Effective Pair Potentials and Structure of Water

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Classical Monte Carlo calculations have been performed in order to investigate the ability of the TIP4P, SPC, and SPCE water models to reproduce the structural features of liquid water. The simulations were carried out in the NPT ensemble at 4 thermodynamic conditions. The results are compared with recent neutron diffraction data. Essentially, the three models capture equally well the thermodynamic and structural features of water. Although they were parametrized to reproduce the water properties at ambient conditions, the agreement with the experimental pair correlation functions was even better at supercritical conditions. This is because the effective pair potentials have some difficulty to reproduce cooperative interactions, like hydrogen bonds. These interactions are less effective at supercritical conditions, where the liquid behaves roughly like a gas.

Key words: Monte Carlo Simulation; Non-polarizable Water Models; Radial Distribution Functions; Hydrogen-bonds.

Introduction

In spite of the long-standing attention devoted to the study of water, its macroscopic properties are not yet completely understood. Experimental results have provided a detailed picture of the way in which water molecules are arranged in pure water and around particles dissolved in it [1], but from a theoretical point of view, many questions remain still open. This situation is a consequence of the complexity of the intermolecular interactions and the lack of spatial symmetry characteristics of the liquid state. For water, in particular, these difficulties are stressed due to its hydrogen-bond network [2].

In the last 20 years, Monte Carlo (MC) and molecular dynamics (MD) calculations have become popular [3–5], and many models that reproduce the water behavior have been proposed. Rigid models are the most popular ones [6–9], but models including polarization have also been tested [10–15]. Most recently, improved models that include various sites in the water molecule have been developed [16, 17]. None of them, however, is able to describe the liquid as it approaches the freezing point. This is due to the cooperative nature of the H-bonding interactions and the multibody aspect of the electronic polarization forces [2, 18]. Three of these models have had the most success to capture many of the dynamical and structural properties of water [19–27]. They are the simple point charge (SPC) [9] and the extended simple point charge (SPCE) [8] models of Berendsen et al. and the transferable intermolecular potential (TIP4P) model of Jorgensen et al. [7]. All of them are empirical effective pair potentials with parameters fitted to pressure or ambient density and heat of vaporization. The SPC model takes the contribution of the induced dipoles to the potential energy into account [8].

A good effective pair potential must be able to incorporate the average many-body interactions into the interaction between pairs. The aim of this work was to investigate the performance of the TIP4P, the SPC, and the SPCE models to reproduce the structure of liquid water at various thermodynamic conditions. Several papers have been published in which the pair correlation functions of water obtained by simulation have been compared with experimental results [19–26, 28]. The three models represent very well the water O-O pair correlation function at various T-P conditions, observing that in general the first peak is too high when compared with the experimental one. In recent years, Soper and coworkers have determined the experimental site-site radial distribution function for water by neutron diffraction, from 25° to 400°C [29]. They have used a new formalism based on the minimum noise principle to estimate g(r), in which systematic errors, which may otherwise cause deviations in the rdf’s, can be minimized [30]. In this work, results obtained with the three models investigat-
ed at several \( T-p \) conditions have been compared with the results reported by Soper et al. [29].

**Details of the Simulations**

**The Intermolecular Potential Functions**

Following usual procedures in force field calculations [4], the energy \( E_{ab} \), between molecules \( a \) and \( b \) was represented by a sum of Coulomb and Lennard-Jones potentials centered on the sites, that is

\[
E_{ab} = \sum_{ij} \left[ \frac{A_{ij}}{r_{ij}^6} - \frac{B_{ij}}{r_{ij}^{12}} + q_i q_j/r_{ij} \right],
\]

where \( r_{ij} \) is the distance between site \( i \) and \( a \) and site \( j \) in \( b \) and \( q_i \) and \( q_j \) are point charges located respectively on the \( i \) and \( j \) molecular sites. For each site \( k \), the parameters \( A_{kk} \) and \( B_{kk} \) were given by \( A_{kk} = 4 \varepsilon_k \sigma_k^6 \) and \( B_{kk} = 4 \varepsilon_k \sigma_k^12 \), where \( \varepsilon_k \) and \( \sigma_k \) are the Lennard-Jones parameters for the \( k \)-th site.

**Monte Carlo Simulations**

The simulations were carried out in the isothermal-isobaric ensemble using Metropolis importance sampling [31] and periodic boundary conditions with the DIA-DORIM code developed by Freitas [32]. Table 1 shows the thermodynamic conditions investigated. The systems consisted of 400 molecules in a cubic cell. The initial volume of the box was calculated assuming the experimental density of water.

The simulations were started with an equilibration phase with every 500th attempted molecular move. After volume changes, the center of mass coordinates of all molecules in the reference box were scaled in the usual way [34]. Ranges for translating and rotating the molecules and for volume moves were adjusted to yield an acceptance/trial ratio between 0.40 and 0.45 for new configurations. Each calculation started with an equilibration phase with 1.2x10^7 configurations, and the averages were then obtained after a new segment with other 1.2x10^7 configurations. Statistical uncertainties were calculated from separate averages over blocks of 2x10^5 configurations. The calculations were performed in IBM RISC 6000 workstations.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Density (g/cm^3)</th>
<th>H-bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>1</td>
<td>0.99</td>
<td>3.58</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>1900</td>
<td>0.99</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>100</td>
<td>0.92</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>2800</td>
<td>0.92</td>
<td>3.06</td>
</tr>
</tbody>
</table>

* The experimental results are from [29].
Results and Discussion

Densities obtained from the simulations are listed in Table 2. The three models present good agreement with the experimental data in the studied range of temperature and pressure, although the SPC model seems to have some difficulty to capture the experimental value of this property. This is already noticed observing earlier reports for 1 atm and 25 °C [7, 8, 41]. Figure 1 shows the experimental results for the OO and OH site-site pair correlation functions at different thermodynamic conditions. The curves at 423 K and 100 atm were not plotted for clarity. There are no serious differences between them and those at 423 K and 1900 atm. These results have been analyzed by Soper and coworkers [1, 29]. As a general trend, there is a decrease in pair correlation functions, and the second hydration shell vanishes at higher temperatures. These findings characterize the loss of tetrahedral order as one moves away from the ambient conditions [42]. Beside this, the peaks seems to move to larger radius values. The result reported by Soper et al. [29] for the OO rdf at ambient conditions is not significantly different from that obtained by Narten and Levy using X-ray diffraction, reported by Jorgensen et al. [7].

The OO and OH site-site correlation functions obtained with the investigated models are compared with the experimental ones in Figs. 2 and 3, respectively. The three models present basically the same results and behavior. The SPC model shows a better agreement with the experimental result at ambient conditions, but at supercritical temperatures the models are completely equivalent. All of them, in spite of having been parame-trized at ambient temperature and pressure, capture better the experimental behavior in conditions away from the ambient ones. In such conditions, when the liquid behaves as a non hydrogen-bonded liquid, its structural feature is equally captured by the three models. So, one can conclude that in such thermodynamic conditions, an intermolecular potential with reasonable values of Lennard-Jones parameters and site charges can reproduce the actual structure of water. In fact, the problem at low temperatures is the strong H-bonds, insufficiently reproduced by a pairwise effective potential. We have tried to improve the Lennard-Jones $\epsilon$ parameter. This way these

Table 2. Theoretical densities and hydrogen-bonds (H-bonds) obtained with the investigated models.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>TIP4P</th>
<th>SPCE</th>
<th>SPC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-bonds</td>
<td>Density</td>
<td>H-bonds</td>
</tr>
<tr>
<td>1</td>
<td>3.7</td>
<td>1.01</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>3.4</td>
<td>0.99</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>0.89</td>
<td>3.3</td>
</tr>
<tr>
<td>4</td>
<td>2.9</td>
<td>0.90</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Errors in the density are between 0.02 and 0.03.

Fig. 1. The experimental OO (left) and OH (right) site-site pair correlation functions of water at the thermodynamic conditions shown in the pictures.
models agree better with experimental values of the OO rdf at room conditions (results not shown). The results show that it is possible to lower the first peak of the OO correlation without losing agreement of density and heat of vaporization, but the peak corresponding to the second hydration shell vanishes quickly. So, since this peak is the main evidence of the tetrahedral order [42], one can conclude that the value of the $\varepsilon$ parameter is fundamental for the construction of the H-bond network in this models. At 573 K and 2800 atm the experimental OO and OH rdfs present shoulders that are not shown by the calculations. In the same way, the models do not show the movement to larger distances with increase in temperature and pressure shown in the experiments. In Table 2
is also reported the number of hydrogen bonds in the water obtained by integrating the first peak in the OH site-site correlation function up the first minimum. The general trend is that the number of hydrogen bonds obtained by the simulations at ambient pressure and temperature is greater than the experimental one. This is rather a consequence of the overestimation in the OH site-site correlation function of all models. On the other hand, some analyses suggest that the area of the OH peak is not a reliable measure of the OH coordination in water [20, 43], so the figures shown can have some intrinsic errors.
Conclusions

The SPC, SPCE and TIP4P show roughly the same ability to describe the properties of water in the T-p conditions investigated. The SPC model shows a better agreement with the experimental rdf at ambient conditions, but at supercritical temperatures the models are completely equivalent. All of them, in spite of having been parametrized at ambient temperature and pressure, capture better the experimental behavior in conditions away from the ambient one, because these the network of H-bonds is dismantled.

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