Molecular simulation of water along the liquid–vapor coexistence curve from 25 °C to the critical point

Juan J. de Pablo and John M. Prausnitz
Department of Chemical Engineering, University of California, Berkeley and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley

Henry J. Strauch and Peter T. Cummings
Department of Chemical Engineering, University of Virginia, Charlottesville

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Previous work has shown that the simple point-charge (SPC) model can represent the experimental dielectric constant of water. In this work, we present results of Monte Carlo simulations of SPC water in the isothermal–isobaric (NPT) ensemble and in the Gibbs ensemble. Long-range intermolecular interactions are included in these simulations by use of the Ewald summation method. When Ewald sums are used, simulated, uniphasic liquid potential energies are slightly lower (in absolute value) than those obtained for a simple spherical cutoff of the intermolecular potential. The coexistence curve of SPC water is obtained from 25 to 300 °C. The critical constants of SPC water are estimated by adjusting the coefficients of a Wegner expansion to fit the difference between simulated liquid and vapor orthobaric densities; the estimated critical temperature is 314 °C and the estimated critical density is 0.27 g/cm³.

I. INTRODUCTION

Because of its unique importance in science and technology, a large number of molecular-simulation studies of water have appeared in the literature. Water molecules are generally modeled as neutral particles having partial charges; these charges interact through Coulomb potentials. Since these are long-range potentials, it is not immediately clear how best to perform the molecular simulations under periodic boundary conditions.

The simplest way to simulate the properties of fluids whose molecules interact through long-range intermolecular forces is either to apply a spherical truncation to the intermolecular potential, or to use a minimum-image convention. These methods are simple, efficient, and often yield satisfactory results. Unfortunately, however, neglecting longer-range contributions to the potential energy can have severe adverse effects on some of the properties of the simulated fluid, particularly those which depend on orientational correlations between molecules (i.e., dielectric constant). Further, these relatively simple methods suffer from the additional disadvantage of strong dependence on system size and cutoff radius. For vapor–liquid simulations in the Gibbs ensemble, the size and density of each “phase” are not known a priori; it is not satisfactory to define an arbitrary cutoff radius for each phase, because the choice of cutoff may have a strong effect on the computed orthobaric densities. Liquid-phase densities might be computed with reasonable accuracy because, from previous simulations of liquid water, we have a good idea of what the density and the cutoff radius should be. Vapor-phase densities, however, may vary significantly with system size and cutoff radius.

The mean reaction field (RF) method provides an attractive and theoretically sound alternative for simulation of dipolar systems. Neumann has explored the application of the RF method to several models of water. Neumann’s results are encouraging but the RF method also has some shortcomings discussed elsewhere.

In this work we use the Ewald summation (ES) method, where a slowly converging Hamiltonian is replaced by an equivalent mathematical expression that is more rapidly converging. The advantage of the ES method over other methods is that Coulombic systems can be simulated with a “full” Hamiltonian, without having to resort to arbitrary truncations of the intermolecular potential.

We show results of NPT as well as Gibbs-ensemble simulations of water. These results correspond to molecular simulations using the ES method. To analyze the influence of different truncation schemes on the simulated properties, we compare our simulation results to those obtained by Jorgensen et al. who used a spherical cutoff of the intermolecular potential. An assessment of the size dependency of simulation data is crucial for simulations in the Gibbs ensemble; to study the effect of system size on the simulated properties, some of the calculations presented here were repeated using different numbers of particles.

Recent studies of the dielectric properties of water indicate that the SPC model yields a dielectric constant in reasonable agreement with experiment at 25 °C. Since our aim is eventually to simulate phase equilibria for electrolyte solutions, we use the SPC model in this work. Note, however, that the SPC model of water (as most simple models of water) has a dipole moment different from the gas-phase value of real water. Also note that we have not included polarizability effects in our simulations.

To the best of our knowledge, the calculated coexistence data presented here constitute the only available simulation information on vapor–liquid equilibria for water; since these data could not be verified by comparison with previous stud-
ies of water, two computer codes for the simulation of water were developed completely independently at the University of California, Berkeley, and at the University of Virginia. Agreement between results from these two codes was later verified by carrying out independent calculations at several temperatures.

II. THE Ewald-Summary Method

Consider two identical molecules $i$ and $j$. Each molecule contains $m$ sites; those on molecule $i$ are designated by $a$ and those on molecule $j$ by $b$. The intermolecular potential is of the form

$$u_{ij} = \sum_{a}^{m} \sum_{b}^{m} \left( \frac{e^{q_{a}^{i}}}{r_{ab}^{ij}} + 4\epsilon_{ab}^{ij} \left[ \left( \frac{\alpha_{ab}}{r_{ab}^{ij}} \right)^{12} - \left( \frac{\alpha_{ab}}{r_{ab}^{ij}} \right)^{6} \right] \right),$$

(1)

where $q_{a}^{i}$ is the charge on site $a$ of molecule $i$, and $r_{ab}^{ij}$ is the distance between sites $a$ and $b$ located at molecules $i$ and $j$, respectively. [Note that $a$ and $b$ are not exponents in Eq. (1).] In addition to Coulombic interactions between the charged sites of a molecule, sites of different particles can interact through a Lennard-Jones potential; $\epsilon_{ab}$ and $\sigma_{ab}$ are the energy and size parameters for the Lennard-Jones interaction between a site $a$ and a site $b$. Figure 1 shows the geometry of the SPC model and the corresponding parameters.

Consider a system containing $N$ molecules. Under periodic boundary conditions, the Hamiltonian for the simulated system becomes

$$H = \frac{1}{2} \sum_{i=0}^{N} \sum_{i=1}^{N} u_{ij} (\vec{r} + \vec{n}L),$$

(2)

where $L$ is the edge of a cubic simulation box, and where the sum over lattice vectors $\vec{n}$ enforces these boundary conditions. The prime indicates that for $\vec{n} = 0$, the $i = j$ terms are omitted from the sum.

As discussed by De Leeuw et al., the sum in Eq. (2) is conditionally convergent for potentials proportional to $r^{-d}$ when $0 < d < 3$. To achieve absolute convergence, the sum is broken into two separate, more rapidly converging components. The first of these components is a sum over lattice vectors in real space. The second is a sum over lattice vectors in reciprocal space. After substitution of Eq. (1) into Eq. (2), and after some mathematical manipulations described elsewhere, the Hamiltonian in Eq. (2) can be written as

$$H = \frac{1}{L} \sum_{i,j=1}^{N} \sum_{a=1}^{m} \sum_{b=1}^{m} q_{a}^{i} q_{b}^{j} \sum_{n=0}^{\infty} \left( \frac{\text{erfc}(\alpha|\vec{r}_{ab}^{ij}/L + \vec{n}|)}{|\vec{r}_{ab}^{ij}/L + \vec{n}|} \right) + \frac{1}{2L} \sum_{i=1}^{N} \sum_{a=1}^{m} (q_{a}^{i})^{2} \sum_{n=0}^{\infty} \frac{\text{erfc}(\alpha|\vec{n}|)}{|\vec{n}|}$$

$$+ \frac{1}{2L} \sum_{i,j=1}^{N} \sum_{a=1}^{m} \sum_{b=1}^{m} q_{a}^{i} q_{b}^{j} \sum_{n=0}^{\infty} \frac{\text{erfc}(\alpha|\vec{r}_{ab}^{ij}/L + \vec{n}|)}{|\vec{r}_{ab}^{ij}/L + \vec{n}|} - \frac{1}{|\vec{r}_{ab}^{ij}/L|}$$

$$+ \frac{1}{2L} \sum_{i,j=1}^{N} \sum_{a=1}^{m} \sum_{b=1}^{m} q_{a}^{i} q_{b}^{j} \sum_{n=0}^{\infty} \frac{1}{|\vec{n}|^{2}} e^{-|\vec{n}|^{2}/\alpha^{2}} e^{2\pi\alpha n \cdot \vec{r}_{ab}^{ij}/L} - \frac{\alpha}{L^{\alpha/2}} \sum_{i=1}^{N} \sum_{a=1}^{m} (q_{a}^{i})^{2} + \frac{2\pi N \mu^{2}}{3L^{2}}$$

(3)

In deriving Eq. (3), we have assumed that the periodically replicated simulation box is surrounded by a conductor (tin foil boundary conditions). Parameter $\alpha$ is a mathematical artifact needed to obtain Eq. (3). By mathematical construction, the full Hamiltonian should be independent of the value of $\alpha$. In practice, however, to make simulations feasible in a reasonable amount of time, the summations over $\vec{n}$ in Eq. (3) must be truncated after a few terms; parameter $\alpha$ dictates how many terms should be kept in each of these summations.

The complementary error function erfc decays to zero for increasing arguments; in practice, $\alpha$ is chosen large enough so that the first three summations in Eq. (3) can be truncated beyond the minimum image ($\vec{n} = 0$). However, $\alpha$ must not be too large, lest the number of terms that must be kept in the complex summation also be too large. We truncate the complementary-error-function sums after $\vec{n} = 0$, instead of truncating the complex-space sums after $\vec{n} = 0$, because the latter can be coded in such a way that one of the sums over particles is avoided, thereby making calculations much faster.

In agreement with previous work on water, we find

$q(O) = -0.82$ esu
$q(H) = 0.41$ esu
$\langle\text{HOO}\rangle = 109.47^{\circ}$
$r$(OH) = 1.0 Å
$\varepsilon$ (O) = 0.155 kcal/mol
$\sigma$(O) = 3.167 Å

FIG. 1. SPC model of water. The molecule has one van der Waals interaction site located at the oxygen atom. In addition, the molecule has electrostatic charges: two positive charges are located at the hydrogen atoms (H), and one negative charge is located at the oxygen atom.
that for $\alpha = 5.0$ the erfc terms in Eq. (3) can be truncated beyond the minimum image for both liquid and vapor densities. Four terms in the complex-space summations appear to yield potential energies accurate to five significant figures. Whether such a high accuracy is necessary or not depends on the properties of interest. While some authors have kept only four terms (256 vectors) or less in the complex sums for their simulations of the dielectric properties of water,\textsuperscript{9,10} other authors claim that four terms do not yield results of sufficient accuracy to warrant calculation of the dielectric constant of water.\textsuperscript{14} Recent results for the dielectric constant of water by Strauch and Cummings,\textsuperscript{10} however, indicate that four terms are enough. Further, additional terms should not have a noticeable effect on the calculation of orthobaric densities.

III. NPT SIMULATIONS

Isobaric–isothermal (NPT) Monte Carlo simulations with metropolis sampling were performed for systems of 64, 108, and 216 water molecules, respectively. Volume moves were attempted after cycles of 300 particle displacements. Both the maximum particle and volume displacements were adjusted to yield 50% of successful moves. All simulations comprised at least a period of $10^6$ moves for equilibration.

Table I shows results of NPT simulations, with the ES method for systems of 64, 108, and 216 particles. All simulations in Table I were performed at 298 K and 1 atm. Four terms (or 256 vectors) were kept in the Fourier series [fourth term on right-hand side of Eq. (3)]. Contrary to the results of simulations using the SC method, the energies and densities given in Table I are, within the accuracy of our results, only slightly dependent on the size of the system. This finding suggests that water simulations in the Gibbs ensemble might be performed on small systems, without significant loss of accuracy.

IV. GIBBS-ENSEMBLE SIMULATIONS

Recently, De Pablo and Prausnitz\textsuperscript{4} have presented results of Gibbs-ensemble simulations of vapor–liquid equilibria for lower alkanes and for water. In this study, however, only a spherical cutoff was applied to the intermolecular potential, and therefore the results for water were dependent on the size of the system. In this work, simulations were performed using the ES method to include long-range forces properly.

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**TABLE I. Results of NPT simulations for liquid water at 298 K and 1 atm.**

<table>
<thead>
<tr>
<th>Run</th>
<th>No. moves</th>
<th>No. particles</th>
<th>Density g/cm$^3$</th>
<th>Potential energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$750 \times 10^3$</td>
<td>64</td>
<td>0.964 ± 0.021</td>
<td>-9.72 ± 0.09</td>
</tr>
<tr>
<td>2</td>
<td>$1000 \times 10^3$</td>
<td>108</td>
<td>0.969 ± 0.026</td>
<td>-9.82 ± 0.06</td>
</tr>
<tr>
<td>3</td>
<td>$1000 \times 10^3$</td>
<td>216</td>
<td>0.963 ± 0.008</td>
<td>-9.93 ± 0.03</td>
</tr>
</tbody>
</table>

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**TABLE II. Results of NPT simulations at 300 K and 1 atm for different truncation methods.**

<table>
<thead>
<tr>
<th>Run</th>
<th>Truncation method</th>
<th>No. moves</th>
<th>No. particles</th>
<th>Density g/cm$^3$</th>
<th>Potential energy kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>ES</td>
<td>$1000 \times 10^3$</td>
<td>108</td>
<td>0.969 ± 0.026</td>
<td>-9.82 ± 0.06</td>
</tr>
<tr>
<td>4*</td>
<td>SC</td>
<td>$1000 \times 10^3$</td>
<td>125</td>
<td>0.971 ± 0.007</td>
<td>-10.18 ± 0.03</td>
</tr>
</tbody>
</table>

*Run 4 corresponds to results reported by Jorgensen et al. (Ref. 2) for SPC water at 298 K and 1 atm. The cutoff radius used by these authors was 7.5 Å.*
TABLE III. Orthobaric densities and potential energies. Results of Gibbs-ensemble simulations for systems of 140 and 200 particles.*

<table>
<thead>
<tr>
<th>Run</th>
<th>T K</th>
<th>No. particles</th>
<th>% transfers</th>
<th>Liquid density g/cm(^3)</th>
<th>Vapor density g/cm(^3)</th>
<th>Potential energy liquid kcal/mol</th>
<th>Potential energy vapor kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>5V</td>
<td>300</td>
<td>140</td>
<td>0.1</td>
<td>0.958 (15)</td>
<td>0.000 0251 (28)</td>
<td>- 9.81 (13)</td>
<td>- 0.0531 (41)</td>
</tr>
<tr>
<td>6V</td>
<td>373</td>
<td>140</td>
<td>0.1</td>
<td>0.893 (15)</td>
<td>0.000 648 (111)</td>
<td>- 8.90 (35)</td>
<td>- 0.136 (88)</td>
</tr>
<tr>
<td>6'B</td>
<td>373</td>
<td>200</td>
<td>0.1</td>
<td>0.899 (11)</td>
<td>0.000 711 (56)</td>
<td>- 8.82 (7)</td>
<td>- 0.16 (9)</td>
</tr>
<tr>
<td>7B</td>
<td>423</td>
<td>200</td>
<td>0.4</td>
<td>0.833 (12)</td>
<td>0.002 75 (15)</td>
<td>- 8.17 (7)</td>
<td>- 0.46 (10)</td>
</tr>
<tr>
<td>8B</td>
<td>473</td>
<td>200</td>
<td>1.0</td>
<td>0.745 (32)</td>
<td>0.011 0 (17)</td>
<td>- 7.39 (19)</td>
<td>- 0.85 (20)</td>
</tr>
<tr>
<td>9B</td>
<td>523</td>
<td>140</td>
<td>1.7</td>
<td>0.647 (40)</td>
<td>0.049 6 (55)</td>
<td>- 6.54 (18)</td>
<td>- 2.14 (35)</td>
</tr>
<tr>
<td>9'B</td>
<td>523</td>
<td>200</td>
<td>1.7</td>
<td>0.658 (25)</td>
<td>0.047 6 (60)</td>
<td>- 6.64 (15)</td>
<td>- 2.09 (22)</td>
</tr>
<tr>
<td>10B</td>
<td>573</td>
<td>200</td>
<td>5.2</td>
<td>0.408 (49)</td>
<td>0.078 9 (140)</td>
<td>- 5.14 (26)</td>
<td>- 2.30 (34)</td>
</tr>
</tbody>
</table>

*The numbers in parentheses indicate the uncertainty in units of the last decimal digit (or digits). Letter B indicates that the results correspond to the Berkeley code, while letter V indicates that they correspond to the Virginia code.

The Gibbs-ensemble simulations discussed here were performed on systems of 140 or 200 particles, depending on the temperature. Since the Gibbs-ensemble method has been the subject of a recent review\(^{16}\) it need not be described again. Here it suffices to say that all simulations consisted of cycles of 1000 particle-displacement attempts, followed by a volume-change attempt and a series of particle transfer attempts (attempts to move a particle from one coexisting phase to the other). Depending on the temperature, the required number of transfer attempts was adjusted in such a way that only a few molecules were created or destroyed during a single cycle (not more than 2% of the total number of molecules in each phase). The insertion or removal of too many molecules can disrupt the structure of water, thereby giving rise to low liquid densities. The fourth column of Table III indicates the percentage of successful transfer attempts between coexisting phases. Additional details concerning the specific case of Gibbs-ensemble simulation of water are given elsewhere.\(^4\)

All the averages shown in Table III were obtained over periods of 10\(^6\) moves; 10\(^8\) moves were required for equilibration.

Runs 6 and 6' and 9 and 9' indicate that system size does not have a significant effect on the simulated orthobaric densities. In view of the length of these type of simulations, this result is important for future work with water in the Gibbs ensemble.

Figure 2 shows the experimental and the simulated coexistence curves for real and SPC water, respectively. To estimate the coordinates of the critical point of SPC water, the coefficients of a Wegner expansion\(^{17}\) were adjusted to fit the difference between simulated orthobaric densities. When truncated after the third term, these series can be written as

$$|\rho_i - \rho_c| = B_0 \Delta t^\beta (1 + B_1 \Delta t^\beta + B_2 \Delta t^{2\beta} + ...),$$

$$\Delta t = \frac{T - T_c}{T_c},$$

where $B_0$, $B_1$, and $B_2$ are substance-dependent coefficients, where $\Delta$ is a correction-to-scaling exponent equal to 0.5, and where $\beta$ is a critical exponent also equal to 0.5.\(^{17,18}\) This procedure gave an estimate of the critical temperature $T_c = 587$ K. A rectilinear diameter extrapolation for this critical temperature yields a critical density of $\rho_c = 0.27$ g/cm\(^3\). However, because of the statistical uncertainty of simulation results, particularly near the critical point, these estimates should be used with caution.

The experimental values are $T_c = 647.3$ K and $\rho_c = 0.32$ g/cm\(^3\). Upon increasing the temperature, disagreement between experiment and simulation becomes more pronounced; the simulated critical temperature for SPC water is well below the experimental value. Agreement could be improved by making the interaction parameters slightly temperature dependent, due to small changes in molecular structure as temperature rises. Such adjustments, however, are beyond the scope of this work.

![Experimental and Simulation Data](image-url)
V. CONCLUSIONS

For Monte Carlo simulations in the NPT ensemble, the density and potential energy of SPC water are only weak functions of system size provided that Ewald summations are used for proper inclusion of electrostatic interactions. The results of these simulations indicate that the ES method yields liquid energies that are about 2% lower than those obtained with the SC method (for the SPC model).

Recent studies of the dielectric properties of water suggest that the SPC model is superior to other simple models of water. To mimic the dielectric properties of water adequately, either the ES method or the RF method must be used. When the ES method is used, simulated liquid densities at normal conditions are about 3% lower than experiment.

Gibbs-ensemble simulations of polar fluids, such as water, require the use of Ewald summations, lest the results be highly dependent on the size of the simulated system. We find that if the ES method is used, systems of 140 water molecules are large enough to yield results of reasonable accuracy for the orthobaric properties.

Based on a Wegner-expansion extrapolation, we estimate the critical constants of SPC water to be $T_c \approx 587$ K and $\rho_c \approx 0.27$ g/cm$^3$.

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