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Authors

Pablo, J.J. de
Prausnitz, John M.
Strauch, H.J.
et al.

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J.J. de Pablo, J.M. Prausnitz, H.J. Strauch,
and P.T. Cummings

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Molecular Simulation of Water Along
the Liquid-Vapor Coexistence Curve from
25°C to the Critical Point

J.J. de Pablo and J.M. Prausnitz
Department of Chemical Engineering
University of California
and
Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

and
H.J. Strauch and P.T. Cummings
Department of Chemical Engineering
University of Virginia
Charlottesville, VA

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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

ABSTRACT

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, uniphase 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 (1). These methods are simple, efficient, and often yield satisfactory results (2,3). 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 (2). Vapor-phase densities, however, may vary significantly with system size and cutoff radius (4).

The mean reaction field (RF) method (1,5,6) provides an attractive and theoretically sound alternative for simulation of dipolar systems. Neumann (7,8) 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 (1).

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 (16) 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. (2) who used a spherical cutoff of the intermolecular potential. An assesment 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 (6,9,10) indicate that the *SPC* model (11) 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.

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 studies 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-Summation 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

$$u_{ij} = \sum_a^m \sum_b^m \left(\frac{q_i^a q_j^b}{r_{ij}^{ab}} + 4 \epsilon^{ab} \left(\left(\frac{\sigma^{ab}}{r_{ij}^{ab}} \right)^{12} - \left(\frac{\sigma^{ab}}{r_{ij}^{ab}} \right)^6 \right) \right) , \quad (1)$$

where q_i^a is the charge on site *a* of molecule *i*, and r_{ij}^{ab} is the distance between sites *a* and *b* located at molecules *i* and *j*, respectively. (Note that *a* and *b* are not exponents in Equation 1). In addition to coulombic interactions between the charged sites of a molecule, sites of different particles can interact through a Lennard-Jones potential; ϵ^{ab} and σ^{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

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

where L is the edge of a cubic simulation box, and where the sum over lattice vectors \bar{n} enforces these boundary conditions (1). The prime indicates that for $\bar{n} = 0$, the $i=j$ terms are omitted from the sum.

As discussed by De Leeuw et al.(12), the sum in Equation (2) is conditionally convergent for potentials proportional to r^{-d} when $0 < d \leq 3$. 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 Equation (1) into Equation (2), and after some mathematical manipulations described elsewhere (12,13), the Hamiltonian in Equation (2) can be written as

$$\begin{aligned} H = & \frac{1}{L} \sum_{i < j}^N \sum_a^m \sum_b^m q_i^a q_j^b \sum_{\bar{n}=0}^{\infty} \left(\frac{\text{erfc}(\alpha |\bar{r}_{ij}^{ab}/L + \bar{n}|)}{|\bar{r}_{ij}^{ab}/L + \bar{n}|} \right) \quad (3) \\ & + \frac{1}{2L} \sum_i^N \sum_a^m (q_i^a)^2 \sum_{\bar{n} \neq 0}^{\infty} \frac{\text{erfc}(\alpha |\bar{n}|)}{|\bar{n}|} \\ & + \frac{1}{2L} \sum_{i=1}^N \sum_{a \neq b}^m \sum_b^m q_i^a q_i^b \left(\sum_{\bar{n}=0}^{\infty} \frac{\text{erfc}(\alpha |\bar{r}_{ii}^{ab}/L + \bar{n}|)}{|\bar{r}_{ii}^{ab}/L + \bar{n}|} - \frac{1}{|\bar{r}_{ii}^{ab}/L|} \right) \\ & + \frac{1}{2L} \sum_{i=1}^N \sum_{j=1}^N \sum_a^m \sum_b^m q_i^a q_j^b \sum_{\bar{n} \neq 0}^{\infty} \frac{1}{\pi |\bar{n}|^2} e^{-\pi^2 |\bar{n}|^2 / \alpha^2} e^{2\pi i \bar{n} \cdot \bar{r}_{ij}^{ab} / L} \\ & - \frac{\alpha}{L\pi^{1/2}} \sum_{i=1}^N \sum_{a=1}^m (q_i^a)^2 + \frac{2\pi N\mu^2}{3L^3} \\ & + \sum_{i < j}^N \sum_a^m \sum_b^m 4\epsilon^{ab} \left(\left(\frac{\sigma^{ab}}{r_{ij}^{ab}} \right)^{12} - \left(\frac{\sigma^{ab}}{r_{ij}^{ab}} \right)^6 \right) \end{aligned}$$

Parameter α is a mathematical artifact needed to obtain Equation (3). By mathematical construction, the *full* Hamiltonian should be independent of the value

of α . In practice, however, to make simulations feasible in a reasonable amount of time, the summations over \bar{n} in Equation (3) must be truncated after a few terms; parameter α 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, α is chosen large enough so that the first three summations in Equation (3) can be truncated beyond the minimum image ($\bar{n}=0$). However α 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 $\bar{n}=0$, instead of truncating the complex-space sums after $\bar{n}=0$, 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 (9), we find that for $\alpha = 5.0$ the *erfc* terms in Equation (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 (9,10), other authors claim that four terms do not yield results of sufficient accuracy to warrant calculation of the dielectric constant of water (14). Recent results for the dielectric constant of water by Strauch and Cummings (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 Equation (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.

Table I - Results of NPT Simulations for Liquid Water at 298K and 1atm. Systems of Different Sizes				
Run	# moves	# particles	density g/cm^3	potential energy kcal/mol
1	$750 * 10^3$	64	0.964 ± 0.021	-9.72 ± 0.09
2	$1000 * 10^3$	108	0.969 ± 0.026	-9.82 ± 0.06
3	$1000 * 10^3$	216	0.963 ± 0.008	-9.93 ± 0.03

Without the use of Ewald sums, the simulated dielectric properties of water are in very poor agreement with experiment. Since most of the unusual properties of water (such as its ability to dissolve electrolytes) are precisely a result of its high dielectric constant, it is important for our purposes to reproduce the experimental dielectric constant, even if it is at the expense of liquid densities that are about 3% lower than the experimental values.

Our results for the energy are slightly different from those of Jorgensen et al.(2). For systems of 125 SPC water molecules, with a spherical truncation and no cutoff corrections, these authors report a density of $0.971 (g/cm^3)$ and a potential energy of $-10.18 (kcal/mol)$ at $25 \text{ }^\circ C$ and 1 atm. Table II shows these results. In principle, use of the ES method is responsible for the difference between our results for the potential energy and those of Jorgensen et al. (2).

In their molecular-dynamics simulations of SPC water, Alper and Levy (6) have observed that, when using a reaction field, internal energies are $\approx 3 \%$ more positive than those obtained in the absence of the reaction field. The results of our NPT simulations of water using the ES method are consistent with the observations

of Alper and Levy; including long-range contributions to the potential energy results in more positive potential energies.

Table II - Results of <i>NPT</i> Simulations at 300K and 1 atm for Different Truncation Methods					
Run	Truncation Method	# moves	# particles	density <i>g/cm³</i>	potential energy <i>kcal/mol</i>
2	ES	1000 * 10 ³	108	0.969 ± 0.026	-9.82 ± 0.06
4	SC	1000 * 10 ³	125	0.971 ± 0.007	-10.18 ± 0.03

* Run 4 corresponds to results reported by Jorgensen et al.(2) for SPC water at 298 K and 1 atm. The cutoff radius used by these authors was 7.5 Å.

Recently, Linde and Andersen (15) have discussed the advantages and disadvantages of several truncation methods. These authors found that upon completely neglecting the reciprocal-space terms in Equation (3) (fourth term on right-hand side of Equation (3)) satisfactory results were obtained for fused electrolytes. This method (spherical Ewald truncation [SET]) and its variations (i.e. keeping only one term in the reciprocal-space summations of Equation 3) provide intermediates between the full ES method and the simpler, SC method; they provide an interesting alternative to the time-intensive, full ES method and could be useful for the simulation of the thermodynamic properties of water and aqueous mixtures.

IV) Gibbs-Ensemble Simulations

Recently, De Pablo and Prausnitz (4) have presented results of Gibbs-ensemble simulations of vapor-liquid equilibria for lower alkanes and for water. In that 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.

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).

Table III - Orthobaric Densities and Potential Energies. Results of Gibbs-Ensemble Simulations for Systems of 140 and 200 Particles

Run	T K	# particles	% transfers	liquid density g/cm^3	vapor density g/cm^3	potential energy liquid kcal/mol	potential energy vapor kcal/mol
5V	300	140	0.1	0.958 (15)	0.0000251 (28)	-9.81 (13)	-0.0531 (41)
6V	373	140	0.1	0.893 (15)	0.000648 (111)	-8.90 (35)	-0.136 (88)
6'B	373	200	0.1	0.899 (11)	0.000711 (56)	-8.82 (7)	-0.16 (9)
7B	423	200	0.4	0.833 (12)	0.00275 (15)	-8.17 (7)	-0.46 (10)
8B	473	200	1.0	0.745 (32)	0.0110 (17)	-7.39 (19)	-0.85 (20)
9B	523	140	1.7	0.647 (40)	0.0496 (55)	-6.54 (18)	-2.14 (35)
9'B	523	200	1.7	0.658 (25)	0.0476 (60)	-6.64 (15)	-2.09 (22)
10B	573	200	5.2	0.408 (49)	0.0789 (140)	-5.14 (26)	-2.30 (34)

* 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.

All the averages shown in Table 3 were obtained over periods of 10^6 moves; 10^6 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

$$|\rho_l - \rho_v| = B_0 \Delta t^\beta \left(1 + B_1 \Delta t^\Delta + B_2 \Delta t^{2\Delta} + \dots \right) \quad (4)$$

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

where B_0 , B_1 and B_2 are substance-dependent coefficients, where Δ is a correction-to-scaling exponent equal to 0.5, and where β is a critical exponent also equal to 0.5 (17,18). This procedure gave an estimate of the critical temperature $T_c = 587K$. 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 $T_c = 647.3K$ 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.

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 $T_c \approx 587K$ and $\rho_c \approx 0.27g/cm^3$.

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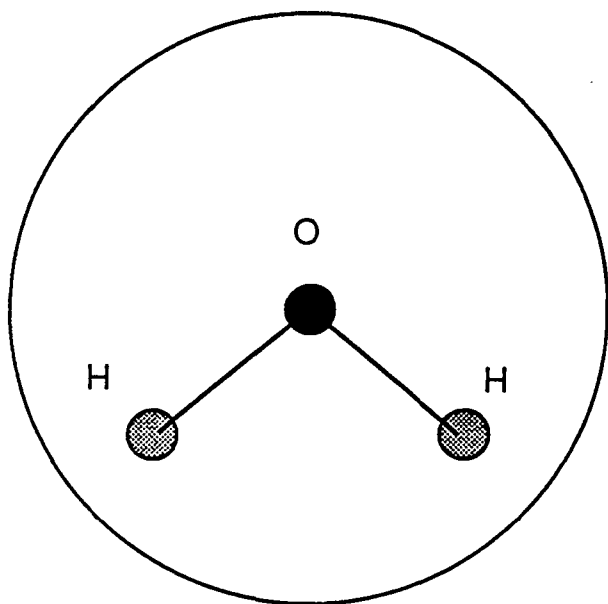
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FIGURE 1

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.

FIGURE 2

Coexistence curve of water. The open squares show experimental data. The solid circles show results of Gibbs-ensemble simulations.

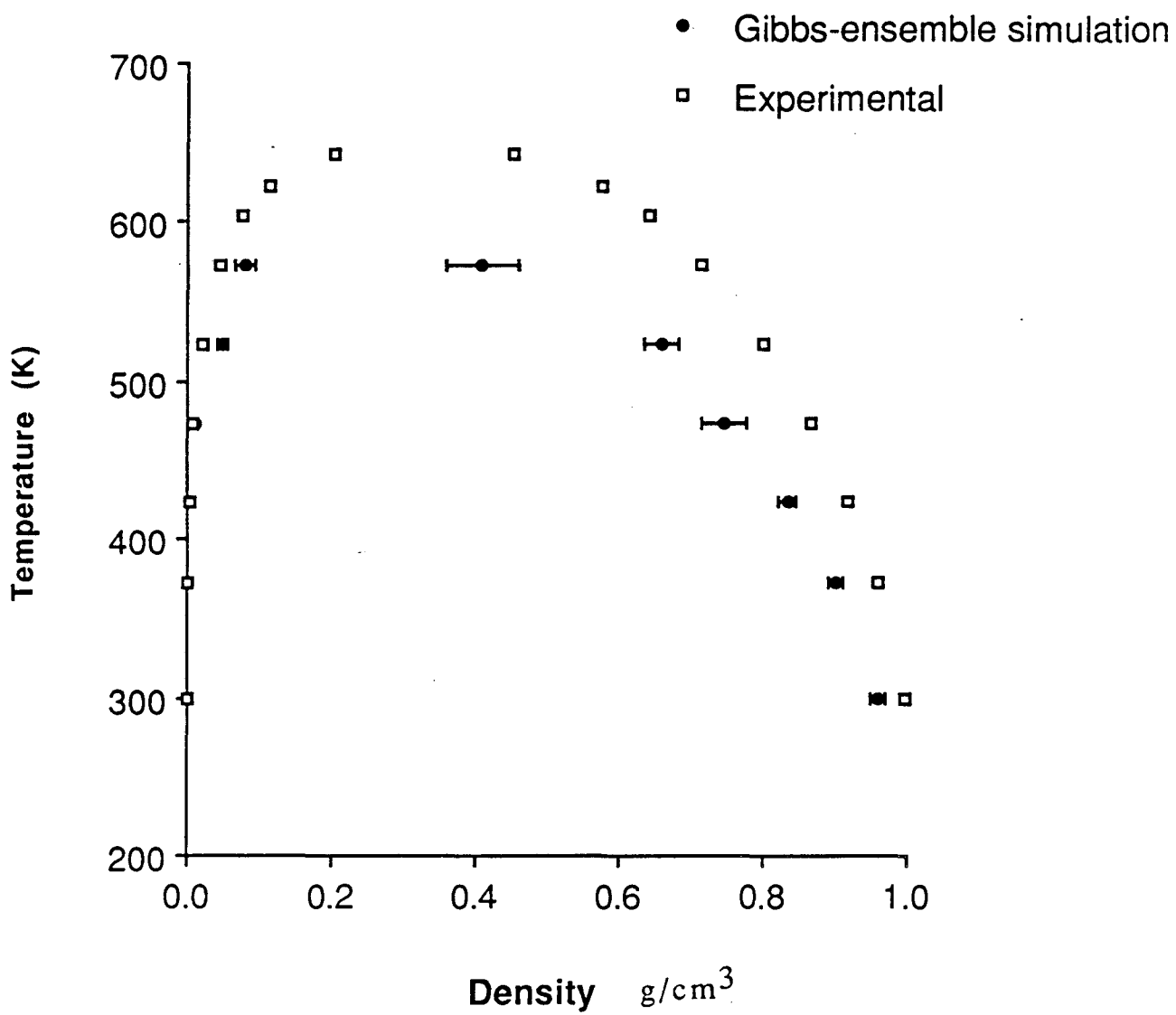


$$q(\text{O}) = -0.82 \text{ esu}$$
$$q(\text{H}) = 0.41 \text{ esu}$$

$$\langle \text{HOH} \rangle = 109.47^\circ$$

$$r(\text{OH}) = 1.0 \text{ \AA}$$

$$\epsilon(\text{O}) = 0.155 \text{ kcal/mol}$$
$$\sigma(\text{O}) = 3.167 \text{ \AA}$$



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