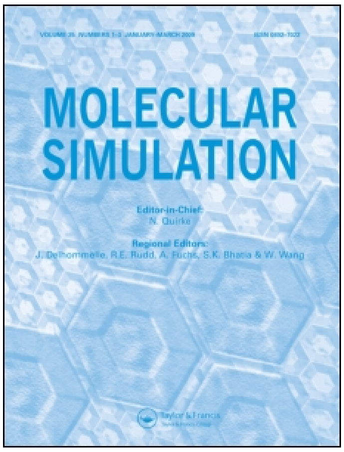

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Molecular Dynamics Simulations with Interaction Potentials Including Polarization Development of a Noniterative Method and Application to Water

T. P. Straatsma[a]; J. A. McCammon[a]
[a] Chemistry Department, University of Houston, Houston, Texas, USA

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MOLECULAR DYNAMICS SIMULATIONS WITH INTERACTION POTENTIALS INCLUDING POLARIZATION

Development of a noniterative method and application to water

T.P. STRAATSMA and J.A. McCAMMON

Chemistry Department, University of Houston, 4800 Calhoun Road, Houston, Texas 77204-5641, USA

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A general method is suggested for the implementation of polarization in molecular dynamics simulations of small molecules. Induced dipole moments are evaluated on selected polarizability centers and represented by separation of charges. The positive polarization charges reside on the selected atoms. The negative polarization charges are treated as additional particles. The positions of these polarization charges are determined from the electrical fields due to the permanent charges of the system. Thus the induction is treated explicitly, while the higher order contributions, the polarization due to induced dipoles, are taken into account in an average way by modification of potential parameters. The forces can be evaluated for the new charge distribution in the conventional way. As an illustration of this approach initial results are reported for the development of a polarizable water model. The higher order polarization is treated in an average way by slight increase of the permanent charges as compared to the values that would give the gas phase dipole moment. The increase in CPU time is comparable to the addition of one atom per polarizable center.

KEY WORDS: Molecular dynamics, polarization, water.

1. INTRODUCTION

The potential field used in molecular simulations is generally based on the assumption of pairwise additivity of interactions. Although the importance of non-pairwise-additive contributions is recognized, the computational expense associated with the self consistent solution of the induced dipoles often has been a reason for not including in molecular simulations the evaluation of interactions beyond two-body terms. For simulations of bulk liquids the average effect of polarization is isotropic, and effective pair models have been developed that include the mean non-pairwise-additive effects. Parameters for these models are usually optimized by reference to experimentally determined thermodynamic properties. These models may give correct results for simulation of bulk liquids, but a correct description of solutions or wall effects can not be expected.

Several attempts have been made to improve on the effective pair potentials through inclusion of non-additive contributions, among others, by Caillol *et al.* [1, 2] and Murad and coworkers [3]. One of the most studied liquids is water, for which several pair potentials and effective pair potentials have been developed and proved to be reasonably adequate in molecular simulations. Methods to treat nonadditive effects in simulations of water have been suggested by a number of authors. Explicit treatment of three-body interactions as suggested by Wojcik and Clementi [4] may become rather cumbersome when applied to complex systems. The polarizable electropole model developed by Barnes *et al.* [5] correctly treats the electrostatic interactions up to the level of quadrupole moments. The model includes Lennard-Jones, point dipole, point quadrupole and point polarizability interactions. The interactions in this model are rather complicated compared to the much simpler point charge models. Rullman and van Duijnen [6] added an anisotropic point polarizability to the simple point charge model SPC developed by Berendsen *et al.* [7], using charges that reproduce the vacuum dipole moment of water. Stillinger [8] proposed a water model consisting of individually polarizable atoms that form a water molecule that is allowed to dissociate. The electric fields in this model are damped for decreasing distance between two polarizable centers so as to prevent the polarization catastrophy, the infinite polarization of two point polarizabilities that come too close together.

In all the above schemes, and other related ones such as that of Lybrand and Kollman [9], the induced moments depend on all other induced moments and therefore have to be evaluated self consistently, usually by an iterative procedure until convergence has been achieved. The complex charge-dipole and dipole–dipole interactions make it quite demanding in terms of computer time to calculate the forces.

Recently Sprik and Klein [10] developed a model for polarizable water in which the polarizability is represented by four point charges treated as a Gaussian charge distribution.

In this work a potential model implementation is described that includes polarization explicitly to first order only. Higher order polarization is treated in an average way, very similar to the treatment of the average effect of the total polarization effects by the effective pair potential models. The level of approximation of the method thus lies between the simpler effective pair models and the more rigorous and more CPU extensive self consistent field approaches. To circumvent the complex evaluation of forces involving the dipoles, the induced dipoles are represented by a separation of charges. This allows for the calculation of forces involving charges only. For each polarizable center one additional point charge is added to the system.

The method is illustrated on a simulation of liquid water, for which potential parameters are optimized to give the experimental density and vaporization energy. The method suggested is not specific for water. Any small molecule where it seems reasonable to assign a polarizability to one particular atom can, in principle, be treated using this approach.

2. THEORY

The basic theory of the interactions between polarizable molecules is well known [11, 12]. A summary of the derivation of the formulae most relevant to this article will be given. Consider a point charge Q at a distance R from an isotropic point polarizability α. The electrical field at the position of α due to the presence of the point charge Q is

$$\mathbf{E} = \frac{1}{4\pi\varepsilon_0}\frac{Q}{R^3}\mathbf{R} \qquad (1)$$

At the position of the point polarizability, the electrical field will induce a dipole, with dipole moment

$$\boldsymbol{\mu}^{ind} = \alpha\mathbf{E} = \frac{\alpha}{4\pi\varepsilon_0}\frac{Q}{R^3}\mathbf{R} \tag{2}$$

This induced dipole can be represented by two charges q and $-q$, separated a distance $\mathbf{r}$ in the direction of the local field $\mathbf{E}$,

$$\boldsymbol{\mu}^{ind} = q\mathbf{r} \tag{3}$$

If the assumption is made that $r \ll R$, then $R - \frac{1}{2}r \approx R$ and $R + \frac{1}{2}r \approx R$. The force exerted on the charge q by the point charge Q is then

$$\mathbf{F}_q = \frac{1}{4\pi\varepsilon_0}\frac{qQ}{R^3}\mathbf{R} \tag{4}$$

If the system is at equilibrium at the charge separation r, this force is compensated for by an opposite force, equal in magnitude but with opposite sign, that drives the separation of charges back towards the original position of α,

$$\mathbf{F} = -\frac{1}{4\pi\varepsilon_0}\frac{qQ}{R^3}\mathbf{R} = -\frac{\boldsymbol{\mu}^{ind}q}{\alpha} = -\frac{q^2}{\alpha}\mathbf{r} \tag{5}$$

For a collection of charges Q_i and isotropic point polarizabilities α_j the potential at position k is given by

$$V_k = \sum_{i \neq k}\frac{Q_i}{4\pi\varepsilon_0 r_{ik}} + \sum_{j \neq k}\frac{\mathbf{r}_{jk}\cdot\boldsymbol{\mu}^{ind}}{4\pi\varepsilon_0 r_{jk}^3} \tag{6}$$

where $\mathbf{r}_{mn} = \mathbf{r}_m - \mathbf{r}_n$. The induced dipole moments $\boldsymbol{\mu}_j^{ind}$ arise from the local electrical field at j,

$$\boldsymbol{\mu}_j^{ind} = \alpha_j\mathbf{E}_j \tag{7}$$

This electrical field is due to all charges and induced dipoles,

$$\mathbf{E}_k = \sum_{i \neq k}\frac{Q_i\mathbf{r}_{jk}}{4\pi\varepsilon_0 r_{jk}^3} + \sum_{j \neq k}\frac{(3\mathbf{r}_{jk}\mathbf{r}_{jk} - \mathbf{I}r_{jk}^2)\boldsymbol{\mu}_j^{ind}}{4\pi\varepsilon_0 r_{jk}^5} \tag{8}$$

These equations represent a system of linear equations in $\boldsymbol{\mu}_j^{ind}$.

3. IMPLEMENTATION IN MOLECULAR DYNAMICS

The treatment given above suggests that polarization can be included by adding an additional particle carrying charge only to each polarizable atom in the system. This additional particle would be bound to the polarizable atom with the usual harmonic bond interaction, with a zero equilibrium distance and a force constant q^2/α. To be able to use this particle in Newton's equations of motion it would also need to have mass. Because of the added inertia, the polarization charge will not adjust its position instantaneously to the changing electric field as is required if it is to represent an induced dipole. To remedy this problem the positions of the polarization charges could be energy minimized prior to the evaluation of forces. This has to be done every dynamic step and will make simulations rather inefficient.

Another possible solution to this problem is given by the following approach. Given a configuration of molecules, the electrical field on all polarizable atom positions is evaluated. This can be performed for the permanent charges in a single step. With the calculated electrical fields $\mathbf{E}_k$, the position $\mathbf{r}_l$ of an additional particle l, carrying a charge q_l only, can be evaluated from

$$\mathbf{r}_l = \mathbf{r}_k + \frac{\alpha_k \mathbf{E}_k}{q_l} \tag{9}$$

At this point the procedure could be repeated, using the permanent charges and the polarization charges representing the induced dipoles, to obtain a new set of electrical fields $\mathbf{E}_k$, from which new polarization charge positions can be evaluated. Repeating this step until convergence will yield, within the approximation of representing the induced dipoles by separated charges, the solution to equation (8).

The contribution of the permanent atomic charges in the first step will be the most important. Analogous to effective pair potentials, in which the average total effect of polarization is represented by modified potential parameters, the average effect of polarization due to induced dipoles can be represented by modified parameters. A model is then obtained that explicitly treats the first order polarization, without the need for iterative solution of the total induced dipole moments.

With the new set of coordinates all forces can be evaluated using standard procedures since no additional interaction types are present. The force between polarization charges and their corresponding polarizable atoms can be represented by a harmonic force with force constant q^2/α. This is not really necessary, however. The net force on the polarization charges will to a reasonable approximation be in the direction of the electric field at the polarizable atoms. Since the evaluated polarization charge positions are in equilibrium, the net reacting opposite force is equal in magnitude. Therefore it seems justifiable to add the evaluated forces on the polarization charges directly to the forces on the corresponding polarizable atoms and subsequently perform the time step for the atomic centers only. This approximation will be reasonable if the charge separation is small, i.e. if the polarization charge is large. If a charge comes close to a polarizability, the charge separation may be large. In that case the influence of the other charges in the system will be small and the polarization charge will be put on the line connecting the charge and the polarizability. The force on the polarization charge will then still be approximately in the direction of the electrical field on the polarizable center and the displacement of the forces will still be allowed.

Since the induced dipoles are represented by separated charges, an additional term in the energy expression is needed, corresponding to the energy it costs to distort the molecule to its polarized state [12]. This energy is given by

$$U^{pol} = \frac{1}{2} \sum_i \frac{\mu_i^2}{\alpha_i} \tag{10}$$

4. A POLARIZABLE WATER MODEL

Results will be given in this section on the application of the above outlined approach to water. The simulations reported are for a system of 216 water molecules. Cubic periodic boundary conditions are applied. The cut-off distance is 0.9 nm. Simulations were performed for the isothermal-isobaric ensemble, using weak coupling to an external heat and pressure bath to maintain temperature and pressure [13] at 300 K and 10^5 Pa. The coupling relaxation times are 0.2 and 0.5 ps for temperature and pressure, respectively. The timestep for the integration of the equations of motion, using a leapfrog algorithm [14], is 1 fs.

The water geometry is the SPC geometry, with bondlengths of 0.1 nm and the tetrahedral bond angle [7]. The molecular interactions are described by electrostatic interactions between point charges on the positions of the atoms, and a Lennard-Jones type non-bonded interaction between oxygen atoms. In the simulations the bond lengths and bond angle of this water model are held fixed using SHAKE [15].

The water molecule is given one polarizability on the oxygen position. The electrical fields determining the induced dipole moments are evaluated to first order, i.e. from the permanent charges only. The influence of induced dipoles on the electrical fields is represented in an average way by slightly enhancing charges on hydrogen and oxygen compared to the charges that give the experimental vacuum dipole moment of water. The Lennard-Jones repulsion, the hydrogen charge and the polarization charge are available as adjustable parameters to fit thermodynamic properties to experimental values.

The polarization charge was fixed to $-8.0\,e$, while the Lennard-Jones repulsion and hydrogen charge are fitted to give the experimental density and vaporization energy. After optimization of the parameters, the following results are obtained from a simulation of the system for 50 ps, following a 50 ps equilibration run. Results are given in Table 1 with label STR/1. For comparison published results for the SPC and SPC/E models for water are also given [12]. The radial distribution functions for oxygen–oxygen, oxygen–hydrogen and hydrogen–hydrogen are given in Figures 1, 2 and 3. Also shown are the distribution functions obtained for the SPC/E water model [12] and experimental distribution functions obtained from neutron diffraction measurements by Soper and Phillips [16]. The general shape of the oxygen–oxygen radial distribution function is correct. The first peak in this distribution is shifted to

Table 1 Molecular dynamics simulation results for SPC, SPC/E and STR/1 water models.

	SPC	*SPC/E*	*STR/1*	*Experiment*
q_H/e	0.41	0.4238	0.351739	
q_{pol}/e			−8.0	
C6/10^{-3} kJ·mol^{-1} nm^6	2.61691	2.61691	2.66191	
C12/10^{-6} kJ·mol^{-1} nm^{12}	2.63324	2.63324	3.01500	
$\alpha\cdot(4\pi\varepsilon_0)^{-1}$/nm^3			0.001445	0.001445
Run length/ps	20.0	27.5	50.0	
T/K	308.0	306.0	303.6	
p/10^5 Pa	−1.	6.	1.7	
U^{pot}/kJ·mol^{-1}	−37.7	−41.4	−41.61	−41.5
U^{pol}/kJ·mol^{-1}			12.78	
U^{pol}_{corr}/kJ·mol^{-1}	3.74	5.22	0.21195	
ρ/kg·m^{-3}	970.0	998.0	994.9	995.0 (305 K)
μ_{ind}/10^{-30} Cm			2.564	
μ_{perm}/10^{-30} Cm	7.585	7.841	6.509	6.171 (vac)
μ_{total}/10^{-30} Cm	7.585	7.841	8.972	
Diff. const./10^{-9} m^2 s^{-1}	4.3	2.5	3.1	2.7 (305 K)

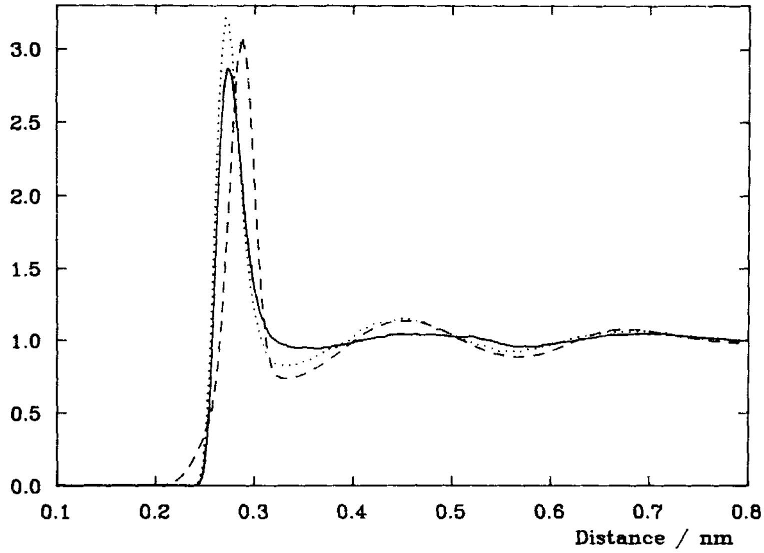

Figure 1 Radial oxygen–oxygen distribution function for the STR/1 model (solid line), SPC/E model (dashed line), and from experiment (dotted line).

smaller distance, as is the case in most water models. The height of the first peak is comparable to the experimental findings. Over the entire range this radial distribution function is very similar to the function obtained for the frequently used SPC model for water. For both SPC and the present model the structure beyond the first peak is

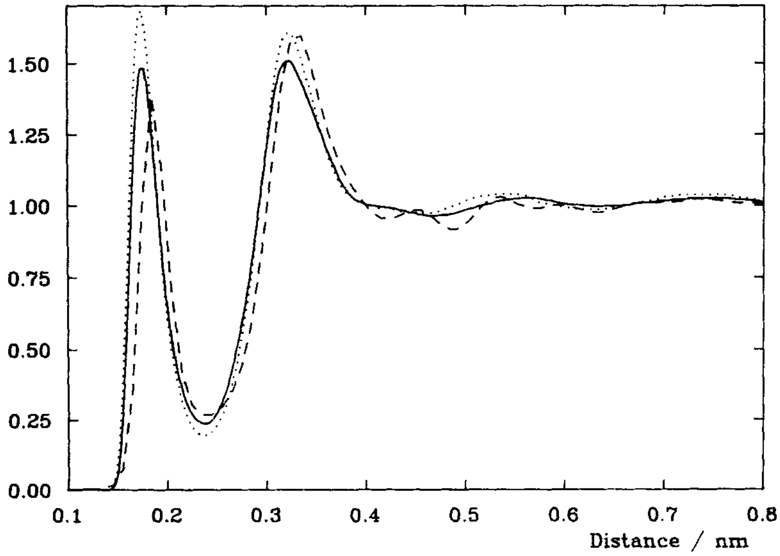

Figure 2 Radial oxygen–hydrogen distribution function for the STR/1 model (solid line), SPC/E model (dashed line), and from experiment (dotted line).

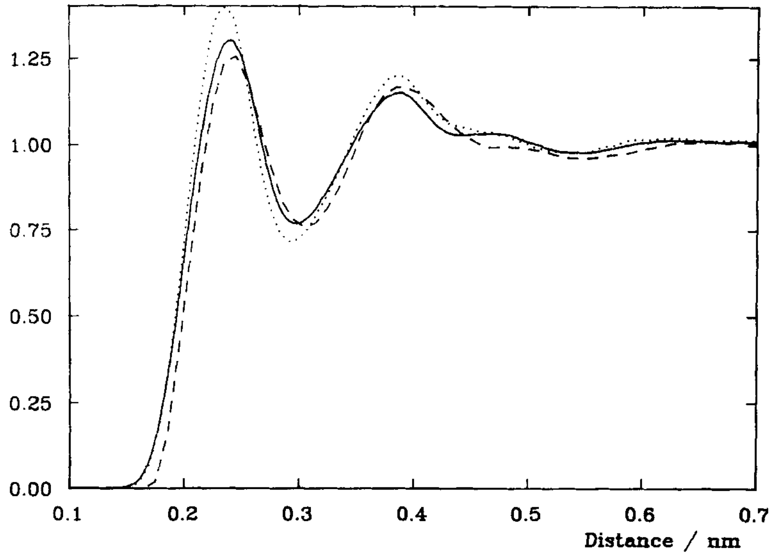

Figure 3 Radial hydrogen–hydrogen distribution function for the STR/1 model (solid line), SPC/E model (dashed line), and from experiment (dotted line).

much less pronounced than the experimental curve. This structure is better resolved by the enhanced SPC/E water model for which the radial distribution functions are also shown. The oxygen–hydrogen and hydrogen–hydrogen radial distribution functions are, both for the present model and the SPC/E water model, in excellent

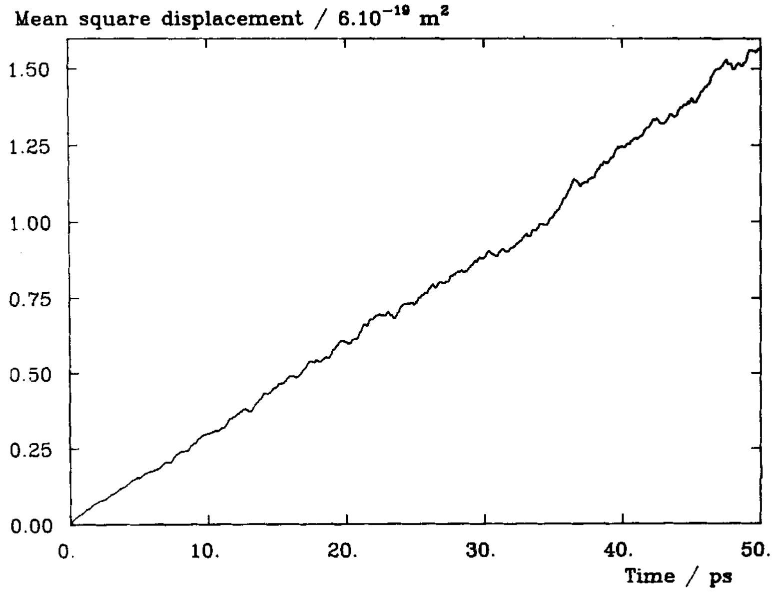

Figure 4 Mean square displacement for STR/1 water model.

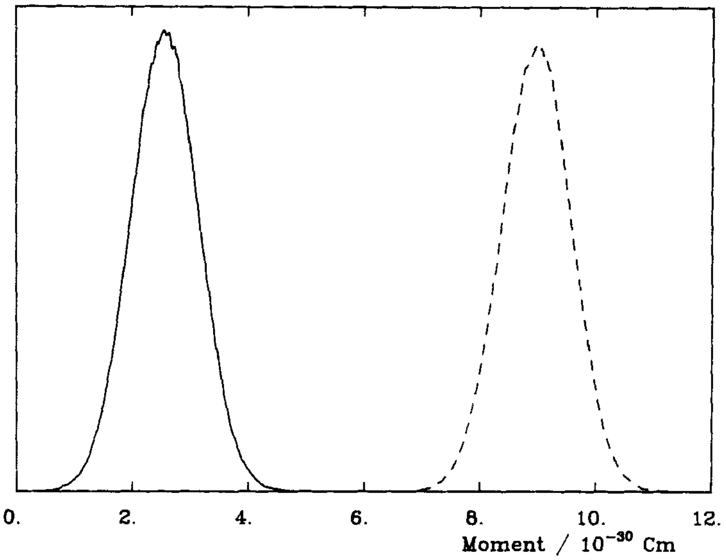

Figure 5 Induced (solid line) and total (dashed line) dipole moment distribution of STR/1 water.

agreement with the experimentally found curve. For the dipole-dipole correlation distribution and the center of mass velocity autocorrelation functions only minor diferences were found between the present model and the SPC/E water model. The diffusion coefficient, as evaluated from the mean square displacement plotted in Figure 4, is $3.1\,10^{-9}\,\mathrm{m}^2\mathrm{s}^{-1}$ and compares well to the experimental value of $2.7\,10^{-9}\,\mathrm{m}^2\mathrm{s}^{-1}$. The induced dipole moment and total dipole moment distributions

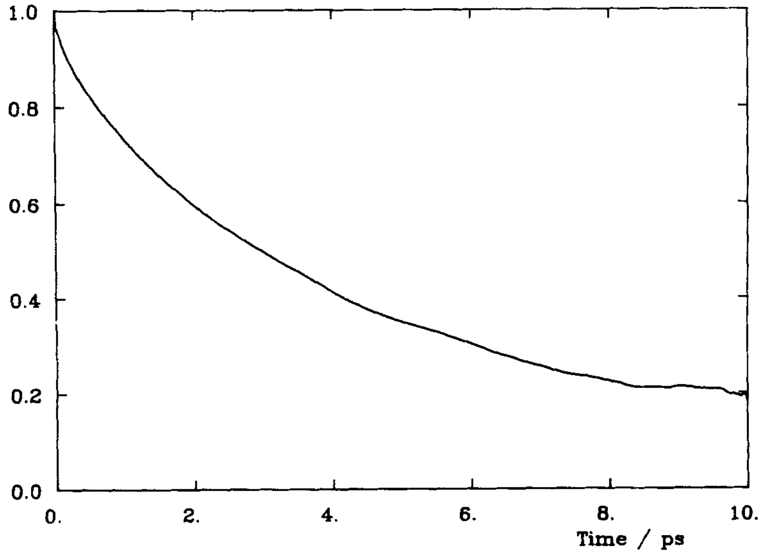

Figure 6 Induced dipole autocorrelation function.

are shown in Figure 5. The average dipole moments are $2.564\,10^{-30}$ and $8.972\,10^{-30}$ Cm for the induced and total dipole moment respectively. The average charge separation is 0.016 nm, which corresponds to one tenth of the smallest non-bonded oxygen–hydrogen distance. The autocorrelation function of the induced dipole moment is shown in Figure 6. It is obvious from the extremely high correlation shown by the autocorrelation function that the electric field changes only very slowly in time.

The value for the polarization charge was arbitrarily chosen to be -8.0 *e*. This rather high value ensures that the charge separation is in the direction of the electric field at the position of the oxygen atom, and therefore allows for the shift of the polarization charge forces to the corresponding oxygen atom. Changing the value of the polarization charge will change the polarization charge separation from the oxygen nucleus. Changing the polarization charge, however, does not noticeably alter the radial distribution functions, as determined from simulations using $-2.0\,e$ and $-10.0\,e$ for the polarization charge.

The charges on oxygen and hydrogen, although much smaller than in the widely used effective pair models for water, are still somewhat enhanced over the values that would give the correct vacuum dipole moment for water. This charge enhancement is needed to account for the dipole moments induced by the presence of other induced dipole moments. This enhancement is much smaller than in the effective pair models, in which the average effect of the total induced dipole moments is represented by larger charges. If the induced dipole moments are evaluated from permanent charges and induced dipoles, requiring a more CPU intensive, iterative solution of the electrical field, this enhancement of charges is not needed.

The distribution and density of the angle between the first order induced dipole and the permanent dipole of the molecule are shown in Figure 7. Although the induced

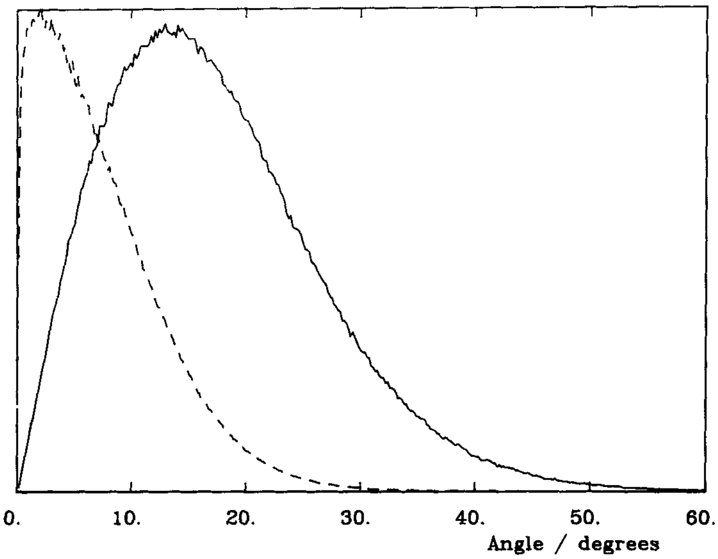

Figure 7 Distribution (solid line) and density (dashed line) of the angle between the induced dipole and the permanent dipole in bulk STR/1 water.

dipoles clearly tend to be aligned with the permanent dipole, there is a significant dispersion about this direction. That the density drops to zero at an angle of zero likely reflects the poor sampling of the small bins of solid angle in this region. The average angle is 17.3°. The angle density is rather broad. This indicates that effective pair models, in which the polarization is treated by enhancing the charges leading to a permanent dipole moment that includes the average effect of polarization, is indeed an approximation. This will also be true for the treatment of the polarization due to the first order induced dipoles by slight enhancement of the charges in the present model. In an iterative fashion the induced dipole moments were evaluated using not only the permanent charges but also the polarization charges, using the same potential parameters. The fully converged induced dipoles were found to have an average angle of 4 degrees with the first order induced dipoles.

5. CONCLUSION

The implementation of polarization in molecular dynamics simulations described in this article gives encouraging results for the application for water. The structural properties for bulk water are reasonably well reproduced, although there is no real improvement over the effective pair potentials. In the effective pair potentials for water the average effect of polarization is described by enhanced atomic charges. Not taking the spread in the direction of induced dipoles into account will enforce a more constantly directed influence on the environment of each water molecule, leading to a more ordered structure of its surroundings. This may explain the more pronounced second peak in the oxygen-oxygen radial distribution function as obtained using effective pair models, as compared to the present model. On the other hand, the structure of the oxygen-oxygen radial distribution function is considerably improved from the SPC model to the SPC/E model, although the difference between the two models is only a small change of about $0.02e$ in the charges.

Since the directions of the fully converged induced dipoles were found to be actually closer to the direction of the first order induced dipoles than to the direction of the permanent dipoles, the model can possibly be refined by enhancing also the polarizability rather than the permanent charges only, in order to better take into account the average effect of polarization by the first order induced dipoles. Other refinements may be possible, e.g. by changing the location of the fixed atomic charges. On the other hand the present model may behave quite differently from effective pair potentials in simulations of aqueous solutions.

The objective of the present study is the introduction and initial development of a general potential model for use in molecular dynamics simulations that includes polarization in a simple and computationally inexpensive way. The CPU time needed in the case of water is for the STR/1 model about twice the time for the SPC/E efffective pair model. The three center effective pair model leads to 9 interactions per water molecule pair. In the STR/1 model there is one additional polarization charge per molecule, leading to 16 water molecule pair interactions.

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APPENDIX

The calculations described in this article were performed using the ARGOS molecular dynamics package, developed and copyrighted by T.P. Straatsma [17]. The force field as it is used in ARGOS is of the form,

$$V(\{\mathbf{r}_i\}) = \sum_{n=1}^{N_b} \tfrac{1}{2} C_{b,n}(b_n - \mathrm{b}_{0,n})^2 \tag{11}$$

$$+ \sum_{n=1}^{N_\theta} \tfrac{1}{2} C_{\theta,n}(\theta_n - \theta_{0,n})^2 \tag{12}$$

$$+ \sum_{n=1}^{N_\xi} \tfrac{1}{2} C_{\xi,n}(\xi_n - \xi_{0,n})^2 \tag{13}$$

$$+ \sum_{n=1}^{N_\phi} C_{\phi,n}[1 + \cos(m_n \phi_n - \delta_n)] \tag{14}$$

$$+ \sum_{i<j}^{N} \left[\frac{C_{12,ij}}{r_{ij}^{12}} - \frac{C_{6,ij}}{r_{ij}^{6}} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right] \tag{15}$$

The terms in this equation represent covalent bond stretching, bond angle bending, harmonic improper dihedral bending, sinusoidal proper dihedral torsion, and non-bonded van der Waals and electrostatic interactions. External electrical fields and reaction fields are implemented. Distance constraints can be treated using SHAKE [15] or a method described by Edberg *et al.* [18]. The program package allows for equilibrium molecular dynamics simulations, free energy perturbation calculations, free energy thermodynamic integrations in which derivatives of the Hamiltonian are obtained from single configurations or ensemble averages, energy minimizations using a steepest descent technique or a conjugate gradient method, and adiabatic mapping.

The equations of motion are solved using a leap-frog algorithm [14]. Pressure and temperature can be maintained constant through coupling with an exernal heat and pressure bath [13]. In the course of simulations a range of properties and distribution functions can be calculated.

The most CPU time consuming part of MD simulations is the calculation of non-bonded forces. This part is broken up in the generation of the pair lists and the calculation of the forces using these pair lists. Since atoms are usually displaced slightly from one time step to the next, the expensive generation of the pair lists does not have to be done every dynamics step. The, usually small, solvent molecules will move faster than large solute molecules. An additional advantage of separating calculations for solute and solvent interactions is therefore that pair lists for the solute–solute non-bonded interactions can be updated less frequently than the pair lists involving solvent molecules. The generation of the pair lists is based on particle distances.

The data structure and the order in which operations are performed allow for very efficient implementation on vector processing computers. The program was initially developed on a NEC SX-2/400 supercomputer [19]. The vectorization ratio that can be obtained ranges from 98% for a simulation of 216 SPC/E water molecules in a cubic periodic box to 86% for a simulation of myoglobin, a 1530 atom protein, in 3128 SPC/E water molecules in a rectangular periodic box.

Details of the implementation and vectorization of the ARGOS program will be published elsewhere [17].

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