Applied Radiation and Isotopes 83 (2014) 115–121

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Simulating liquid water for determining its structural and transport properties

Daniel Arismendi-Arrieta, Juan S. Medina, George S. Fanourgakis [1], Rita Prosmiti [*], Gerardo Delgado-Barrio

Instituto de Física Fundamental, IFF-CSIC, Serrano 123 28006 Madrid, Spain

HIGHLIGHTS

- Transport properties of liquid water are important in bio-simulations.
- Self-diffusion coefficient, shear and bulk viscosities calculations from NVE molecular dynamics simulations.
- Their comparison with experimental data provides information on intermolecular forces, and serve to develop water models.

ARTICLE INFO

Available online 20 January 2013

Keywords:
Water models
Theoretical simulations
Transport coefficients

ABSTRACT

Molecular dynamics simulations are carried out for calculating structural and transport properties of pure liquid water, such as radial distribution functions and self-diffusion and viscosity coefficients, respectively. We employed reparameterized versions of the *ab initio* water potential by Niesar, Clementi and Corongiu (NCC). In order to investigate the role of the electrostatic contribution, the partial charges of the NCC model are adjusted so that to reproduce the dipole moment values of the SPC/E, SPC/Fw and TIP4P/2005 water models. The single and collective transport coefficients are obtained by employing the Green–Kubo relations at various temperatures. Additionally, in order to overcome convergence difficulties arising from the long correlation times of the stress-tensor autocorrelation functions, a previously reported fitting scheme was employed. The present results indicate that there is a significant relationship between the dipole moment value of the model, and the calculated transport coefficients. We found that by adjusting the molecular dipole moment of the NCC to the value of the TIP4P/2005, the obtained values for the self-diffusion and viscosity coefficients are in better agreement with experiment, compared to the values obtained with the original NCC model. Even though the predictions of the present model exhibits an overall correct behavior, we conclude that further improvements are still required. In order to achieve that, a careful reparameterization of the repulsion–dispersion terms of the potential model is proposed. Also, the effect of the inclusion of many-body effects such as polarizability, should also be investigated.

1. Introduction

One of the major motivation for research on liquid water is due to its ubiquity in our environment, and thus its presence among a variety of research areas, from industrial applications to environmental, planetary and natural sciences, *e.g.* biology, chemistry and physics. So, as early as 1933 Bernal and Fowler (1933) proposed the first molecular model for water, and since then numerous of them have been reported with an increasing degree of complexity, *e.g.* from rigid to flexible and from pairwise to polarizable, based on empirical (Berendsen et al., 1987; Jorgensen et al., 1983; Wu et al., 2006) or *ab initio* data (Niesar et al., 1990; Fanourgakis and Xantheas, 2006; Bukowski et al., 2008; Kumar et al., 2010).

During the last years in several review papers the performance of different water models has been assessed and discussion on the aspects of their forms have been reported (Finney, 2001; Guillot, 2002; Vega and Abascal, 2011). Finney (2001) has presented four particular aspects of the forms used for water models in terms of four myths related to the tetrahedral structure, the spherical repulsive core of water molecule, the electrostatic nature of water-water hydrogen bond, and the pair-additive form for the water–water interactions. Next year Guillot (2002) in his

---

[*] Corresponding author. Tel.: +34 915616800x941131.
E-mail address: rita@iff.csic.es (R. Prosmiti).

[1] Present address: Computation-based Science and Technology Research Center (CaSToRC), The Cyprus Institute, P.O. Box 27456, 1645 Nicosia, Cyprus.

0969-8043/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.apradiso.2013.01.020

extensive review on what we have learned from computer simulations on water, concluded that, modeling of water still leaves a taste of incompletion, and discussed some guidance for possible improvement. Recently, Vega and Abascal (2011) have also reported a variety of properties predicted with rigid, non-polarizable water models. They have proposed an evaluation test consisting on 17 different properties of water in order to assess the overall performance of a water model. Among five water models they examined, the TIP4P/2005 (Abascal and Vega, 2005) was found to be the most accurate rigid non-polarizable water model with an average score 7 out of 10. This model (Abascal and Vega, 2005) can be regarded as a small variation of the first water model proposed by Bernal and Fowler (1933), although it took more than 70 years its optimum parameterization and the accurate analysis of its capacity. The overall score of the TIP4P/2005 still leaves space for considerable improvements (Vega and Abascal, 2011) and in this direction, the accurate description of the many-body polarization effects is considered to have the most important contribution. A second factor that is currently examined is the flexibility of the water monomer, although in a recent study (González and Abascal, 2011) it was found that its inclusion in the TIP4P/2005f model did not substantial improve the performance of the original (TIP4P/2005) model. Finally, the performance of quantum instead of classical molecular simulations in order to explicitly account for the nuclear quantum effects, may significantly affect the performance of the model.

Moreover, apart from empirical water models, which are parameterized for reproducing experimentally determined properties of liquid water, progress has been made on the ones following an *ab initio*-based strategy. These latter water models are improved representations, accounting explicitly for electrostatic interactions, dispersion, exchange repulsion, polarizability, and monomer flexibility, while their parameters were obtained by fitting to high-level *ab initio* calculations for water clusters. In particular, such potentials have been first reported by Clementi and coworkers (see references Matsuoka et al., 1976; Niesar et al., 1990 for the MCY and NCC models, respectively), and most recently by Fanourgakis and Xantheas (2006, 2008) the TTM2.1-F and TTM3-F models, Bukowski et al. (2008) the CC-pol model, and from Jordan group (Kumar et al., 2010) the DPP2 one. Nowadays, it is also possible to approach the problem of water modelling by carrying out direct DFT calculations, although current functionals are still not so successful, and development of new ones is currently in progress (Wang et al., 2011; Yoo and Xantheas, 2011). Moreover, we should point out that the computational cost increases rapidly as we go from rigid empirical models to more sophisticated models, and to the DFT ones. Unfortunately, up to now no significant improvement to the predicted properties has been achieved by increasing the degree of complexity of the water model, and thus, rigid empirical models, which are easy to implement and computationally inexpensive for simulations studies, are still the most commonly used (Vega and Abascal, 2011).

Here we are interested in the study of transport properties of liquid water which are in general difficult to model accurately, using molecular simulation for their prediction, and aiming to understand the links between molecular structure and macroscopic behavior of liquid water. The central goal for this work is to reveal the capabilities and limits of a simple rigid model for predicting self-diffusion and viscosity coefficients of liquid water at various temperatures. As for non-polarizable models, the use of an enhanced dipole moment with respect to that in the gas phase can be regarded as a possible way of accounting for many-body effects in a condensed environment, we consider here only the two-body part of an *ab initio*-based water model, namely NCC proposed by Niesar et al. (1990). NCC is a four-site model as it places the negative charge on an extra dummy atom (M-site) along the bisector of the HOH angle of the water molecule. We choose this interaction model as in contrast to several other commonly used water models, it includes anisotropy in the repulsive interactions, by replacing the Lennard–Jones (LJ) oxygen centered term by exponential ones for both oxygen and hydrogen atoms, as well as for the M-site. By changing the values of the atomic charges we adjust its dipole moment value to that of four commonly used water models, and more specifically to the rigid NCC (NCC without polarizability part (Niesar et al., 1990), and we called it NCC^a here), TIP4P/2005 (Abascal and Vega, 2005), and SPC/E (Berendsen et al., 1987) with values of 1.85 D, 2.305 D, and 2.35 D, respectively, and the flexible SPC/Fw (Wu et al., 2006) with $\mu = 2.39$ D. The results presented in this paper could provide insight into the effect of the dipole moment in the transport properties of the liquid water as a function of the temperature. A detailed analysis of them could serve to limit the directions for an improvement searching, *e.g.* to define more appropriate functional forms, and/or to propose target properties in the process for developing empirical potential models.

The paper is organized as follows: the next section describes the protocol used in the molecular dynamics simulations and provides details for the procedure was employed for the calculation of the structural and transport properties of water. In Section 3 the results obtained in this study for a range of different thermodynamical conditions are presented and compared with the experimental data available in the literature, while a short discussion is also provided. Finally, the summary and some conclusive remarks constitute the closing section.

2. Computational details

The molecular dynamics (MD) simulations were carried out using the program MOLDY (Refson, 2000). A cubic box containing 256 water molecules with standard periodic boundary conditions in the three directions and density adjusted to the experimental value was used to simulate liquid water (Lide, 1990). Short-range intermolecular interactions were truncated at a distance $r_c = 10$ Å. The shifted-force potential was applied for the van der Waals interactions, while for the treatment of the long-range electrostatic interactions the standard Ewald summation technique was employed (Ewald, 1921). The modified Beeman algorithm (Refson and Pawley, 1987) was used to integrate the equations of motion with a time step of 0.1 fs, and the temperature was controlled using a velocity scaling procedure.

Radial distribution functions (RDFs) and transport properties were estimated for temperatures between 273 and 373 K. First, a constant volume and temperature (NVT ensemble) MD simulation was performed to compute the average energy of the system at the given temperature, following the procedure described in reference Medina et al. (2011). Then a set of 20 independent constant volume and energy (NVE) simulations were carried out for a total time of 200 ps each, with a tolerance of $\Delta E/E \leq 10^{-4}$ in the energy value.

Equilibrium MD simulations and the Green–Kubo (GK) formula were used to calculate the self-diffusion viscosities along with the shear and bulk viscosities (Chen et al., 2009). This formalism establishes a direct relation between a transport coefficient and the equilibrium time autocorrelation function X_{ACF} of the microscopic flux in the system. For the self-diffusion coefficient, D, the GK equation reads

$$D = \frac{1}{3}\int_0^{\infty} V_{\mathrm{ACF}}(t)\, dt, \tag{1}$$

where

$$V_{\mathrm{ACF}}(t) = \frac{1}{N_m}\sum_{i=1}^{N_m} \langle v_j(t) \cdot v_j(0) \rangle, \tag{2}$$