Dependence of the liquid-vapor surface tension on the range of interaction: A test of the law of corresponding states

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The validity of the principle of corresponding states is investigated for the case of a potential with more than one intrinsic length scale. The planar surface tension of coexisting liquid and vapor phases of a fluid of Lennard–Jones atoms is studied as a function of the range of the potential using both Monte Carlo simulations and density functional theory (DFT). The interaction range is varied from $r_c^*=2.5$ to $r_c^*=6$ and the surface tension is determined for temperatures ranging from $T^*=0.7$ up to the critical temperature in each case. The simulation results are consistent with previous studies and are shown to obey the law of corresponding states even though the potential has two intrinsic length scales. It is further shown that the corresponding states principle can also be used to enhance the accuracy of some, but not all, DFT calculations of the surface tension. The results show that most of the cutoff dependence of the surface tension can be explained as a result of changes in the cutoff-dependent phase diagram and that corresponding states can be a useful tool for explaining differences between theory and simulation. © *2009 American Institute of Physics.*
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I. INTRODUCTION

One of the most fundamental properties of a fluid is the surface tension at the liquid-vapor interface. Aside from its obvious physical importance, the surface tension is also one of the most accessible quantities for comparison between liquid-state theory and computer simulation. It is clearly hopeless to make quantitative predications of, e.g., nucleation rates, based on a theory that does not properly describe the planar surface tension. For simple two-body potentials, with single energy and length scales, some inadequacies of theoretical calculations can be corrected by making use of the law of corresponding states. However, it is unclear that this is useful for more complicated potentials that involve multiple length and/or energy scales. An important class of such potentials is the truncated form of the simple pair potentials. Truncation is primarily a computational convenience employed to make computer simulation less costly but, because of the different truncations used, it has the negative effect of making it difficult to compare the results of different simulation studies if the range of truncation differs. On the positive side, however, it is extremely useful as a test of theoretical models to have such a diversity of results as a base line. In this paper, we show that for the important case of a truncated Lennard–Jones (LJ) potential, the law of corresponding states can still be used to correlate simulation studies at different values of truncation as well as in comparison to theoretical calculations.

It would seem that such a fundamental property would be an ideal candidate for study via computer simulation. However, the determination of the surface tension from simulation turns out to be frought with difficulties so that even today there is still a substantial amount of effort directed toward the development of more reliable algorithms and the refinement of the reported values even for the paradigmatic case of a simple fluid modeled with the LJ interaction.[1] Because the surface tension is very sensitive to the cutoff, an important part of the development of algorithms has focused on the calculation of the corrections needed to get the infinite-ranged limit from data obtained using a truncated potential (see, e.g., Refs. 1–7). This sensitivity is a nuisance when the goal is to get the infinite-range result, but, as noted above, it can be made useful. In particular, one of the important reasons to determine the surface tension from simulation is that it provides a base line against which theories of inhomogeneous liquids can be tested.[8,9] For this application, the sensitivity of the surface tension to the range of the potential can be used as a test of the generality of a theory which was probably motivated in the first place by its agreement with some existing simulation data. Furthermore, there has recently been a significant increase in interest in short-ranged potentials in their own right. This is due to the fact that certain complex fluids, in particular globular proteins, can, in a first approximation, be modeled as a simple fluid with a very short-ranged interaction.[10] It is therefore interesting to study the properties of fluids with these kinds of interactions and to test that existing theories work in this new domain of interest. For these reasons, we

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TABLE I. Surface tension determined from simulation as a function of temperature for different cutoffs.

Temperature	$r_c^*=2.5$[a]	$r_c^*=3$[a]	$r_c^*=4$[a]	$r_c^*=4$[b]	$r_c^*=6$[b]
0.70	0.584(27)	0.770(21)	0.964(46)	0.914(30)	1.070(13)
0.72	0.561(26)	0.726(25)	0.899(22)		1.034(7)
0.75	0.511(20)	0.698(28)	0.825(31)		0.959(8)
0.80	0.421(19)	0.608(16)	0.748(25)	0.736(32)	0.847(13)
0.85	0.315(13)	0.480(12)	0.633(24)		
0.90	0.228(13)	0.384(15)	0.542(16)	0.484(33)	0.638(8)
0.95	0.181(11)	0.314(12)	0.443(22)		
1.0	0.106(7)	0.234(8)	0.348(11)	0.313(59)	0.438(15)
1.05		0.156(11)	0.258(23)		
1.1		0.111(16)	0.200(12)		0.261(13)
1.15		0.074(10)	0.108(14)		
1.2		0.054(6)	0.067(15)	0.063(19)	0.105(5)

[a]Using approximately 2000 atoms.
[b]Using approximately 8000 atoms.

present in this paper a systematic study of the dependence of the surface tension of a LJ fluid as a function of the range of the potential.

The motivation of the present work is therefore three-fold. First is the modest goal of making available a systematic simulation study of the dependence of surface tension on the range of a truncated LJ potential for use as a base line for the development of theoretical methods. The second is to show empirically that even a potential with two length scales can still be well described by the law of corresponding states. This is intended to aid in the common problem of making comparisons of data obtained from simulations with different truncations. The final goal is to apply the same scalings to theoretical models, specifically density functional theory (DFT) calculations, and to show that in some, but not all, cases, the theoretical calculations also obey a law of corresponding states. This is a useful observation as it allows one to improve the quantitative accuracy of theoretical calculations that are often based on intrinsically inaccurate equations of state. These demonstrations, which are all of an empirical nature, are made for the case of surface tension but it is hoped that the concepts may prove more generally applicable.

In this paper, we describe the results of Monte Carlo (MC) simulations of a LJ fluid with the potential truncated at several different points. We have chosen to truncate and shift the LJ potential, $v_{LJ}(r)$, so that the potential used in this work is $v(r;r_c)=v_{LJ}(r)-v_{LJ}(r_c)$ for $r<r_c$ and $v(r)=0$ for $r\geq r_c$. The choice to shift the potential is made with a view to applications where such a shift is often made, but the study could equally well have been performed with an unshifted potential. We do not shift the force, i.e., we do *not* use $\tilde{v}(r;r_c)=v_{LJ}(r)-v_{LJ}(r_c)-(r-r_c)v'_{LJ}(r_c)$ with $v'_{LJ}(r)=dv_{LJ}(r)/dr$ inside the cutoff, as is usually done in molecular dynamics simulations to avoid impulsive forces: our potential is truncated and shifted but the force is not shifted. This choice was made in order to allow for comparison with previous MC studies.

In the simulations a slab of liquid is bounded on both sides by vapor. The surface tension is determined using the method of Bennett[11,12] as there seems to be some evidence

that this method is more robust than other commonly used techniques.[13] It is often the case that the quantity of interest is the surface tension for the infinite-ranged potential. Since simulations almost always make use of truncated potentials, various techniques have been developed to approximate the so-called long-range corrections, i.e., the difference between quantities calculated with the truncated potential and the infinite-ranged quantities.[4] We do not include any such corrections here since our goal is actually to study the truncated potentials. Thus, each value of the cutoff defines a different potential with its own coexistence curve and thermodynamics.

In Sec. II, we present the simulation techniques used in our work. Section III contains a discussion of our results including a comparison to previous work. Since one of the motivations for this work is to provide a base line for testing theories of the liquid state, we illustrate this by comparing our results to DFT calculations and by testing the law of corresponding states. We give our conclusions in the last section.

II. SIMULATION METHODS

Simulations are performed with a standard metropolis MC algorithm (MC-*NVT*) for a system of N particles of mass m at temperature T in a volume $V=L_xL_yL_z$, where L_x, L_y, and L_z are the dimensions of the rectangular simulation cell. Periodic boundary conditions are used in all directions. Particles interact via the LJ potential,

$$v_{LJ}(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right), \tag{1}$$

which is truncated and shifted so that the potential simulated is

$$v(r) = \begin{cases} v_{LJ}(r) - v_{LJ}(r_c), & r < r_c \\ 0, & r \geq r_c, \end{cases} \tag{2}$$

where r_c is the cutoff radius. The minimum dimension of the box must be larger than twice the cutoff to avoid self-interactions via the periodic boundaries so two different system sizes were used: a system of 2000 atoms for cutoffs
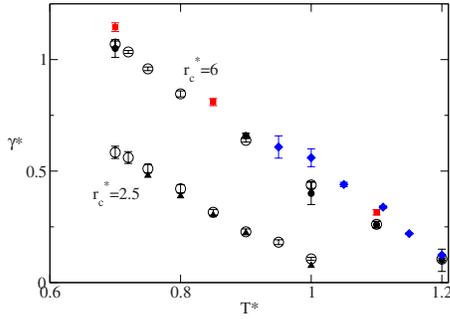
FIG. 1. (Color online) The surface tension as a function of temperature for two different cutoffs. The open circles are our data, the filled circles are from Duque *et al.* (Ref. 16), the squares are from Mecke *et al.* (Ref. 1), the diamonds are from Potoff and Panagiotopoulos (Ref. 17), and the triangles are from Ref. 15. Note that the Mecke and Potoff data both include long-ranged corrections.

FIG. 3. (Color online) The fit of the difference in liquid and vapor densities, as determined from simulation (symbols), to the renormalization group functional form (lines). The data are shown as circles ($R_c=6.0$), open squares ($R_c=4.0$, larger cell), filled squares ($R_c=4.0$, smaller cell), diamonds ($R_c=3.0$), and triangles ($R_c=2.5$).

$r_c/\sigma \leq 4.0$ and 8000 atoms for cutoffs $r_c/\sigma \geq 4.0$. The use of both systems for $r_c=4.0\sigma$ allows for a check of finite-size effects. Each simulation starts from a rectangular box ($L_x=L_y=L$, $L_z=4L$ for the smaller systems or $L_x=L_y=2L$ for the larger systems) filled with a dense disordered arrangement of particles ($\rho^* \equiv \rho\sigma^3 = 0.8$) surrounded along the z-direction by two similar rectangular boxes containing particles in a low density state ($\rho^* \sim 0.01$) thus giving an overall length of $L_z=12L$. The total simulation box has sides of length $L_x=L_y=9.15\sigma$ (smaller) or twice this for the larger cells and $L_z=109.63\sigma$. The liquid film located in the middle of the box has a thickness $\Delta z \simeq 27\sigma$ so that the two interfaces do not influence each other. The system is first equilibrated during 5×10^5 MC cycles (one cycle=N updates) after which the positions of the particles are saved every 20 cycles during 5×10^5 cycles. This ensemble of 2.5×10^4 configurations is used to compute the density profile and the surface tension by Bennett's method.

Although several methods are available for the computation of the surface tension, Bennett's approach has been chosen because of its accuracy.[13] In Bennett's method the calculation of the surface tension follows from the definition
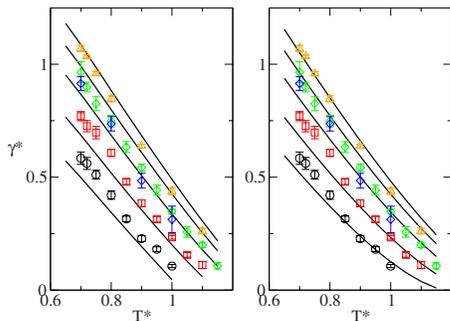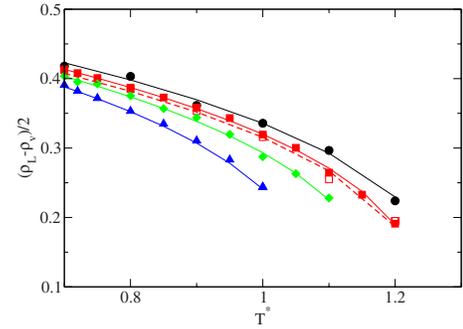

FIG. 2. (Color online) Comparison of our simulation data to a DFT model (Ref. 9). The panel on the left shows the results of the theory using an empirical equation of state while the results on the right were obtained using thermodynamic perturbation theory. The lines are ordered from the smallest cutoff (lowest lines) to the largest cutoff (highest lines) and were calculated for $r_c^*=2.5,3,4,6,\infty$. The data are represented by circles (2.5), squares (3), diamonds (4), filled diamonds (4—larger system), and triangles (6).

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{N,V,T}, \tag{3}$$

where F is the free energy and A is the area of the liquid-vapor interface. In its implementation the method requires that one performs two simulations: one for system 0 of interface area A_0, and another for system 1 of interface area $A_1=A_0+\Delta A$. In this work $\Delta A/A=5\times10^{-4}$. The free energy difference ΔF between the two systems is evaluated by the method of acceptation ratio which starts with the computation of $\Delta E_{01}=E_{01}-E_{00}$, which is the difference between E_{00}, the energy of a configuration of system 0, and E_{01}, the energy of a new configuration obtained from the previous one by rescaling the positions of the particles:[12,14] $x'=x(A_1/A_0)^{1/2}$, $y'=y(A_1/A_0)^{1/2}$, and $z'=z(A_0/A_1)$. Similarly one computes $\Delta E_{10}=E_{10}-E_{11}$ obtained from a configuration of system 1 following an inverse rescaling of the positions. ΔF is obtained by requiring that

$$\sum_{n_0} f(\Delta E_{01} - \Delta F) = \sum_{n_1} f(\Delta E_{10} + \Delta F), \tag{4}$$

where Σ_{n_0} (Σ_{n_1}) is a sum over the configurations of systems 0 (1), and $f(x)=(1+\exp(\beta x))^{-1}$. Then, taking into account the fact that the system contains two flat interfaces, the value of the surface tension is given by $\gamma=\Delta F/(2\Delta A)$.

III. RESULTS

A. Comparison to previous results

Our results for the surface tension as a function of the cutoff are given in Table I. Note that all quantities are reported in reduced units so that the reduced temperature is $T^*=k_BT/\epsilon$, the reduced cutoffs are $r_c^*=r_c/\sigma$, and the reduced surface tension is $\gamma^*=\gamma\sigma^2/\epsilon$. In Fig. 1 we show our results for cutoffs of $r_c^*=2.5$ and 6.0 compared to the MC data of Haye and Bruin[15] for the shorter cutoff and to the MD data of Duque *et al.*[16] (who appeared to shift the forces) and Potoff and Panggiotopoules[17] and Mecke *et al.*[1] The latter two are shown even though they include long-ranged corrections. Our data are seen to be very consistent with the MC data obtained without long-ranged corrections and to lie slightly below the corrected data, as expected.

TABLE II. The critical points for the LJ potential truncated at different values. The theoretical values were determined using the empirical JZG equation of state (Ref. 18) and the first order BH perturbation theory.

R_c^*	MC		Theory-JZG		Theory-BH	
	T_c^*	ρ_c^*	T_c^*	ρ_c^*	T_c^*	ρ_c^*
2.5	1.10(1)[a]	0.31(9)[a]	1.03	0.233	1.18	0.301
3.0	1.18(1)[a]	0.31(7)[a]	1.16	0.317	1.28	0.300
4.0	1.26(1)[a]	0.31(5)[a]	1.24	0.317	1.35	0.298
4.0	1.25(2)[b]	0.30(6)[b]	⋯	⋯	⋯	⋯
6.0	1.30(2)[b]	0.32(9)[b]	1.28	0.317	1.39	0.297
∞	1.31[c]	0.317[c]	1.30	0.317	1.41	0.297

[a]Using approximately 2000 atoms.
[b]Using approximately 8000 atoms.
[c]From Ref. 27.

B. Comparison to DFT

In Fig. 2, we compare our results to the predictions of a recently proposed DFT model.[9] The DFT requires knowledge of the bulk equation of state and the figure shows results using two different inputs: the 33-parameter equation of state of Johnson *et al.*[18] and first order Barker–Henderson (BH) thermodynamic perturbation theory.[19,20] Both versions of the theory are in good qualitative agreement with the data, showing the decrease in surface tension as the range of the potential decreases. It might be thought that the use of an empirical equation of state should automatically give superior results to an approximation, such as thermodynamic perturbation theory, but this is not necessarily the case since the equation of state is fitted to data for the infinite-ranged potential. The finite cutoff is accounted for using simple mean-field corrections[12,18] and these become increasing inaccurate as the cutoff becomes shorter and, for fixed cutoff, as the fluid density becomes higher. The latter condition means, in the present context, increasing inaccuracy as the temperature decreases. Both of these trends are confirmed by the figure. The decrease in accuracy with decreasing cutoff can be seen in the fact that the critical point (corresponding to the temperature at which the surface tension extrapolates to zero) is less accurately estimated for the smaller cutoffs than for the larger cutoffs.

The perturbation theory, on the other hand, takes the cutoff into account more accurately and consistently so that no strong change in accuracy is expected as the cutoff decreases. However, the theory itself is expected to be less accurate for higher densities so again a drop in accuracy with decreasing temperature would be expected and that is indeed seen in the figure. Furthermore, perturbation theory is in general going to be inaccurate near the critical point as it does not take into account renormalization effects which tend to lower the critical point. These effects are less pronounced for shorter-ranged potentials and indeed the perturbation theory seems more consistent with shorter-ranged potential.

C. Corresponding states

The principle of corresponding states is a generalization of the results of the van der Waals equation of state.[21] The idea is that the properties of simple liquids should be universal functions of the state variables, density, and temperature, scaled to the critical point. In this section, we test this hypothesis by applying it to the surface tension in the case of a potential with two intrinsic length scales. The first step is therefore to determine the critical temperatures and densities of the various truncated potentials. Since the theoretical calculations require an equation of state as input, the critical points are easily determined. To determine them from the simulations, we took five independent averages over 5000 configurations and fitted the density profiles in each case to a hyperbolic tangent and then from these extract the coexisting vapor and liquid densities at each temperature. A study of the size dependence of the critical properties of small systems led Wilding[22] to conclude that for temperatures more than about 5% lower than the critical temperature, the coexistence densities obtained from simulation are well described by the nonclassical relation $\rho_\pm = \rho_c + A(T_c - T) \pm B(T_c - T)^{0.325}$, where the liquid (vapor) corresponds to the plus (minus) sign and where ρ_c is the critical density. The nonclassical exponent is the best estimate from renormalization group theory.[23,24] Based on such results, which imply that the mean-field behavior expected to be found for small system is
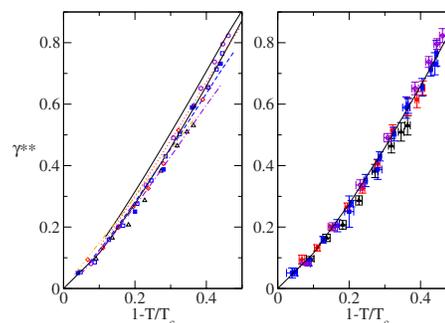

FIG. 4. (Color online) The scaled surface tension, $\gamma^{**} \equiv \gamma / T_c \sigma^{2/3}$, as a function of distance from the critical temperature. The left panel includes the theoretical curves based on the empirical JZG equation of state, shown as full line ($R_c^*=\infty$), dotted line ($R_c^*=6$), dashed line ($R_c^*=4$), dashed-dotted line ($R_c^*=3$), and dashed-dotted-dotted line ($R_c^*=2.5$) and the simulation data, shown as circles ($R_c^*=6$), filled squares. ($R_c^*=4,2000$ atoms), open squares ($R_c^*=4$, 8000 atoms), diamonds ($R_c^*=3$), and triangles ($R_c^*=2.5$). The right hand panel shows only the data from simulation as well as the estimated error. In both cases, the thin line is a best fit to all of the data (theory and simulation) of the form $\gamma^{**}=\gamma_0^{**}(1-T/T_c)^{1.26}$ with $\gamma_0^{**}=2.09$.
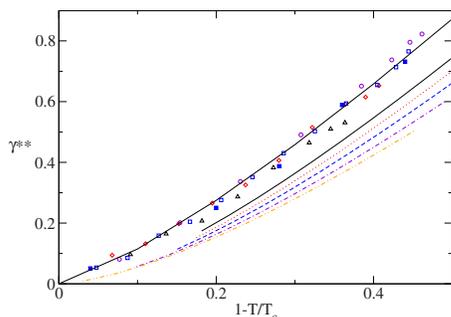
FIG. 5. (Color online) The same as Fig. 4 (left panel) but using the surface tension calculated with the perturbative equation of state.

confined to temperature near the critical temperature, several authors[25,26] used this expression to determine critical properties from simulations and we have followed the same procedure. Thus, the critical temperatures were from $\frac{1}{2}(\rho_l-\rho_v)=2B(T_c-T)^{0.325}$ after which the critical density was determined using the law of the rectilinear diameter, $\frac{1}{2}(\rho_l+\rho_v)=\rho_c+A(T_c-T)$. The results of these fits are illustrated in Fig. 3 and summarized in Table II. The largest errors in this procedure are in the determination of the critical density. Noting that the critical density is virtually the same in all of the calculations, except the case of Johnson *et al.* and a cutoff of 2.5σ, which is known to be anomolous,[18] we can minimize errors by not using the critical density in the corresponding states scaling.

Figure 4 shows the surface tensions, as determined from simulation and theory using the Johnson, Zollweg, and Gubbins (JZG) equation of state, scaled to the critical temperature as a function of distance from the critical temperature. Despite wide range of cutoffs and the mixture of data from simulations and theory, it is nevertheless seen that the data do in fact obey the law of corresponding states to a good approximation. However, the same scaling of the theoretical calculations using the equation of state from thermodynamic perturbation theory, shown in Fig. 5, does not give a single curve. It would appear that care must therefore be taken in the application of the corresponding state mapping to particular DFT models.

IV. CONCLUSIONS

We have presented our determination of the liquid-vapor surface tension in a LJ fluid as a function of the range of the potential. The data give a systematic picture of the variation of surface tension with the cutoff and are in agreement with previous studies. It is hoped that this can serve as a useful benchmark for the development of theories of inhomogeneous liquids. Indeed, the results were compared here to calculations made using a recently developed DFT and the

strengths and weaknesses of the theory are evident; while it gives a good semiquantitative estimate of the surface tension for all cutoffs, errors on the order of 10% are present indicating that further improvement is possible.

We have also tested the law of corresponding states by showing our results from both simulation and theory scaled to the critical density and temperature. For the simulation data and the theoretical calculations based on an empirical equation of state, the law of corresponding states appears to be obeyed. Høwever, the calculations based on the equation of state from first order perturbation theory do not appear to scale well at all. These results indicate that care must be exercised before assuming that the law of corresponding states applies to particular theoretical models.

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