

Long Range Corrections in Inhomogeneous Simulations

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An improved method for the treatment of the long range corrections in molecular simulations of inhomogeneous systems with planar interfaces is presented. To evaluate the quality of this approach, Monte Carlo simulations of the Lennard–Jones fluid are performed in the temperature range $T^* \in \langle 0.7, 1.25 \rangle$. The attention is focused especially on the values of the surface tension, which represents a property significantly sensitive to the truncation of the intermolecular interactions. When the presented approach is employed, the values of coexisting densities and surface tensions obtained with the cutoff distance $R_c = 2.5\sigma$ are within experimental errors identical with those obtained for cutoff distance $R_c = 5.5\sigma$.

1. Introduction

Canonical simulations of systems with a planar interface represent a simple method to study vapor–liquid phase equilibria (VLE).¹ Compared with the more sophisticated techniques which enable one to study the phase equilibria without having the coexisting phases in physical contact (e.g., thermodynamic integration² and Gibbs ensemble Monte Carlo³), this method can directly offer important information about the interface between the coexisting phases. On the other hand, since the indirect techniques avoid the formation of a vapor–liquid interface, they are more effective to determine the bulk properties of coexisting phases.

The direct canonical simulations of two coexisting phases in one common box were used for the first time more than thirty years ago.^{4,5} They represent standard isothermal–isochoric Monte Carlo (MC) or molecular dynamics (MD) simulations in a box with one elongated edge and a decreased total number density of the system. Under the critical temperature, the system naturally splits into two phases of different densities which correspond to the vapor and liquid phases. The interfaces between these phases tend to have minimal surface area, and that is why they are perpendicular to the elongated edge of the box.

During molecular simulations, a truncation of intermolecular interactions is applied. It is well-known that this truncation influences different properties of liquids to various extents. When for a Lennard–Jones (LJ) fluid at reduced temperature $T^* = 0.92$ the truncation of the pair potential at distance $R_c = 2.5\sigma$ is used, then a difference less than 1% in the excess internal energy can be observed (compared to the full LJ potential). However, the density of the coexisting liquid phase at this temperature is affected approximately by 5%; the vapor pressure is affected by 20%, and in the case of the surface tension, this difference is over 50%.⁶

There is a standard simple way to include the corrections due to the truncation of dispersion interactions in simulations of homogeneous systems.¹ This method is based on assumptions that the radial distribution function equals unity beyond the cutoff radius and that the density of all components is not

dependent on the position. Correction terms to particular thermodynamic quantities are evaluated according to simple formulas and added after the simulation run. In the case of direct canonical simulations of phase equilibria, the system is not homogeneous (the density depends on the position) and this simple “bulk” approach does not reflect that the long range corrections to the energy of a molecule in the liquid phase are different from those for a molecule in the vapor phase (or, in other words, the long range contribution to the force acting on a molecule in the interfacial region cannot be neglected). This shows the effect that the densities of the coexisting phases (and other equilibrium properties) are different from those obtained using any indirect simulation technique within which the corrections due to the truncation of intermolecular interactions are involved.

For long ranging Coulombic interactions, the lattice sum method (Ewald summation) is quite well elaborated. This method can be simply modified for inhomogeneous systems.^{7,8} In the case of water (and aqueous solutions containing ions), the electrostatic forces are several orders higher than the dispersion forces and the behavior of such systems is not considerably affected by improper treatment or neglect of the long range contributions due to truncated dispersion interactions.⁹ For most other polar liquids, the dispersion interactions are about equal in magnitude to the electrostatic interactions and the treatment of long range corrections plays an important role. In the case of nonpolar fluids, the inclusion of long range corrections becomes crucial, as was well demonstrated by Trokhymchuk and Alejandre in their article dealing with the problems with truncation of intermolecular interactions in inhomogeneous simulations of the Lennard–Jones fluid;⁶ in this case, different forms of truncation caused considerably different phase behavior.

Several approaches were suggested to minimize or eliminate the influence of truncation in inhomogeneous simulations in order to enable adequate determination of interfacial properties. One of the most important of such properties is the surface tension. It is a quantity which has a clear meaning; it is simply accessible experimentally, and as was mentioned above, it is very sensitive to the truncation of intermolecular interactions. Potoff et al.¹⁰ used histogram-reweighting Monte Carlo simula-

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tions and determined the surface tension values of LJ fluid up to the critical point. This method is a bulk (homogeneous) simulation, and thus, their data should represent the values corresponding to the full LJ potential.

Holcomb et al.¹¹ and later Blokhuis et al.¹² employed a formula for the tail corrections to the surface tension values obtained in inhomogeneous simulations for different cutoff distances, and from these corrected values, they extrapolated the value corresponding to the full Lennard–Jones potential. At reduced temperature $T^* = 0.92$, they concluded that it is necessary to have at least $R_c = 5\sigma$ to obtain values of the surface tension not affected by truncation; for smaller values of the cutoff distance, this method does not work because the densities of coexisting phases and consequently the values of “noncorrected” surface tension are strongly dependent on R_c .

It seems to be necessary to include the long range corrections (lrc’s) already into the simulation algorithm in order to obtain density profiles which correspond to the nontruncated potential model. Guo et al.^{13,14} suggested an approach based on the assumption of local dependence of thermodynamic properties. Mecke et al.¹⁵ have included the long range corrections within MD simulation by adding an additive force contribution in the direction perpendicular to the interface. Especially the approach of Mecke et al. offers better results in comparison with simulations without any lrc’s. Nevertheless, for reduced temperatures higher than 1.0, the obtained density profiles and surface tension values show a significant dependency on the cutoff radius for $R_c < 4.4\sigma$ (Guo et al.) or $R_c < 5.0\sigma$ (Mecke et al.), respectively.

López-Lemus et al.^{16,17} used the lattice sum technique for the dispersion part of the Lennard–Jones potential in inhomogeneous simulations to study the thermodynamic and transport properties of the Lennard–Jones fluid. As this technique is an analogy of the Ewald method for potential with an r^{-6} dependence, it increases the computational time considerably. Despite this, the method seems to be more efficient than simulations with larger cutoff distances since smaller system sizes and numbers of particles are necessary.

We have improved the approach of Mecke et al.¹⁵ for involving long range corrections into the simulation algorithm. Moreover, we have derived expressions for lrc’s to the components of the virial tensor in inhomogeneous simulations with a planar interface. Using this approach, the values of the surface tension and of the coexisting densities are within identical experimental errors for cutoff radii between 2.5σ and 5.5σ . In the next section, we briefly describe the main features of this approach and bring in the derived formulas. After that, we present the results of our simulations for Lennard–Jones fluid accompanied by a short discussion.

2. Theory

Within this study, we are concerned with systems of Lennard–Jones (LJ) particles. These are particles interacting through the well-known LJ potential:

$$u_{ij} = u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where σ and ϵ are potential parameters and r is the distance between the centers of particles i and j . The reduced quantities are introduced in the standard way: the temperature, $T^* = k_b T / \epsilon$; the density, $\rho^* = \rho \sigma^3$; and the surface tension, $\gamma^* = \gamma \sigma^2 / \epsilon$. In the presented formulas, we will use the full notation in order to preclude any confusion.

The total potential energy of a system of N particles interacting via pairwise additive interactions can be written as

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N u_{ij} = \frac{1}{2} \sum_{i=1}^N U_i \quad (2)$$

where u_{ij} is the interaction energy between particles i and j and $U_i = \sum_{j=1}^N u_{ij}$ can be seen as the potential energy of molecule i . Because of the truncation of intermolecular interactions, this energy has to be split into two parts; the first one is the directly counted interactions with molecules inside the cutoff sphere around the i th molecule, and the second one represents the long range corrections (lrc’s):

$$U_i = \sum_{j \in R_c(i)} u_{ij} + U_i^{\text{lrc}} \quad (3)$$

In the case of systems with a planar interface parallel to the xy -plane, the simulation box can be divided into strips parallel to this interface. The potential energy of all molecules in one strip then has on average an identical value which depends on the z -coordinate only. The long range term is also a function of the z -position of the molecule only, and it can be expressed as a sum of contributions from all the strips

$$U_i^{\text{lrc}}(z_i) = \sum_k^{n_k} \Delta u_{i,k}^{\text{lrc}}(z_i, z_k) \quad (4)$$

where $\Delta u_{i,k}^{\text{lrc}}(z_i, z_k)$ represents the interaction energy between particle i and those of particles from strip k which are outside the cutoff sphere; the total number of strips is usually on the order of several hundreds. Assuming uniform particle–particle distribution beyond the cutoff distance

$$g(z_i, z_j, r_{ij}) = 1 \quad \text{for } r_{ij} \geq R_c \quad (5)$$

the particular contributions to $U_i^{\text{lrc}}(z_i)$ due to interaction with k th slab can be calculated in following way:

$$\Delta u_{i,k}^{\text{lrc}}(z_i, z_k) = \int_V u(r) \rho(z_k) dV \quad (6)$$

where $\rho(z_k)$ is the number density in the strip located at position z_k and the integration is performed over the part of volume of the strip for which $r > R_c$. For homogeneous systems, $\rho(z) = \rho$, we can recover the standard expression for long range corrections to the energy of molecule i used in bulk simulations by evaluating following integral:

$$U_i = \rho \int_{R_c}^{\infty} 4\pi r^2 u(r) dr \quad (7)$$

The two cases which can arise in inhomogeneous systems with a planar interface are schematically shown in Figure 1. In the upper part, a case when a fraction of particles from the k th strip lies inside the cutoff sphere for molecule i ; the intersection of this strip and the cutoff sphere must be excluded from integral 6. In the second case, the integration is performed over the whole volume of the strip. With the help of quantities θ , R , r , and $\xi = |z_k - z_i|$, we can express the contribution $\Delta u_{i,k}^{\text{lrc}}(z_i, z_k)$ as

$$\Delta u_{i,k}^{\text{lrc}}(z_i, z_k) = \int_{R_0}^{\infty} u(r) \rho(z_k) 2\pi R dR \Delta z = - \int_{\cos \theta_0}^{\cos(\pi/2)} u(r) \rho(z_k) 2\pi \xi^2 \frac{d(\cos \theta)}{\cos^3 \theta} \Delta z \quad (8)$$

where the symbol $j \in R_c(i)$ means again all particles inside the cutoff sphere of molecule i . The long range correction term to the virial tensor component due to forces acting on particle i can be again expressed as

$$\Pi_{\alpha\alpha}^{\text{lrc}}(z_i) = \sum_k^{n_k} \rho(z_k) \pi_{\alpha\alpha}(|z_k - z_i|) \Delta z \quad (20)$$

where the functions $\pi_{xx}(\xi)$, $\pi_{yy}(\xi)$, and $\pi_{zz}(\xi)$ are determined likewise as in the case of corrections to the internal energy. We should only note that in order to obtain the formulas for functions $\pi_{xx}(\xi)$ and $\pi_{yy}(\xi)$ the integration with respect to the azimuthal angle ϕ does not give trivial contribution 2π , but it must be explicitly performed. That is why the resulting formulas are of a slightly more complicated form:

$$\pi_{xx}(\xi) = \pi_{yy}(\xi) = \begin{cases} 2\pi\epsilon \left[\frac{6R_c^2 - 5\xi^2}{5} \left(\frac{\sigma}{R_c}\right)^{12} - \frac{3R_c^2 - 2\xi^2}{2} \left(\frac{\sigma}{R_c}\right)^6 \right] & \xi \leq R_c \\ 2\pi\epsilon \left[\frac{\xi^2}{5} \left(\frac{\sigma}{\xi}\right)^{12} - \frac{\xi^2}{2} \left(\frac{\sigma}{\xi}\right)^6 \right] & \xi > R_c \end{cases} \quad (21)$$

and

$$\pi_{zz}(\xi) = \begin{cases} 4\pi\epsilon\xi^2 \left[\left(\frac{\sigma}{R_c}\right)^{12} - \left(\frac{\sigma}{R_c}\right)^6 \right] & \xi \leq R_c \\ 4\pi\epsilon\xi^2 \left[\left(\frac{\sigma}{\xi}\right)^{12} - \left(\frac{\sigma}{\xi}\right)^6 \right] & \xi > R_c \end{cases} \quad (22)$$

From these relations, the formula for the tail correction to the surface tension can be recovered by inserting for π_{xx} and π_{zz} into

$$\Delta\gamma^{\text{lrc}} = \int \int \rho(z) \rho(z') (\pi_{zz}(|z - z'|) - \pi_{xx}(|z - z'|)) dz dz' \quad (23)$$

and performing the integration with any suitable approximation of the density profile $\rho(z)$. To our thinking, the resulting formula will be uselessly complicated so we followed a more straightforward way and determined the lrc's directly to the three components of the virial tensor according to eq 20; at any time they were evaluated and stored, the values included long range corrections.

3. Results

To test the above-described approach, we performed a set of MC simulations for particles interacting via the Lennard–Jones potential in the range of reduced temperatures $T^* = 0.7$ – 1.25 . For temperatures up to $T^* = 1.10$, the system contained 2048 Lennard–Jones molecules in box; at higher temperatures, $T^* = 1.20$ and $T^* = 1.25$, we had to increase the number of particles to 2500 in order to have sufficiently thick layers of both phases. The dimensions of the simulation box were $11\sigma \times 11\sigma \times 66\sigma$. Orea et. al.¹⁸ have observed strong oscillations of the surface tension values with dependence on the lateral dimensions of the simulation box. This effect becomes important at low temperatures and can reach more than 10% of the surface tension value even for boxes with the x - and y -dimensions equal to 8σ . Our values $B_x = B_y = 11\sigma$ should be sufficiently large (at least for $T^* > 0.85$).

The simulation procedure was started from a random configuration in a parallelepiped box with dimensions $11\sigma \times 11\sigma \times 22\sigma$. After an initial isothermal–isobaric equilibration of

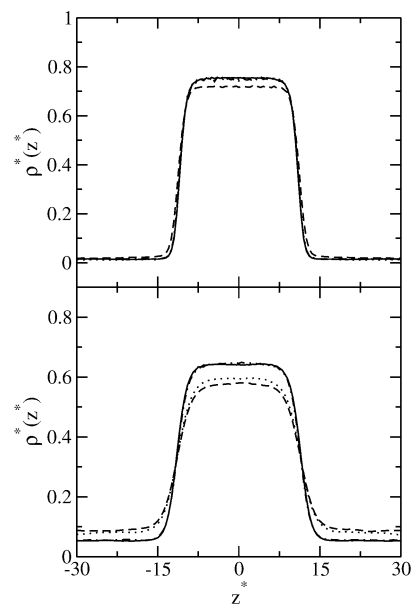


Figure 2. Density profiles for LJ fluid obtained with different treatments of the long range corrections for $T^* = 0.9$ (upper part) and $T^* = 1.1$ (lower part): (solid line) our approach; (dotted line) Mecke et al.;¹⁵ (dashed line) Guo et al.¹³ (all with $R_c = 2.5\sigma$); (dashed–dotted line) our approach with $R_c = 5.5\sigma$.

10 000 MC cycles (moves per molecule) accompanied by 10^4 volume changes performed in the z -direction only, free space was added to obtain the final size of the box. After a run of 100 000 cycles to stabilize the interface, a production run of 250 000 MC cycles was performed. The maximum displacement varied between 0.1σ and 0.4σ to get the acceptance ratio 25–50%. The simulation box was divided into 660 strips of 0.1σ thickness into which the density profiles were accumulated after 10 MC cycles were finished. With the same frequency, the components of the virial tensor and their long range corrections were evaluated.

The long range contributions to the energy were calculated at every MC step (an attempt to move one molecule) according to eq 11. The evaluation of the sum of 660 elements in every MC step caused an approximately 20% increase of the computational time when the cutoff distance was equal to 2.5σ ($T^* = 1.0$, 2048 particles); for $R_c = 5.5\sigma$, this accrue was about 5%. We should note that the absolute times consumed for the evaluation of the lrc's are in both cases the same; the difference is caused by the considerably large time necessary for the simulation with $R_c = 5.5\sigma$.

The density profiles with different treatments of lrc's at $T^* = 0.9$ and $T^* = 1.1$ are compared in Figure 2. The solid curve is our new approach, the dashed line was obtained by the method of Guo et al.,¹³ and the dotted line was obtained by MC simulation with the treatment of lrc's analogous to that used in the MD study by Mecke et al.¹⁵ All curves show density profiles obtained with $R_c = 2.5\sigma$. The dashed–dotted line is a density profile obtained with $R_c = 5.5\sigma$ with the evaluation of the lrc's according to the new method. To obtain comparable courses of the density profiles, we performed all simulations with identical numbers of particles in the same box geometry.

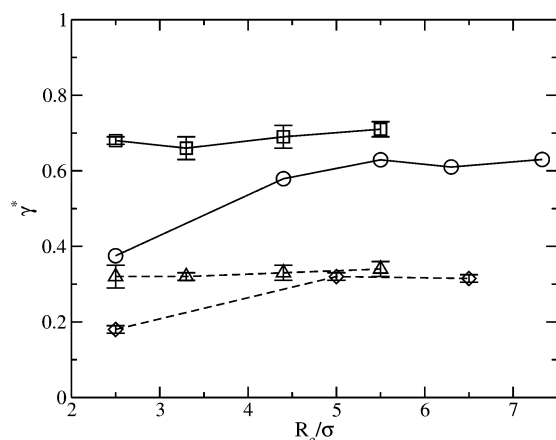
While for $T^* = 0.9$ only the curve according to Guo et al. has a slightly different course from the others, at $T^* = 1.10$ also the treatment of lrc's according to Mecke et al. provides a density profile which is different from that with $R_c = 5.5\sigma$. The new method gives for both cutoff distances identical curves at both temperatures which is a prerequisite for good calculation of other equilibrium properties.

TABLE 1: Surface Tension Values at $T^* = 0.92$ and $T^* = 1.1$ Obtained with Different Values of the Cutoff Radius

R_c	γ^*	
	$T^* = 0.92$	$T^* = 1.10$
2.5σ	0.68 ± 0.02	0.33 ± 0.02
3.3σ	0.66 ± 0.03	0.32 ± 0.01
4.4σ	0.69 ± 0.03	0.33 ± 0.02
5.5σ	0.71 ± 0.02	0.34 ± 0.02

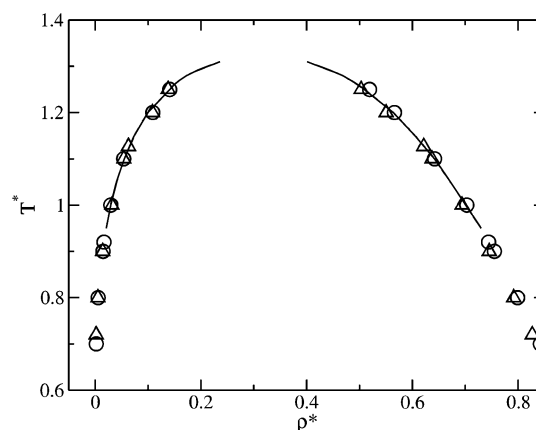
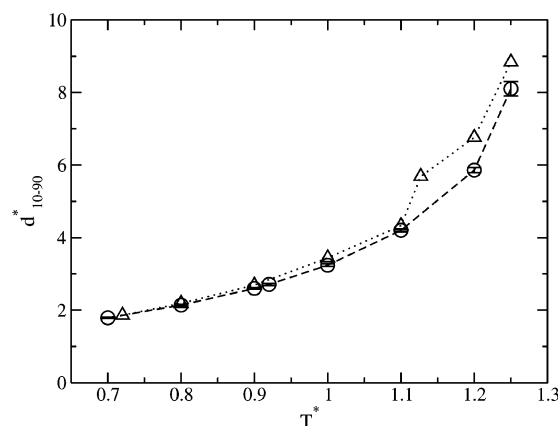
TABLE 2: Surface Tension, Interfacial Thickness, and Coexisting Densities for an LJ Fluid from MC Simulations at Different Temperatures^a

T^*	γ^*	d_{10-90}^*	ρ_l^*	ρ_g^*
0.7	1.21 ± 0.02	1.79 ± 0.02	0.842 ± 0.001	0.0021 ± 0.0002
0.8	0.94 ± 0.01	2.14 ± 0.02	0.799 ± 0.001	0.0058 ± 0.0003
0.9	0.74 ± 0.02	2.60 ± 0.02	0.755 ± 0.001	0.0149 ± 0.0003
0.92	0.68 ± 0.02	2.71 ± 0.03	0.744 ± 0.001	0.0167 ± 0.0003
1.0	0.51 ± 0.01	3.24 ± 0.03	0.703 ± 0.001	0.0296 ± 0.0004
1.1	0.33 ± 0.02	4.20 ± 0.04	0.642 ± 0.001	0.054 ± 0.001
1.2	0.16 ± 0.02	5.86 ± 0.07	0.566 ± 0.001	0.109 ± 0.002
1.25	0.10 ± 0.02	8.1 ± 0.2	0.519 ± 0.001	0.141 ± 0.002

^a $R_c = 2.5\sigma$.**Figure 3.** Effect of the cutoff radius on the values of surface tension: (circles) Trokhymchuk et al. (no lrc's);⁶ (squares) this work (both with $T^* = 0.92$); (diamonds) Mecke et al.;¹⁵ (triangles) this work (both with $T^* = 1.1$). The lines only highlight the orientation in the figure.

The values of the surface tension obtained with different cutoff radii are listed in Table 1. They are compared with some literature data in Figure 3. The upper set (for $T^* = 0.92$) is a comparison between our results (squares connected by a solid line) and the data of Trokhymchuk et al.⁶ and Nijmeijer et al.¹⁹ which do not include any long range corrections (circles connected by a solid line). The significant difference even for large cutoffs is surprising. The lower set is our results at $T^* = 1.10$ (triangles connected by a dashed line) compared with the corrected values given by Mecke et al.¹⁵ (diamonds connected by a dashed line). Since the approach of Mecke et al. does not involve all interactions with molecules outside the cutoff sphere, it is expectable that their values of surface tension will be lower than ours. Nevertheless, for sufficiently large cutoffs, this difference is on the order of the variance of our data.

The values of the surface tension, coexisting densities, and 10–90 thickness at different temperatures obtained within this work with $R_c = 2.5\sigma$ are listed in Table 2. The variances of the surface tension values were determined as 3 times the standard deviation of 10 block averages obtained from the total ensemble of the 20 000 actual values; for coexisting densities, the variations were estimated from several (5–10) average values in slabs of 1σ thickness at different positions in the bulk phases

**Figure 4.** Vapor–liquid coexistence curve for Lennard–Jones fluid: (circles) this work; (triangles) López-Lemus et al.;¹⁶ (solid line) Potoff et al.¹⁰**Figure 5.** Temperature dependence of the 10–90 thickness: (circles) this work; (triangles) López-Lemus et al.¹⁶

and those for the 10–90 thickness are represented by the ranges between the minimal and maximal estimates of these thicknesses.

The vapor–liquid coexistence curve is shown in Figure 4. The solid line represents the results of Potoff et al.,¹⁰ the circles are results of this work, and the triangles are data obtained by López-Lemus et al.¹⁶ using inhomogeneous simulations with the lattice sum technique. At higher temperatures, a small shift of liquid densities of this work toward higher values can be observed.

In Figure 5, the temperature dependence of the 10–90 thickness, d_{10-90} , is shown. The circles are results of this work, while the triangles are values calculated from the interfacial thicknesses δ reported by López-Lemus et al.¹⁶ These two quantities can be recalculated using a simple formula: $d_{10-90} = 1.09861\delta$. The deviated value at $T^* = 1.127$ in the set of López-Lemus et al. is probably caused by a misprint in ref 16; the reported value fit much better to the temperature $T^* = 1.17$. Similar deviation can be seen also for the surface tension value at $T^* = 1.127$ in that work. In the whole range, our values are systematically slightly lower which means that the interface is more narrow. As well as the small difference in coexisting density, this is an indication that our results correspond to a less volatile system.

Several different literature sets of data on the temperature dependence of the surface tension are compared in Figure 6. To make the figure less complicated, we omitted the error bars in all sets. The open circles connected by a dotted line represent the results of this work; open diamonds with a dashed line are

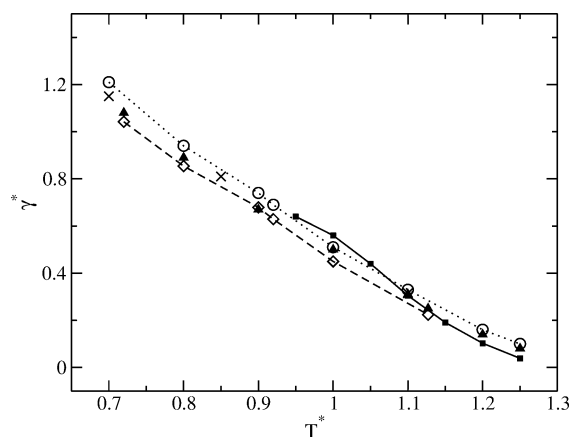


Figure 6. Comparison of obtained values of the surface tension with the literature data: (open circles) this work; (open diamonds) Trokhymchuk et al.;⁶ (filled triangles) López-Lemus et al.;¹⁶ (filled squares) Potoff et al.;¹⁰ (crosses) Mecke et al.¹⁵ The dashed, dotted, and solid lines connecting symbols are only guides for the eye. At temperature $T^* = 1.1$, the value of Mecke et al. (cross) is overlapped by that of López-Lemus (filled triangle).

the data of Trokhymchuk et al.⁶ obtained with $R_c = 5.5\sigma$ without any long range corrections; crosses are the values reported by Mecke et al.¹⁵ ($R_c = 5.0\sigma + \text{Irc's}$); the filled triangles are the results of López-Lemus et al.¹⁶ obtained by using the lattice sum technique in inhomogeneous simulations; the filled squares are the data of Potoff et al.¹⁰ calculated using the histogram-reweighting method.

The observed tendency $\gamma(\text{Trokhymchuk}) < \gamma(\text{Mecke}) < \gamma(\text{this work})$ could be expected since it is in this order that a larger fraction of long range contributions is included. Nevertheless, it was found that the values of the surface tension obtained with spherically truncated and truncated and shifted potentials with $R_c = 5.5\sigma$ are nearly identical;⁶ accordingly, Trokhymchuk et al. concluded that the surface tension value for the full Lennard–Jones potential should not be very different from that obtained with $R_c = 5.5\sigma$. This is also supported by simulations at $T^* = 0.92$ with even larger cutoffs of $R_c = 6.3\sigma$ by Holcomb et al.¹¹ and $R_c = 7.33\sigma$ by Nijmeijer et al.¹⁹ Despite the fact that the simulation of Nijmeijer et al. may be affected by a small systematic error since it was performed in a box of improper geometry, we tend toward the opinion that the correct value of the surface tension at this temperature should be smaller than our result 0.68 ± 0.02 . Together with the fact that the extrapolation of our data to the critical temperature of LJ fluid ($T_c^* = 1.312$) yields a nonzero value, we can conclude that our approach slightly overestimates the attractive contribution of intermolecular interactions. This effect can be probably caused by the fact that near $r = 2.5\sigma$ the radial distribution function of the Lennard–Jones fluid in bulk liquid phase has a minimum and taking $g(r) = 1$ leads then to the over valuation of the attractive part of the intermolecular energy. On the other hand, the values obtained by Potoff et al. in the temperature range

$0.95 \leq T^* \leq 1.1$ are even higher than our results. To clarify these problems along with studying the synchronous influence of the lateral dimension of the simulation box and the thickness of the liquid film represents one of the aims of our contemporary work.

Conclusion

A new simple method for treating the truncation of intermolecular energy in inhomogeneous simulations was suggested. To test the ability of this method to describe the equilibrium properties, we simulated a film of Lennard–Jones particles in equilibrium with its vapor for different cutoff distances at temperatures $T^* = 0.92$ and $T^* = 1.1$. For the shortest truncation radius used $R_c = 2.5\sigma$, we obtained values of coexisting densities and surface tension comparable with those obtained with R_c values larger than 5σ when no long range corrections are included. In the temperature range $\langle 0.7, 1.25 \rangle$, we obtained stable density profiles and reasonable values of other equilibrium properties.

The suggested approach can be simply extended to models of molecular fluids with different interaction sites of the Lennard–Jones type or to mixtures of different compounds. It can be also used in simulations of the liquid–liquid interface between two immiscible liquids.

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