

Water Model Simulation

Tong Sze Chai

1155064701

2017-2018 CUHK PHYS4610

Physics Final Year Project

Abstract

Water model is mainly used to simulate liquid water. Molecular dynamics and Monte Carlo methods are popular techniques on computer simulation [1]. In the simulation, the system usually included few hundred to few thousand water molecules. Since the statistical mechanical averages can be generated from the coordinates, the “exact” answer can be obtained. The characteristics of the simulation mainly depends on the potential function on the Hamiltonian that govern the interaction of molecules. Water model have many usages. For example, in bio-molecular simulations, which predict the physical properties of biological molecules in their aqueous environments [2].

1 Introduction

There are many types of water model. Water model can be classified by their nature. In general, the nature include: i) the interaction points called site, ii) whether the water model is flexible or rigid, iii) whether the model consider the polarization effect [1]. In this paper, simple water model will be our focus. Simple water models are rigid and do not consider the polarization effect. The charges on the site are fixed. Different kinds of simple water models have different numbers of interaction site. TIP4P and SPC/E are some examples of simple model.

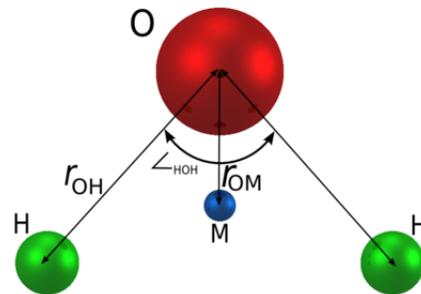


Fig. 1. TIP4P Model

1.1 TIP4P Model

In TIP4P model a single Lennard-Jones (LJ) interaction site is located at the position of the oxygen atom [3]. In Fig.1 [4], two positive point charges are located in the positions of the hydrogen atoms. A negative charge is located at M-site, which is 0.15 \AA away from the oxygen along the H-O-H bisector in the direction of the positive charges. Parameters of TIP4P model are shown in Table 1.

1.2 SPC/E Model

In Fig.2 [5,6], the SPC/E model has a LJ interaction site and the negative charge are located at the position of the oxygen atom. Positive charges are located on the hydrogen atoms. Parameters of SPC/E model are shown in Table 1.

Parameters	TIP4P	SPC/E
$\Upsilon_{OH}(\text{\AA})$	0.9572	1.000
$\Upsilon_{OM}(\text{\AA})$	0.15	—
$\angle_{HOH}(\text{deg})$	104.52	109.47
$\sigma(\text{\AA})$	3.154	3.166
$\epsilon/\kappa(K)$	78.00	78.19
$q_o(e)$	0	-0.8476
$q_H(e)$	0.52	0.4238
$q_M(e)$	-1.04	—

Table 1. Parameters of TIP4P and SPC/E model

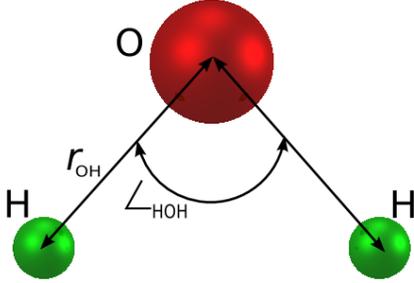


Fig. 2. SPC/E Model

2 Potential Function of Water Model

Potential function of water model is important to determine the motion of the water molecule [1]. From Eqn.(1), the force acting on each water molecule is known after the potential $V(x, y, z)$ is defined.

$$F = -\nabla V(x, y, z) \quad (1)$$

Where x, y, z are the coordinates of the centre-of-mass of a water molecule.

2.1 Total molecular interaction

The total molecular interaction is as follow:

$$V_{tot} = V_{ele} + V_{ind} + V_{dis} + V_{exc} \quad (2)$$

The total molecular interaction in Eqn.(2) can be divided into four parts. V_{ele} is electrostatic interaction. V_{ind} is induced dipole interaction. V_{dis} is dispersion interactions and V_{exc} is exchange repulsion.

2.1.1 Electrostatics interaction

The first-order perturbation electrostatics interaction can be written as follow [7]:

$$\hat{V}_{AB} = \frac{q_A q_B}{R} + q_A \nabla \left(\frac{1}{R} \right) \mu_B - q_B \nabla \left(\frac{1}{R} \right) \mu_A + \dots \quad (3)$$

In Eqn.(3), where q_A is the total charge on molecule A and q_B is the total charge on molecule B. The total dipole moment of molecule A and molecule B are, respectively, denoted by μ_A and μ_B . R is the distance between the centre-of-masses of molecule A and molecule B.

2.1.2 Induced dipole interaction

Induced dipole interaction can be written as follow [8, 9]:

$$V_{ind} = -\frac{1}{2} \Delta \mu_A E_A \quad (4)$$

In Eqn.(4), where E_A is the electric field at molecule A and $\Delta \mu_A$ is the induced dipole moment on molecule A.

2.1.3 Dispersion Interactions

Using London's original work and the Taylor expansion of the interaction operators, the approximate dispersion energy is as follow [9, 10]:

$$V_{dis} = -\frac{1}{4} \bar{\epsilon} \sum_{\alpha\beta\gamma\delta} \alpha_{\alpha\beta}^A \alpha_{\gamma\delta}^B \nabla^2 \left(\frac{1}{R} \right)_{\alpha\gamma} \nabla^2 \left(\frac{1}{R} \right)_{\beta\delta} \quad (5)$$

In Eqn.(5), where $\bar{\epsilon}$ is an average molecular excitation potential. The polarizabilities α^A and α^B are obtained from the corresponding monomer wave functions. R is the distance between the centre-of-masses of molecule A and molecule B.

2.1.4 Exchange Repulsion

The first-order approximation to the exchange repulsion can be written in terms of the overlap integrals as follow [11]:

$$V_{exc} = c_1 S^2 + c_2 S^4 + c_3 S^6 + \dots \quad (6)$$

In Eqn.(6), where c_1 , c_2 and c_3 are some expansion coefficients, and S is the overlap integral between two orbitals on atoms A and B. For fermions, it is sometimes called Pauli repulsion.

3 Water Model Hamiltonian

The water molecules may be treated as rigid asymmetric rotors specified by configurational vectors with six degrees of mechanical freedom [12]. Three specify the center-of-mass position and three Euler angles fix the spatial orientation. The classical Hamiltonian H_N for simple water model can be written as follow:

$$H_N = \frac{1}{2} \sum_{j=1}^N (m|v_j|^2 + \omega_j \cdot I_j \cdot \omega_j) + V_N(x_1 \dots x_N) \quad (7)$$

In Eqn.(7), the first part of the Hamiltonian corresponding to the translational kinetic energy. The molecules all have mass m . The linear velocity denoted by v_j . The second part corresponding to the rotational kinetic energy. ω_j represent the angular velocity and the inertial moment tensors are symbolized by I_j . The last part associate with the potential energy where $x_1 \dots x_N$ are the configurational vectors.

Computer resource is limit. It is very time consuming to evaluate potential energy V_N which consist of N molecules. In order to speed up the simulation, V_N can be approximates by a pair function V_{eff} .

$$V_N(R_1 \dots R_N) \approx \sum_{ij} V_{eff}(R_i, R_j) \quad (8)$$

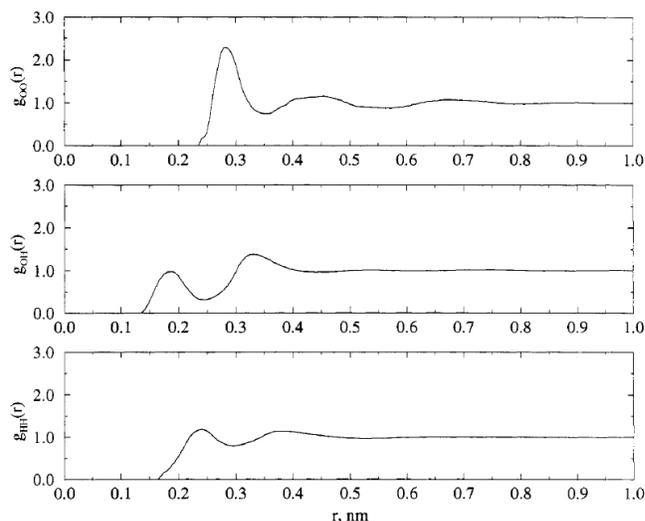


Fig. 3. Experimental water radial distribution functions followed by O-O pair, O-H pair and H-H pair at 298K.

Combining Eqn.(7) and Eqn.(8), the new Hamiltonian become:

$$H_N = \frac{1}{2} \sum_{j=1}^N (m|v_j|^2 + \omega_j \cdot I_j \cdot \omega_j) + \sum_{i<j=1}^N V_{eff(2)}(x_i, x_j) \quad (9)$$

The subsequent motion of the water molecule in the simulation can be evaluated by Eqn.(9).

4 Radial distribution function

Radial distribution function describes how density varies as a function of distance from a reference particle. It is widely used in presenting a water model result. There are 3 kinds of radial distribution function of water model such as O-O pair, O-H pair and H-H pair. A good water model simulation should match the radial distribution function with the experimental result.

In Fig.3 [13], the positions of the principal maximum of $g_{OO}(r)$ at 0.28 nm and the secondary maximum at 0.45 nm is a signature of tetrahedrally coordinated water molecule. Since each water molecule has only one oxygen atom, the radial distribution function of water and $g_{OO}(r)$ would be quite similar. As a result, $g_{OO}(r)$ is commonly



Fig. 4. Spatial distribution function of TIP4P model

used in representing the simulation result.

There are two maxima of $g_{OH}(r)$ at 0.19 nm and at 0.33 nm just because each water molecule has two hydrogen atom. The first maximum in $g_{OH}(r)$ indicate the existence of hydrogen bond. The second maximum in $g_{OH}(r)$ is also a mark of tetrahedral coordination of water molecules.

5 The Spatial Distribution Function in Liquid Water

Radial distribution functions have been commonly used in presenting computer simulation result. However, water molecule does not have spherical symmetry. Radial distribution functions cannot be interpreted unambiguously to provide the spatial order in a molecular liquid [14]. The spatial structure of TIP4P in the liquid state is demonstrated here (Fig.4).

The spatial distribution function is denoted by (Fig.4) $g_{OO}(r, \Omega)$ for TIP4P at 25°C. The isosurfaces corresponding to $g_{OO}(r, \Omega) = 1.4$. The enclosed regions have average oxygen densities at least 40% greater than that of the bulk. The central molecule has been included to define the local frame. The colors indicate the distance r from the central molecule. Orange to yellow

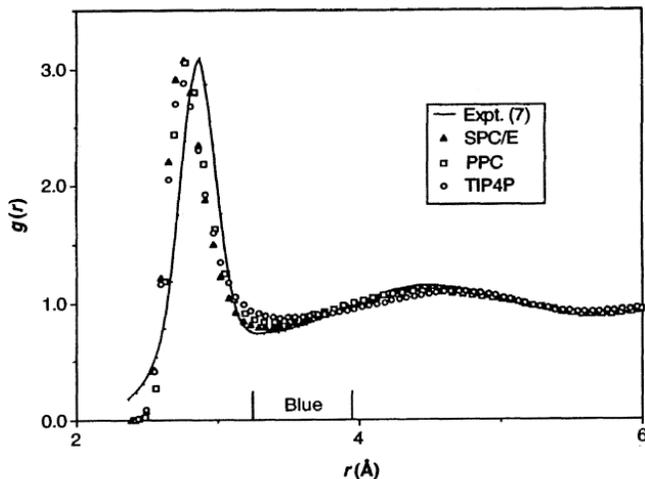


Fig. 5. The oxygen-oxygen pair radial distribution functions of water models at 298K. (The range of blue color is consistent with Fig.4)

represents to $r < 3.2\text{\AA}$. Green to blue and back to green represents to $3.2\text{\AA} < r < 4.0\text{\AA}$. Yellow to red corresponds $4.0\text{\AA} < r < 5.0\text{\AA}$.

In Fig.4, the two distinct caps above the hydrogens of the central molecule are two hydrogen bond accepting neighbours. The single cupped below the oxygen are two hydrogen bond donating neighbours. The two predominately blue features due to additional non-tetrahedral coordination. The non-tetrahedral coordination have local maxima in oxygen density occur at the first minimum in $g_{OO}(r)$ (Fig.5) [15]. The non-tetrahedral local maxima in oxygen density can only be observed in spatial distribution function.

6 Phase Diagram of Water Model

The phase diagram of water as obtained from computer simulations for simple water model TIP4P and SPC/E [16]. (NpT) Monte Carlo simulations were used for the liquid phase. Anisotropic NpT Monte Carlo simulations were performed for the solid phases [17]. Since phase diagram is a stringent test for any water potential function, it may help to develop better water models. Moreover, the experimental phase diagram of water is shown as below (Fig.6).

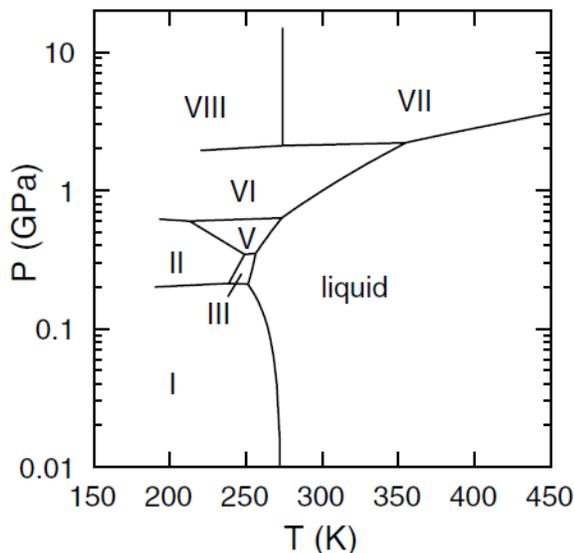


Fig. 6. Experimental Phase Diagram of Water

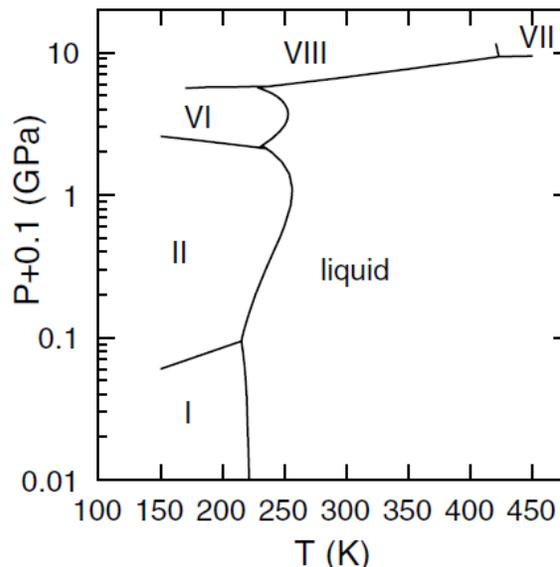


Fig. 8. Simulated Phase Diagram of SPC/E Model

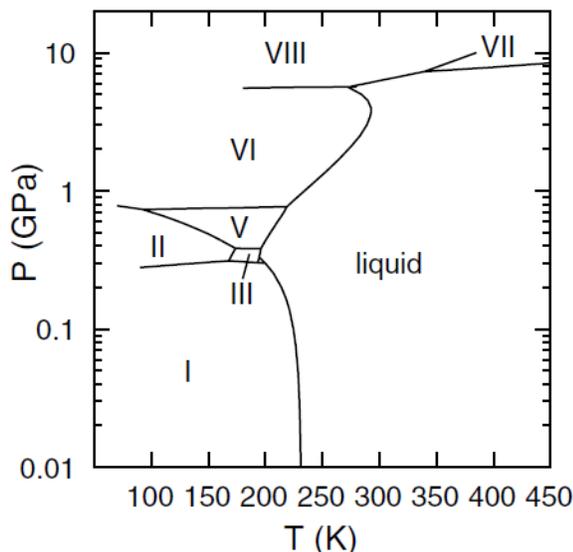


Fig. 7. Simulated Phase Diagram of TIP4P Model

Fig.7 shows the phase diagram of the TIP4P model. Ices I, II, III, V, VI, VII, and VIII are found to be stable phases for the TIP4P model. Ice IV and IX are clearly metastable phases for the TIP4P model so they do not show up in the phase diagram.

Fig.8 shows the phase diagram of the SPC/E model. Concerning the SPC/E model, ices II, VI, VII, VIII are stable solid phases while ices IV and IX are metastable. The SPC/E model predicts

that ices III and V are metastable, which shows disagreement with experimental result. At low pressure, ice II shows extraordinary stability in SPC/E model.

In summary, the TIP4P provide a better description of phase diagram than SPC/E. TIP4P and SPC/E model have only one major difference, which is the location of the negative charge. The negative charge of TIP4P is located on M-site while the negative charge of SPC/E is located on the oxygen. This is the key factor that TIP4P reduces the stability of ice II with respect to its competitors (ice I, III, V) [18]. Although the phase diagram of TIP4P shows good agreement with experimental result, fails to describe high density ice VII and VIII. It is just because TIP4P is designed for liquid molecular simulation.

7 TIP4P/ε, TIP4P Refinement

TIP4P model [19], which are developed to fit the liquid density and heat of vaporization at 298K. TIP4P aims to evaluate thermodynamics properties include the liquid density, temperature of maximum density, heat of vaporization, self-diffusion coefficient, pair distribution functions, critical parameters, and dielectric constant. However, TIP4P fails to reproduce liquid density

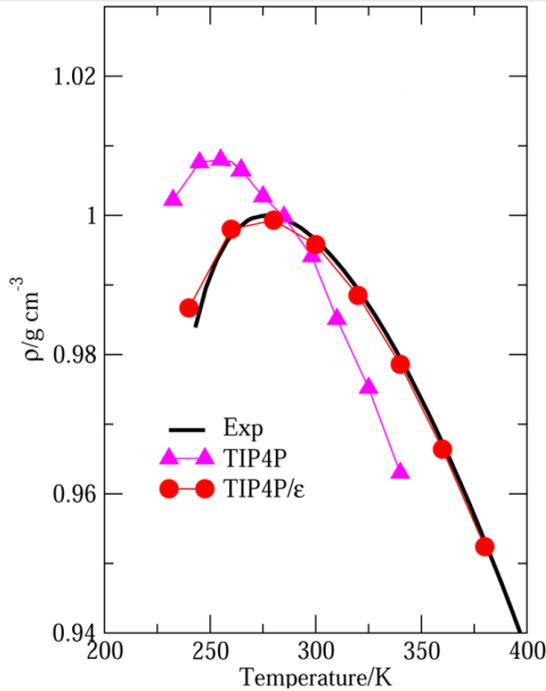


Fig. 9. Liquid density of water as a function of temperature for rigid force fields of water

at various temperature and dielectric constant at 298K (Fig.9 & 10) [20].

TIP4P/ε is developed by parameterizing the static dielectric constant at room temperature and the temperature of maximum density simultaneously (Fig.10 & 11). TIP4P/ε has the same geometry of the TIP4P model [20]. The simulations perform at 240K where a molecular dipole moment μ of minimum density is found (Fig.12). The minimum is shifted to larger values of μ as the distance between the oxygen atom and M-site decreases. The parameters that define the dipole moment are adjusted to reproduce the experimental dielectric constant. After that, the Lennard-Jones parameters are varied to match the temperature of maximum density (Fig.11). The only difference between the TIP4P/ε with TIP4P is the values of the interaction parameters. Parameters are shown in Table 2.

The intermolecular force of the simulation is based on Eqn.(10). The first term is the LJ interaction and the second term is the Coulomb interaction. The M-site is massless, but the force acting

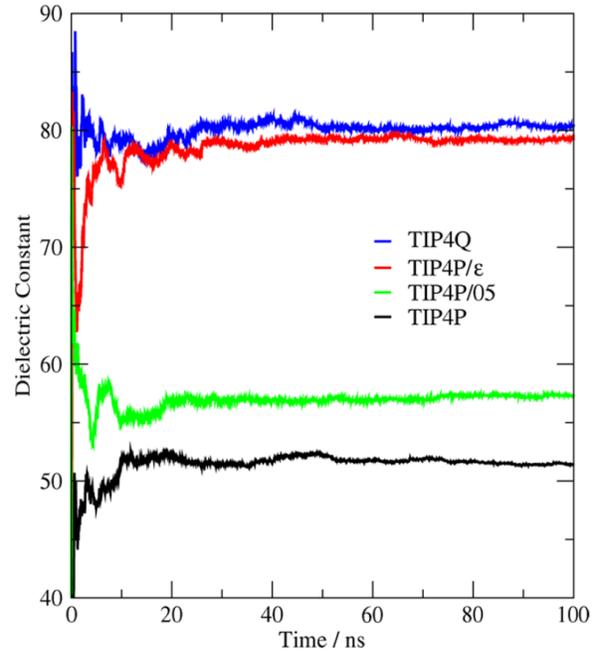


Fig. 10. Dielectric constant as a function of time at 298K. The experimental Dielectric constant of water is 78.54K at 298K. [21]

Parameters	TIP4P	TIP4P/ε
$\Upsilon_{OM}(\text{\AA})$	0.15	0.105
$\sigma(\text{\AA})$	3.154	3.165
$\epsilon/\kappa(K)$	78	93.0
$q_o(e)$	0	0
$q_H(e)$	0.52	0.527
$q_M(e)$	-1.04	-1.054
$\mu(D)$	2.177	2.4345

Table 2. Force Field Parameters of TIP4P & TIP4P/ε

on it is distributed among the whole molecule.

$$\mu(r_{ij}) = 4\epsilon_{OO} \left[\left(\frac{\sigma_{OO}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{OO}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^3 \sum_{j=1}^3 \frac{q_i q_j}{r_{ij}} \quad (10)$$

where r_{ij} is the distance between sites i and

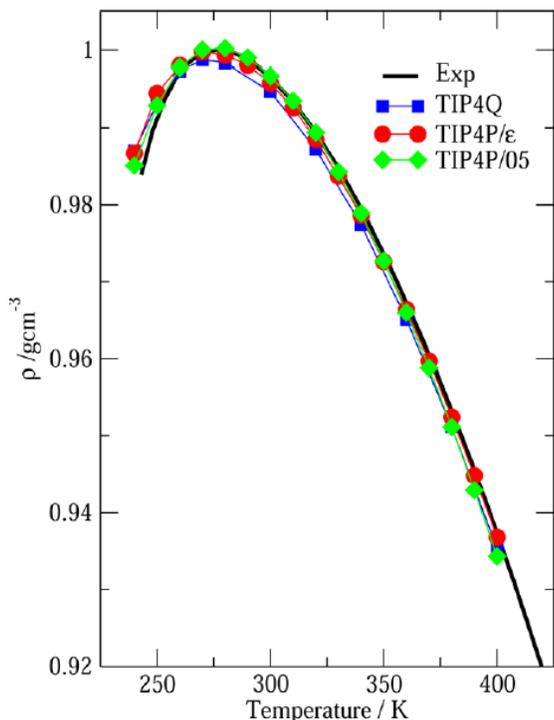


Fig. 11. Density as a function of temperature for rigid water models.

j , q_i is the electric charge of site i , ϵ_{OO} is the LJ energy scale, ϵ_0 is the permittivity of a vacuum, and σ_{OO} is the diameter for an OO pair.

In summary, TIP4P/ε reproduces the dielectric constant, thermodynamics, and dynamical and structural properties at different temperatures and pressures are in good agreement with experimental data [22].

8 A Hybrid Density Functional-Classical Molecular Dynamics Simulation

Solute-solvent interactions is important in chemical processes such as equilibria and reactions [23]. There are two main approaches, which include continuum models [24] and statistical simulations [25]. Most of the research conduct statistical simulations such as Monte Carlo or Molecular Dynamics, which can handle a great numbers of molecules. However it cannot give a very accurate description of the electronic structure of the solute when chemical reactions are involved [26]. Continuum models are effective

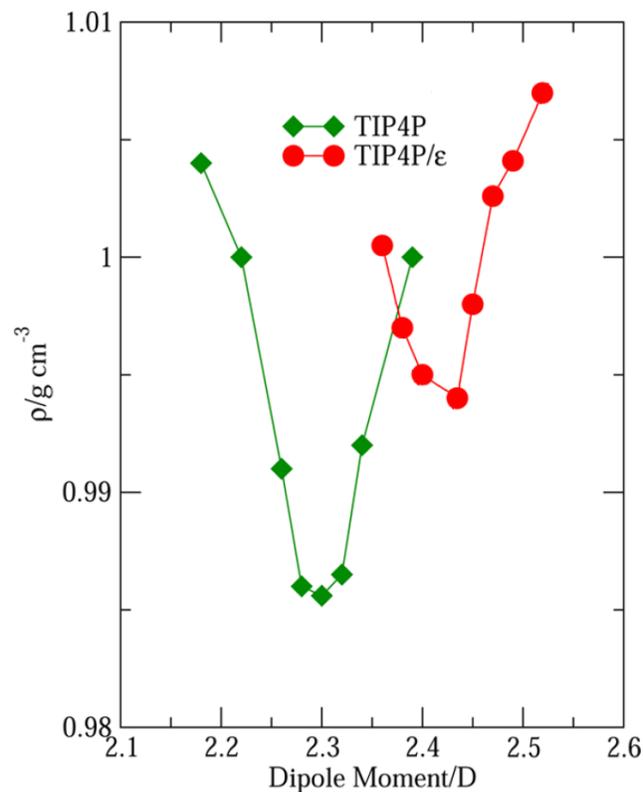


Fig. 12. Liquid density of water as a function of molecular dipole moment at 240K

to implement quantum treatments characterized by a dielectric constant, with a detailed electronic description of the solute. However, the computing time would be too large.

The development of hybrid models that combine some of the advantages of the two previous approaches. These hybrid models consist in the statistical treatment of a large system and a small part is studied at the quantum mechanical level. This approach allows the investigation of polarization effects and reactive processes in solution. Density Functional Theory (DFT) [27] techniques is a method of obtaining an approximate solution to the Shrödinger equation of a many-body system. DTF and and molecular mechanics (MM) [28] contribute to the semiempirical hamiltonian [29].

For a computer simulation involve a classical subsystem constituted by 128 TIP3P water molecules and a quantum subsystem of a single

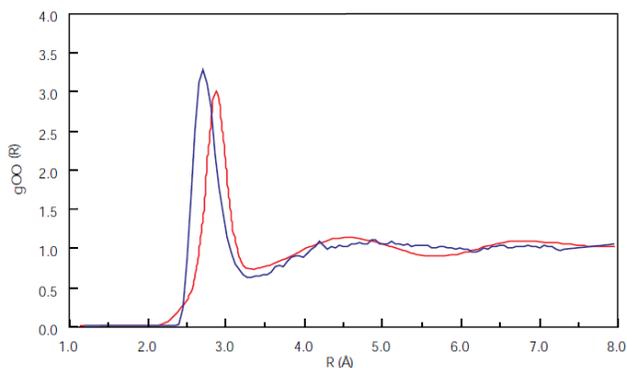


Fig. 13. Oxygen-oxygen radial distribution functions: DFT/ TIP3P (blue line) and experimental (red curve)

water molecule. The total energy of the system can be written as Eqn.(11):

$$E(R_n, R_s) = E_{dft}(R_n) + E_{mm}(R_s) + E_{dft/mm}(R_n, R_s) \quad (11)$$

where R_n is the position of the quantum mechanical nuclei and R_s the position of the solvent interaction sites.

$E_{dft}(R_n)$ is the energy of the subsystem described quantum mechanically. It can be written in terms of which are all functionals of the charge density. The terms are ion-electron potential energy, ion-ion potential energy, electron-electron energy, kinetic energy and exchange-correlation energy. $E_{mm}(R_s)$ is the energy of the system described at the classical mechanical level. It involves only two terms, which are LJ interaction and Coulomb interaction. $E_{dft/mm}(R_n)$ is interaction between the DFT and the MM portions. It combines with LJ interaction, Coulomb interaction and ion-electron potential energy.

In the hybrid molecular dynamics algorithm, the simulation results for the radial distribution functions (Fig.13), solvation energy and solute polarization that are in good agreement with experimental data [26]. It also gives a better description of polarization effects on the quantum molecule.

Conclusions

In water model computer simulation, there are mainly two factors to give an accurate description, the types of the model and the methods of the simulation. Different types of water model are designed to show different features. No model reproduce all thermodynamics properties. TIP4P is designed for liquid molecular simulation, which fails to reproduce high pressure ice properties. Refinement can be done to show a better description on some properties, such as TIP4P/ε shows a better liquid density of water as a function of temperature compare to TIP4P. Moreover, the methods of the simulation are limited by the computer resources. For example, the computing time for continuum models would be large but give a better description than statistical simulations. In conclusion, the type of the model and the method of the simulation should be chosen carefully with respect to the simulation conditions.

References

- [1] Anders Wallqvist and Raymond D. Mountain *Molecular Models of Water: Derivation and Description*
- [2] Hans W. Horn, William C. Swope, and Jed W. Pitera *Development of an improved four-site water model for biomolecular simulations: TIP4P-Ew*
- [3] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R.W.Impey, and M. L. Klein, *J. Chem. Phys.* 79, 926 (1983).
- [4] TIP4P model of water page on SklogWiki, http://www.sklogwiki.org/SklogWiki/index.php/TIP4P_model_of_water
- [5] H. J.C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* 91, 6269 (1987).
- [6] SPC/E model of water page on SklogWiki, http://www.sklogwiki.org/SklogWiki/index.php/SPC/E_model_of_water
- [7] A.D.Buckingham, in *Intermolecular Forces.*, J. O. Hirschfelder, Ed., *Advances in Chemical Physics.*, Wiley, New York, 1967
- [8] A.D.Buckingham, in *Intermolecular Interactions: From Diatomics to Biopolymers*,

- B. Pullman, Ed.*, Wiley, New York, 1978,
- [9] C. G. Grey and K. E. Gubbins, *Theory of Molecular Fluids: Fundamentals*, Clarendon Press, Oxford, 1984, Vol. 1
- [10] A. Wallqvist, P. Ahlstrom, and G. Karlstrom, *J. Phys. Chem.*, 94, 1649 (1990). A New Intermolecular Energy Calculation Scheme: Applications to Potential Surface and Liquid Properties of Water.
- [11] D. E. Williams and D. J. Craycroft, *J. Phys. Chem.*, 91, 6365 (1987). Nonbonded H . . H Repulsion Energy from Ab Initio SCF Calculations of Methane, Ammonia, Water and Methanol Dimers.
- [12] Aneesur Rahman, and Frank H. Stillinger *Molecular Dynamics Study of Liquid Water*
- [13] A. K. Soper, F. Bruni, and M. A. Ricci, *J. Chem. Phys.*, 106, 247 (1997). Site-Site Pair Correlation Functions of Water from 25 to 400": Revised Analysis of New and Old Diffraction Data.
- [14] Peter G. Kusalik* and Igor M. Svishchev *The Spatial Structure in Liquid Water*.
- [15] A. K. Soper and M. G. Phillips *Chem. Phys.* 107, 47 (1986).
- [16] E. Sanz, C. Vega, J. L. F. Abascal, and L.G. MacDowell *Phase Diagram of Water from Computer Simulation*.
- [17] D. Frenkel and B. Smit, *Understanding Molecular Simulation*. Academic Press, San Diego, 1996
- [18] O. Matsuoka, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, 64, 1351 (1976).
- [19] Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; *J. Chem. Phys.*, 1983, 79, 926935. Klein, M. L. Comparison of Simple Potential Functions for Simulating Liquid Water.
- [20] Abascal, J. L. F.; Vega, C. A. *J. Chem. Phys.*, 2005, 123, 144504 144512. Relation Between the Melting Temperature and the Temperature of Maximum Density for the Most Common Models of Water.
- [21] Diego P. Fernandez, Y.Mulev, A.R.H Goodwin and J.M.H Levelt Sengers *A Database for the Static Dielectric Constant of Water and Steam*
- [22] Raul Fuentes-Azcatl and Jose Alejandro *Non-Polarizable Force Field of Water Based on the Dielectric Constant: TIP4P/ε*
- [23] Reichardt, C. *in Solvents and Solvent Effects in Organic Chemistry*; VCH, Weinheim, 1988.
- [24] Onsager, L. *J. Am Chem. Soc.* 1936, 58, 1486.
- [25] Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* 1985, 107, 154
- [26] Iaki Tun, Marilia Teresa C. Martins-Costa, Claude Millot and Manuel F. Ruiz-Lpez *A Hybrid Density Functional-Classical Molecular Dynamics Simulation of a Water Molecule in Liquid Water* 25 September 1995
- [27] Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
- [28] Warshel, A.; Levitt, M. *J. Mol. Biol.* 1976, 103, 227
- [29] Bash, P.; Field, M. J.; Karplus, M. *J. Am. Chem. Soc.* 1987, 109, 8092