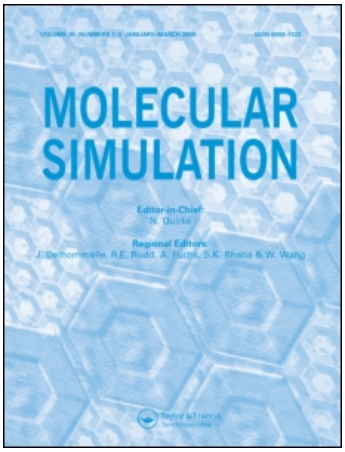

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On the Implementation of Friedman Boundary Conditions in Liquid Water Simulations

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ON THE IMPLEMENTATION OF FRIEDMAN BOUNDARY CONDITIONS IN LIQUID WATER SIMULATIONS

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We have applied the image approximation to the reaction field as suggested by H.L. Friedman [*Mol. Phys.*, **29**, 1533 (1975)] by investigating appropriate cavity sizes and system parameters for use in molecular simulations. The energy of and the structure around a central simple point charge (SPC) water molecule in a dielectric cavity was found to be in good agreement with the properties of a liquid sample. To confine the water molecules within the cavity, we introduced a short-range repulsion between a real charge and its image as the Lennard-Jones repulsive potential between oxygen atoms of the SPC potential. For a system of 65 water molecules a cavity radius of 10.45 Å is appropriate; this radius is altered to 12.00 Å for a cavity surrounding 113 molecules. The effect of the boundary is restricted to the outermost water layer which is in contact with the dielectric continuum.

KEY WORDS: Friedman boundary conditions, liquid water, SPC potential

1 INTRODUCTION

The long-range nature of dipolar interactions has caused some concern as to appropriate boundary conditions for simulating liquid water [1–12]. Periodic boundary conditions impose a long-range ordering between different cells, a phenomenon which may introduce non-physical results for strongly solvated dipoles or ions in water. This effect is present whether the interactions are truncated or smoothly tapered off within the unit box. Exact calculation of the long-range electrostatic forces in a periodic system is possible using Ewald sums [13]. The reaction field method [14], which truncates the long-range dipole-dipole interactions and replaces it with a new short-range contribution, does not circumvent the periodicity of the system.

In the method suggested by Friedman [1], a sample of polar fluid is enclosed in a dielectric medium with the same dielectric constant as the fluid. The reaction field caused by the polarization of the dielectric medium is approximated by image charges. This is accurate when the dielectric constant of the system is large. Dielectric cavities have also been used in quantum chemical calculations of proton transport [15] and in the study of conformational equilibrium [16].

Other non-periodic boundaries proposed introduce a hydrophobic surface layer, either with water-boundary forces calculated from an explicit shell of fixed atoms [17] or from a mean field approach [18, 19], enveloping the region of interest. An outer buffer zone governed by Langevin dynamics acts as buffer and heat reservoir.

Neither of these models includes long-range interactions caused by the reaction field.

This work is thus intended to establish practical implementation of the image boundary conditions and to test the method on liquid water.

2 SIMULATIONS

In the image approximation to the reaction field [1] of a spherical cavity of radius a, the reaction potential generated by a real charge, e, located at $\mathbf{r}$ relative to the cavity center, is that of an image charge of magnitude,

$$e_{im} = -(\varepsilon - 1)/(\varepsilon + 1)a/r\, e \tag{1}$$

located at,

$$\mathbf{r}_{im} = (a/r)^2\mathbf{r}. \tag{2}$$

Higher order terms to the image approximation add corrections on the order of $(\varepsilon + 1)^{-1}$, which for water becomes negligible due to the high dielectric constant of water. The reaction potential is the sum of all images of the sources within the cavity. The effective interaction of all charged particles in the cavity is then,

$$U(\mathbf{R}) = U^d(\mathbf{R}) + \sum \sum u_{jk}(\mathbf{r}_j, \mathbf{r}_k) \tag{3}$$

where $U^d(\mathbf{R})$ signifies all direct charge and Lennard-Jones interactions between the set of $\mathbf{R}$ molecules within the cavity, and $u_{jk}(\mathbf{r}_j, \mathbf{r}_k)$ is the interaction between the j:th real charge within the cavity and the k:th image charge,

$$u_{jk}(\mathbf{r}_j, \mathbf{r}_k) = 1/2\, e_j e_k / |\mathbf{r}_j - \mathbf{r}_k|, \tag{4}$$

where the double summation runs over all charged particles. As a charge approaches the cavity boundary the u_{jj} term becomes infinitely attractive and it is necessary to augment Equation 4 with a short-range repulsive term, u^*_{jj}. For the simulations presented here this was chosen to be the short range A/r^{12} repulsive term of the oxygen-oxygen interaction of the water model.

The water potential used was that of the Simple Point Charge (SPC) model constructed by Berendsen et al. [20] which has been shown to give reliable results for liquid water properties. The equations of motion in the molecular dynamics simulation were integrated using the velocity Verlet algorithm [21] with a timestep of 1.0 femtosecond. The molecules were treated as rigid, and the internal bond and angles were maintained by a Shake and Rattle scheme [22]. The temperature was kept at 300 K by periodically rescaling the velocities. The initial configurations were taken from an equilibrated sample of liquid water in which the edge molecules have been shaved off to fit into the cavity. One molecule located at the origin of the cavity was kept fixed. As the dielectric constant of SPC water is roughly 70 [23–26] we chose to set the ratio $(\varepsilon - 1)/(\varepsilon + 1)$ equal to one. It is only for models with disparately low dielectric constants [27, 28] one needs to use the correct ratio. An initial 30 picosecond equilibration was the followed by a 200 picosecond sampling run in which the properties of the central molecule was monitored. The three systems analyzed here consist of 65 water molecules with cavity radii of 9.75 (system

A) and 10.45 (system **B**) Ångström, and a 113 molecule system with a 12.00 Ångström radius (system **C**).

3. RESULTS AND DISCUSSION

With the image approximation boundary method the particle density number is not exactly $N/(4\pi a^3/3)$, as the available volume for the particles is not easily defined. The standard density for liquid water is ~ 0.034 molecules/Å^3, a value which would lead to a cavity radius of 7.7 Å for the 65 particle system. We have tested different cavity radii empirically in order to achieve the correct liquid water structure around the central molecule. In Figure 1 we plot the oxygen-oxygen radial distribution function of the central molecule with the surrounding molecules inside the cavity for different system specifications. This is also compared to a simulation of 216 water molecules using periodic boundary conditions [12]. The structure of the fluid is sensitive to the location of the dielectric boundary. Using cavity radii between 7.7 and 9.0 Å for the 65 particle system leads to a very strong correlation of water molecules at the cavity boundary and non-physical liquid water properties. As seen in Figure 1 at a radius of 9.75 Å (system **A**) the aggregation of molecules at the surface is not present and the first peak has approximately the right intensity. However the second peak, indicative of the tetrahedral ordering of liquid water, is conspicuously absent. Extending the radius to 10.45 Å (system **B**) alters neither the first peak position nor its intensity but does restore the tetrahedral coordination. The first two layers are thus correctly modelled, but as seen in Figure 1 the structure after 6 Å is affected by the boundary. In enlarging the system with one more layer of water molecules to 113 molecules we fine-tuned the cavity radius to 12.00 Å (system **C**) to give the liquid optimal water structure. In this system the peak positions and intensities are reproduced up to the third peak in the oxygen-oxygen distribution function.

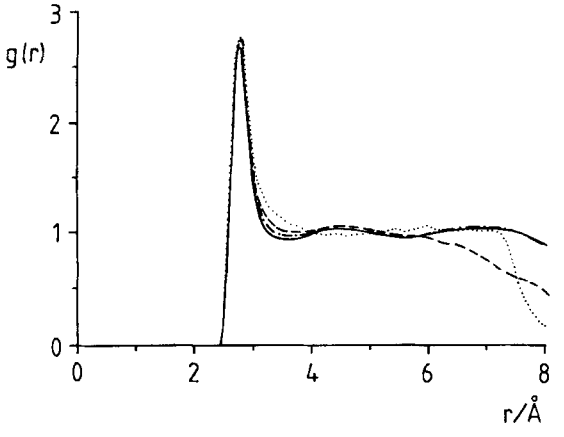

Figure 1 The oxygen-oxygen radial distribution function of the central water molecule with surrounding waters for N = 65, a = 9.75 Å (···), N = 65, a = 10.45 Å (– – –), N = 143, a = 12.00 Å (– · – · –), and compared to a simulation of 216 molecules employing periodic boundary conditions (———).

The information from the oxygen-hydrogen radial distribution function is similar to that of the oxygen-oxygen distribution function but does not reveal the removal of tetrahedral structure for the compressed cavity. The strength of the hydrogen bond between the central molecule with its neighbor is virtually the same for all systems investigated here. Thus the influence of too small a dielectric cavity is rather subtle with the second nearest neighbor coordination of the liquid changed.

The potential energy of the central molecule with the surrounding water and dielectric media is -41.5 and -41.7 kJ/mole for the N = 65, $a = 10.45$ Å and N = 113, $a = 12.00$ Å systems, respectively. This can be compared to the range of values between -41.1 to -41.9 kJ/mole for periodic systems with 125 to a 1000 water molecules, using either a truncation of the potential or an Ewald summation of the electrostatic interaction [12]. Thus the potential energy is reproduced satisfactorily with the image boundary conditions.

Image boundary conditions are feasible to use in computer simulations of liquid water systems. The primary drawbacks are that water molecules in the outermost rim layer are affected by the cavity, which means that at least a shell of two water layers is required to remove any spurious effects from the boundary conditions. Secondly, the method does not lend itself for usage in systems with low symmetry such as solvation of elongated molecules. Finally a rough knowledge of the dielectric constant of the model system is necessary. The advantages are that the reaction field can be correctly included in the simulation to order of $(\varepsilon + 1)^{-1}$, and that possible misleading effects of long range correlations are removed.

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