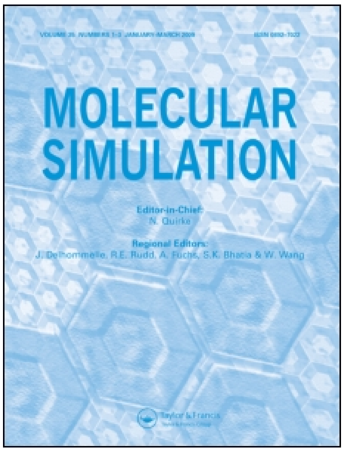

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A ROBUST WATER POTENTIAL PARAMETERISATION

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We compare molecular dynamics simulation results for the properties of liquid water predicted by four novel water potential models. These models are designed as a combination of parameters taken from the dedicated but brittle TIP3P water potential, and the more flexible but less accurate parameterisations such as the Dreiding and Universal force fields. We find that a hybrid of Dreiding and TIP3P delivers the best results, yielding a density, diffusion coefficient and radial distribution function in good agreement with experiment, performing in some respects even better than the dedicated reference TIP3P model. Another Dreiding based force field predicts semi-quantitative results for the water structure and dynamics while the Universal force field based models are incapable of simulating a condensed phase of water at all, continuing to expand indefinitely. These observations are useful for selecting and designing robust water force field parameterisations that can be used for general simulation purposes.

Keywords: Flexible water potentials, molecular dynamics simulations

INTRODUCTION

The simulation of the bulk properties of water has proved to be a major challenge to computational chemists over several decades. Highly popular and successful potential models for liquid water include TIP3P, TIP4P [1] and SPC [2] potentials. These models are regarded as the best available today.

Nevertheless, force fields which are too highly optimised for a given application (*e.g.* to simulate/reproduce the bulk properties of water), are usually found to be 'brittle' when extended to other systems – in particular, when new atoms are introduced which were not originally present when the potential model was designed (and indeed under different conditions of temperature and /or pressure). With the growth in accessibility of computational chemistry techniques, and their application to an ever growing range of systems, there is a pressing need for much more flexible, less brittle, force field parameterisations which can be relied upon in new and often unforeseen circumstances. There is evidently going to be a trade-off in meeting this new demand – a sacrifice in quantitative accuracy for the sake of qualitatively correct trends, a fact widely accepted in the simulation community [3].

One attempt to address this issue is exemplified in the work of Goddard and coworkers, who have sought to generate force field parameterisations that could be applied to a much wider range of atoms than most conventional force fields are designed to handle. Thus the Dreiding force field was introduced by Mayo *et al.* [4] as a general force field for describing organics, but it also includes parameters for a number of atoms more usually encountered in inorganic chemistry, such as Na, Cl, Fe and Zn.

More ambitiously still, Rappé *et al.* [5] have sought to extend this conceptual approach across the full periodic table, offering parameterisations of a large number of atoms, which are all intended to be mutually self-consistent. Indeed, the Universal force field (as well as Dreiding) is now incorporated as part of a commercially available computational chemistry package [6]. A user can dial up the Universal force field in an almost unlimited range of simulations, from simple molecular mechanics to full blown grand canonical Monte Carlo and molecular dynamics applied to dense systems.

It is therefore important to address the question as to the validity of these force fields in general applications. In the present note, we report on the performance of these force fields in predicting the bulk properties of water, such as water density, diffusion coefficient and radial distribution function. We compare their predictions with a well established but dedicated water force field, namely TIP3P.

SIMULATIONS

We have performed molecular dynamics simulations of liquid water using the Cerius^2 software package [6]. The potential energy of the water molecules is expressed as a sum of bonded and non-bonded interactions. The (intramolecular) bonded interactions include harmonic potentials for bond stretching and bending interactions [5]. The (intermolecular) non-bonded interactions are pairwise additive and are described by Coulombic and Lennard-Jones 6–12 parameters:

$$v(r) = \sum_{ij} (q_i q_j / r_{ij}) - D^0_{ij}\{2(R^0_{ij}/r_{ij})^6 - (R^0_{ij}/r_{ij})^{12}\} \tag{1}$$

Within the Cerius^2 environment bonded parameters and non-bonded van der Waals (Lennard-Jones) parameters are available from the Universal (UFF) and Dreiding force fields. It is these parameters which provide the self-consistent parameterisation across the periodic table. Atomic charges and geometry parameters (bond lengths and angles) can be obtained from quantum chemical calculations for a water monomer, using the semi-empirical MOPAC code [7]. Another source of force field parameters for water is the TIP3P potential. This potential successfully reproduces the bulk properties of liquid water, but it is not optimised to be used in combination with many other chemical components. In order to combine the best of both worlds, that is the flexibility of the Dreiding and UFF force fields and the accuracy of the TIP3P potential, we have designed four different force fields for water, as a combination of the available UFF, Dreiding, TIP3P, and MOPAC parameters. These are listed in Table I. We want to investigate to what extent these parameterisations reproduce the properties of bulk liquid water, and compare these to the TIP3P results as a reference case. Our aim is to select a potential parameterisation which shows the correct behaviour for liquid water and is transferable to more complex systems.

We should point out that the TIP3P model, as well as SPC and TIP4P, actually are rigid models; that is, there are no bond stretching or bending interactions involved. These rigid models reproduce the thermodynamic and structural properties of bulk water very well [8]. However, the Cerius^2 software currently does not allow rigid body (constraint) dynamics, so that we were obliged to use flexible water potentials in the present work. A relatively small (and thus computationally expensive) integration time step

TABLE I Four different force fields for water and reference model TIP3Pf

Parameterisation	*geometry + charges*	*vdWaals*	*bonded*
UFF/MOP	MOPAC	UFF	UFF
DREI/MOP	MOPAC	Dreiding	Dreiding
UFE/TIP	TIP3P	UFF	UFF
DREI/TIP	TIP3P	Dreiding	Dreiding
TIP3Pf	TIP3P	TIP3P	UFF

of 1 fs was therefore chosen to capture high frequency bond vibrations. In a recent paper on the merits of flexible water models [9] it is concluded that flexible models may be computationally inefficient, but do reproduce structural and dynamical properties of water correctly. The bonded parameters employed can be found in refs. [4,5]. In Table II the geometry and non-bonded parameters are listed for the relevant potential functions.

Initially, a computational box was generated containing 128 water molecules, which were randomly positioned and oriented within the box. The initial density was chosen to be approximately equal to the bulk water density of 1 g/cm^3. Subsequently the configuration thus generated was subject to energy minimisation, in order to remove spurious strain. Then for all four potential models, MD simulations were performed in the isothermal-isobaric (NpT) ensemble. The temperature was maintained at 300 K by the Nosé temperature scaling method [10], while the pressure was kept at 0.1 MPa. Periodic boundary conditions were applied in three dimensions. After equilibration, atomic coordinates were recorded every 100 integration time steps, which were used later to calculate macroscopic quantities as averages over the generated time series.

In order to handle the slowly converging long-range forces in these simulations (specifically the dipole-dipole interactions between the water molecules) in a satisfactory way, two different techniques were employed:

- a spline switching function to cut off non-bonded interactions, coming in at 11 Å and vanishing at 14 Å;
- an Ewald summation technique, which splits the interaction of a molecule with all its periodic images into a real space part for nearest neighbour interactions, and a reciprocal space part for further regions. Both partial summations are rapidly converging and therefore truncated beyond 6 Å and 0.5 Å^{-1} respectively [11].

TABLE II Geometry and non-bonded parameters for potential functions, as used in Eq. 1

	UFF	*Dreiding*	*TIP3P*	*MOPAC*
D_O^0	0.060	0.0957	0.1521	
R_O^0 (Å)	3.500	3.4046	2.5789	
D_H^0 (kcal/mol)	0.044	0.0152	0.0000	
R_H^0 (Å)	2.886	3.1950	0.0000	
q(O)			−0.834	−0.326
q(H)			0.417	0.163
r_{OH}(Å)			0.9572	0.943
∠HOH (deg)			104.52	106.8

The advantage of using the Ewald summation technique is that it treats long-range interactions more precisely than the spline cut-off function; the disadvantage is that the Ewald technique is computationally much more demanding. Therefore we have chosen to perform MD simulations for 50 ps using the spline cut-off, and for 20 ps using the Ewald summation technique.

For comparison with the TIP3P reference model, we have performed simulations for the flexible TIP3P model (including UFF bonded parameters) using the Ewald summation technique. This model will be called TIP3Pf, whereas the rigid TIP3P model from the literature (without bonded interactions) will be referrerd to as TIP3P. In the next section we will show that the simulation results for the TIP3Pf model are in close agreement with those of the TIP3P model.

RESULTS AND DISCUSSION

In order to validate the proposed potential models for liquid water, we have compared our simulation results with experimentally measurable, macroscopic properties. For this purpose we have calculated the bulk water density and self-diffusion coefficient as averages over the stored time series of particle coordinates. These values are listed in Table III for both the spline function cut-off and Ewald summation techniques. Literature values obtained for various dedicated water potentials are also given in Table III, as well as the experimental values.

Overall, the calculated water densities are in reasonable agreement with the experimental value of 1.0 g/cm^3, the Ewald summation yielding slightly

TABLE III Bulk density ρ and diffusion coefficients D of water at 300 K for various potential models and treatment of long-range interactions (spline and Ewald)

	spline		*Ewald*	
model	$\rho(g/cm^3)$	$D(10^5cm^2/s)$	$\rho(g/cm^3)$	$D(10^5cm^2/s)$
DREI/TIP	0.96	0.23	0.97	1.88
DREI/MOP	0.94	4.85	0.95	3.02
UFF/TIP	1.07	4.83	0.61	9.12
UFF/MOP	0.31	5.76	0.38	93.9
TIP3Pf			1.02	3.35
expt.	1.00	2.4	1.00	2.4
TIP3P			0.98	3.98
SPC			0.97	3.6
TIP4P			1.00	3.3

better results than the spline function. There are a few exceptions: the UFF/MOP potential yields an average density which is much too low. In fact, during the MD simulations we observed a continuous and indefinite expansion of the computational box, indicating that this potential parameterisation is unable to simulate a condensed phase of water at all. The same holds, to a lesser extent, for the UFF/TIP parameterisation using Ewald summation.

Self-diffusion coefficients were obtained by monitoring the displacement of a water molecule as a function of time, averaging over all molecules and all choices of time origin t_0. The mean square displacement is then calculated as:

$$\langle \Delta r^2(t) \rangle = \langle |\mathbf{r}(t_0 + t) - \mathbf{r}(t_0)|^2 \rangle \tag{2}$$

Diffusion coefficients D were then obtained using the Einstein relation:

$$D = \lim_{t \to \infty} \frac{\langle \Delta r^2(t) \rangle}{6t} \tag{3}$$

The calculated diffusion coefficients for the various potential models are listed in Table III. Our reference TIP3Pf model yields a value of 3.35×10^{-5} cm^2/s, which compares nicely with the literature TIP3P value of 3.98×10^{-5} cm^2/s. The experimental value however is considerably lower. Indeed, the DREI/TIP model combined with Ewald summation delivers a diffusion coefficient which is in better agreement with experimental results than the dedicated TIP3P model. The same holds for the DREI/MOP – Ewald model. Also the DREI/MOP and UFF/TIP models combined with the spline function yield reasonable results. On the other hand, it appears that the values for UFF/MOP and UFF/TIP – combined with Ewald – are too high in comparison with the experimental value of 2.4×10^{-5} cm^2/s. [8]. This corresponds with the very low bulk densities of these water models. In general, the parameterisations yielding the proper water density all give results in reasonable agreement with the experimental diffusion coefficient and the reference TIP3P value. Only DREI/TIP – spline produces too small a value, which is probably due to exaggerated hydrogen bond formation between water molecules.

As a measure of the water structure at the molecular level, the radial distribution function (or pair correlation function) $g(r)$ was calculated. This radial distribution function (rdf) gives the probability of finding a pair of atoms a distance r apart, relative to the probability expected for a completely random distribution at the same density. The simulated rdfs can be compared to rdfs derived from x-ray or neutron scattering experiments, as a Fourier transform of the structure function $S(k)$. In order to get good statistical accuracy, the rdfs were calculated by averaging over all the particle coordinates and all sampled time frames. In Figures 1 and 2 the rdfs for the various water potential models are presented, using the spline switching function and Ewald summation techniques respectively. Only the oxygen-oxygen pair correlations are shown.

The rdf for the TIP3Pf parameterisation, drawn as a dotted line in these figures, serves as a reference model. The TIP3Pf result is very similar to the literature TIP3P rdf [1]: for both these models, the first peak, indicating the organisation of water within the first hydration shell, is located at 2.75 Å, with a height of about 3. However, neutron [12,13] and x-ray diffraction [14] data indicate that the first peak should be located at 2.9 Å. Indeed, the DREI/TIP parameterisation shows a first maximum at this value, for both the Ewald and spline techniques. Furthermore, TIP3P (and TIP3Pf) give too little structure beyond the first peak, as compared with the experimental rdf. The DREI/TIP model on the other hand displays signs of a second

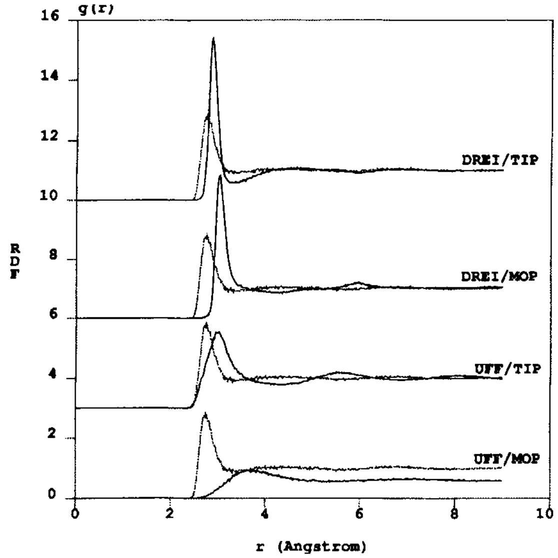

FIGURE 1 Oxygen-oxygen radial distribution functions for various water potential models using a spline function to cut off non-bonded interactions; the result for the reference TIP3Pf parameterisation is drawn as a dotted line in each of the four graphs. The potential model names are described in Table I.

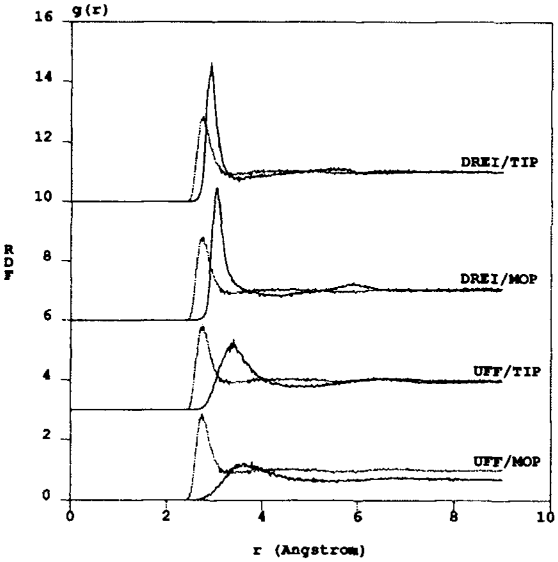

FIGURE 2 Oxygen-oxygen radial distribution functions for various water potential models using an Ewald summation technique to handle non-bonded interactions; the result for the reference TIP3Pf parameterisation is drawn as a dotted line in each of the four graphs. The potential model names are described in Table I.

hydration shell, which is in better agreement with experimental results and also with simulation results using the dedicated four-site TIP4P potential [1]. (Note that it is not yet possible within the Cerius^2 software to use the four-centered TIP4P parameterisation, due to the lack of rigid body dynamics.)

Of the four new potentials, the DREI/TIP model shows the best agreement with experimental water structure data, and performs in some respects even better than the TIP3Pf reference model. The other models display first peaks at larger distances, but the rdfs are generally still in qualitative agreement with experiment. Only the UFF/MOP model yields unsatisfactory results: with increasing distance *r*, the rdfs should go asymptotically to a value of 1, the macroscopic bulk water density. The UFF/MOP model does not satisfy this condition; indeed, we have already observed that this model produces a bulk water density which is much too low.

CONCLUSIONS

We have analysed four possible potential models for the simulation of liquid water. These models are designed to be flexible, in the sense that they can also be used in more complex systems with other chemical components, in particular within commercial simulation packages such as the Cerius^2 environment. The performance of these models has been investigated in predicting the bulk properties of liquid water, such as the bulk water density, self-diffusion coefficient and radial distribution function. We have compared these properties with a highly regarded but dedicated water potential, the TIP3P model, and judged the various models on their merits.

It appears that all models, except UFF/MOP, yield water densities in agreement with experiment. Overall, the use of the DREI-based models should be preferred over UFF-based water potentials, as these fail to simulate a condensed phase of water at all. The DREI/TIP parameterisation, combined with the Ewald summation technique, yields the best results for both the structure and dynamics of water. Indeed, the DREI/TIP simulation results for the radial distribution function and diffusion coefficient are in better agreement with experimental data than the dedicated TIP3P potential. The application of the Ewald summation technique makes this model computationally expensive; as a cheaper alternative, the spline function equivalent of the DREI/TIP model still possesses the required structural properties for water, but the dynamics degrade somewhat. Alternatively, the DREI/MOP model delivers simulation results which are still qualitatively correct.

Summarising, we feel encouraged to use some of these robust water potential models in our future simulations. Particularly in the case of the DREI/TIP-Ewald model, it seems possible to employ a flexible water parameterisation without sacrificing quantitative accuracy completely. Indeed, we have already been using some of these flexible water potentials to good effect; for example, we find trends in qualitative to semi-quantitative agreement with experiment in our simulations of clay-water-organic systems [15] and layered double hydroxides [16].

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