Vapor–liquid equilibrium simulations of the SCPDP model of water

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Abstract

Molecular simulations were carried out using the self-consistent point dipole polarizability model (SCPDP) of water in the region of vapor–liquid equilibrium. The methods of isothermal–isochoric molecular dynamics (NVT–MD) and Gibbs ensemble Monte Carlo (GEMC) were employed to calculate orthobaric densities and vapor pressures; NVT–MD also yields surface tensions and interface thickness. Agreement was found between the two methods, particularly at lower temperatures, but compared with experimental results, this model over-predicts vapor pressures and densities, and under-predicts the liquid density, surface tension, and interface thickness. The interface thickness predicted by the SCPDP model showed better agreement with experimental results than a simpler extended point charge model (SPC/E). © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Simple point charge models [1,2] are used widely to study condensed phases and phase equilibrium of water. Their major shortcoming is that the effects of polarization, which play an important role in physico-chemical processes in water, are not explicitly included. Polarizable models incorporate the effect of polarizability by having polarizable sites [3]; depending on the model, point dipoles or point charges are induced at these sites in response to electrostatic fields due to surrounding molecules. Among polarizable models, the SCPDP model accurately describes the pressure and configurational energy at ambient temperature, while retaining the experimental value for the permanent isolated dipole moment. The structure predicted by this model at ambient conditions agrees well with neutron scattering experiments [3]. Although this model is more detailed than simple point charge models, a significant improvement in the description of phase equilibrium at higher temperatures has not been observed [4].

There are several studies in the literature using polarizable models in inhomogeneous environments using molecular dynamics methods. The effect of polarizability has been included by...
Wallqvist [5] to study the behavior of water close to hydrophobic molecules. Chang and Dang [6] applied the NVT–MD method to study the liquid–liquid mass transfer coefficients for the system tetrachloromethane–water, using polarizable models for both components. Motakabbir and Berkowitz [7] studied the orientation of molecules of a polarizable model of water at the vapor–liquid interface. There are also in the literature results of simulations using the GEMC method in the vapor–liquid region for several polarizable models of water, including the SCPDP model [4,8], and the polarizable version of the SPC model by Chen et al. [9]. These simulations showed that most of these models under-, and over-predict the liquid and vapor orthobaric densities, respectively. Although the SPC/E and the polarizable version of SPC produced better coexisting densities compared to other complex polarizable models, they fail to predict other properties in the vapor phase (SPC/E) and the structure of the liquid phase (SPC polarizable).

The NVT–MD method is a useful and practical tool to study properties in the bulk and at the interface formed between the vapor and liquid phases. It has been applied to study polar [10] and non-polar [11] molecules, and its mixtures [12]. Compared with the GEMC method, NVT–MD requires more computing time because it simulates a thin liquid film between two vapor phases. This approximation to a bulk vapor–liquid system requires larger systems than the GEMC method, which simulates two systems in the corresponding bulk phases in thermodynamic equilibrium. The advantage of NVT–MD over GEMC is that NVT–MD includes an interface allowing it to be used to study interfacial properties.

2. Potential model and methodology

The SCPDP water model developed by Chialvo and Cummings [3] consists of four sites, two of them (H) located at the hydrogen atoms are positively charged, one Lennard-Jones site at the oxygen atom (O), and one site negatively charged (M) along the H–O–H bisector, 0.1 Å away from the oxygen atom. The model has a planar configuration with an H–O–H angle of 109.5°, and an O–H bond length of 1.0 Å. The magnitude and location of the charges correspond to a permanent dipole moment of 1.855 D [13], which agrees with the dipole momentum of an isolated molecule of water. The interactions of this model consist of Lennard-Jones interactions between O–O pairs \( r = 3.221 \text{ Å}, \epsilon/\kappa = 92.56 \text{ K}, \kappa = \text{Boltzmann constant} \), and M–M, M–H, and H–H electrostatic pair interactions. An isotropic point-dipole polarizability is included at the center of mass to account for the many-body polarizable effects.

The induced dipole moment \( p_i \) at the center of mass of molecule \( i \) is given by

\[
p_i = \alpha E_i = \alpha (E_i^q + E_i^p),
\]

where \( \alpha = 1.444 \text{ Å}^3 \) [13] is the scalar molecular polarizability, \( E_i \) is the total electric field at the center of mass of molecule \( i \), and \( E_i^q, E_i^p \) are the contributions from the permanent charges and induced dipoles, respectively.

NVT–MD simulations of the vapor–liquid interface were carried out using a Gear’s fourth-order predictor corrector algorithm [14] with a Nosé thermostat [15] in the NVT ensemble. Systems simulated employed 1000 molecules of water. The simulation cell was a rectangular parallelepiped of dimensions \( 25.77 \times 25.77 \times 128.85 \text{ Å}^3 \). The initial configuration consists of a cubic cell in an FCC arrangement. The range of temperatures studied was 300–520 K, and the cutoff radius was 12.88 Å. Periodic boundary conditions were used along with the minimum image criterion. Statistical averages of the properties were made using 400 000 configurations, with previous 200 000 configurations for equilibration.

The molecular reaction field [3,16,17] with a dielectric constant of 78 [18] was used to correct long ranged electrostatic interactions. Corrections to the Lennard-Jones forces due to the inhomogeneity of the system in the \( z \)-direction were applied using the expression developed by Meeke et al. [19], i.e.,

\[
\Delta F_{iz}/8\pi = -\int_{-\infty}^{-r_c} dz_i \rho(z_i) (z_i^{11} - z_i^{-5}) - \int_{r_c}^{\infty} dz_i \rho(z_i) (z_i^{-11} - z_i^{-5}),
\]

(2)
where \( \Delta F \) is the additional force acting on particle \( i \) in the \( z \)-direction, \( z_i \) is the component of the distance between oxygen atoms in the \( z \)-direction, and \( \rho(z) \) is the local density, which can be obtained from the density profile. The system is homogeneous in the \( x \)- and \( y \)-directions.

Vapor and liquid densities were obtained by fitting the density profile \( \rho(z) \) to a hyperbolic tangent function [20] of the form

\[
\rho(z) = 0.5(\rho_L + \rho_V) - 0.5(\rho_L - \rho_V) \times \tanh \left( \frac{z - z_0}{d} \right),
\]

(3)

where \( \rho_L, \rho_V \) are the liquid and vapor densities, \( z_0 \) is the position of the Gibbs’ dividing surface, and \( d \) is a parameter related to the thickness of the interface.

The element \( P_{ab} \) of the molecular pressure tensor [21] is given by

\[
VP_{ab} = \sum_{i=1}^{N} \sum_{j=1}^{N} m_i \langle v_i \rangle_a \langle v_j \rangle_b \times \langle r_{iajb} \rangle_z \langle f_{iajb} \rangle_\beta,
\]

(4)

where \( V \) is the volume of the system, \( m_i \) and \( v_i \) are the mass and velocity of molecule \( i \); \( r_{iajb} \) and \( f_{iajb} \) are the separation and force between site \( a \) in molecule \( i \) and site \( b \) in molecule \( j \), respectively. The vapor pressure was calculated using the component \( P_{ZZ} \), which represents the normal pressure of the system. Surface tension values were obtained by

\[
\gamma = \frac{1}{2A} \left[ P_{ZZ} - 0.5(P_{XX} + P_{YY}) \right],
\]

(5)

where \( A \) is the surface area of the interface.

For comparison purposes, the coexisting densities and vapor pressure were also calculated using the GEMC method. Details concerning these calculations and the method used can be found in [8].

### 3. Results

Results for the simulations using the NVT–MD method for thermophysical and interfacial properties are listed in Table 1 for temperatures in the range of 300–500 K. The corresponding thermophysical properties using the GEMC method are listed in Table 2 for temperatures in the range of 350–520 K. The interface formed by the NVT–MD method was unstable with respect to thermal fluctuations for temperatures above 500 K.

The resulting \( T-\rho \) phase envelope using GEMC and NVT–MD methods is shown in Fig. 1 for the SCPDP model of water, in comparison with experimental data [22], published results using the GEMC method [4], and published results using the NVT–MD method for the SPC/E model of water [23]. Results from this work using GEMC and NVT–MD methods agree for vapor densities, and for liquid densities agree from 300 to 450 K; beyond this temperature the liquid densities exhibit small differences. Published results using the GEMC method from Kiyohara et al. [4] agree with our results using the same method for vapor densities, and there are small deviations for liquid densities. Compared with experimental results, the SCPDP model of water under- and over-predicts liquid and vapor densities respectively. At 300 K the absolute error in vapor and liquid densities are 0.024 and 0.0125 g/cm\(^3\), at 500 K the errors are 0.054 and 0.211 g/cm\(^3\), respectively. The SPC/E model predicts coexisting densities in better agreement with experimental results [23] than the SCPDP model. The critical temperature and den-

<table>
<thead>
<tr>
<th>( T ) (K)</th>
<th>( \rho_L ) (g/cm(^3))</th>
<th>( \rho_V ) (g/cm(^3))</th>
<th>( P_V ) (bar)</th>
<th>( \gamma ) (mN/m)</th>
<th>( t ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.984</td>
<td>0.001</td>
<td>0.15</td>
<td>51.5</td>
<td>3.16</td>
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<tr>
<td>350</td>
<td>0.937</td>
<td>0.002</td>
<td>3.30</td>
<td>39.2</td>
<td>4.42</td>
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<tr>
<td>400</td>
<td>0.868</td>
<td>0.010</td>
<td>9.97</td>
<td>25.0</td>
<td>6.14</td>
</tr>
<tr>
<td>450</td>
<td>0.779</td>
<td>0.022</td>
<td>37.16</td>
<td>17.2</td>
<td>8.14</td>
</tr>
<tr>
<td>480</td>
<td>0.699</td>
<td>0.040</td>
<td>67.02</td>
<td>12.4</td>
<td>10.34</td>
</tr>
<tr>
<td>500</td>
<td>0.621</td>
<td>0.067</td>
<td>95.73</td>
<td>8.1</td>
<td>11.66</td>
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</table>
sity of the SCPDP model of water are 538 K and 0.32 g/cm$^3$ [4]. The phase envelopes using reduced temperatures ($T/T_c$) are shown in Fig. 2. The temperatures of each phase envelope were reduced using its own critical temperature. In reduced units, the phase envelope produced by the SCPDP model is in better agreement with the experimental data than the phase envelope produced by the SPC/E model.

Results for vapor pressures using GEMC and NVT–MD methods are shown in Fig. 3, with published results using GEMC method [4], and experimental data [22]. Results from this work using GEMC and NVT–MD methods agree for temperatures up to 400 K; beyond this temperature the vapor pressures calculated using NVT–MD are higher than those obtained by the GEMC method. Published results from Kiyohara et al. [4] using the GEMC method in the range of temperatures between 480 and 510 K agree with our calculations using the same method. Compared with experimental results, all simulations over-predict the experimental vapor pressures in the range of temperature studied. Using reduced temperatures (Fig. 4), the corresponding vapor pressures under-predict the experimental data; these results are consistent with their corresponding phase envelope (Fig. 2), where the vapor densities under-predict the experimental data.

The results for surface tension of the SCPDP model are shown in Fig. 3, in comparison with experimental data [24], and published results for the SPC/E model [23]. Our results for the SCPDP model are well below the experimental results; the absolute error is almost the same for the whole range of temperatures studied, and this is around 22 mN/m. Published results using the SPC/E model from Alejandre et al. [23] agree with ex-

![Table 2](image)

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\rho_L$ (g/cm$^3$)</th>
<th>$\rho_V$ (g/cm$^3$)</th>
<th>$P_V$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>0.927</td>
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<tr>
<td>400</td>
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<td>0.004</td>
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<td>450</td>
<td>0.797</td>
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<td>0.719</td>
<td>0.031</td>
<td>53.93</td>
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<tr>
<td>500</td>
<td>0.653</td>
<td>0.061</td>
<td>98.05</td>
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<tr>
<td>510</td>
<td>0.577</td>
<td>0.077</td>
<td>116.21</td>
</tr>
</tbody>
</table>

![Fig. 1](image)

Fig. 1. Liquid–vapor coexistence curve of water. The solid line represents the experimental data [19]. Squares and circles represent results from this work using NVT–MD, and GEMC methods, respectively. Crosses represent results for the GEMC method from Kiyohara et al. [4]. Diamonds represent results for the SPC/E model from Alejandre et al. [20].

![Fig. 2](image)

Fig. 2. Liquid–vapor coexistence curve of water (reduced temperature). Symbols as in Fig. 1.
experimental results. A simple linear regression was performed on our results, which is shown as a dashed line in Fig. 3; an extrapolation of this curve to a value of 0 mN/m of surface tension produced a value of 532.54 K for the critical temperature, which differs by 1% from the value reported by Kiyohara et al. [4]. In terms of reduced temperatures (Fig. 4), our results are in better agreement with experimental results, particularly at higher temperatures.

The thickness of the interface was calculated using the data obtained from the fitting of the density profiles to Eq. (2). The thickness $t$, is related to the parameter $d$ in Eq. (2) by $t = 2.1792d$ [20]. Results of these calculations are shown in Fig. 3 with published results for the SPC/E model [23] for comparison. The thickness of the interface can be obtained indirectly from ellipsometric and X-ray reflective experiments; results of these experimental studies reported by Matsumoto and Kataoka [25] are also shown in Fig. 3, and compared with our results; the absolute error is around 2.2 Å and is effectively constant for temperatures between 300 and 400 K. Compared with results for the SPC/E model, the SCPDP results are closer to the experimental values. Using reduced temperatures (Fig. 4), results of both models agree with each other, but they do not agree with the experimental data.

4. Conclusions

We have presented new calculations for the SCPDP model of water in the region of vapor–liquid coexistence using NVT–MD and GEMC methods. Results from both methods agree at lower and medium temperatures. At higher temperatures, where we expect system size problems
with NVT–MD, the methods disagree. As expected based on previous phase equilibria studies compared with simpler models like SPC/E, the SCPDP model of water produces inferior results for phase equilibria, particularly at elevated temperatures, for almost all thermodynamic and interfacial properties studied. The only property that seems to be improved is the interfacial thickness. In terms of reduced temperatures, using the critical temperature of each model to reduce, this model produces better results, which are in concordance with results of the SPC/E model. These results show that the major problem of the SCPDP model is that it produces a very low critical temperature, making the predictions for other properties be in disagreement with experimental data.

Although the SCPDP model has the ability to reproduce properties at ambient conditions, it appears to have limited success in predicting vapor–liquid coexistence. The specific shortcomings of the SCPDP potential are difficult to pinpoint. Generally, polarizable models of water underpredict the phase envelope while simultaneously improving the prediction of other properties. We are exploring alternative parameterizations of the SCPDP model to attempt to obtain globally better predictions for the model.

Acknowledgements

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References