The liquid-vapor equilibria of TIP4P/2005 and BLYPSP-4F water models determined through direct simulations of the liquid-vapor interface

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In this paper, the surface tension and critical properties for the TIP4P/2005 and BLYPSP-4F models are reported. A clear dependence of surface tension on the van der Waals cutoff radius (r_{vdw}) is shown when van der Waals interactions are modeled with a simple cutoff scheme. A linear extrapolation formula is proposed that can be used to determine the infinite r_{vdw} surface tension through a few simulations with finite r_{vdw} . A procedure for determining liquid and vapor densities is proposed that does not require fitting to a profile function. Although the critical temperature of water is also found to depend on the choice of r_{vdw} , the dependence is weaker. We argue that a r_{vdw} of 1.75 nm is a good compromise for water simulations when long-range van der Waals correction is not applied. Since the majority of computational programs do not support rigorous treatment of long-range dispersion, the establishment of a minimal acceptable r_{vdw} is important for the simulation of a variety of inhomogeneous systems, such as water bubbles, and water in confined environments. The BLYPSP-4F model predicts room temperature surface tension marginally better than TIP4P/2005 but overestimates the critical temperature. This is expected since only liquid configurations were fit during the development of the BLYPSP-4F potential. The potential is expected to underestimate the stability of vapor and thus overestimate the region of stability for the liquid. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922166>]

I. INTRODUCTION

The liquid-vapor equilibrium of water has profound significance in many laboratory and industrial processes. In addition, protein has a low dielectric constant; an isolated water molecule in protein thus bears much resemblance to water in the vapor phase.¹ It is important to verify the ability of a water model to describe the liquid-vapor equilibrium.

The liquid-vapor equilibria of several water models have been investigated computationally. Many of these simulations rely on equilibrating the chemical potential (μ) of the liquid and vapor phases by Gibbs Ensemble Monte Carlo (GEMC) simulations.^{2–7} Other methods, such as histogram reweighting Grand-Canonical Monte Carlo (GCMC), were also used.^{3,8} Due to the difficulty in inserting and deleting particles in the liquid phase, advanced Monte Carlo (MC) trial moves, such as the configuration biased sampling method,⁹ are frequently applied. The application of such an advanced trial move procedure is especially important for larger molecules, such as organic solvents. This is because the difficulty of a successful particle insertion increases sharply as the size of the molecule increases.

Vega *et al.*¹⁰ obtained the liquid-vapor equilibrium curve using the Gibbs-Duhem equation that does not require particle insertions. However, in order to apply the Gibbs-Duhem equation, the liquid-vapor equilibrium at one temperature and pressure has to be obtained accurately with a more traditional method.

Although MC based phase equilibrium studies are very popular, another straightforward method to investigate the liquid-vapor equilibria is by a direct coexistence simulation of a liquid-vapor interface, frequently done with Molecular Dynamics (MD). MD does not require challenging particle insertions and is able to provide kinetic information, such as evaporation rates. Another benefit of a direct interface simulation is the ability to model interface fluctuations, which may be important as surface tension drops when the critical temperature is approached.

We also want to mention the relative simplicity of MD based methods. Although public domain MC codes are available, high performance MD programs are more popular and easy to use. Establishing a simple MD based procedure for liquid-vapor simulation and critical point determination will be very beneficial to the simulation community.

Several MD based liquid-vapor interface simulations have been reported.^{10–14} While long-range electrostatic interactions are typically modeled with Ewald summation, one challenge for a direct simulation of a liquid-vapor interface is the proper treatment of long-range van der Waals interactions. Alejandro and Chapela used Ewald summation also for Lennard-Jones interactions.¹⁴ Although several schemes for the Ewald summation of the Lennard-Jones interactions have been developed,^{15,16} the actual implementation is still not widely available in MD programs. This might be related to the relatively large computational cost of Ewald summations or a lack of proper appreciation of the importance of explicit treatment of long-range van der Waals contributions. For homogeneous system, a simple long-range correction term performs admirably,¹⁷

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however, the importance of proper treatment of long-range van der Waals for inhomogeneous systems is less explored.

For a two dimensional slab, analytical formulas for long-range van der Waals corrections do exist.^{18,19} The application of such a formula requires a density profile function as input. Additional approximations have to be made for such a density profile function. Furthermore, it has been argued that such corrections have to be applied self-consistently,¹⁴ which involves an additional term in the force component normal to the slab surface. This force correction term is not widely implemented in MD programs. For simulation of other inhomogeneous systems, such as water droplets and confined water, analytical long-range correction terms are, to the best of our knowledge, yet to be derived.

It will be beneficial to establish a sufficiently accurate procedure for studying the liquid-vapor equilibria before rigorous treatment of long-range van der Waals becomes readily available in MD simulation packages. In this work, we show, quantitatively, the effect of incomplete treatment of long-range van der Waals for surface tension and critical property calculations through a liquid-vapor slab simulation. We show that it is possible to provide a good estimate of the critical point with a cutoff scheme for van der Waals interactions. A linear extrapolation formula is proposed to estimate the surface tension (γ) with two to three cutoff based slab simulations with different van der Waals cutoff radius r_{vdw} . We hope some of our conclusions can be used to study other inhomogeneous systems, such as water droplets, water confined in nanopores or nanotubes. Droplet studies are important for addressing fundamental questions, such as the curvature dependence of surface tension²⁰ and the contact angle of fluid on substrate surfaces.

In this particular study, we will utilize the Gromacs program due to its speed. At the same time, our method can be used with any MD packages that support NVT simulations of an interface, and is able to calculate the system Virial.

In this work, we will study the liquid-vapor equilibria of the TIP4P/2005 model²¹ and the BLYPSP-4F model.²² The liquid-vapor equilibria of the TIP4P/2005 model have been investigated previously by several groups and can be used as a validation of our method. The BLYPSP-4F model was developed by force-matching electronic structure calculations without fitting to any experimental property.²³ The BLYPSP-4F water has a freezing temperature of 258 K and a room temperature dielectric constant of 76.²⁴ A previous study of the BLYPSP-4F model likely underestimated its surface tension due to the use of a relative small van der Waals cutoff of 0.9 nm.²⁴ This study provides a refined estimate of the surface tension, boiling temperature, and critical point for this model.

Around room temperature, which is the condition of parameterization of the BLYPSP-4F model, our new simulation indicates that the BLYPSP-4F model gives a surface tension in good agreement with experimental results, performing slightly better than the TIP4P/2005 model. The revised estimate of the critical temperature is higher than the experimental value. This is expected since BLYPSP-4F was optimized to best reproduce the quantum partition function of the liquid. By optimizing only for the liquid, the simple point-charge energy expression used in BLYPSP-4F is unable to properly describe

the gas phase, leading to an underestimation of the relative stability of the gas. Consequently, the boiling temperature and critical temperature are over-estimated by up to 7% in the Kelvin scale.

The paper is organized in four sections: computational details of the direct interface simulations including the technique used for density determination will be described in Sec. II, results and discussion are presented in Sec. III, and a summary and conclusion is included as Sec. IV.

II. COMPUTATIONAL DETAILS OF THE DIRECT INTERFACE SIMULATIONS

Water slabs were created with the liquid-vapor interfaces in the X-Y plane. The X-Y cross section of the box has the shape of a square. When the interface is small, longer wavelength capillary waves are suppressed. In order to assess the importance of interface fluctuations, four simulation boxes were investigated with the X and Y dimension varying from 3.0 nm to 4.5 nm in increments of 0.5 nm. The number of water molecules in the box was chosen so that the slab will be 3.3 nm thick assuming liquid density at 300 K. The same number of water molecules is used for all the temperatures for each box size, except for the TIP4P/2005 model at 600 K. For the TIP4P/2005 model, 600 K is sufficiently close to the critical point. The interface thickness increases as water approaches the critical point, leading to an underestimation of the liquid density unless the number of water molecules is increased. After a convergence study with as much as 8 nm thick of liquid at 600 K, we increased the number of water molecules by approximately 25% at 600 K for the TIP4P/2005 model. When the interface is removed, a bulk simulation with this amount of water fills a thickness of approximately 5.7 nm. The Z-dimension of all slab simulations was chosen to be 10.0 nm, except for TIP4P/2005 water at 600 K. With the thicker liquid slab, a box thickness of 12.0 nm is used for this simulation.

A canonical ensemble simulation was performed with the temperature controlled using the Nosé-Hoover thermostat with a relaxation constant of 2 ps. Each simulation trajectory is 20 ns long and statistics were collected only from the last 15 ns. Up to two independent trajectories were performed in each simulation condition to reduce the error bar. Surface tensions are measured once every 100 MD steps during the production run.

The electrostatic interaction was treated using the particle-mesh Ewald (PME) method²⁵ in 3 dimensions. A spline order of 6 and a real space Ewald precision of 10^{-6} was used; the reciprocal space electrostatics was integrated with a Fourier mesh density of 0.12 nm^{-1} . Since BLYPSP-4F is a flexible water potential, a time step of 0.5 fs was used to ensure good energy conservation. For the TIP4P/2005 model, a time step of 1.0 fs was used with the monomer geometry constraint by the shake algorithm with a tolerance of 10^{-6} . Although this tolerance has been used with the TIP4P/2005 model, it actually leads to a small drift in the conserved quantity of the Nosé-Hoover integrator in our simulation. The fastest drift rate was observed for the 4.5 nm box at 600 K. The drift rate, when normalized to per mole water, was $1.18 \times 10^{-4} \text{ kJ}/(\text{mol}\cdot\text{ps})$. This drift can be eliminated with a shake tolerance

of 10^{-7} . Since the tighter shake convergence only improves the conserved quantity and has no observable influence on any other properties investigated, all TIP4P/2005 simulations reported in this work still use a tolerance of 10^{-6} .

The standard formula for long-range van der Waals correction should not be used for interface simulations. Although long-range corrections for liquid-vapor interface have been derived, proper application of these corrections should be done self-consistently by including a correction term to atomic forces.¹⁴ Such a correction term is not implemented in Gromacs. In order to quantitatively access the error introduced by a simple van der Waals cutoff scheme, a series of van der Waals cutoff distances, r_{vdw} , was tested for each box ranging from 0.9 nm to either 2.0 nm or the maximum r_{vdw} allowed by each simulation box. The maximum r_{vdw} supported by the Gromacs program is half the simulation box size in the shortest dimension. Although Gromacs supports the use of a smooth function to switch the van der Waals energy and forces to zero, we used a simple cutoff scheme. This is appropriate since no sign of energy drift can be attributed to van der Waals truncation in any of our simulations. We anticipate our conclusions to be valid regardless whether a switching function is used.

One popular method for calculating the critical point is through a scaling law of the density difference between the liquid and the vapor phases. For example, the Wegner expansion has the form²⁶

$$\rho_l - \rho_g = A_0|\tau|^{\beta_c} + A_1|\tau|^{\beta_c+\Delta} + A_2|\tau|^{\beta_c+2\Delta} + \dots, \quad (1)$$

where ρ_l and ρ_g are the densities of the liquid and the vapor, respectively. τ is defined by

$$\tau = 1 - \frac{T}{T_c}. \quad (2)$$

A_0 , A_1 , A_2 , β_c and Δ are scaling parameters, with β_c being 0.325 and Δ being 0.5 according to the 3D Ising universality class.^{27,28}

Application of this procedure requires the measurement of ρ_l and ρ_g . This is frequently accomplished by fitting the density distribution across the interface using a profile function. Both the hyperbolic tangent function and the error function have been used to fit the density profile.^{29,30} While the use of the hyperbolic tangent function can be justified with the mean field theory,³¹ the error function has been argued to provide a better fit. This argument was made since the surface tension determined using the capillary wave method will only be consistent with a standard stress tensor based measurement if the surface was fit using the error function.³⁰ In this work, we will avoid the use of a profile function; we will explore the feasibility of an intuitive approach for measuring the density at the center of the liquid.

In our calculations, the z density was measured using bins of 0.1 nm in width. It will be inappropriate to simply pick the largest N bins to estimate the density of the liquid, since the density fluctuates even for a liquid due to the finite compressibility. Picking regions with the largest density will bias our sampling. In order to avoid such a bias, we use two separate widths: one for identifying the liquid region and the other for measuring the density. The first width is chosen so

FIG. 1. Illustration of the procedure of obtaining the liquid and gas densities from the z -density profile.

that a small part of the interface is included in a window of this width. In practice, a width of 3 nm is used for all slabs except for TIP4P/2005 at 600 K, where a 5 nm window is used. The liquid slab is identified by requiring the first region to have the maximum integrated z -density. The center of the slab will be defined as the center of this region. This region should include part of the interface on both sides. After the slab is located, we obtain ρ_l by measuring water density in a 1 nm wide region in the center of the first window. Our data suggest that it is a good assumption that there is at least 1 nm of liquid in the center of the slab. The use of two widths decouples the determination of the maximum density region and the actual measurement of density, thus avoiding possible biases. After the center of the liquid is identified, ρ_g is measured exactly half way ($L_z/2$) from the center of the liquid using a 1 nm window. The procedure of obtaining ρ_l and ρ_g is illustrated in Figure 1.

Since water evaporates constantly from the interface, the evaporation may lead to a small drift of the center of mass of the liquid slab. However, the center of mass velocity remains small since evaporation and deposition probabilities are identical for both surfaces. We extract an average liquid density profile once every 500 ps to avoid any possible complication due to center of mass drift. Longer intervals could also be used and the duration of the intervals has no discernible effect beyond statistical noise.

Once the liquid and gas densities were measured, the critical temperature (T_c) was determined by fitting a truncated Wegner expansion keeping only the first three terms on the right side of Eq. (1). The critical density (ρ_c) was determined by fitting the equation,³²

$$\rho_l + \rho_g = 2\rho_c + D_{1-\alpha}|\tau|^{1-\alpha} + D_1|\tau|. \quad (3)$$

We took $\alpha = 0.11$ following the previous work³² and $D_{1-\alpha}$ and D_1 are parameters to be fit. The pressure of the system can be measured using the pressure normal to the liquid-vapor interface. System pressure was fitted with the Antoine's equation,

$$\ln(P/P^o) = A + \frac{B}{T + C}, \quad (4)$$

where A , B , and C are fitting parameters and P^0 was chosen to be 1 bar. After T_c was determined from the Wegner expansion, the critical pressure P_c was determined using Antoine's equation. Similarly, the boiling temperature was calculated by solving the Antoine equation for temperatures that gave a pressure of 1 atm.

The surface tension (γ) was determined with the mechanical method using the formula¹¹

$$\gamma = \frac{L_Z}{2} \left(P_Z - \frac{P_X + P_Y}{2} \right), \quad (5)$$

where P_X , P_Y , and P_Z are the diagonal elements of the stress tensor and the prefactor $1/2$ is due to the presence of two liquid-vapor surfaces.

As a consistency check, the T_c was also determined by fitting the temperature dependent surface tension with the expression³³

$$\gamma = c_1 \left(1 - \frac{T}{T_c} \right)^\mu \left[1 - c_2 \left(1 - \frac{T}{T_c} \right) \right], \quad (6)$$

where c_1 and c_2 are fitting parameters and the exponent μ was originally proposed by Guggenheim²⁷ to be 11/9. This equation was later adopted by the International Association for Properties of Water and Steam (IAPWS) with a μ of 1.256 to interpolate the surface tension of water.³⁴ In this work, we will use the μ of 11/9 following Vega and de Miguel.³³ All error bars reported in this work indicate 95% confidence interval. Unless otherwise noted, the error bars were determined with the bootstrapping method, where the simulated data are resampled with replacement.³⁵

III. RESULTS AND DISCUSSIONS

Figure 2 reports the surface tension of TIP4P/2005 water as a function of van der Waals cutoff, r_{vdw} , calculated using the 4.5 nm box. The previous estimates for this model by Vega³³ and Alejandre¹⁴ are also shown. Clearly, γ depends on the choice of r_{vdw} . It is well established that, for a homogeneous system, the long-range correction to the pressure scales according to $(1/r_{vdw})^3$, if the tail of the potential scales as $1/r^6$. It is likely that γ also scales according to the power of $1/r_{vdw}$ for an infinite slab. Figure 3 shows γ as a function of $(1/r_{vdw})^2$. The

FIG. 2. Surface tension (γ) of TIP4P/2005 water as a function of r_{vdw} for various temperatures from 300 to 600 K for the 4.5 nm box. The previous literature results are also shown as references.

FIG. 3. γ as a function of $(1/r_{vdw})^2$ for the TIP4P/2005 model for various temperatures from 300 to 600 K for the 4.5 nm box. The solid lines are the linear regressions of the data points.

square of Pearson's correlation R^2 and the surface tension γ_∞ extrapolated to $r_{vdw} = \infty$ are reported in Table I. The reported error bars were calculated using linear regression. The correlations of all the fits are close to one suggesting a robust linear scaling. The extrapolated γ_∞ is close to previously published γ for the TIP4P/2005 model obtained with properly modeling of long-range van der Waals interactions.

Figure 4 shows the liquid density as a function of r_{vdw} . When r_{vdw} increases, the liquid density also increases, consistent with the need for a correction force in the direction normal to the slab. The density reaches the asymptotic value with a r_{vdw} of at least 1.5 nm. At different r_{vdw} , the thickness of the slab is different due to the dependence of liquid density on r_{vdw} . It is interesting to note that the simple $(1/r_{vdw})^2$ scaling of γ holds despite the different slab thicknesses.

Figure 4 also reports the gas density and the normal pressure as a function of r_{vdw} . As r_{vdw} increases, the vapor density and normal pressure decreases. A scaling relation between r_{vdw}

TABLE I. The surface tension extrapolated to $r_{vdw} = \infty$, γ_∞ , for the temperature range from 300 to 600 K for the TIP4P/2005 model. The measured surface tension shows a dependence on $(1/r_{vdw})^2$. The square of Pearson's correlation (R^2) is reported showing the linearity of the fit. Prior surface tension estimates are summarized for comparison. The error bars represent 95% confidence interval.

T (K)	γ_∞	R^2	Vega ¹⁰	Alejandre ¹⁴
300	68.20 ± 0.30	0.9953		68.4 ± 1.1
400	51.20 ± 0.44	0.9883		51.9 ± 1.3
420	47.41 ± 0.32	0.9931		
440	43.52 ± 0.22	0.9977		
450	41.29 ± 0.30	0.9951	41.8 ± 1.3	41.2 ± 1.1
460	38.99 ± 0.21	0.9979		
480	34.74 ± 0.35	0.9897		
500	30.22 ± 0.38	0.9865	30.9 ± 0.8	30.2 ± 0.9
520	25.85 ± 0.29	0.9943		
540	21.26 ± 0.07	0.9998		
550	19.20 ± 0.23	0.9968	19.2 ± 1.0	19.0 ± 1.0
560	16.97 ± 0.18	0.9970		
580	12.18 ± 0.18	0.9955		
600	8.84 ± 0.40	0.9793		8.1 ± 1.0

FIG. 4. Liquid density (ρ_l) as a function of r_{vdw} . The TIP4P/2005 model is used to perform the study at 400, 500, 600 K using the 4.5 nm box.

and densities and pressure is not investigated due to the larger statistical uncertainty in these values.

The dependence of surface tension on r_{vdw} has been reported in the past.^{36–38} The analysis of the previous data shows that similar linear dependence of γ to $(1/r_{vdw})^2$ can also be observed in methane³⁶ described with a united atom Lennard-Jones potential. The square of the Pearson's correlation coefficient R^2 for the methane simulation is 0.979. The extrapolated liquid methane surface tension of 13.54 mN/m agrees well

FIG. 5. Critical temperature (T_c) as a function of the van der Waals cutoff (r_{vdw}) for the TIP4P/2005 model. The error bars represent 95% confidence interval.

with that of 13.4 mN/m to 13.8 mN/m obtained with proper correction of long-range van der Waals interactions. Detailed information and the scaling figures are reported in the supplementary materials.³⁹ Figure 5 shows the T_c determined using the Wegner expansion for different choices of r_{vdw} . It is clear that the fitted T_c increases as the cutoff increases until around a 1.75 nm. The difference between r_{vdw} of 1.75 nm and 2.0 nm is smaller than the statistical noise in this work. The calculated T_c of 637 K agrees well with the estimate of 640 K reported by Vega. The dependence of T_c on r_{vdw} is not surprising. The surface tension disappears at the liquid vapor critical point. By underestimating γ , the T_c is also underestimated with smaller r_{vdw} .

Figure 6 reports the T_c of the TIP4P/2005 model as a function of the size of the simulation box (L) in the X and Y dimensions. T_c estimated using all the choices of r_{vdw} are reported to provide more data points. From this figure, it is clear that the box size has much smaller influence on T_c than r_{vdw} . The overall trend indicates that given the same r_{vdw} values, a larger box will lead to a lower T_c ; however, it is difficult to state with certainty considering the error bars. We argue that any box 3.5×3.5 nm² or larger will produce similar T_c when the same r_{vdw} is used. Even with proper treatment of long-range van der Waals interaction, we recommend not to use a box as small as

FIG. 6. Critical temperature (T_c) of TIP4P/2005 water as a function of the box size (L) for various choices of r_{vdw} . The error bars represent 95% confidence interval.

FIG. 7. Extrapolated surface tension (γ_∞) and surface tension with a r_{vdw} of 1.75 nm ($\gamma_{1.75}$) of TIP4P/2005 water as a function of temperature. The solid lines, which terminate at T_c , are fits to Eq. (6) with a μ value of 11/9. The results from Vega and de Miguel³³ and Alejandre and Chapela¹⁴ are also plotted as a comparison.

3.0 nm in the X-Y dimension for a direct interface simulation since the fitted T_c suggests a possible overestimation with this box size.

Figure 7 shows γ_∞ as a function of temperature; available results from Vega and Alejandre are also shown for comparison. The agreement of γ_∞ to previously reported surface tension of TIP4P/2005 water is excellent. It is worth emphasizing that the extrapolation procedure used to obtain γ_∞ does not rely on a density profile function.

Surface tension calculated with a r_{vdw} of 1.75 nm, $\gamma_{1.75}$, is also shown on Figure 7. As discussed previously, with a r_{vdw} of 1.75 nm, the surface tension is underestimated. However, we argue that $\gamma_{1.75}$ is an acceptable approximation to γ_∞ , underestimating γ_∞ by approximately 1.4–2.0 mN/m at all temperatures, which is about 3% around ambient condition. We note the underestimation of $\gamma_{1.75}$ is approximately constant across all temperatures, thus, the percentage error at higher temperature can be appreciable. For simulations of inhomogeneous systems, such as liquid slab, water droplet, or liquid under confinement, a minimum r_{vdw} of 1.75 nm is a probably good compromise for the TIP4P/2005 model especially at ambient or lower temperatures.

The lines in Figure 7 are fits to Eq. (6), which gives a T_c of 644.6 ± 1.8 K when γ_∞ is used. When $\gamma_{1.75}$ was fit to the equation, a T_c of 640.7 ± 2.3 K was obtained, agreeing fairly well with the γ_∞ estimate. When a r_{vdw} of 1.75 nm is used, the Wegner expansion method gives a T_c of 637.2 ± 1.8 K, which is in excellent agreement the estimate obtained with $\gamma_{1.75}$.

Figure 8 shows the γ of the BLYPSP-4F model as a function of $(1/r_{vdw})^2$ for r_{vdw} from 0.9 to 1.75 nm and extrapolated to infinite r_{vdw} . At 300 K, the γ_∞ for BLYPSP-4F is 68.64 ± 0.28 mN/m, which is marginally larger than that of TIP4P/2005 at 68.20 ± 0.30 mN/m but is smaller than the experimental value at 71.69 mN/m.³⁴

Figure 9 shows the γ_∞ and $\gamma_{1.75}$ as a function of temperature along with fits to the γ - T equation (Eq. (6)). The experimental curve is also shown for comparison. The $\gamma_{1.75}$

FIG. 8. γ of BLYPSP-4F water as a function of $(1/r_{vdw})^2$ for various temperatures from 300 to 600 K.

underestimates γ_∞ by 0.5 to 1.9 mN/m. With γ_∞ , the γ - T equation gives a T_c of 690.2 ± 2.7 K. When $\gamma_{1.75}$ is used to approximate the surface tension, a T_c of 686.2 ± 2.0 K was obtained. Similarly, the Wegner expansion fit to the density difference obtained with a r_{vdw} of 1.75 nm results in a T_c of 685.1 ± 3.8 K in good agreement with the estimated obtained with $\gamma_{1.75}$.

The BLYPSP-4F model shows a smaller temperature dependence of the surface tension when compared with experimental results. It underestimates γ at lower temperatures but overestimates it at higher temperature. This is consistent with BLYPSP-4F underestimates the stability of the gas and overestimates T_c .

We anticipate the T_c obtained with γ_∞ to be of higher quality. However, the difference of T_c obtained with $\gamma_{1.75}$ and γ_∞ is comparable to the error bar. The critical temperature, density, and pressure and the boiling temperature of both TIP4P/2005 and the BLYPSP-4F models obtained with a r_{vdw} of 1.75 nm are summarized in Table II. The TIP4P/2005 critical properties compare well with previous published results. The BLYPSP-4F model overestimates the critical temperature by about 38 K and produces a critical vapor pressure approximately 15% too

FIG. 9. BLYPSP-4F surface tension extrapolated to $(1/r_{vdw})^2 = 0$ (γ_∞) and obtained with a r_{vdw} of 1.75 nm ($\gamma_{1.75}$) as a function of temperature. The solid lines, which terminate at T_c , are fits to Eq. (6) with μ value of 11/9. The experimental values and the TIP4P/2005 values are also reported as a comparison.

TABLE II. The critical temperature (T_c), critical density (ρ_c), critical pressure (P_c), and the boiling temperature (T_b) of the BLYPSP-4F and TIP4P/2005 models calculated in the $4.0 \times 4.0 \times 10.0$ nm box with a r_{vdw} of 1.75 nm. Previous published results from the Vega group and the experimental values are reported for comparison. The error bars represent 95% confidence interval.

Model	BLYPSP-4F	TIP4P/2005	TIP4P/2005 [Vega] ¹⁰	H ₂ O ⁴⁴
T_c (K)	685.1 ± 3.9	639.7 ± 2.4	640	647.1
ρ_c (mol/L)	16.28 ± 0.25	15.96 ± 0.20	17.21	17.87
P_c (bar)	189.8 ± 48.7	147.7 ± 17.5	146	220.64
T_b (K)	398.7 ± 13.1	393.2 ± 7.8	401	373.15

low. Although the BLYPSP-4F P_c is significantly better than the TIP4P/2005 model, this could simply be a consequence of the overestimation of T_c . Overall, the BLYPSP-4F model underestimates the stability of the gas, leading to lower vapor pressure and higher critical temperature; this is consistent with the BLYPSP-4F model only being optimized for the liquid. The fixed charge model failed to properly capture true many-body effects required for a liquid potential to be transferable to the gas phase.

We argue that smallest r_{vdw} acceptable for simulation of the TIP4P/2005 model is 1.75 nm when long-range van der Waals correction is not used. Although long-range van der Waals correction is straightforward for homogeneous systems, for inhomogeneous systems, such as liquid slab, bubbles, and confined systems, proper treatment of long-range van der Waals can be challenging. We note the minimal acceptable r_{vdw} was argued based on the observation of acceptable γ and T_c . For the simulation of other properties, the minimal r_{vdw} may be different or may not exist. However, considering the surface tension of liquid being a key term in many thermodynamic equations involving interfaces. We anticipate the 1.75 nm r_{vdw} being a good starting point before more comprehensive study is performed.

Moreover, the minimal acceptable r_{vdw} should depend on the force field model being used. For the TIP4P/2005 model, both the $1/r^{12}$ and $1/r^6$ terms in the Lennard-Jones potential are truncated in our simulations. Since the contribution due to the $1/r^{12}$ term decays much faster than the $1/r^6$ term, it is commonly accepted that only long-range contributions from the $1/r^6$ term are influencing macroscopic properties. The BLYPSP-4F model used the Buckingham potential for non-bonded interactions. The exponential function in the Buckingham potential decays faster than $1/r^{12}$ at large separations. It is safe to assume that only the $1/r^6$ term is responsible for the observed r_{vdw} dependence for the BLYPSP-4F model too.

Since the TIP4P/2005 uses a C_6 parameter of 736.05 kcal·Å⁶/mol, which is on the larger side of all published water models, we anticipate a r_{vdw} of 1.75 nm will be an acceptable compromise for most water models. With the Lennard-Jones expression, the TIP4P/2005 model has a σ of 0.315 89 nm. A 1.75 nm is slightly larger than 5σ proposed for studying the equation of state for Lennard-Jones systems.⁴⁰ This is consistent with a previous study by Goujon *et al.*, where the asymptotic behavior can be observed with a r_{vdw} of 1.8 nm for Ar, which was modeled with a σ of 0.339 52 nm.³⁷ Thus, we

anticipate a r_{vdw} of 5σ might be sufficient also for other systems. However, for model potentials that do not use the standard Lennard-Jones term, the definition of σ might be ambiguous. Since σ scales to the 6th root of C_6 for the Lennard-Jones potential, we propose that a good compromise in computational cost and accuracy can be achieved if C_6/r_{vdw}^6 is less than 0.1 J/mol.

IV. SUMMARY AND CONCLUSION

In this study, we established a procedure to measure the critical point of water with molecular dynamics without assuming a functional form for the z-density profile. It is shown that proper treatment of long-range van der Waals interactions is important for surface tension and critical point calculations. Since many existing computational programs still have not implemented algorithms for proper modeling of long-range van der Waals interactions for inhomogeneous system, we showed that it is possible to estimate the surface tension of a liquid by a linear extrapolation procedure. Moreover, for most water models, a r_{vdw} of 1.75 nm seems to be reasonable compromise at least for temperatures at or below ambient condition. A 1.75 nm r_{vdw} underestimates the surface tension of water by no more than 2 mN/m and produces a good estimate of the liquid-vapor critical point. For other inhomogeneous systems, we recommend to use a r_{vdw} so that C_6/r_{vdw}^6 is no more than 0.1 J/mol.

By fitting only to electronic structure forces on liquid configurations sampled from 0 to 40 °C following the adaptive force matching procedure.^{22,41–43} The BLYPSP-4F model potential gives a surface tension comparable and marginally better than TIP4P/2005, underestimating the experimental value by 4.5% at 300 K. However, the γ of BLYPSP-4F water shows a weaker temperature dependence and becomes larger than the experimental value at higher temperature. The critical point of the BLYPSP-4F model is about 685 K at 190 bar using the Wegner expansion. Comparing to the experimental critical point at 647 K and 221 bar, the BLYPSP-4F model predicts a higher T_c and lower P_c . The larger region of stability for the liquid and the underestimation of the vapor pressure indicate a lower relative stability for the gas. This is consistent with the neglect of gas phase configurations in the development of BLYPSP-4F model. Due to a lack of a more rigorous treatment of polarization and by optimizing only for the liquid, BLYPSP-4F shows poor transferability for modeling water vapor.

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