The Second Virial Coefficients for Water from Monte Carlo Integration Using Reduced Effective Charges

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THE SECOND VIRIAL COEFFICIENTS FOR WATER FROM MONTE CARLO INTEGRATION USING REDUCED EFFECTIVE CHARGES

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The reduction of the dipole moment of effective pair potentials of rigid water models enables accurate second virial coefficients to be determined over the whole temperature range. Subsequent Isothermal-Isobaric (NPT) ensemble simulations of water vapour have shown that there is a significant difference in vapour densities between the modified water potentials.

1 INTRODUCTION

An important feature of effective pair potential models for water is that they have large dipole moments which take into account many body induced polarization interactions. The most common potential model for rigid water consists of a Lennard Jones centre at the oxygen and three or four charged centres. In this work we confine attention to models with three charged centres of the type shown in Figure 1. The two body effective potential energy is given by equation 1, where ε and σ are the usual well depth and hard sphere parameters, ε_0 is the permittivity of vacuum and $r_{\alpha\beta}$ is the distance between a pair of point (partial) charges α and β on different molecules.

$$U = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \sum_{\alpha}\sum_{\beta}\frac{q_{\alpha}q_{\beta}}{4\pi\varepsilon_0 r_{\alpha\beta}} \tag{1}$$

The partial charges and distances which characterise the SPC [1], TIPS2 [2], TIP3P [3] and TIP4P [3] models are given in Table 1. These parameters have been optimized with respect to liquid water at normal densities and temperatures, details of the optimization being given in the cited references. One consequence of the optimization, is that if accepted values of ε and σ are chosen, the effective dipole in these models is considerably greater than the dipole of an isolated water molecule (1.85D). Enhanced effective dipoles are regarded as reasonable on the grounds that collective induced interactions would polarize water molecules in such a way as to increase the effective dipole compared to the bare dipole.

Pablo *et al.* [4] have reported Gibbs ensemble simulations for the SPC model and show that an effective dipole moment would yield lower liquid densities and higher vapour densities than experiment. Strauch *et al.* [5] found that using the bare dipole of water 1.85D in the vapour box gave better agreement with experimental vapour densities [6].
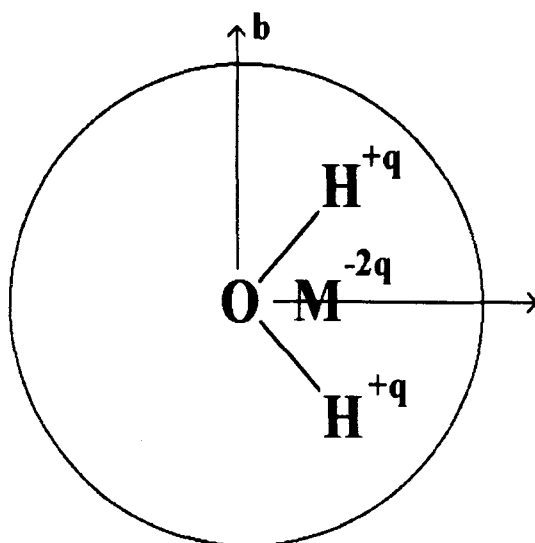
Figure 1 The geometry of three charged centre rigid water potentials.

Table 1 The partial charges and distance which characterise rigid water potentials.

	SPC	TIPS2	TIP3P	TIP4P
$r_{OM}/\text{Å}$	0	0.15	0	0.15
$r_{OH}/\text{Å}$	1	0.9572	0.9572	0.9572
$\angle HOH/°$	109.47	104.52	104.52	104.52
q_H/e	0.41	0.535	0.417	0.52
q_M/e	-0.82	-1.07	-0.834	-1.04
$\varepsilon/\text{kJmol}^{-1}$	0.65066	0.54216	0.63669	0.64912
$\sigma/\text{Å}$	3.16560	3.2407	3.15066	3.15358

Although using a bare dipole moment of 1.85D produces vapour densities in better agreement with experiment these are still consistently lower than the experimental values. Since it is improbable that the ε and σ parameters would be different in the two phases, this suggests that the reduced dipole in the vapour phase should be higher than the bare dipole. In this work we use numerical integration to calculate the second virial coefficients for water for a number of different models and compare these with experimental results. It is found that the vapour state is well represented by an SPC model with a dipole lower than the optimum liquid state value, but higher than the bare dipole.

2 METHOD

A virial expansion can be written to describe non ideal fluids (Equation 2). Where $\langle p \rangle$ is the mean pressure and ρ is the number density. For low density fluids the third term and higher may be ignored.

$$\beta \langle p \rangle = \rho + B\rho^2 + C\rho^3 + \ldots \simeq \rho + B\rho^2 \qquad (2)$$

The second virial coefficient per molecule B is given by Equation 3:

$$B = -\frac{V}{2}\left(\frac{Z_2}{Z_1^2} - 1\right) \qquad (3)$$

Where V is the volume, Z_1, the singlet configurational integral and Z_2 is the doublet configurational integral. This can be expressed as in Equation 4.

$$B = -\frac{1}{128\,\pi^2\,V}\iint (e^{-\beta u_{12}} - 1)\,dq_1 dq_2 \qquad (4)$$

Where $q \equiv (r, \omega)$ and r, ω are translational and rotational coordinates respectively. u_{12} is the pair interaction between particle 1 and 2. This integral may be simplified by writing B as a function of the separation between two molecules and averaged over all orientations (Equation 5):

$$B = -2\pi \int f_{12}(r)r^2\,dr = -\frac{V}{2N_{cfg}}\sum_{i=1}^{N_{cfg}} f_i \qquad (5)$$

Where $f_{12}(r) = \langle \exp(-\beta u_{12}) - 1 \rangle$, is the orientationally averaged Mayer function, r is the particle separation, i is the index number of a configuration and N_{cfg} is total number of configurations.

Monte Carlo numerical integration was used to evaluate the integrals for various modified SPC water models at a number of different temperatures. The integral was evaluated in three parts. In the first region from $0\,\text{Å} < r < 2\,\text{Å}$, it was assumed that f_{12} is approximately -1. In the second region $2\,\text{Å} < r < 4\,\text{Å}$ f_{12} was calculated by generating 1.5×10^6 positions and orientations randomly and B determined from the mean f_{12} multiplied by $-V/2$. This procedure was repeated for the third region, $4\,\text{Å} < r < 10\,\text{Å}$ using 7.5×10^5 configurations.

Monte Carlo simulations consisting of 50 vapour molecules at various temperatures were made using the modified SPC water models. The models included those listed in table 1, and a series of SPC models with partial charges modified so as to give the dipole moment shown in Figure 3. The Isothermal-Isobaric (NPT) ensemble was used with the pressure fixed at the experimental saturated vapour pressures, and one volume trial move was attempted for every 50 phase trial moves. The systems were allowed to equilibrate over about 5×10^7 phase moves and sampling was made over a further 1×10^8 phase moves.

In making the choice of pressure for the NPT studies, two possibilities were considered. The first was that the pressure should be the saturation vapour pressure for model water with the specified dipole moment. This pressure therefore changes as the effective dipole moment is altered. This choice was rejected on the grounds that in comparing the coordination numbers the result would be very strongly affected by the accompanying density change, therefore obscuring the effect we seek to examine. The second was to maintain the pressure fixed at the experimentally determined saturation vapour pressure for real water, whatever the value of the effective dipole moment. Results for this method are all at the same density and so do not suffer from the disadvantage mentioned above. A further advantage of the second approach is that it does not require expensive lengthy determination of

the saturation vapour pressure by the Gibbs' method for each value of the effective dipole moment.

3 RESULTS AND DISCUSSION

Figure 2 compares the experimental virial coefficients with B calculated for models in table I using the 'liquid' state effective dipole. It is clear that neither the temperature dependence of B nor the agreement at high temperature is good. Figure 3 shows the second virial coefficients for the SPC model with various effective dipoles. A reduced effective dipole moment of 2.085D was found to produce the closest agreement with experimental [7] second virial coefficient values. Calculations were repeated for the TIPS2, TIP3P and TIP4P water potentials models, and optimum reduced effective dipoles of 2.085D, 2.139D and 2.025D respectively were obtained.

Thus in all cases the optimum reduced effective dipole moments of rigid water models are greater than the bare dipole moment. Since we have accepted the ε and σ values adopted in the optimized potentials it follows that this implies that in the vapour phase, water molecules are not entirely isolated and an effective pair potential would need to include polarization effects.

Numerical integration of the oxygen-oxygen radial distribution functions, $g(r)$ obtained from the simulations Figure 4 was used to determine the coordination number of the water molecules in the vapour:

$$n_c = \int_0^r 4\pi r^2 g(r)\rho dr \qquad (6)$$

Where ρ is the calculated mean number density of the water vapour at that temperature. The maximum limit of r was fixed at 2.86Å, which gave a coordination number of 4.5 for liquid water at 298.15K. Obviously the coordination number depends on the range of r, but this is not important, since here, we are interested only in the relative values of n_c for the different dipoles investigated. The coordination numbers are plotted in Figure 5 and give evidence that some clustering occurs in the simulated water vapour for the bare dipole moment and rather more strongly for higher effective dipole moments. Further evidence of molecular clustering is provided by "snapshots" of the simulations (Figure 6).

The integration and simulation were partly performed on a Naga 33MHz i80486DX and a single 25MHz T800 transputer.

4 CONCLUSION

The reduction of the dipole moment of effective pair potentials of rigid water models enables accurate second virial coefficients to be determined over the normal temperature range. The optimum reduced effective dipole moment is greater than the bare dipole moment of 1.85D, implying that polarization effects would be important in small clusters. Of course an alternative deduction would be to insist that water in the vapour phase must have the bare dipole, and to optimize ε and σ on this basis. It would then follow that a new parameterization would be needed for the liquid state (using the optimised ε, σ pair).
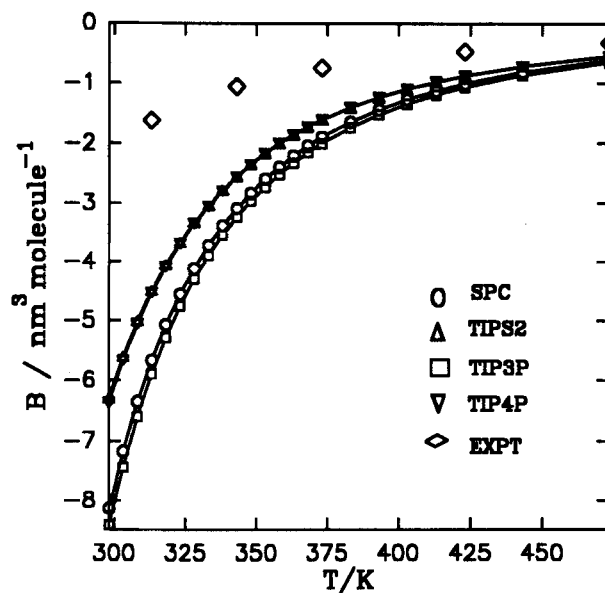
Figure 2 Calculated second virial coefficients of water models at different temperatures.
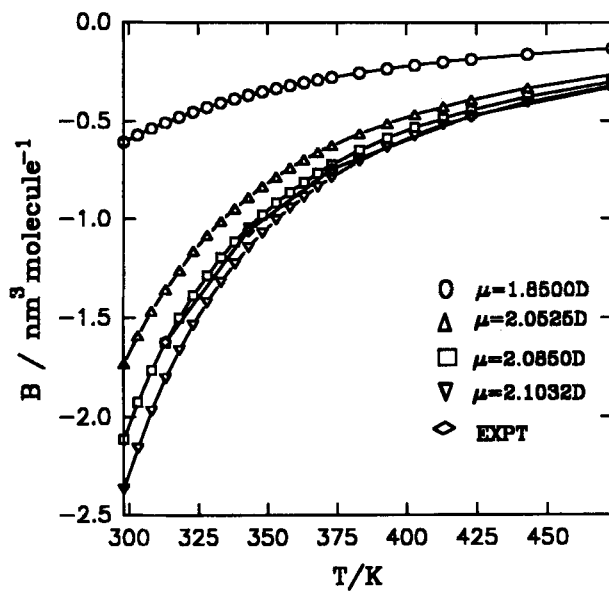

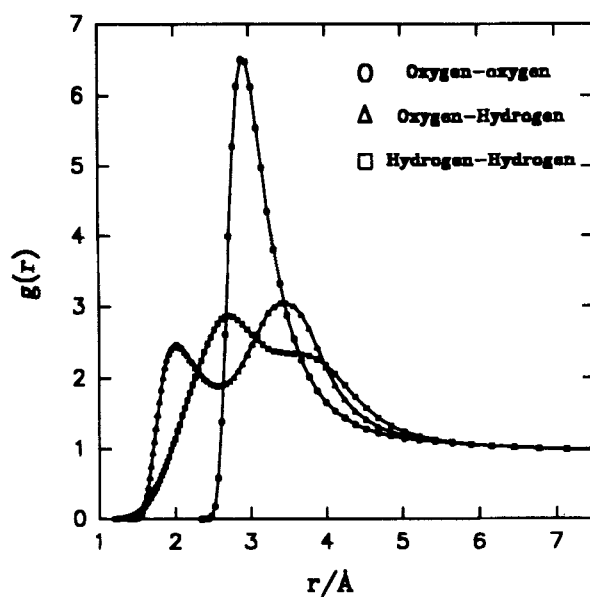**Figure 3** Calculated second virial coefficients of modified SPC water at different temperatures.

Figure 4 Calculated radial pair distribution function of modified SPC water ($\mu = 2.085$ D) in the vapour phase at 473.15K.
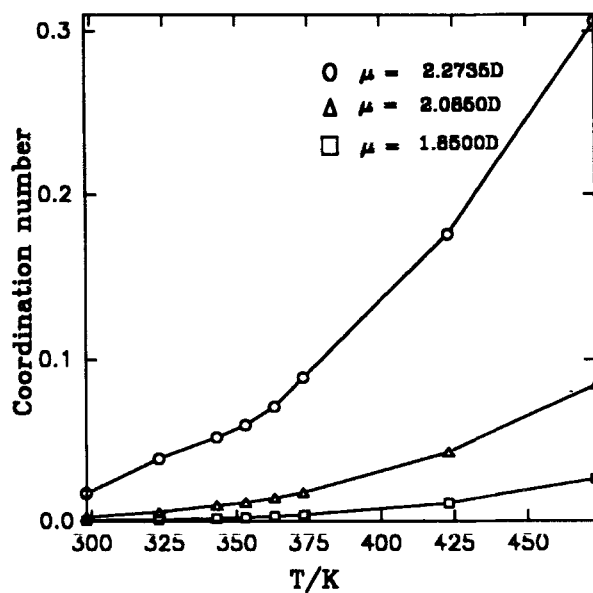

Figure 5 Calculated coordination numbers of modified SPC water vapour as a function of temperature for different choices of dipole.

Figure 6 Simulation snapshot of the modified SPC water ($\mu = 2.085D$) at 473.15K.

The Isothermal-Isobaric (NPT) ensemble simulations of water vapour show that there is a significant difference in vapour densities between the modified water potentials. The coordination numbers of the modified SPC water models confirm that some degree of clustering occurs in the vapour phase using these models.

Acknowledgements

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