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LETTERS TO THE EDITOR

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NOTES

Monte Carlo simulation of vapor–liquid binodal of water

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Among many popular potential models of water, the nonpolarizable four-site TIP4P potential¹ is one of the more widely used. Recently, two new potential models of water on the basis of the TIP4P potential have been developed. One is the four-site Dang–Chang polarizable potential² and another is the five-site TIP5P potential.³ The former is designed to describe not only bulk and interfacial properties of liquid water but also microclusters of water. The nonpolarizable TIP5P potential is the latest version in the TIP series from the Jorgensen group. Compared with the TIP4P potential, for example, the TIP5P potential gives a much improved description of the so-called temperature of maximum density. Recently we used the TIP4P, SPC/E⁴ and Dang–Chang potentials to study ion-induced droplet formation.⁵ The supersaturation was not evaluated due to the lack of vapor–liquid coexistence density for the Dang–Chang model. In this note, we report Gibbs ensemble Monte Carlo (GEMC) simulation^{6,7} of vapor–liquid coexistence densities (the binodal curves) for the TIP5P and Dang–Chang models of water. Similar simulations have been carried out for the SPC/E water in the presence of uniform external electric fields.⁸

The molecular parameters for TIP5P and Dang–Chang potentials are listed in Table I. Specifically, the pairwise TIP5P potential is given by the sum of the Lennard-Jones and Coulomb interactions,

$$U_{\text{pair}} = \sum_i \sum_{j>i} \left(4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right), \quad (1)$$

where r_{ij} is the distance between site i of one molecule and site j of another molecule; q_i is the charge of site i ; σ and ϵ are the Lennard-Jones parameters for the oxygen site. In addition, the Dang–Chang model has a molecular polarizability α of 1.444 Å.³ The nonadditive polarizable energy of the system U_{pol} is then given by

$$U_{\text{pol}} = -\frac{1}{2} \sum_i \vec{\mu}_i \cdot \vec{E}_i^0, \quad (2)$$

where \vec{E}_i^0 is the electric field produced by all permanent charges in the system at site i ,

$$\vec{E}_i^0 = \sum_{j \neq i} \frac{q_j \vec{r}_{ij}}{r_{ij}^3} \quad (3)$$

and $\vec{\mu}_i$ is the induced dipole at site i , which is given by

$$\vec{\mu}_i = \alpha_i \vec{E}_i = \alpha_i \left[\vec{E}_i^0 + \sum_{j \neq i} \mathbf{T}_{ij} \cdot \vec{\mu}_j \right], \quad (4)$$

where \vec{E}_i is the total electric field at site i , and \mathbf{T}_{ij} is the dipole tensor, i.e.,

$$\mathbf{T}_{ij} = \frac{1}{r_{ij}^3} \left(\frac{3\vec{r}_{ij}\vec{r}_{ij}}{r_{ij}^2} - \mathbf{I} \right), \quad (5)$$

where \mathbf{I} is the unit tensor. We used a standard iterative self-consistent field procedure to evaluate the induced dipole with Eq. (4). The iterations were stopped when the maximum difference in the induced dipoles between successive iterations is less than 0.0001 D/site. In all simulations, the water–water interactions were truncated at a molecular separation of 9 Å.

To calculate the vapor–liquid coexistence densities (binodal curves), we employed the Gibbs ensemble Monte Carlo simulation method of Panagiotopoulos.^{6,7} In the GEMC method, two simulation cells are used, each representing a portion of one coexisting phase. Three types of MC moves are taken in the simulation: molecular displacement and rotation to assure internal equilibrium; variation of cell volume to satisfy equal pressure conditions; and molecular exchange between two cells to enforce equal chemical potential conditions. We used a 432 water molecule system. We found that this system size is reasonably large to prevent some large density fluctuation due to the molecule exchange. In all simulations, each MC cycle consists of 432 attempts of displacement and rotation, one volume rearrangement attempt, and one molecule exchange attempt. The number of MC cycles in the equilibration run typically ranged from 100 000 to 1 000 000 to assure the system is in the equilibrium state. After the equilibration run, another 1 000 000 cycles were then used for data collection in the case of the TIP5P model. In the case of the Dang–Chang model, 100 000 cycles were

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TABLE I. Molecular parameters for TIP5P and Dang–Chang water models. The TIP5P water model has two negative charge sites (denoted M) located at two lone-pair interaction sites. The Dang–Chang model has one negative charge site which is shifted from the position of the oxygen site (the Lennard-Jones site) by r_{OM} toward the direction of the permanent dipole. α is the molecular polarizability.

	TIP5P	Dang–Chang
r_{OH} (Å)	0.9572	0.9572
r_{OM} (Å)	0.70	0.215
θ_{HOH} (deg)	104.52	104.52
θ_{MOM} (deg)	109.47	
ϵ_{LJ} (kcal/mol)	0.16	0.1825
σ_{LJ} (Å)	3.12	3.234
q_H (e)	0.241	0.519
q_M (e)	−0.241	−1.038
α (Å ³)		1.44

used due to the much longer computational time needed for the polarizable model. The simulation results are shown in Table II.

Because the critical point cannot be determined directly from the GEMC simulation, we fitted the vapor–liquid coexistence densities (ρ_v and ρ_l), except those of 298.15 K, to the scaling law

$$\rho_l - \rho_v = A(T_c - T)^\beta \quad (6)$$

and the rectilinear law,

$$\frac{\rho_l + \rho_v}{2} = \rho_c + B(T_c - T), \quad (7)$$

where T_c is the critical temperature, ρ_c is the critical density, and A and B are two associated coefficients. For three-dimensional systems, the critical exponent β is 0.326. The final estimated T_c is 546 and 590 K for the TIP5P and the Dang–Chang model water, respectively.¹⁰ Note that both values of T_c are lower than the experimental value of 647 K.¹¹

In Fig. 1, we plot the binodal curves of the TIP5P and Dang–Chang model water, along with the binodal curves of TIP4P and SPC/E model water (Ref. 9). Compared with the TIP4P model ($T_c = 579$ K), the TIP5P model gives a lower T_c of 546 K whereas the Dang–Chang model yields a higher T_c (590 K). It is known that a fluid with a stronger dipole

TABLE II. Vapor–liquid coexistence densities of TIP5P and Dang–Chang model water. Numbers in parentheses denote the error of the simulation data.

T (K)	TIP5P		Dang–Chang	
	ρ_g (g/cm ³)	ρ_l (g/cm ³)	ρ_g (g/cm ³)	ρ_l (g/cm ³)
298.15	0.000 054 9(11)	0.989(4)	0.000 048 8(4)	0.997(13)
323	0.000 221(4)	0.970(3)	0.000 219(2)	0.967(6)
373	0.001 48(4)	0.908(3)	0.001 49(1)	0.917(11)
423	0.006 11(27)	0.824(3)	0.007 97(24)	0.851(7)
473	0.024 1(12)	0.711(6)	0.024 9(13)	0.764(8)
503	0.056 4(8)	0.622(13)		

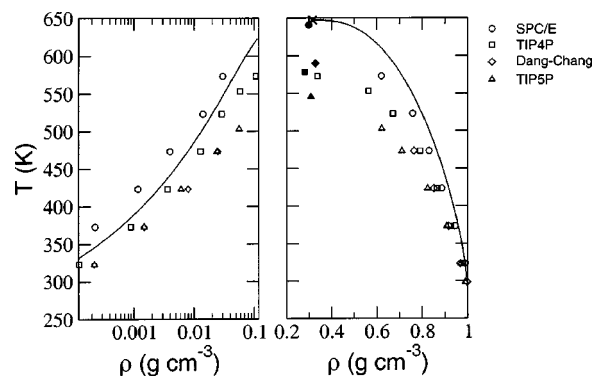


FIG. 1. Vapor–liquid binodal curves of TIP5P and Dang–Chang model water. Simulation results are compared with those of TIP4P and SPC/E model water. The solid line represents experimental values (Ref. 11). The open circles, squares, diamonds, and triangles are simulation results of SPC/E, TIP4P, Dang–Chang, and TIP5P model, respectively (Ref. 9). The closed symbols represent the estimated critical point for each water model by using Eqs. (6) and (7). The cross denotes the measured critical point of water from experiments.

moment tends to have a higher T_c . Indeed, the polarizable Dang–Chang model has effectively stronger dipole moment (permanent plus induced dipole)² than that of TIP4P (2.18 D). On the other hand, the dipole moment of TIP5P model (2.29 D) is slightly higher than TIP4P and yet the T_c of TIP5P water is lower than that of TIP4P. This apparently peculiar behavior can be understood on the basis¹² that the five-site TIP5P model has much smaller quadrupole moments Q_{xx} and Q_{yy} ($1.65 \times$ and -1.48×10^{-26} esu cm², respectively) in magnitude than those of TIP4P ($2.20 \times$ and -2.09×10^{-26} esu cm²) as well as those of the Dang–Chang model ($2.24 \times$ and -2.05×10^{-26} esu cm²).

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