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COMMENTS

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

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In an earlier paper[1] [hereafter referred to as I], de Pablo *et al.* reported Gibbs ensemble Monte Carlo (GEMC) simulations of SPC water with long-range intermolecular interactions computed using the Ewald summation method. The coexistence curve of SPC water was obtained from 25 to 300 °C. At each temperature simulated, the liquid densities obtained in the simulation were consistently lower than the corresponding experimental quantities and the vapor densities consistently higher. By fitting the simulation results to a Wegner expansion for the difference between simulated liquid and vapor orthobaric densities, the estimated critical temperature was $T_c = 587$ K and the estimated critical density was $\rho_c = 0.27$ g/cm^3. This differs substantially from the experimental quantities values of $T_c = 647.3$ K and $\rho_c = 0.32$ g/cm^3.

One of the features of the SPC model which makes it accurate at ambient conditions is that it has a dipole moment of 2.24 D. Since the bare dipole moment of a water molecule is 1.8 D, it is clear that the higher dipole moment of SPC is an effective dipole moment that includes the effect of polarizability that is important at high density. However, in GEMC one of the phases is a vapor phase where it seems more appropriate to use the bare dipole moment of 1.8 D rather than the higher effective value.

Hence, we repeated the simulations reported in I with the modification that the molecules in the vapor phase interacted with a slightly modified SPC potential. All the interactions in the modified SPC were the same as for the regular SPC except that the magnitudes partial charges were reduced by a factor of $\sqrt{(1.8/2.24)}$. The reader is referred to I for details of the simulation methodology. With this modification, we obtained the results given in Table II and illustrated in Fig. 1. If we compare the results from I, Table I, with the present results, Table II, we see that the vapor phase densities at the three temperatures $T = 473$, 523, and 573 K and the liquid phase density at $T = 573$ K differ in a statistically significant way, and in each case in the direction of greater agreement with experiment. Using the Wegner expansion, we find that the critical point can be estimated from the simulation results to be $T_c = 606$ K and $\rho_c = 0.27$ g/cm^3, which is considerably closer to the experimental results.

It is apparent from the results presented here that taking into account the difference in effective dipole moment between the liquid and vapor phases has a substantial positive effect on the predictions of the SPC model. However, there is clearly a physical inconsistency in the simulations presented here which becomes evident as the critical point is approached since in this limit the dipole moment used in the two phases should become equal. In order to model the physical situation properly, we require that the effective dipole moment in the two phases should be temperature and density dependent in such a way that the two are equal above the critical point and approach each other as the critical point is neared. A more rigorous approach is to use the bare dipole moment in each phase and use polarizability, though this would result in longer simulation runs since polarizability results in a many body calculation which must be performed at each configuration. The present results suggest that it is worthwhile to pursue one or both of these two directions in developing intermolecular potentials for water that can be used effectively in phase equilibria calculations.

The state dependence of the SPC potential used in this work amounts to assuming a density independent value for the dipole moment in each phase. This is similar in spirit to the approach taken by de Pablo *et al.*[2] in work presented subsequent to the completion of the simulations reported in

TABLE I. GEMC simulation results for vapor–liquid equilibrium of SPC water using the same dipole moments in liquid and vapor phases. Estimated uncertainties in the results are given in parentheses. Letter V indicates that the results correspond to the Virginia code, while the letter B indicates that they correspond to the Berkeley code.

Run	Molecules	T(K)	Vapor phase		Liquid phase	
			U kcal/mole	ρ g/cc	U kcal/mole	ρ g/cc
1V	140	373	− 0.136(88)	0.000648(111)	− 8.90(35)	0.893(15)
1′B	140	373	− 0.16(9)	0.000711(56)	− 8.82(7)	0.899(11)
2B	200	423	− 0.46(10)	0.00275(15)	− 8.17(7)	0.833(12)
3B	200	473	− 0.85(20)	0.0110(17)	− 7.39(19)	0.745(32)
4V	140	523	− 2.14(35)	0.0496(55)	− 6.54(18)	0.647(40)
4′B	200	523	− 2.09(22)	0.0476(60)	− 6.64(15)	0.658(25)
5B	200	573	− 2.30(34)	0.0789(140)	− 5.14(26)	0.408(49)

TABLE II. GEMC simulation results for vapor–liquid equilibrium of SPC water using different dipole moments in liquid and vapor phases. Estimated uncertainties in the results are given in parentheses.

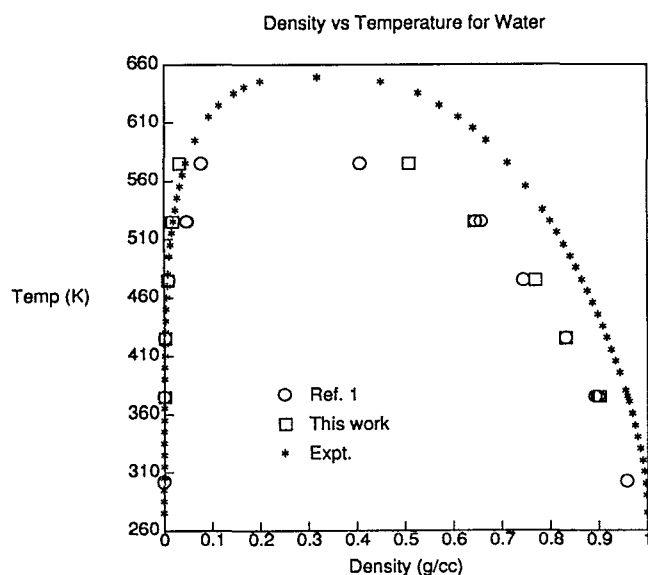| Run	Molecules	T(K)	Vapor phase		Liquid phase	
			U kcal/mole	ρ g/cc	U kcal/mole	ρ g/cc
1	140	373	− 0.011(53)	0.000651(56)	− 8.86(17)	0.901(16)
2	140	423	− 0.032(28)	0.00250(21)	− 8.14(31)	0.831(24)
3	140	473	− 0.074(32)	0.0075(16)	− 7.37(23)	0.769(32)
4	140	523	− 0.165(52)	0.0175(55)	− 6.57(14)	0.644(33)
5	140	573	− 0.765(188)	0.0384(120)	− 5.62(18)	0.504(28)

FIG. 1. Gibbs ensemble Monte Carlo simulation results for SPC water with the same dipole moment in each phase (O, from Ref. 1) and with different dipole moments in each phase (□, this work) compared with experimental data.

this manuscript. De Pablo *et al.* have proposed using linear functions of density in the liquid and vapor phases for the energy parameter in Lennard-Jones potentials for alkanes to account for many body forces whose importance increases with density. In the de Pablo *et al.* work, the use of density dependent energy parameters did not appreciably affect pure fluid properties but led to much better agreement with experiment in mixtures of disparate size (such as methane/pentane).

[1] J. J. de Pablo, J. M. Prausnitz, H. J. Strauch, and P. T. Cummings, J. Chem. Phys. **93**, 7355 (1990).

[2] J. J. de Pablo, M. Bonnin, and J. M. Prausnitz. Phase equilibria for polyatomic fluids from computer simulation, pure hydrocarbons and mixtures. Presented at the 11th International Symposium on Thermophysical Properties, Boulder, Colorado, 1991, Fluid Phase Equilibria (submitted).