Gibbs ensemble Monte Carlo simulations of coexistence properties of a polarizable potential model of water

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Abstract

The vapor pressure, heat of vaporization and liquid/vapor densities along the coexistence curve of the polarizable water model of Dang and Chang (J. Chem. Phys. 106, 8149, 1997) were calculated by using Gibbs ensemble Monte Carlo simulation techniques. Long-range interactions such as charge-charge, charge-dipole, and dipole-dipole were evaluated by using Ewald summation techniques. The model yields good agreement with the corresponding experimental data in the lower temperature region, but only moderate agreement in the higher temperature region. The critical temperature and density were estimated to be 565 K and 0.28 g/ cm$^3$, compared to experimental $T_C = 647$ K and $\rho_C = 0.32$ g/ cm$^3$. 
We recently developed a potential model for water that includes many-body effects by using molecular dynamics simulation techniques. Our model provides good descriptions of the optimized structural and energetic properties for water clusters and for the thermodynamic and the structural properties of liquid water at ambient conditions. In this Letter to the Editor, as a part of our long-term interest in the development of potential models for water, which are able to describe the interactions in widely varying environments. We evaluate the coexistence properties of this water model by using Gibbs ensemble Monte Carlo simulation techniques. Toward this end, we computed the liquid/vapor coexistence density, the vapor pressure, and the heat of vaporization of water and compared our results to the experimental data and previous computational studies of coexistence properties using different water models.

The Gibbs ensemble Monte Carlo simulation technique was employed to determine the vapor/liquid coexistence and equilibrium properties of our water model. The theoretical basis and detailed procedures for calculation of thermodynamic and phase coexistence properties have been described elsewhere. This method has been used successfully in calculating thermodynamic properties for water and water-mixtures. The simulations were carried out by using a set of modified programs originally written by Errington and Panagiotopolous. For our system, which consists of 216 water molecules, an Ewald summation technique was used to evaluate the long-range charge-charge, charge-dipole, and dipole-dipole interactions. We note here that the Lennard-Jones parameters have been slightly modified from our original water model to compensate for the differences between the Ewald summation and the molecule-molecule truncation approaches used in calculating liquid densities and energies of the liquid water. The final parameters for the modified version of the water model are presented in Table I.

The calculated densities of coexistence phase, the vapor pressure, and the heat of vaporization as a function of temperature for our model are shown in Figures 1-3.
Overall, our model predicted these properties quite well for the temperature ranges between 300 and 450 K, but a significant deviation from the experimental data was observed above 450 K. This deviation was expected, however, because our potential model was developed to reproduce the experimental liquid water properties at ambient conditions (i.e., at 300K and 1 atm). We estimated the approximate values of the critical temperature and density by fitting the simulation results to the law of rectilinear diameters and a scaling law, assuming that the models obey the Ising exponent $\beta = 0.325$). The estimated critical temperature is 565 K, and the critical density is 0.28 g/cm$^3$. These results can be compared to the corresponding experimental critical temperature and density of 647 K and 0.32 g/cm$^3$. It has been recognized in our previous work that our simulation results near the critical region are associated with non-negligible uncertainties. Therefore, the simulated numerical values of the critical properties should be taken with care. During the MC simulations, the averages total dipole moments of the water molecules along the coexistence curve were also evaluated. We found the values of $\mu$ decrease from 2.75 D to 2.35 D in the liquid phase and $\mu$ increase from 1.85 D to 2.05 D in the vapor phase as the temperatures increased.

In addition to Gibbs ensemble Monte Carlo simulations, we also carried out molecular dynamics simulations at room temperature using the new version of the potential parameters. We found the computed radial distribution functions, $g_{oo}$, $g_{oh}$, and $g_{hh}$ slightly improved over the original model when compared to the corresponding experimental data. The computed dielectric constant is about 100 $\pm$ 20 and the computed self-diffusion constant is 1.8 $\pm$ 0.2 cm/ sec$^2$. These results can be compared to the corresponding experimental dielectric constant and self-diffusion constant of 80 and 2.3 cm/ sec$^2$. It is well known that the length scale describing the correlation of the macroscopic system (correlation length) begins to diverge as the critical point is
approached. Because of the constraint of finite simulation size, the molecular simulations may have difficulties in capturing this divergence. To this end, finite size scaling method has been used to extrapolate critical properties from finite system simulations. Therefore, in the present work; the evaluation of critical parameters from a single simulation may be subject to errors. In addition, it has been pointed out by Panagiotopoulos and coworkers that the critical properties of water are very sensitive to small changes in the potential parameters. Since our potential model was developed to reproduce the experimental liquid water properties at ambient conditions (i.e., at 300K and 1 atm), this model may not be suitable at the near critical conditions. Many efforts have been devoted to reparametrize water potentials to give accurate descriptions of both vapor-liquid coexistence properties over a wide temperature range as well as bulk liquid properties at ambient condition. However, these models are only satisfactory at best. This may indicate that the Lennard-Jones and other similar potential function forms are not adequate in describing the water interactions.
References


7. U. Grigull, J. Straub and P. Schiebener, Steam Tables in SI Units (Berlin: Springer-Verlag).


10. This work was performed in the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL) under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy. EMSL is a national scientific user facility located at PNNL, which is operated by Battelle for the Department of Energy. Computer resources were provided by the Division of Chemical Sciences and by the Scientific Computing Staff, Office of Energy Research, at the National Energy Research Supercomputer.
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Table I. The optimized potential parameters for water-water interactions used in the molecular dynamics simulation. \( \sigma \) and \( \varepsilon \) are the Lennard-Jones parameters, \( q \) is atomic charge, and \( \alpha \) is the molecular polarizability.

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<th>( q (\text{e}) )</th>
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**Figure Captions:**

Figure 1. Comparison between computed coexistence density using Gibbs Monte Carlo simulation techniques (solid circles) and the corresponding experimental result (solid lines).

Figure 2. Comparison between computed vapor pressure using Gibbs Monte Carlo simulation techniques (solid circles) and the corresponding experimental result (Open circles).

Figure 3. Comparison between computed heat of vaporization using Gibbs Monte Carlo simulation techniques (solid circles) and the corresponding experimental result (Open circles).
Saturated vapor and liquid densities

\[ \rho, \text{g/cm}^3 \]

\[ T/\text{K} \]
Heat of vaporization

\[ \Delta H / \text{KJ-mol}^{-1} \]

\[ T / \text{K} \]

- **Ex**
- **MD**