Effective Pair Potentials and Structure of Water

J. M. M. Cordeiro

Depto. de Física e Química, Faculdade de Engenharia de Ilha Solteira, UNESP, Av. Brasil Centro, 56,
C.P. 31, 15385-000 Ilha Solteira, SP, Brazil

Reprint requests to Dr. J. M. M. Cordeiro; E-mail: cordeiro@fqm.feis.unesp.br

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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 Carle 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 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 SPCE 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 investigated 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

$$E_{\mathrm{ab}} = \sum_{ij} \left[A_{ij}/r_{ij}^{12} - B_{ij}/r_{ij}^{6} + q_i\, q_j/r_{ij}\right] , \qquad (1)$$

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 $A_{kk} = 4\,\varepsilon_k\, \sigma_k^{12}$ and $B_{kk} = 4\,\varepsilon_k\, \sigma_k^{6}$, where ε_k and σ_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 DIADORIM 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. In the calculation of the total configurational energy using (1), the full intermolecular interaction was considered whenever any of the site-to-site distances r_{ij} fell below a cut-off radius of 9.5 Å. It was shown in a recent work that the thermodynamic properties are little dependent on the approach used to take into account the long range share of the interactions [33]. All models used in the present work were parametrized using the cutoff methodology. The contributions of Lennard-Jones interactions beyond the cut-off radius were considered using the formalism presented by Allen and Tildesley [34]. In the methodology discussed by these authors, the long range contribution from the Lennard-Jones potential is included by integrating the potential function from the cut-off radius to infinity, assuming that the pair correlation function is unitary. In previous papers we have found that the long-range contribution from the Lennard-Jones potential amounts to 1 to 2% of the total interaction energy [35–38]. Several methods are used to take into account long-range Coulombic interactions. Such contribution can be introduced, for instance, using the reaction field formalism (RF) discussed by Newman [39]. For liquid simulations, the RF may be superior to the Ewald sum correction in the sense that an artificial long-range correlation is not introduced in liquid simulations by the RF formalism [40]. A detailed investigation of the influence of including long-range corrections using RF methodology in the values of thermodynamic properties obtained in liquid simulation has been performed in our research group [40]. As a general trend, it was found that the effects in thermodynamic and structural properties are very small. Therefore, long range corrections for Coulombic interactions beyond the cut-off radio were not included in the present work. As discussed elsewhere, site-site pair correlation functions, thermodynamic properties and single particle dynamics of polar liquids appear to be quite insensitive to the long range forces in the system [4], which is in accord with results obtained by us using the RF formalism [40]. Starting from the initial distribution of molecules in the central box, new configurations were generated by randomly translating and rotating a randomly chosen molecule along Cartesian co-ordinates. As the calculations were carried out in the NPT ensemble, new configurations were also generated by probing the density of the liquid with volume changes. A volume move was tried on 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 $1.2{\times}10^7$ configurations, and the averages were then obtained after a new segment with other $1.2{\times}10^7$ configurations. Statistical uncertainties were calculated from separate averages over blocks of $2{\times}10^5$ configurations. The calculations were performed in IBM RISC 6000 workstations.

Table 1. Thermodynamic conditions of the simulations with experimental density and number of hydrogen bonds per water molecule (H-bonds)[a].

Simulation	Temperature (°C)	Pressure (atm)	Density (g/cm^3)	H-bonds
1	25	1	0.99	3.58
2	150	1900	0.99	–
3	150	100	0.92	–
4	300	2800	0.92	3.06

[a] 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].

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

Simulation	TIP4P		SPCE		SPC	
	H-bonds	Density	H-bonds	Density	H-bonds	Density
1	3.7	1.01	3.7	1.03	3.6	1.00
2	3.4	0.99	3.5–	1.00	3.3	0.98
3	3.0	0.89	3.3	0.92	3.0	0.87
4	2.9	0.90	3.0	0.92	2.9	0.89

Errors in the density are between 0.02 and 0.03.

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 parametrized 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 ε parameter. This way these

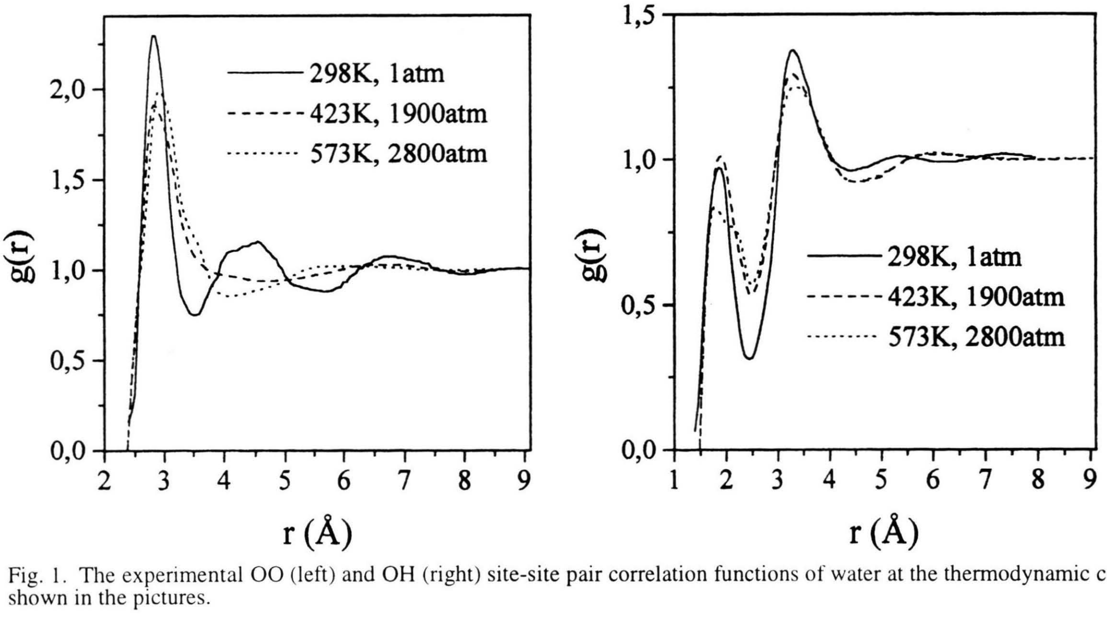

Fig. 1. The experimental OO (left) and OH (right) site-site pair correlation functions of water at the thermodynamic conditions shown in the pictures.

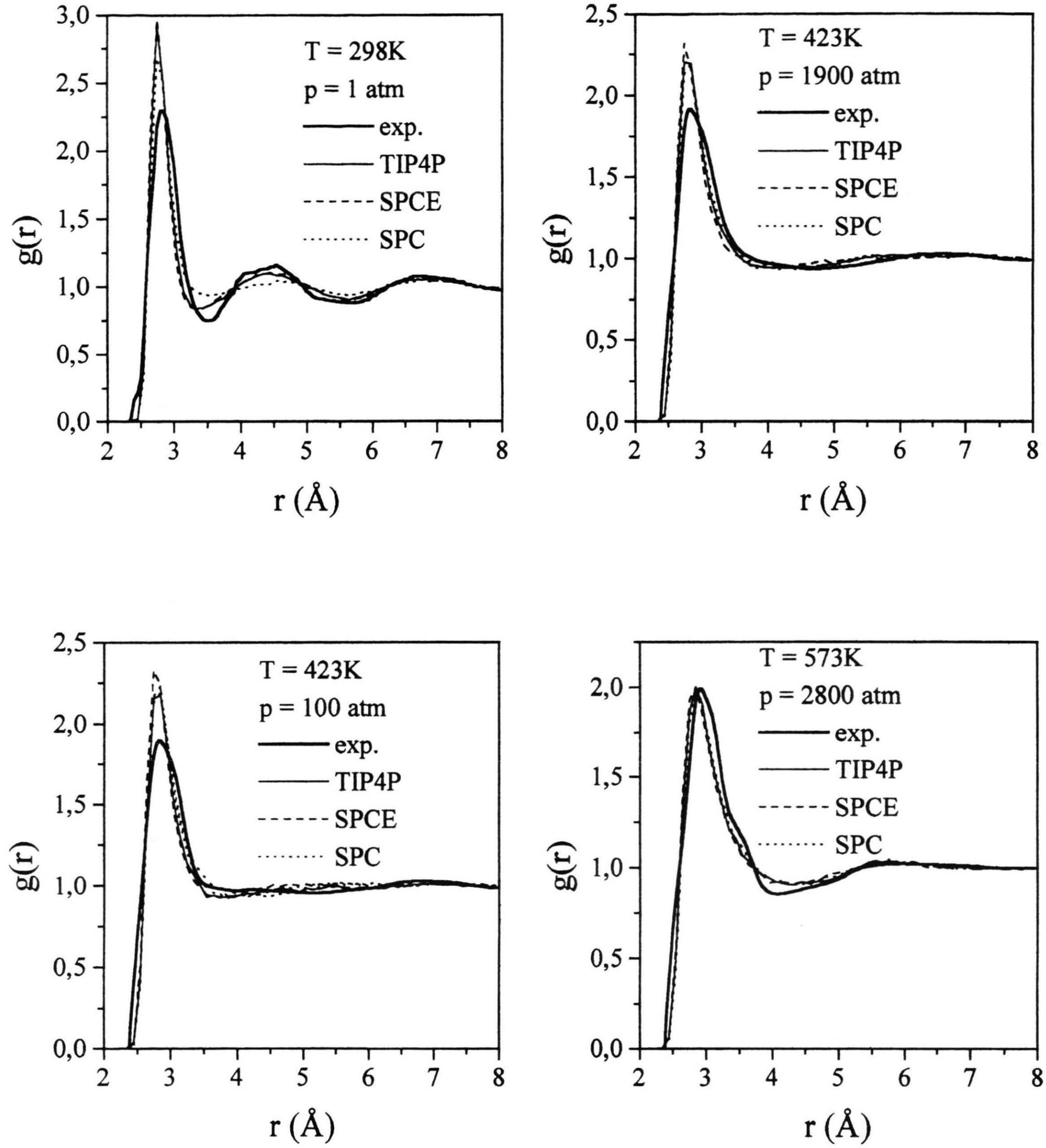

Fig. 2. The OO site-site correlation functions of water at the thermodynamic conditions shown in the pictures.

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 ε 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

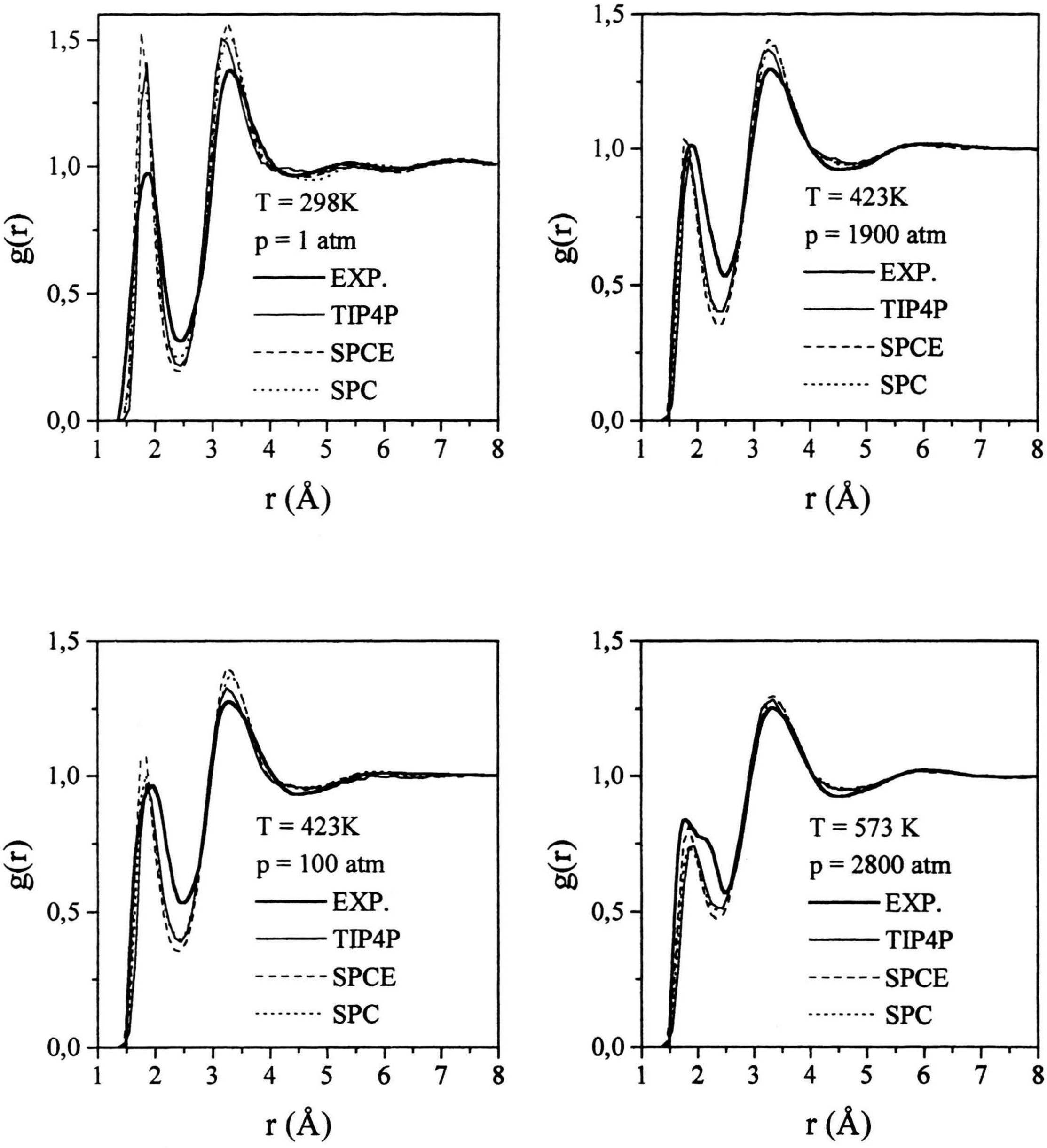

Fig. 3. The OH site-site correlation functions of water at the thermodynamic conditions shown in the pictures.

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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