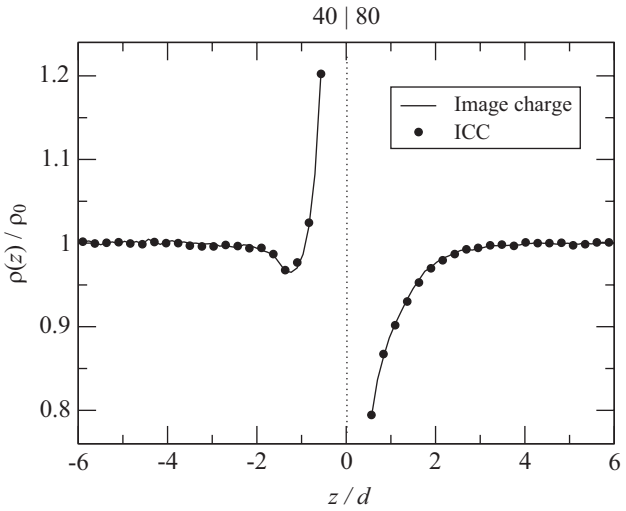

Figure 1. Normalized density profiles for ions in two dielectric half spaces (40 in the left and 80 in the right) separated by an impermeable dielectric boundary. The curve and points give the simulation results with the electrostatic images and ICC methods, respectively.

impenetrable so that ions cannot move from the left half space to the right half space and vice versa. The agreement of the ICC results with those base on the method of electrostatic images is excellent.

In Fig. 2 we show results, again for ions of diameter 0.3 nm, for the case of two dielectric boundaries, where the dielectric coefficient is ε_1 in the left and right half spaces that are separated by a slab of thickness 1 nm, whose dielectric coefficient is ε_2. We use the notation $\varepsilon_1|\varepsilon_2|\varepsilon_1$ to specify the system. Ions on the left cannot enter the slab or the right half space. Similarly, ions on the right cannot enter the slab or the left half space. In contrast to the geometry of Fig. 1, the matrix A is not diagonal.

4. Summary

The ICC method, outlined here, is now being applied to a wide variety of problems, including the interactions between colloidal particles, electrochemistry, and the selectivity of physiological membrane channels. Previously, such boundary element methods were virtually unknown in physico-chemical and biophysical particle simulations.

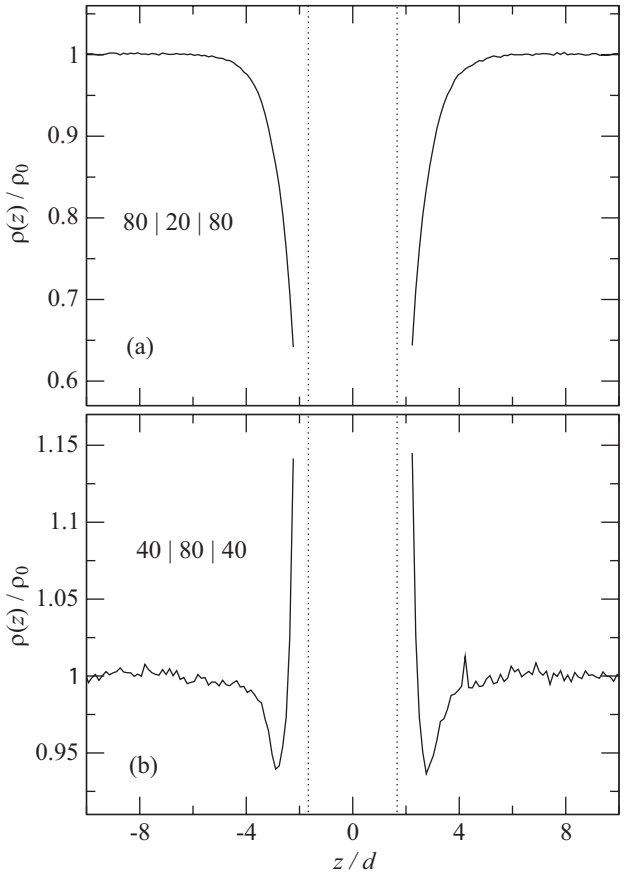

Figure 2. Normalized density profiles for ions on either side of a slab with a different dielectric coefficient. The curves in part (b) are less smooth because they are the result of a shorter run.

5. References

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