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Non-Polarizable Force Field of Water Based on the Dielectric Constant: TIP4P/ε

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S *Supporting Information*

ABSTRACT: The static dielectric constant at room temperature and the temperature of maximum density are used as target properties to develop, by molecular dynamics simulations, the TIP4P/ε force field of water. The TIP4P parameters are used as a starting point. The key step, to determine simultaneously both properties, is to perform simulations at 240 K where a molecular dipole moment of minimum density is found. The minimum is shifted to larger values of μ as the distance between the oxygen atom and site M, l_{OM}, decreases. First, the parameters that define the dipole moment are adjusted to reproduce the experimental dielectric constant and then the Lennard-Jones parameters are varied to match the temperature of maximum density. The minimum on density at 240 K allows understanding why reported TIP4P models fail to reproduce the temperature of maximum density, the dielectric constant, or both properties. The new model reproduces

some of the thermodynamic and transport anomalies of water. Additionally, the dielectric constant, thermodynamics, and dynamical and structural properties at different temperatures and pressures are in excellent agreement with experimental data. The computational cost of the new model is the same as that of the TIP4P.
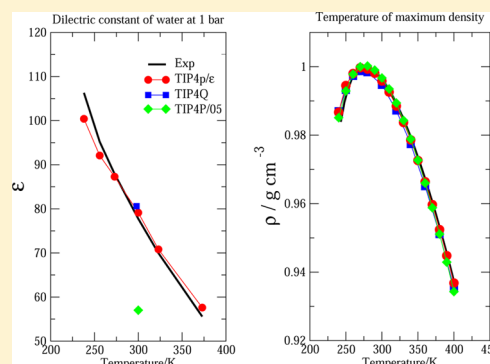
1. INTRODUCTION

Water is found everywhere and plays an important role in several areas such as biology, electrochemistry, environmental physics, geology, etc. Water has a different behavior than molecules of around the same size and molecular structure. The structure of water in a liquid or in a solid is dictated by the geometry and polarity. Molecular dynamics (MD) and Monte Carlo (MC) methods are useful tools to understand water at different thermodynamic conditions from molecular interactions. Guillot in 2002 reviewed[1] most of the simulations of water using rigid, flexible, and polarizable potentials performed with MC and MD methods. The popular rigid SPC/E,[2] TIP3P,[3] and TIP4P[3] models, which were developed to fit the liquid density and heat of vaporization under ambient conditions, were some of the analyzed models. The target properties chosen by Guillot to evaluate the performance of the force fields were the liquid density, temperature of maximum density, heat of vaporization, self-diffusion coefficient, pair distribution functions, critical parameters, and dielectric constant. He found that none of the models reproduced all the properties. Large differences were found for the same property using different models. In 2009, Vega et al.[5] published a review to analyze results from TIP3P, TIP4P, TIP4P/2005,[6] and TIP5P[7] force fields. The TIP5P and TIP4P/2005 matched the experimental temperature of maximum density. Apart from the properties analyzed by Guillot, they included the coexisting densities at the liquid–vapor phase equilibrium, the surface tension, the equation of state (EOS) at high pressures, the EOS

of ice Ih, and the phase diagram of different ices. They arrived to the conclusion that the TIP4P/2005 model gave results closer to the experimental values for most of the analyzed properties. The model failed to reproduce the dielectric constant, the heat of vaporization, the vapor pressure, and the melting temperature of ice Ih. In 2011, Vega and Abascal[8] made a deeper comparison of the models mentioned above and this time they included the three-site SPC/E force field. Apart from the properties analyzed in 2009, they included the shear viscosity and orientational relaxation time in the comparison. The TIP4P/2005 was able to reproduce the minimum of shear viscosity at 273 K. The TIP4P/2005 force field was the best in that evaluation followed by the SPC/E model.

Alejandre et al. in 2011 developed the TIP4Q force field,[9] a model that had the TIP4P geometry with positive charges on every nucleus and a negative charge at a distance l_{OM} along the bisector of the bending angle. The fourth charge was added to increase the molecular dipole moment. The TIP4Q model was parametrized to match simultaneously the experimental dielectric constant and temperature of maximum density. Excellent agreement was found when its results were compared with those from the TIP4P/2005 model. The TIP4Q model also failed to reproduce the heat of vaporization, the vapor pressure, and the melting temperature of ice Ih. The TIP4Q

model is computationally more expensive than TIP4P because the interaction between two molecules involves the calculation of 16 pair distances in comparison with 10 in the TIP4P. The dielectric constant is a macroscopic property that describes the electrostatic interactions in a liquid. That quantity is important in multicomponent systems where the components are charged or polar, for instance, in electrolyte solutions, mixtures of polar solvents, and so on.

Vega et al.[8] have pointed out some aspects where rigid non-polarizable water models might fail, and they also disscused possible areas of research to improve force fields. The role the dipole/quadrupole moments ratio plays on the phase diagram has been analyzed;[10,11] it is suggested that a ratio close to 1 gives a good description of the phase diagram including the ice phases. Wang and co-workers[12] in a recent work have found that a polarizable model called iMOEBA is able to give at the same time the correct T_{MD} and dielectric constant. That model improves the TIP4P/2005 force field. Although water is one of the most studied systems using molecular simulation methods, it is convenient to know up to what extent a non-polarizable water model with a correct dielectric constant and temperature of maximum density improves or not other physical properties.

The main goal of this work is to provide a systematic procedure to find the parameters of force fields containing four points and to develop the TIP4P/ε model that contains three charges and one Lennard-Jones (LJ) site on the oxygen atom. The TIP4P/ε has the same computational cost as TIP4P. In the new model, the charge distribution is chosen to reproduce the dielectric constant, while the LJ parameters are determined to obtain the temperature of maximum density. The new parametrization involves simulations at 240 K. By using the parameters of the TIP4P model, it is found that for $l_{OM} = 0.15$ Å at 240 K there is a minimum in the plane $\mu-\rho$ (ρ is the liquid density). The liquid density at 240 K is greater at the dipole moment of the original model than at μ_{md}. The minimum is shifted to larger μ values when l_{OM} is decreased. The optimum value of the dipole moment of minimum density, μ_{md}, obtained from the minimum, is chosen to reproduce the dielectric constant at 300 K. The LJ parameters are modified to match the experimental temperature of maximum density. The fitting procedure targets only liquid-phase properties, and the model might fail to give the correct phase diagram of ices. The procedure of minimum density at 240 K allows one to understand why four-site models (TIP4P, TIP4P-Ew, TIP4P/2005) fail to reproduce the dielectric constant, the temperature of maximum density, or both properties. It is found that the μ value used to parametrize the TIP4Q model is the same as μ_{md}. The conclusions drawn in this work might be useful to develop polarizable models; however, we focus the study on the comparison with non-polarizable force fields. Simulation results for the TIP4P/2005, TIP4Q, and TIP4P/ε force fields will be discussed in this work.

The rest of the work is organized as follows: Section 2 gives the force field, section 3 gives the simulation details, the search of parameters is given in section 4, and in section 5 the results are analyzed. Finally, concluding remarks and references are given.

2. THE TIP4P/ε FORCE FIELD OF WATER

The molecule is rigid with the same geometry of the TIP4P model.[3] The bond distance is $r_{OH} = 0.9572$ Å, and the bending angle is $\theta = 104.52°$. The molecules have four sites: two hydrogens, an oxygen, and a site M located at a distance l_{OM} from the oxygen atom along the bisector of the bending angle.

The intermolecular force field between two water molecules is based on the LJ and Coulomb interactions

$$u(r_{ij}) = 4\varepsilon_{OO}\left[\left(\frac{\sigma_{OO}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{OO}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\varepsilon_0}\sum_{i=1}^{3}\sum_{j=1}^{3}\frac{q_i q_j}{r_{ij}} \tag{2.1}$$

where r_{ij} is the distance between sites i and j, q_i is the electric charge of site i, ε_0 is the permittivity of a vacuum, ε_{OO} is the LJ energy scale, and σ_{OO} is the diameter for an OO pair. The site M does not have mass, but the force on it is distributed among the other atoms. The model has one LJ site on the oxygen and three charges: one in every hydrogen atom and one on the site M. The only difference between the TIP4P/ε with TIP4P and TIP4P/2005 models is the values of the interaction parameters. The parameters of the force fields analyzed in this work are given in Table 1.

Table 1. Force Field Parameters of Non-Polarizable Water Models[a]

model	σ (Å)	ε/k_B (K)	q_H (e)	q_O (e)	l_{OM} (Å)	μ (D)
TIP4P	3.154	78	0.520	0.0	0.15	2.177
TIP4P/2005	3.1589	93.2	0.5564	0.0	0.1546	2.305
TIP4Q	3.1666	93.2	0.525	0.5	0.069	2.44
TIP4P/ε	3.165	93.0	0.527	0.0	0.105	2.4345

[a]The charge on site M is $q_M = -(2q_H + q_O)$. The geometry for the isolated molecule is given by $r_0 = 0.9572$ Å and $\theta_0 = 104.52°$.

3. SIMULATION DETAILS

Molecular dynamics simulations are performed using the Gromacs suite of programs.[14] Three types of simulations are carried out to determine properties on the liquid and solid phases, liquid–vapor and solid–liquid phase equilibriums. Liquid simulations are carried out using 500 molecules in the NVT (constant number of particles, volume, and temperature) and in the NPT (constant number of particles, pressure, and temperature) ensembles. The liquid–vapor phase equilibrium and interfacial properties are obtained using slab simulations[15] in the NVT ensemble for systems with 5832 molecules. The simulations for ice Ih[16] and melting temperature[17] of ice Ih are carried out using 768 molecules with the anisotropic NPT ensemble implemented in Gromacs.

All the simulations use periodic boundary conditions in all directions, and the equations of motions are solved using the leapfrog algorithm[14,18] with a time step of 2 fs, otherwise stated. The temperature is kept constant using the Nosé–Hoover thermostat[19] with a parameter of 0.5 ps. The pressure is obtained using the Parinello–Rahman barostat with a parameter of 1.0 ps.[14] The bond distances are kept constant using the LINCS procedure.[20]

The Ewald summation method is used to evaluate the electrostatic interactions.[21] The LJ and the real part of the potential in liquid simulations are truncated at 9.5 Å with added long-range corrections, LRC,[18] to energy and pressure. The simulations at the liquid–vapor interface are performed using a parallelepiped cell with dimensions $L_x = L_y = 54$ Å and $L_z = 184$ Å and a truncation distance of 2.6 nm ($8\sigma_{OO}$) (at that distance, the coexisting densities and surface tension reach the largest

values avoiding finite size effects).[22−24] The LRC are not included in Gromacs for inhomogeneous systems. The molecules are initially allocated in a liquid slab surrounded by a vacuum[15,25] with two symmetrical interfaces. The systems are equilibrated for 0.5 ns, and the average properties are obtained for at least 1.5 ns divided in 5 blocks. At the end of the simulation, the system contains two symmetrical interfaces. The coexistence densities are obtained through the average density profile in the bulk regions.[22] The SPME method[21] is used to calculate the reciprocal interactions with a mesh of reciprocal vectors of 1.2 Å in every direction and a spline of order 4. The maximum number of reciprocal vectors in the longest direction L_z of the simulation cell[15] is $|\mathbf{k}_z^{max}| = (L_z/L_x)|\mathbf{k}_x^{max}|$. It is important to use that relation to obtain the correct surface tension at the liquid−vapor interface[15,22,25] when the Ewald sum is applied.

4. SEARCH OF PARAMETERS

The main idea behind the TIP4P/ε parametrization of water is to choose the dipole moment defined by the geometry, q_H and l_{OM}, to reproduce the experimental dielectric constant and then to determine the LJ parameters to match the temperature of maximum density, T_{MD}. In a previous work, the TIP4Q model was parametrized using also both properties as a target. The model gave a dielectric constant of 80.6 under ambient conditions with a dipole moment of 2.44 D. It also reproduced the T_{MD} and several density anomalies of water.

The TIP4P/ε model has three charges and one LJ interaction between oxygen atoms; thus, the number of pair interactions between two molecules is the same as that in the TIP4P model. In order to reproduce the experimental T_{MD} of water, which is 277 K, the model has to be able to give a density, ρ, at 240 K lower than at 300 K. The TIP4P model gives[4] a density of 1.008 g cm^{-3} at 245 K, and the T_{MD} is found 24 K below the experimental value, i.e., at 253 K. On the other hand, the model gives a molecular dipole moment of 2.17 D and a dielectric constant of 52 at 300 K and 1 bar.

As a starting point, to develop the TIP4P/ε force field, the geometry, the LJ parameters, and the l_{OM} values of the TIP4P model developed by Jorgensen et al.[3] (see Table 1) were kept constant during simulations in the NPT ensemble to obtain the liquid density at 240 K and several values of μ, in other words, several values of q_H in the TIP4P models. The dipole moment involves charges and l_{OM} values, and it allows comparing TIP4P and TIP4Q results. When μ is increased, a minimum is found in the plane $\mu−\rho$, with a density that is smaller than at 300 K. The dipole moment of minimum density, μ_{md}, is 2.3 D; see Figure 1. If μ_{md} is used to perform NPT simulations at temperatures above 240 K, the experimental densities are overestimated but they can be decreased by increasing mainly ε_{OO}. The decrease in density is greater at higher temperatures. A model with $\mu =$ 2.3 D and greater LJ parameters than those from TIP4P is expected to improve the TIP4P model. In order to find the optimum μ_{md} for the TIP4P/ε model, additional NPT simulations were performed, keeping constant the TIP4P Lennard-Jones parameters, for smaller fixed values of l_{OM} and different q_H values. In all of the cases, a minimum was found on the density shifted to larger values of μ. The T_{MD} of these four-point models can match the experimental data when both the l_{OM} and q_H values are obtained from μ_{md} and appropriate LJ parameters are taken. In order to understand the origin of μ_{md}, several properties were analyzed. The number of hydrogen bonds in the minimum is the same as that of systems with other
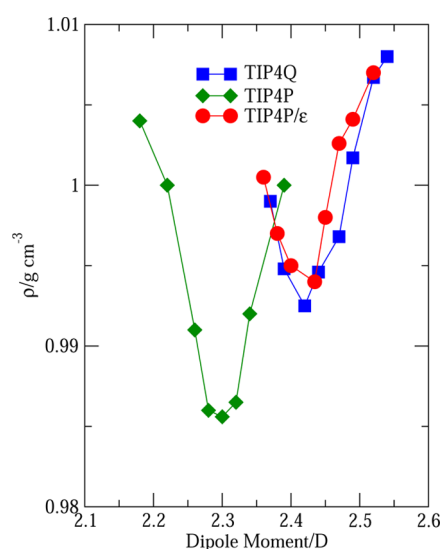

Figure 1. Liquid density of water as a function of molecular dipole moment at 240 K and 1 bar using fixed LJ values from the TIP4P model[3] and different charge distributions. The dipole moment for the TIP4P and TIP4P/ε models is obtained using a l_{OM} value of 0.15 and 0.105 Å, respectively. The results for the TIP4Q model are obtained with $l_{OM} = 0.069$ Å and $q_O = 0.5e$.

charges. The enthalpy as a function of charge shows a linear behavior, that is, the μ_{md} is not a consequence of an energetic factor. The oxygen−oxygen pair distribution function at the minimum density is slightly shifted to larger distances, and the first peak is less high than those from greater densities; i.e., the effective volume of the first shell of waters surrounding a molecule is larger at the minimum density. More work is needed to draw definite conclusions.

The TIP4P/ε parameters were found in a three-step procedure: (1) The charge distribution was fixed using $\mu_{md} =$ 2.4345 D ($l_{OM} = 0.105$ Å, $q_H = 0.527e$), see Figure 1, with LJ parameters from the TIP4P model. A dielectric constant of 76 was found. The densities at high temperatures were much greater than experimental data; see legend TIP4P-A in Figure 2. (2) The ε/k_B value was increased from 78 to 93 K in several steps; the final value coincides with that of the TIP4P/2005 model. The change in density was not symmetric, but larger differences were found at higher temperatures; see legend TIP4P-B in Figure 2. If ε/k_B is greater than 93 K, the densities at high temperatures decreased, but they increased at 240 K; i.e, the predicted densities at 240 K moved away from experimental data. (3) Finally, to match the experimental temperature of maximum density, the σ_{OO} value was increased from 3.154 to 3.165 Å, less than 0.35%; see legend TIP4P/ε in Figure 2. The dielectric constant at 300 K was 79 for $\mu_{md} = 2.4345$ D, close to the TIP4Q model. The final parameters for the TIP4P/ε are given in Table 1. It is interesting that the new q_H value is close to that from the TIP4P, while the new ε_{OO} value is around the same as that from the TIP4P/2005 model. The new model, as it will be seen below, reproduces the experimental dielectric constant, T_{MD}, and several thermodynamic and transport properties.

The μ_{md} analysis is applied to the TIP4P, TIP4P-Ew, TIP4P/2005, and TIP4Q water models to understand the predicted results of T_{MD}, the shape of the $T−\rho$ plane, the dielectric constant, or all of them. The TIP4P model has a dipole moment of 2.17 D, but for $l_{OM} = 0.15$ Å, the dipole moment of
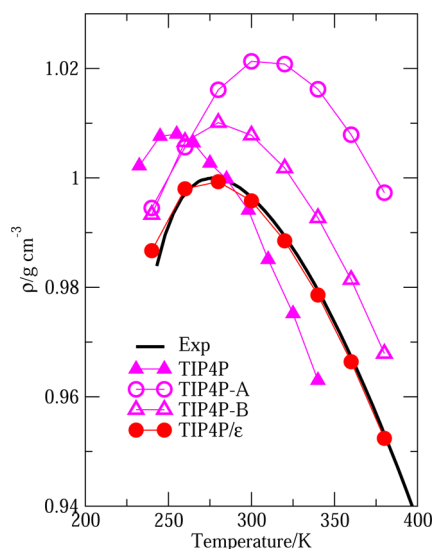
Figure 2. Liquid density of water as a function of temperature for rigid force fields of water. The results for the TIP4P are taken from ref 4. The TIP4P-A is for results using $\mu_{md} = 2.4345$ D ($q_H = 0.527$e and $l_{OM} = 0.105$ Å) with LJ parameters from TIP4P. The TIP4P-B is for results using $\mu_{md} = 2.4345$ D and $\varepsilon/k_B = 93$ K and σ_{OO} from TIP4P. The filled circles are results for the TIP4P/ε with parameters given in Table 1.

minimum density is around 2.3 D at 240 K; see Figure 1. The density of that model at 240 K is not only higher than the minimum density, but it is also higher than that at 300 K. The TIP4P model gives a maximum in the $T-\rho$ plane shifted to lower temperatures where the densities at low temperatures are overestimated and they are underestimated as the temperature increases.[4] The low dipole moment compared with the TIP4P/ε model explains why the TIP4P does not reproduce the dielectric constant. The main change applied to the TIP4P model to parametrize the TIP4P-Ew force field was to decrease l_{OM} from 0.15 to 0.125 Å, which gave $\mu = 2.321$ D. The value of μ_{md} is expected to be around 2.37 D, see Figure 1; therefore, the TIP4P-Ew model should have the same behavior as the TIP4P model; i.e., the density at 240 K is higher than that at the minimum, the reported[13] $T_{MD} = 274$ K is shifted to lower temperatures compared with experimental data, and the densities are overestimated and underestimated for temperatures below and above 274 K, respectively. The TIP4P-Ew model fails to reproduce the dielectric constant because the μ value of the model is lower than that of the TIP4P/ε force field. To develop the TIP4P/2005 force field, the q_H and ε_{OO}/k_B values from the TIP4P model were increased and the rest of the parameters were almost unchanged. The model reproduces T_{MD} because μ of the model is surprisingly μ_{md}, see Figure 1, and the density at 240 K is lower than that at 300 K with $\varepsilon_{OO}/k_B = 93.2$ K. The TIP4P/2005 model gives a dielectric constant of 58, and it fails to reproduce the experimental value because μ is small compared with that of the TIP4P/ε model. The TIP4Q model was fitted to reproduce the T_{MD} and dielectric constant. The μ value of the model is around the same as μ_{md} shown in Figure 1. The use of $\varepsilon_{OO}/k_B = 93.2$ K leads to a density which is lower at 240 K than at 300 K, and therefore. the model reproduces the T_{MD}.

5. SIMULATION RESULTS

The TIP4P/ε force field is developed by finding the charge distribution defined by μ that reproduces the experimental

dielectric constant at 300 K and 1 bar, while the LJ parameters on the oxygen atom are chosen to reproduce the T_{MD} at 1 bar. Once the force field parameters are fixed, other properties are calculated at different temperatures and pressures such as the dielectric constant, isothermal compressibility, thermal expansion coefficient, heat of vaporization, self-diffusion coefficient, shear viscosity, equation of state at high pressures, oxygen−oxygen pair distribution function, liquid−vapor coexisting densities, vapor pressure, surface tension, and equation of state of ice Ih. The results for the TIP4P/ε force field are compared with those of TIP4Q and TIP4P/2005 water models. All the property definitions and numerical data are given as Supporting Information.

5.1. Dielectric Constant, ε. The dielectric constant[26] at 300 K as a function of time is shown in Figure 3 for the rigid
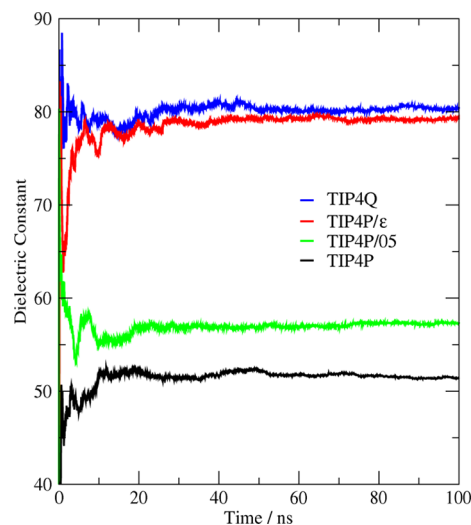

Figure 3. Dielectric constant as a function of time for the TIP4P, TIP4P/2005, TIP4Q, and TIP4P/ε models. All the results are obtained in this work.

water models, and the final results are 52 for TIP4P, 58 for TIP4P/2005, 80.6 for TIP4Q, and 79 for TIP4P/ε. These values are in good agreement with published results.[3,6,9] The proper evaluation of the dielectric constant needs long simulations to have the average dipole moment of the system around zero. Results of ε on the liquid phase are also obtained at other thermodynamic conditions. The dielectric constant results are shown in Figure 4 at different temperatures and 1 bar, in Figure 5 along the coexistence line, and in Figure 6 at different temperatures and pressures. Although the force field parameters are obtained to reproduce ε under ambient conditions, the simulation results are in excellent agreement with experimental data[27] under all thermodynamic conditions.

5.2. Temperature of Maximum Density, T_{MD}. The liquid densities as a function of temperature and 1 bar are shown in Figure 7 for the rigid water models. The liquid densities for the TIP4P/2005 are obtained in this work because there are two publications[6,28] that report slightly different values. The new results compare well with those given in refs 6 and 28 and allow a direct comparison to be made between the results for the TIP4P/ε and TIP4P/2005 models. All the simulation details are the same; the only difference is the value of the force field parameters. The three models, shown in Figure 7, give the same $\rho-T$ shape and around the same T_{MD}. The estimated T_{MD} is 276 K for the TIP4P/2005 and TIP4P/ε models, compared

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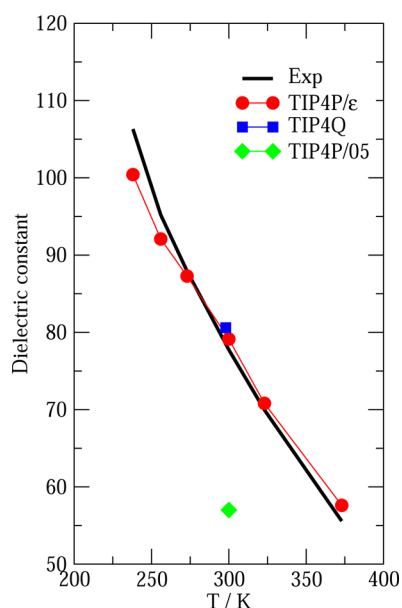dx.doi.org/10.1021/jp410865y | *J. Phys. Chem. B* 2014, 118, 1263−1272

Figure 4. Dielectric constant as a function of temperature at 1 bar for several rigid water models. The continuous line is for experimental data.[27]

Figure 6. Dielectric constant of rigid water models at different temperatures and pressures. The continuous line is for experimental data.[27]
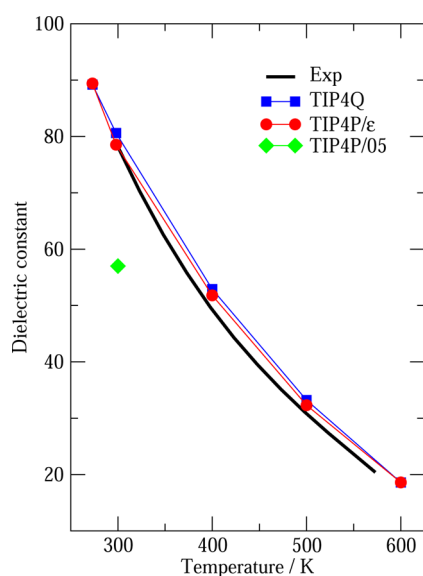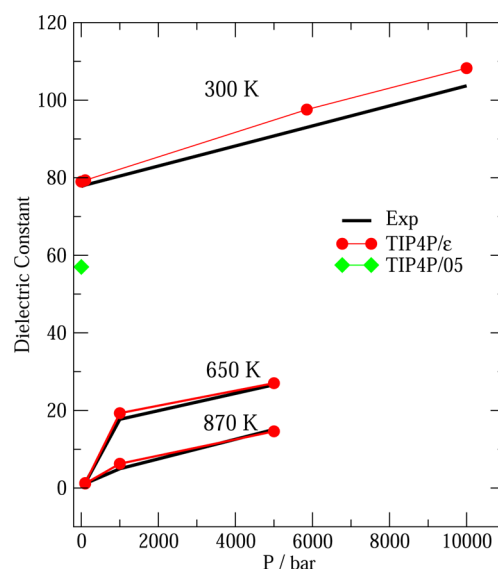

Figure 5. Dielectric constant as a function of temperature for the liquid phase along the liquid–vapor coexistence for systems with 864 molecules. The continuous line is for experimental data.
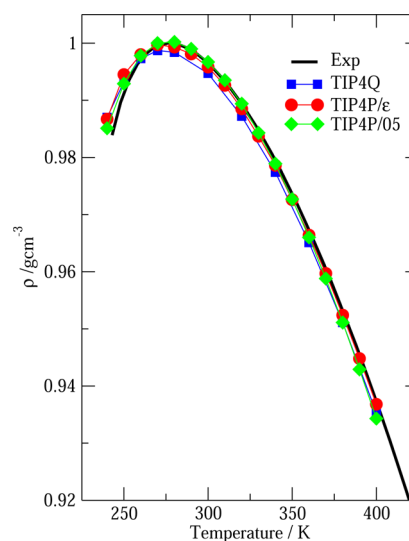

Figure 7. Density as a function of temperature for rigid water models. The simulation results for the TIP4P/2005 model are obtained in this work. The continuous line is for experimental data.[29]

with the experimental value[29] of 277 K. The experimental results for temperatures below 273 K are for the mestastable liquid.

5.3. Isothermal Compressibility, κ_T. The results are shown in Figure 8 for different rigid water models in simulations of 500 molecules, and 40 ns long simulations are needed to have reliable results because that property is obtained through volume fluctuations. Some simulations were performed to analyze the effect that time step has on the isothermal compressibility. Results with 1 and 2 fs were the same, within simulation error, when the average values were obtained by taking the volume fluctuations every 2 ps in both cases. The three models give a minimum on κ at around 310 K. The

results for the TIP4P/ε force field are closer to experimental data[29] than the TIP4P/2005 model.[28]

5.4. Thermal Expansion Coefficient, α_P. The liquid densities shown in Figure 7 are used to calculate α_P by fitting the density results to a polynomial function of degree 5. The results shown in Figure 9 for the three models compare well with experimental data[29] at temperatures greater than 275 K. At lower temperatures, the simulation results are systematically higher due to the small difference between simulation results and experimental data in the ρ–T shape; see Figure 7.

5.5. The Heat of Vaporization, ΔH_v. The heat of vaporization, the enthalpy difference between the vapor and liquid, is a property that has been used as a target property in the parametrization of some force fields such as SPC/E,[2] TIP3P,[3] and TIP4P.[3] These models fail to reproduce the experimental T_{MD} and other thermodynamic and dynamical properties.[1,5,8] Other models such as TIP4P-Ew[13] and TIP4P/
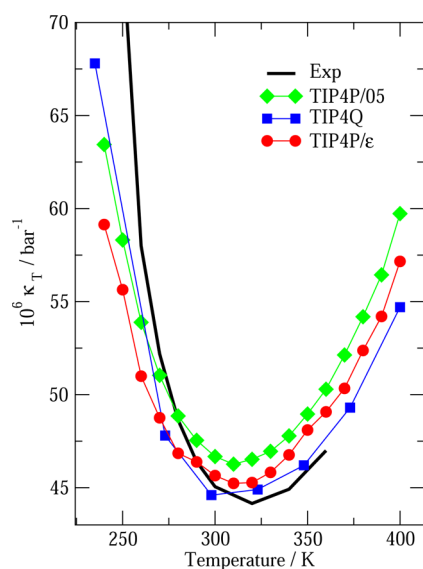
Figure 8. Isothermal compressibility as a function of temperature for rigid water models. The simulation results for the TIP4P/2005 model are obtained in this work. The continuous line is for experimental data.[29]
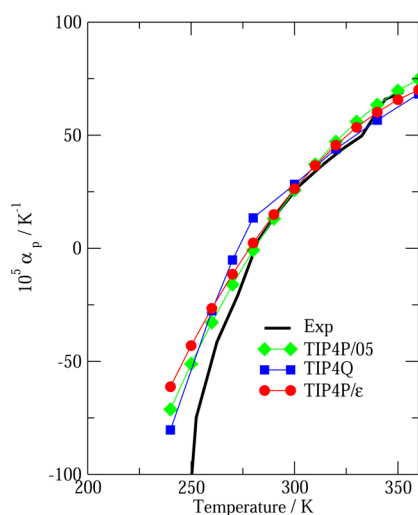

Figure 9. Thermal expansion coefficient as a function of temperature for rigid water models. The simulation results for the TIP4P/2005 model are obtained in this work. The continuous line is for experimental data.[29]

2005[6] that give a better description of T_{MD} and several anomalies of water do not reproduce the experimental ΔH_v. It has been suggested[2,13] that some corrections are needed to compare the results of effective rigid models with experimental data to take into account properly the vapor phase. The ΔH_v values reported in this work are obtained using

$$\Delta H_v = H_{gas} - H_{liq} = RT - U_{liq} - PV_{liq} - E_{pol} + C$$

(5.2)

where R is the gas constant, T is the temperature, U_{liq} and V_{liq} are the potential energy and volume of the liquid phase, and E_{pol} is the polarization correction energy that includes the energetic cost of the effective polarization[1,2]

$$E_{pol} = \frac{1}{2} \frac{(\mu - \mu_g)^2}{\alpha}$$

(5.3)

where μ_g is the dipole moment of water in the gas phase, μ is the corresponding value of the rigid model, and α is the experimental molecular polarizability.

The last term in eq 5.2 is a correction to account for the change in the intramolecular vibrational modes and for nonideal gas behavior; in this work, it is calculated following the description given by Horn et al.[13] The results of ΔH_v, with corrections, are shown in Figure 10. The best agreement with
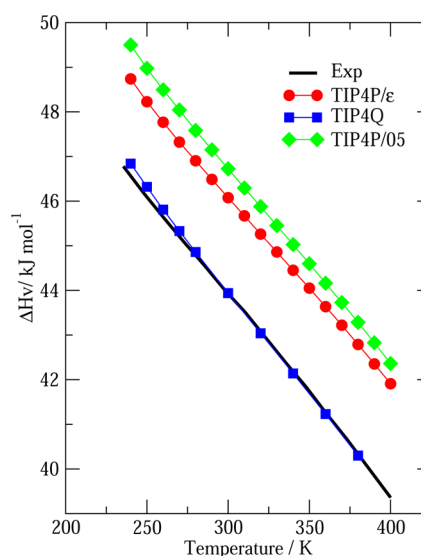

Figure 10. Heat of vaporization for rigid water models at different temperatures. The simulation results for the TIP4P/2005 model are obtained in this work. The results are corrected according to the procedure described by Horn et al.[13] The continuous line is for experimental data.[30]

experimental data[30] is for the TIP4Q model. The results from the TIP4P/ε model improve those from the TIP4P/2005 force field. The ΔH_v results without corrections are also given in the Supporting Information. It has to be emphasized that the polarization correction is not valid in the calculation of surface tension and vapor–liquid equilibria from simulations. A molecule moving from the liquid to the vapor phase does not gain the energy associated with the polarization correction.

5.6. The Self-Diffusion Coefficient, D. The three models give the same results, within the simulation error, which are systematically lower than experimental values[31] for temperatures above 280 K; see Figure 11.

5.7. The Shear Viscosity. The shear viscosity was obtained recently for several water models,[32] and one of the conclusions was that only the TIP4P/2005 model gives results in good agreement with experimental data[33] and it is able to predict the minimum of viscosity at 273 K as a function of pressure.

In this work, NPT simulations are performed for at least 30 million steps with a time step of 1 fs to make a direct comparison with results reported[32] for the TIP4P/2005 model. The pressure components are saved on a disk every 1 fs, and all the configurations are used as a time origin. The upper limit in the integrations is 8 ps in all cases. The results are shown in Figure 12 at different temperatures and pressures. The TIP4P/2005 and TIP4P/ε give the same values, within the simulation error. At 373 K, the simulation values match the experimental
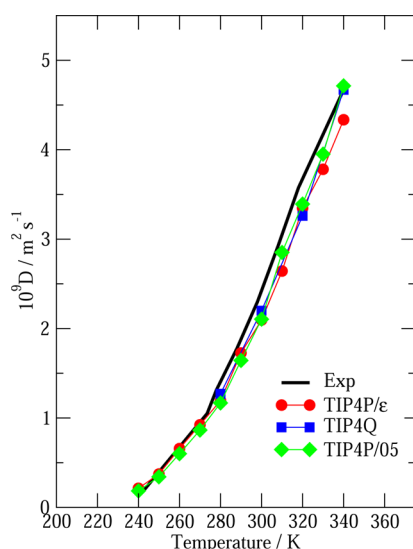
Figure 11. Difussion coefficient of rigid water models at different temperatures. The simulation results for the TIP4P/2005 model are obtained in this work. The continuous line is for experimental data.[31]
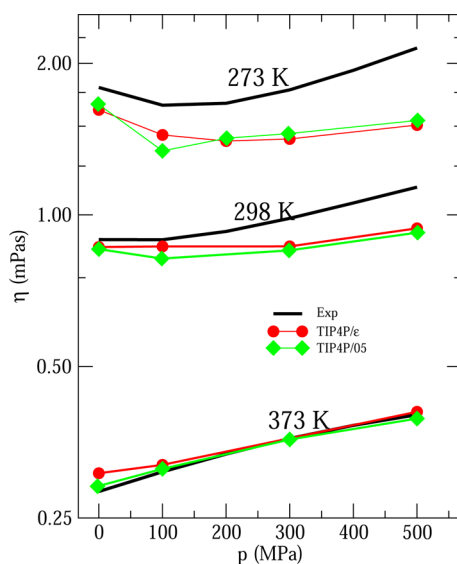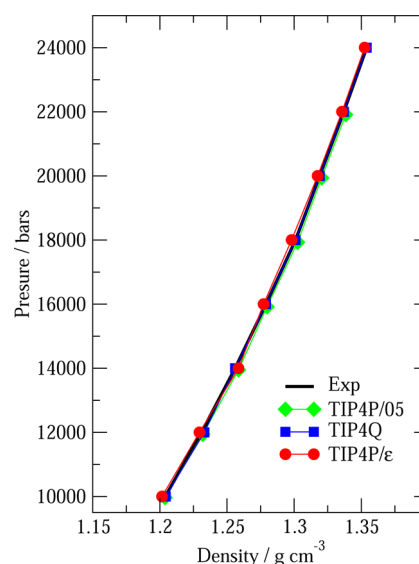

Figure 13. Equation of state at high pressures at 373 K for rigid water models for systems with 864 molecules. The results for the TIP4Q and TIP4P/2005 are taken from the original sources.[6] The continuous line is for experimental data.

Figure 12. Shear viscosity in logarithm scale as a function of pressure at different temperatures for rigid water models. The results for the TIP4P/2005 model are taken from the original sources.[32] The continuous line is for experimental data.[33]
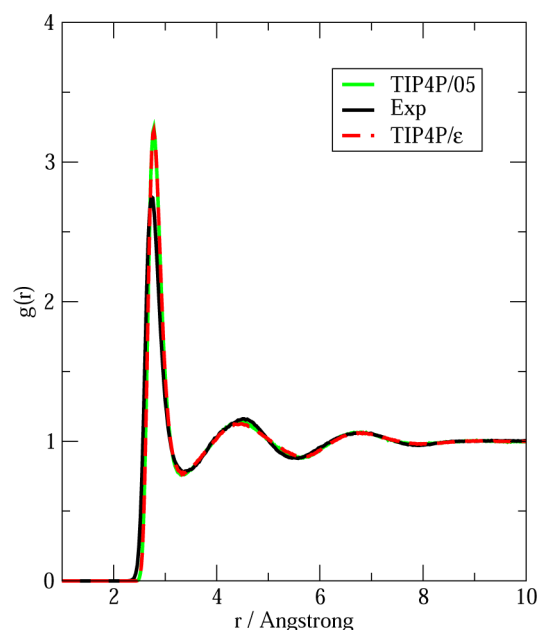

Figure 14. Oxygen−oxygen pair distribution function for rigid water models at 300 K and 1 bar. All the simulation results are obtained in this work. The continuous line is for experimental data.[34]

data;[33] however, at 298 and 273 K, the simulation results are systematically lower; the difference is larger at high pressures. Both models predict the minimum value of shear viscosity at 273 K.

5.8. The Equation of State at High Pressure. The density results as a function of pressure at 373 K are shown in Figure 13. The three models give the same results. The agreement with experimental data is remarkably good.

5.9. The Structure of Liquid Water. The oxygen−oxygen pair distribution function obtained in NPT simulations at T = 300 K and P = 1 bar for liquid water is shown in Figure 14. The results for TIP4P/2005 and TIP4P/ε models give a higher first peak than the experimental results[34] for the liquid. The structures for the ice Ih, not shown, at 250 K are also the same for the two models and compare well with experimental data.

5.10. Coexisting Densities, Vapor Pressure, and Surface Tension. It is important to evaluate if a force field that has been parametrized in the liquid phase reproduces also the experimental data[35] at the liquid−vapor interface. The simulations are carried out in the NVT ensemble using an elongated cell.

The liquid and vapor densities are obtained by fitting the average density profile to a hyperbolic tangent function.[23] The results are shown in Figure 15. The liquid densities obtained for the three models are in good agreement with experimental data[35] at all temperatures. The TIP4Q and TIP4P/ε models give the same results, but they fail to reproduce the vapor density at temperatures above 550 K. Their results are
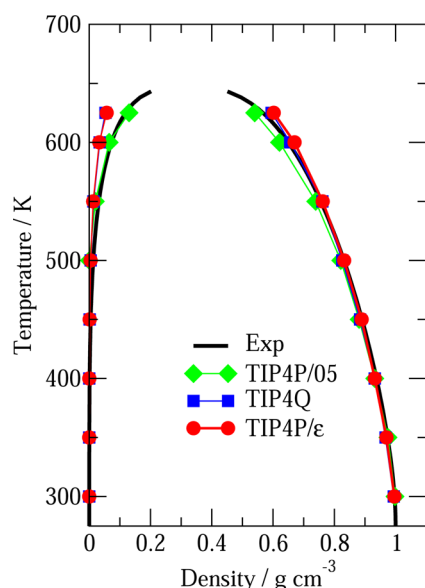
Figure 15. Liquid−vapor phase equilibrium of rigid water models. The results for the TIP4Q and TIP4P/2005 are taken from the original sources.[9,25] The continuous line is for experimental data.[35]

systematically lower that experimental data.[35] The critical parameters for the TIP4P/ε model, obtained by using the rectilinear diameter law with critical exponents $\beta = 0.325$, are ρ_c = 0.32 g cm^{-3} and T_c = 665 K. The corresponding experimental values are ρ_c = 0.322 g cm^{-3} and T_c = 647.1 K. The TIP4P/2005 model is in excellent agreement with experimental data including the region close to the critical point.

The vapor pressure, P_v, is calculated as the normal component of the pressure tensor in the interface simulations. The results as a function of temperature of different rigid water models are shown in Figure 16. All the models underestimate
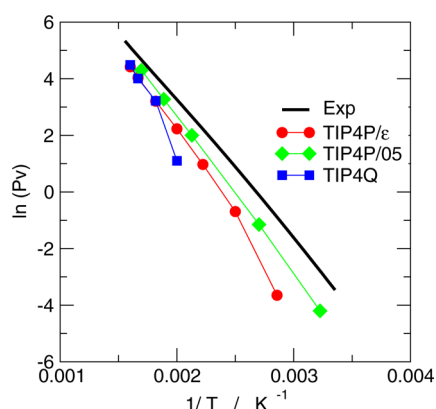

Figure 16. Logarithm of vapor pressure as a function of inverse temperature. The results for the TIP4Q and TIP4P/2005 are taken from the original sources.[9,25] The continuous line is for experimental data.[35]

the vapor pressure compared with experimental data.[35] The best agreement with experiment is for the TIP4/2005 model. The TIP4Q and TIP4P/ε give the same results at high temperatures.

The surface tension[23,36] results are shown in Figure 17. The results for the TIP4P/2005 model[25,37] are in good agreement with experimental data[35] at all temperatures. The TIP4P/ε and
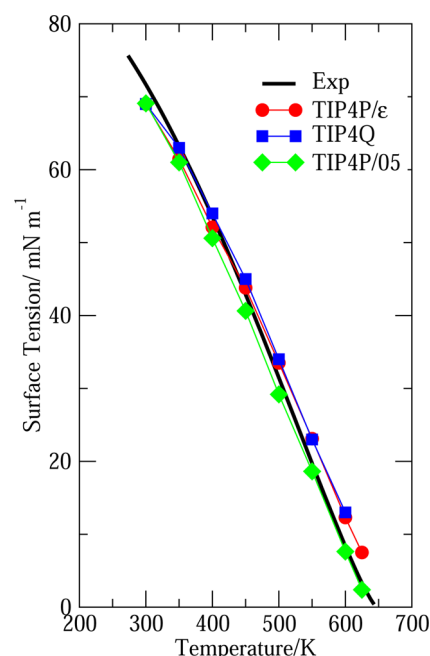

Figure 17. Surface tension as a function of temperature for rigid water models. The results for the TIP4Q and TIP4P/2005 are taken from the original sources.[9,25] The continuous line is for experimental data.[35]

TIP4Q models give the same results, and the agreement with experimental data is good for temperatures less than 500 K but the surface tension is slightly larger than experimental data at higher temperatures.

5.11. Equation of State and Melting Point of Ice Ih. The TIP4P/ε model is not fitted to reproduce ice properties, but it is useful to know how well the model can reproduce the equation of state of ice Ih. The density as a function temperature at 1 bar of ice Ih is obtained for the TIP4P/ε model. In this case, isotropic NPT simulations were performed on systems containing 864 molecules with zero total dipole moment,[38] using the Berendsen thermostat and barostat.[14] The results are shown in Figure 18. The results for the TIP4P/ε are closer to the experimental values[39] than those of the TIP4P/2005 and TIP4P/Ice water models.[6,40] The three models fail to reproduce the shape of the experimental data, and they show a linear behavior with almost the same slope. The curvature has been associated with quantum effects.[41]

The melting temperature, T_m, is also obtained using direct coexistence simulations.[17] Anisotropic NPT simulations, starting from the same initial configuration, at 1 bar and temperatures ranging from 235 to 245 K are carried out in systems containing 870 water molecules in an elongated simulation cell in the z direction, half in the liquid and half in the ice Ih. The Berendsen thermostat and barostat were used with parameters of 0.2 and 0.5 ps, respectively. The result of T_m is estimated to be 240 ± 2 K, the same value as that reported for the TIP4Q model and slightly smaller than 249 K that was reported for the TIP4P/2005 model.[17] The experimental values[35] is 273 K.

6. CONCLUDING REMARKS

The procedure to develop the TIP4P/ε force field of water involves simulations at 240 K using the TIP4P model parameters. The results at 240 K show that optimum charge distributions, defined by molecular geometry and partial
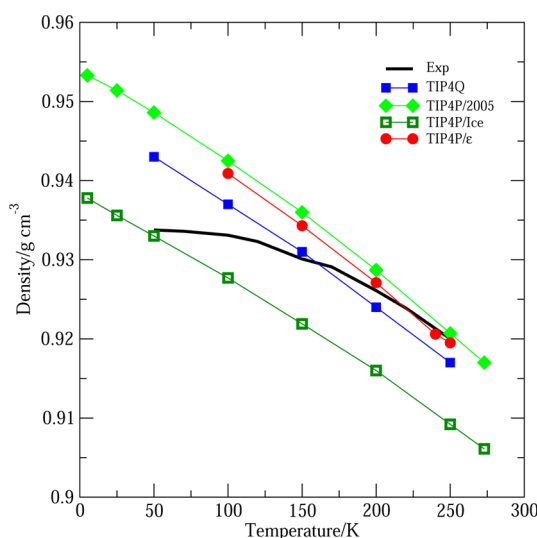
Figure 18. Equation of state of ice Ih at different temperatures and 1 bar for rigid water models. The results for the TIP4Q, TIP4P/2005, and TIP4P/ice are taken from the original sources.[9,40] The continuous line is for experimental data.[39]

charges, can be obtained from the μ_{md} procedure to reproduce the experimental dielectric constant under ambient conditions. The molecular dipole moment of the TIP4Q model is used as a guide to obtain the final values. A second step is to fix μ_{md} and then to increase the LJ parameters on the oxygen atom to match the experimental temperature of maximum density. This finding shows that short- and long-range interactions are independent; i.e., the charge distribution can be chosen to obtain the dielectric constant, a macroscopic property that describes the electrostatic interactions, and then to determine the LJ parameters to reproduce the temperature of maximum density and other physical properties. The μ_{md} procedure allows us to understand why the TIP4P, TIP4P-Ew, and TIP4P/2005 models fail to reproduce T_{MD}, ε, or both properties.

The TIP4P/ε and TIP4Q models are equivalent in the sense that both give around the same results, but the TIP4P/ε model is computationally faster because the interaction between two water molecules involves the calculation of 10 distances, the same number as in the TIP4P model.

There is excellent agreement between the calculated and experimental dielectric constants at different temperatures and pressures for the new model, although the parameters are fitted to obtain ε under ambient conditions. The improvement on the dielectric constant is not reflected on better values of the heat of vaporization, vapor pressure, EOS of ice Ih, or melting temperature of ice Ih. The results from this work go in the opposite direction of the work of Aragones et al.[42] where they stated that the polarization factor (G), which contains information about the orientational dependence of water interactions, is more important than the value of the dielectric constant itself. Therefore, the TIP4P/ε, which reproduces the dielectric constant of water, will fail to reproduce the dielectric constant of ices because it does not reproduce the orientational dependence of the water molecule interactions. Aragones et al. demonstrated that rigid and non-polarizable water models with a dipole/quadrupole ratio deviating from the unit will fail in reproducing the polarization factor, and thus any related properties.

The main difference between the TIP4P/ε and TIP4P/2005 models is for the dielectric constant and results close to the critical point. The critical temperature of the new model is overestimated by around 3%. All other liquid or vapor−liquid properties for these two models are the same, for practical purposes. The differences might be more important in simulation of mixtures where components with partial charges or ionic components are present. Since the melting temperature for the TIP4P/ε is below the experimental value and the dipole/quadrupole moment ratio is around 1.12, it is expected the model might fail to reproduce the stability of the ice phases.

The procedure used in this work is being applied to force fields of water with dipole/quadrupole moment ratios around 1 trying to improve the properties where the TIP4P/ε model fails.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The definitions of properties and numerical values, at different temperatures and pressures, of all the simulation results obtained in this work are given in tables for liquid density, dielectric constant, self-diffusion coefficient, thermal expansion coefficient, isothermal compressibility, heat of vaporization, shear viscosity, surface tension, coexisting densities, and vapor pressure at the liquid−vapor phase equilibrium. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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