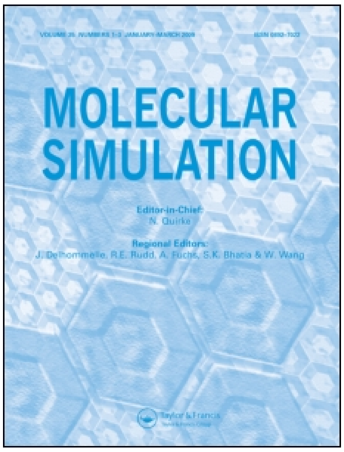

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PREDICTING LIQUID–VAPOUR EQUILIBRIA FOR WATER USING AN *AB-INITIO* POTENTIAL FROM HISTOGRAM REWEIGHTING MONTE CARLO SIMULATIONS

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The coexisting densities for an *ab-initio* model for water have been calculated using grand canonical Monte Carlo simulations with the histogram reweighting technique. Although good agreement with experimental data is found for the radial distribution function at room temperature, the predicted critical density and temperature are well below both the experimental value as well as predictions from semi-empirical potentials. Improvement in the repulsive part of the *ab-initio* potential is suggested as a way to obtain better agreement with experiment.

Keywords: Vapour liquid equilibria; water; histogram reweighting

1. INTRODUCTION

Although numerous intermolecular potentials for water have been developed in an attempt to reproduce the thermodynamic and dynamic properties of water, the complex nature of the interactions that occur between water molecules have limited the range of validity of such models. The accurate prediction and understanding of the behaviour of water is, however, of fundamental importance in many key processes in biology as well as being of great interest in a wide range of technological applications.

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For instance, a reliable estimation of the phase behaviour of water and water mixtures is necessary in the design of industrial separation processes for these mixtures.

From a molecular simulation viewpoint, semi-empirical models have generally been used as a basis for calculating phase coexistence properties. In these models, the parameters of a proposed intermolecular potential are adjusted so that the model predictions agree with experimental results. These potentials can then be used to predict properties at other thermodynamic conditions. However, in practice, it is found that these models are limited with respect to the range of thermodynamic conditions that can be used.

In this work we consider another possibility for estimating the phase behaviour. Instead of using experimental data, we use an *ab-initio* calculation to estimate the intermolecular potential. Since the *ab-initio* calculation is independent of the thermodynamic conditions, it should be generally applicable as well as able to predict all properties of interest. Another advantage is that since the *ab-initio* calculation is developed in a systematic way it is, in principle, possible to consistently refine it to improve agreement with experiment. We show how Monte Carlo simulations in the grand canonical ensemble combined with the histogram reweighting technique can be used to calculate the phase coexistence densities. The results of the *ab-initio* model are then compared against data from semi-empirical potentials such as the SPC, TIP4P/P and SCPDP and the experimental behaviour.

2. MODEL

To model the water–water interactions, we use the MCHO model of Saint-Martin *et al.* In Figure 1 a schematic representation of the model is given.

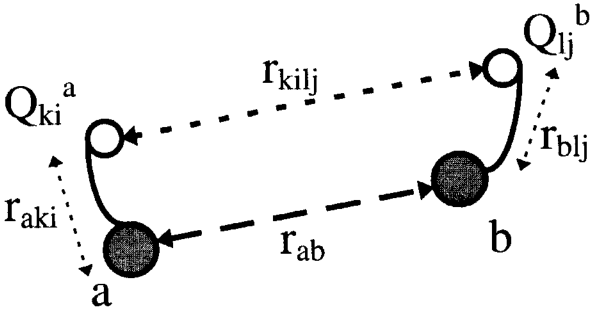

FIGURE 1 Schematic representation of the MCHO model.

As can be seen, this potential is of an atom–atom type and considers mobile charges, Q_{kia}, attached to each atom, a, by an harmonic oscillator term. This feature allows it to treat polarisation and non-additive effects. The functional is similar to semi-empirical potentials and is as follows:

$$U = \sum_{i<j}\left[\sum_{a\in i}\sum_{b\in j}\left(Ae^{-\alpha r_{ab}} + Be^{-\beta r_{ab}}\right) + \sum_{k_i,l_j}\left(C\frac{Q^a_{k_i}Q^b_{l_j}}{r_{k_i l_j}} + \frac{D}{r^n_{k_i l_j}}\right)\right] + \sum_i \sum_{a\in i} H_a r^2_{ak_i}$$

where r is the distance between the centre and charge or between charges on different atoms and A, B, α, β, C, D and n depend on the pair of interacting atoms and the H_a depend only on the type of atom and are taken from the work of Saint-Martin.

The functional form of the MCHO model is relatively simple but allows the water molecules to polarise responding to the electric field around the charge. The parameters were adjusted to reproduce the two-body water–water interaction surface of Matsuoka *et al.* (originally developed for the MCY potential), the three body non-additivity contribution of the surface computed by Clementi *et al.*, and four body non-additivities. The relatively simple form of the potential allows the interactions to be calculated in a reasonable amount of time which permits the application of Monte

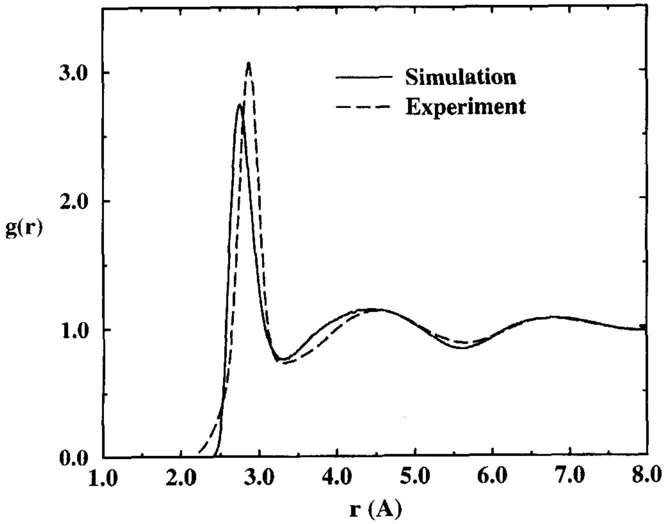

FIGURE 2 Oxygen–oxygen radial distribution function for water at ambient conditions.

Carlo techniques such as the histogram reweighting technique that was used in this work.

The model has proved to give almost quantitative agreement with experimental data for the structure and internal energy at room temperature. For instance, as can be seen in Figure 2, there is good agreement between the oxygen–oxygen radial distribution function for the model prediction and experimental data of Soper and Phillips. It should be noted that there is some controversy in the literature over the precise interpretation of the neutron scattering experiments of the structure of water and more recent works have shown a lowering of the first peak which would give an even better agreement with the predicted radial distribution function.

3. SIMULATION METHODOLOGY

In order to calculate the thermodynamic properties of the model we used multiple histogram reweighting. The basis of this technique lies in the fact that it is possible to calculate, during a single grand canonical Monte Carlo simulation carried out at some temperature, β_0, chemical potential, μ_0, and volume, V, a histogram of the probability of observing a given energy, E, and density, $N, f_0(N, E)$. This histogram can then be used to estimate, within a constant A_0, the density of states, W, for a region of energies and densities.

$$f_0(N,E) = W(N, V, E)\exp(\beta_0\,\mu_0\,N - \beta_0\,E + A_0)$$

By reweighting the original histogram, we can calculate the thermodynamic properties of the system over a range of temperatures, β_1, and chemical potentials, μ_1, relatively close to the values of the original simulation by estimating a histogram, $f_1(N, E)$, at these new conditions.

$$\frac{f_1(N, E)}{f_0(N, E)} = \exp[(\beta_1\mu_1 - \beta_0\mu_0)N - (\beta_1 - \beta_0)E]$$

In order to span a wider range of values, it becomes necessary to sum together several histograms from different simulations. Ferrenberg and Swendsen have proposed an optimal way of doing so in which the error is minimised, as given below:

$$P(N, E) = \frac{\sum_{n=1}^{R} f_n(N, E)\exp(-\beta E + \beta\mu N)}{\sum_{m=1}^{R} K_m \exp[-\beta_m E + \beta_m\mu_m N - C_m]}$$

$$\exp(C_m) = \sum_{E}\sum_{N} P(N, E)$$

where K_m is the number of states sampled in simulation m and $P(N, E)$ is the density probability for a given β and μ and the sum in the second equation is carried out at conditions corresponding to simulation m. In this method it is necessary to calculate a number of constants, C_m, self-consistently which correspond to the difference in free energy between the various simulations.

4. RESULTS

First of all, short runs were carried out to approximately locate the critical point. Afterwards several runs were performed both at the approximate critical point as well as at several sub-critical temperatures close to the estimated coexistence activities. Typical runs were between 30–50 million configurations with a total of 250 million configurations over 8 states. In the Monte Carlo routine, displacement, rotation, and creation/removal steps were used to sample phase space and hence construct the histograms. Further details of the simulations can be found in Mackie *et al.* The Ewald sum was used to include the long range contribution to the electrostatic interactions.

In order to calculate the phase behaviour, it is necessary to search for where the density probability shows a double peak corresponding to a liquid and vapour phase in coexistence. In Figure 3 are shown several such density probability curves for water at several sub-critical temperatures

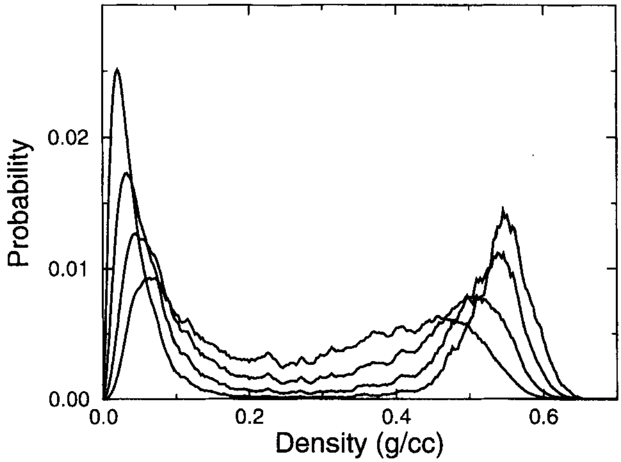

FIGURE 3 Coexistence probability density distributions for the MCHO model near and below the critical point. The curves correspond to temperatures of 480, 470, 460 and 450 K.

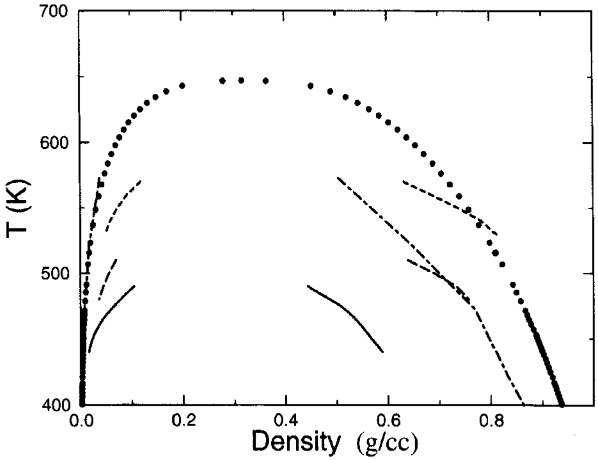

FIGURE 4 Temperature-density phase diagram for water near the critical point. (filled circles) experimental data (solid line) MCHO, (dashed line) TIP4P/P Kiyohara *et al.* (long dashed line) SCPDP Kiyohara *et al.* (dot dashed line) SPC Strauch and Cummings.

for the MCHO potential where, in addition, the chemical potential has been adjusted at a given temperature in order to give the same area under both the liquid and vapour peak and thus equal pressures in both phases. The coexisting liquid and vapour densities can then be calculated by averaging the density for each peak.

In Figure 4 a temperature-density phase diagram for water is given for both the experimental values, the *ab-initio* results following the procedure already described, as well as several semi-empirical potentials. As can be seen, the *ab-initio* model severely underestimates both the critical density and temperature when compared both to the experimental value and to the semi-empirical potentials. However, it should be stressed that no adjustable parameters have been used in the *ab-initio* calculation and that, to our knowledge, this is the first time that the phase behaviour of water has been calculated by an *ab-initio* potential. We suspect that the most probable source of the discrepancy comes from poor sampling in the repulsive region of the potential which becomes increasingly important as the temperature is raised.

5. CONCLUSIONS

In conclusion, we have been able to estimate the phase diagram of an *ab-initio* potential for water by using grand canonical Monte Carlo simulations with multiple histogram reweighting techniques. Although the MCHO model shows good agreement for the structure of water at ambient temperatures, both the predicted critical temperature and density are well below the experimental values as well as those of semi-empirical potentials. We believe that poor sampling in the repulsive part of the potential is the main cause of this deviation and work is currently underway to probe this possibility. By improving the quality of the *ab-initio* intermolecular potential surface it should be possible to systematically improve agreement with experiment, not only for the phase coexistence prediction, but also for the already good agreement for the structure found at ambient conditions.

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