Long Range Corrections to the Vapor-Liquid Equilibrium and Surface Tension of Methane with NVT Molecular Dynamics Simulations

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Abstract

In direct molecular dynamics simulations (MD) of inhomogeneous systems the density is distributed across the interface and, as a result, the conventional long range corrections cannot be used for these systems. In this work, to correct the results of MD simulations for vapor-liquid equilibrium of methane, we have used the slab based corrections to the direction perpendicular to the interface(z-direction) of the force affecting on each particle. All the particles in each slab are considered to have the same coordinate in the z-direction. The density profiles from preliminary simulations with large cut-off distance values were used for the calculation of long range correction terms. New sets of simulation runs, including long range corrections, were then executed with smaller values of cut-off distance. By employing this approach, more accurate results by the cut-off radius $R_c = 2.5\sigma$ in comparison with those produced with the cut-off distance $R_c = 5.5\sigma$ without applying the long range corrections, are observed for the values of the coexisting densities and the surface tension.

Keywords: *Molecular Dynamic Simulations, Inhomogeneous Systems, Long Range Corrections*

1. Introduction

Computer simulations are one of the influential tools that scientists and engineers are trying to use in finding answers for their essential and engineering problems. In fact, they are interested in reproducing such exact data that would enable them to replace molecular simulations by experimental methods.

Molecular experiments like Molecular Dynamics (MD) and Monte Carlo (MC) simulations have been used extensively during the past few decades to attain knowledge on the properties of homogeneous and also inhomogeneous fluids and their mixtures. Several approaches have been developed in order to study the properties of inhomogeneous systems such as coexisting densities and interfacial properties.

Gibbs ensemble Monte Carlo (GEMC) [1]

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and NPT + test particle [2] are two methods for producing phase equilibrium data and are classified in the category of techniques that do not consider the effect of interfaces.As a result,they cannot give any knowledge about the properties of interfacial region, such as surface tension.

Many studies on liquid-vapor interfaces (e. g. two coexisting phases present in one box) via direct molecular simulations using MD and MC techniques have been published[1-12]. In the case of direct molecular simulations the results can be affected by various problems like system size and truncation of interactions.

It is shown by Holcomb et al.[5]and Chen[7] that the liquid and vapor densities do not depend on the size of the system and the surface area of the interface; however, properties like surface tension are strongly dependent on the surface area.Consequently, to set up the simulation box, the number of particles is commonly assumed to be greater than about 1000. The liquid film thickness should be twice the cut-off and the smallest dimension of the box must be greater than 10 times the collision diameter[5].

It is obvious that smaller cut-off radius results in lower computation time;on the other hand, smaller cut-off radius reduces the accuracy of the calculated properties in both homogeneous and inhomogeneous systems. Trokhymchuk and Alejandre[10]have presented a complete discussion about the significant effects of truncation of interactions resulting from small values of cut-off radius, in both MD and MC

simulations.

In order to overcome the inaccuracy resulting from using small values of cut-off radius and obtaining the calculated properties with higher accuracy, the standard long range corrections[13] are commonly used to correct the truncation of interactions in the simulations of homogeneous systems. However, execution of the long range corrections to the evaluation of properties of inhomogeneous systems is affected by the non uniform distribution of density profile along the direction normal to the interface.

Many studies are concerned with performing long range corrections for inhomogeneous fluids. Chapela et al.[3] derived a tail correction for the expressions of surface tension and then added the correction term to the surface tension values obtained at the end of the simulation runs. Holcomb et al.[5] suggested applying the tail correction to the values of surface tension obtained with large cut-off radius. In their approach, application of tail correction introduced by Chapela et al.[3]to the results of simulations with R_c=4.4σ produced the full Lennard-Jones potential surface tensions.Their method was later followed and completed by Blokhuis et al.[6].

Another method is recommended by Guo and Lu[8]. Their correction formulas are introduced to the expressions for calculation of coexisting densities and interfacial properties during the simulation run. They have mentioned that addition of long range corrections during the simulation run results in good agreement between the obtained values of the coexisting densities and those obtained by the GEMC method with smaller values of cut-off distance.

Lotfi et al. [14] added the long range correction term to the expressions of forces acting on a particle and then applied it in MD simulations. Mecke et al.[9]followed this approach and proposed a tail correction to the surface tension and implemented it within the simulation runs. At higher temperatures, their approach is not able to reproduce the same density profiles for cut-off radii 5σ and 2.5σ.Their results show that with a cut-off radius equal to 5σ and a tail correction contribution the surface tension values of a full Lennard-Jones potential can be estimated.

More recently, Janecek[12] proposed expres-sions for long range corrections for configurational energy, the components of the virial tensor, the surface tension and the z-component (the direction perpendicular to the interface) of the force.They executed a series of MC simulations to investigate the effect of the new long range correction terms and calculated surface tension and coexisting densities.In their simulations, the long range terms were calculated for each molecule at every MC step. They showed that their new approach yields the same density profiles for the cut-off values equal to 2.5σ and 5.5σ. Their approach was then used by Shen et al.[15]in MD simulations.They also obtained cut-off independent properties by using the long range corrections proposed byJanecek[12].

Some authors preferred to use the lattice sum method[16, 17] for the dispersion part of the Lennard-Jones potential in their simulations.In the case of Lennard-Jones potential the expressions for this method are introduced byKarasawa and Goddard[18]. In this method, one can use a smaller cut-off

distance and smaller system sizes compared with previous methods.The main disadvantage of this approach is its large computational time. Some works use the multiple-time step method, and particle mesh Ewald[19] is applied to reduce the CPU time.

Escobedo and Mansoori have developed expressions for predicting surface tension of pure fluids and mixtures based on statistical mechanical approach [20, 21]. Their proposed equation covers a wide range of nonpolar and highly polar asymmetric substances and their mixtures.

In this study, we are concerned with the application of long range correction terms to the forces acting on each particle during the MD simulation runs. In Section II of this work, we explain the theory behind the calculations, Section III contains the procedure of simulations, and in Section IV the results of the simulations for methane are discussed.

2. Theory

For inhomogeneous systems including particles interacting via Lennard-Jones potential the truncated force is given by Eq.1.

$$f(r) = -\frac{du(r)}{dr}$$

$$\begin{cases} -\frac{24\varepsilon}{r}\left[2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] & r < R_c \\ 0 & r > R_c \end{cases} \quad (1)$$

Where $f(r)$ is the force and $u(r)$is the pair potential function of interaction between two particles, σ and ε are, respectively, the collision diameter and the depth of the

potential well, r is the distance between the centers of interaction sites and R_c is the cut-off radius.

In order to incorporate the simulation results into full Lennard-Jones potential, long range corrections must be taken into consideration. The standard long range contributions to the energy (U) and pressure (P) for homogeneous systems are evaluated by the following equations[13]:

$$U_{LRC} = 2\pi\rho \int_{R_c}^{\infty} r^2 u(r) g(r) dr \qquad (2)$$

$$P_{LRC} = \frac{-2\pi\rho^2}{3} \int_{R_c}^{\infty} \frac{d(u(r))}{dr} g(r) r^2 dr \qquad (3)$$

Where g (r) is the radial distribution function, ρ is the number density and subscript LRC stands for long range correction.The radial distribution function ($g(r)$) is commonly assumed to be equal to one in the evaluation of long range terms.

Despite homogeneous systems, in direct molecular simulations of vapor-liquid phase equilibria, the density profile is non-uniformly distributed in simulation box in the direction perpendicular to the interface (z-direction). Since Eqs.2 and 3 use uniform average density, they cannot be used in their present form in simulations of inhomogeneous systems with planar interface and must be modified considering the density distribution.

Guo and Lu[8]have developed expressions for the long range contributions for inhomogeneous fluids in MC simulations. In

their work, the simulation cell is divided into k slabs along the z-direction parallel to the interface. Each slab contains N_k particles and is supposed to have a uniform density. The total long range corrections for each property is then obtained in terms of the contributions of all the slabs according to Eq.4.

$$X_{LRC} = \sum_{i}^{k} x_{LRC}(k) \qquad (4)$$

Here, x is the property of interest in each slab, X is its total value in the box and k runs over the number of slabs. For the configurational energy, the local contribution for long range correction in each slab can be expressed by,

$$\frac{u_{LRC}(\mathbf{r}_k)}{N_k} = \frac{1}{2}\int_{R_c}^{\infty} \rho(\mathbf{r})u(r)g(r,z,z_k)dV \quad (5)$$

where $\mathbf{r}$ denotes spherical polar coordinates (r, θ, Φ), ρ ($\mathbf{r}$) is the number density of the fluid in a volume element dVaway from the central molecule in the kth local slab, and z_k is the position of the kth slab. In these calculations it is considered that beyond the cut-off radius of particle i, the slab fluid is uniform, i.e. g (r, z, z_k)=1.With application of this assumption in the spherical polar coordinates the above equation turns into,

$$\frac{u_{LRC}(\mathbf{r}_k)}{N_k} = \pi \int_{R_c}^{\infty} \int_{0}^{\pi} u(r)r^2\rho(\mathbf{r})\sin\theta dr d\theta \quad (6)$$

Since the number density for a system with planar interface varies only in the z-direction, the above integral can be calculated in the following way,

$$\frac{u_{LRC}(z_k)}{N_k} = \pi \int_{R_c}^{\infty} u(r)r^2 dr \int_{-r}^{r} \rho(z)\frac{d\Delta z}{r} \qquad (7)$$

where $\Delta z = z - z_k$. The local configurational energy within each slab is calculated by Eq. 7. Then, using Eq.4, the sum of all these local values is calculated and considered as the total long range correction of the whole system.

According to the Irving and Kirkwood[22] definition, the proper expressions for the components of the pressure tensor are expressed as,

$$P_{zz}^{LRC}(z_k) =$$
$$-\pi\rho(z_k)\int_{R_c}^{\infty} f(r)dr \int_{-r}^{r} \rho(z)(\Delta z)^2 d\Delta z \qquad (8)$$

$$P_{xx}^{LRC} = P_{yy}^{LRC} =$$
$$-\frac{\pi}{2}\rho(z_k)\int_{R_c}^{\infty} f(r)dr \int_{-r}^{r} \rho(z)(r^2 - \Delta z^2)d\Delta z \qquad (9)$$

The details of deriving these expressions and all the assumptions made in their derivation can be found in the original paper of Guo and Lu[8].

Mechanical definition of surface tension proves that it can be related to the diagonal components of the pressure tensor[23]. The appropriate long range correction to the surface tension can then be obtained after straightforward calculations,

$$\gamma_{LRC}(z_k) = \frac{1}{2}\int_{0}^{L_z} \left[P_N(z_k) - P_T(z_k) \right] dz_k \qquad (10)$$

Where P_N is the normal and P_T is the tangential pressure defined by,

$$P_N = P_{zz}, \quad P_T = \frac{1}{2}(P_{xx} + P_{yy}) \qquad (11)$$

In MD simulations of inhomogeneous fluids the long range correction contributions are added to the expressions of forces interacting between molecules as an alternative contribution to the energies[9, 15]. During the MD simulations the forces acting on any particle i inside its cut-off distance are calculated. To consider long range corrections an extra contribution is added to the z-component of the force affecting each particle i. In fact, this contribution accounts for those forces acting on any particle from outside its cut-off distance.

In this work, we have added the long range correction contribution to the expression of forces acting on each particle. The proper estimation to the force in the z-direction is obtained from Eq. 5 by straightforward thermodynamics and is presented by Eq. (12).

$$f_{LRC}(z_k) =$$
$$\int_{R_c}^{\infty} \int_{-r}^{r} 2\pi r^2 \left(-\frac{1}{r}\frac{du(r)}{dr}\mathbf{r} \right)\rho(\mathbf{r})\sin\theta dr d\theta \qquad (12)$$

$$f_{LRC}(z_k) = 2\pi \int_{R_c}^{\infty} f(r)dr \int_{-r}^{r} \rho(z)\Delta z d\Delta z \qquad (13)$$

As mentioned before, LRC terms are calculated for each slab located in position z_k. However, the additional force must be added to each individual particle i, located at z_i, which results in longer simulation runs. In this study, we have calculated $f_{LRC}(z_k)$ at the location z_k of each slab. We have then added it to all the particles located inside the slab

with the same coordinate z_k. In other words, equal contributions of long range correction values are added to all the molecules in each slab.

In order to investigate the effect of addition of f_{LRC} (z_k) to the forces acting on each particle on the calculated thermodynamic properties, we first performed a number of simulation runs by the cut-off distance equal to 5.5σ without using long range corrections. In this way, we obtained the density profile in the z-direction. We then adjusted the obtained values of the density to the corresponding values of position (z) to the form of a hyperbolic tangent function[3, 11] introduced by the following equation,

$$\rho(z) = \frac{1}{2}(\rho_l + \rho_v) - \frac{1}{2}(\rho_l - \rho_v)\tanh\left(2\frac{(z - z_0)}{d}\right)$$

(14)

In Eq. 14, ρ_l and ρ_v are the liquid and vapor bulk densities, z_0 is the position of the Gibbs dividing surface and d is an approximation of the value of the interface thickness. z_0 and d are both considered as adjusting parameters. This equation is then replaced in Eqs. 8, 9 and 13 to obtain the long range correction expressions in our MD simulations of inhomogeneous systems.

3. Simulation details

We have used the reduced parameters in the standard way: $T^* = k_b T / \varepsilon$ for temperature, $P^* = P\sigma^2 / \varepsilon$ for pressure, $\rho^* = \rho\sigma^3$ for density, $\gamma^* = \gamma\sigma^2 / \varepsilon$ for surface tension, where γ is the surface tension, and $z^* = z / \sigma$ for distance in the z direction.

We performed a series of MD simulations in NVT ensemble to study the vapor-liquid thermodynamic properties of methane. We applied the DL_POLY_2.20 simulation package[24] in our studies. In the simulations performed, methane molecules were modeled as a single pseudoatom interacting with each other via Lennard-Jones potential model. The Lennard-Jones parameters for methane are obtained from Martin and Siepmann[25]. The MD simulations were performed at seven values of reduced temperature in the interval $T^* = 0.7$-1.127 introduced in Table 1.

To eliminate the finite system size effect on the simulation properties, all simulations were performed within a parallel epiped box of dimensions $13.41\sigma \times 13.41\sigma \times 39.81\sigma$ containing 2048 particles. Periodic boundary conditions were performed in all three directions. The Leapfrog integration algorithm was used to integrate the equations of motion.

The time step was set equal to 0.003ps, and the temperature was kept constant with Nose-Hoover thermostat. To set up the initial configuration for each simulation, a liquid slab of particles was placed in the cubic simulation box and after 50000 time steps the simulation box was enlarged from both sides in the z-direction to create a parallel epiped box, allocated to establishing the interface. The simulation continued until equilibration of the interface. Average thermodynamic properties were obtained from at least 200000 time steps. The density profiles and the diagonal components of pressure were determined by dividing the simulation box into 296 slabs, each with 0.13σ thickness, parallel to the interface.

We can check that the interface is at mechanical stability if the normal pressure is

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constant along the *z*-axes and is also equal to the tangential pressure away from the interfaces. According to Irving and Kirkwood's [22] definition, the normal and tangential components of the pressure tensor in the *z*-direction are obtained from Eq. 15.

$$P_N(z) = \langle \rho(z) \rangle k_b T$$
$$-\frac{1}{A}\left\langle \sum_i \sum_{j>i} \frac{(z_{ij}^2)}{r_{ij}^2}\frac{du(r_{ij})}{dr_{ij}}\frac{1}{|z_{ij}|}\times\theta\left(\frac{z-z_i}{z_{ij}}\right)\theta\left(\frac{z_j-z}{z_{ij}}\right)\right\rangle \quad (15)$$

Where k_b is Boltzman constant, $A = L_x \times L_y$ is the surface area, $\langle \cdots \rangle$ is the canonical ensemble average and θ is the unit step function, $\theta(x) = 0$ when $x < 0$ and $\theta(x) = 1$ when $x > 0$. The first term in the right hand side of Eq. 15 is the ideal gas contribution and the second term is the contribution of the configuration energy. A subset of DL_POLY programs was modified to calculate these expressions during the simulation runs.

The tangential component of the pressure tensor along the *z*-direction can be obtained by the expression similar to Eq. 15 with $(x_{ij}^2 + y_{ij}^2)/2$ instead of z_{ij}^2. Calculation of these components is redounded to evaluation of surface tension:

$$\gamma(z) = \frac{1}{2}\int_0^{L_z}(P_N(z) - P_T(z))dz \quad (16)$$

Where L_z is the length of the *z*-dimension of the simulation box. The components of the pressure tensor and surface tension were calculated in 10 blocks, each block contains 20000 steps and these profiles were calculated every 100 steps. The long range corrections to the force and diagonal

components of the pressure tensor have been added to the DL_POLY package. The normal component of the pressure tensor is employed for the evaluation of vapor pressure. We used the average normal pressure in the vapor phase for obtaining the vapor pressure.

We first performed two sets of simulations for methane with cut-off radii equal to 5.5σ and 2.5σ at seven values of reduced temperature in the interval $T^*=0.7$-1.127 without considering long range corrections. After reaching the vapor-liquid equilibrium for $R_c=5.5\sigma$, we fitted the obtained values of density to Eq. 14. For each reduced temperature, the constants of Eq. 14 are presented in Table 1. Using the density profile, the long range correction contribution to the force was calculated by Eq. 13 at any position z_k. Then, the contributions to the diagonal components of pressure tensor were calculated from Eqs. 8 and 9.

Table 1. The reduced parameters of Eq. 14 obtained from fitting to density data from simulation with $R_c=5.5\sigma$.

T^*	ρ_l^*	ρ_v^*	z_0^*	d^*
0.7	0.8298	0.0024	6.8792	1.4050
0.72	0.8233	0.0033	6.9678	1.3699
0.8	0.7864	0.0080	7.1699	1.7562
0.9	0.7329	0.0177	7.4844	2.2679
0.92	0.7319	0.0177	7.5040	2.3704
1	0.6819	0.0341	7.7477	2.9963
1.127	0.6011	0.0769	7.9649	5.1657

After the preliminary runs, new sets of simulations with the cut-off radius equal to 2.5σ and with applying the long range corrections were performed at the same values of reduced temperature. During the simulation runs, the long range terms were calculated at each time step and were added to the pressure tensor and to the force acting on each methane molecule. After reaching new vapor-liquid equilibrium the new density profile is obtained. The influence of the addition of the long range correction expressions to the interacting forces on the coexisting densities and also on the interfacial properties is examined and presented in the next section.

4. Results and discussion

As mentioned above, the truncation of interactions as represented by the values of cut-off radius is an assumption with significant effect on the simulation results. The density profile of methane at $T^{*}=0.72$ with two cut-off values without application of long range corrections is shown in Fig.1. Small cut-off radius has led to estimation of lower densities for liquid phase and higher densities for vapor phase by MD simulations. In Table 2 vapor-liquid densities in conjunction with surface tension values obtained from MD simulations are compared with experimental data[26]. It is obvious that with application of small cut-off distance, deviation of equilibrium densities and also surface tension from experimental data is increased and is more noticeable at higher temperatures. The advantage of smaller

values of cut-off distance is the shorter time required for execution of simulation runs. On the other hand, due to truncation of interactions, small values of cut-off distance produce less accurate and less reliable results.

In Fig. 2 the vapor-liquid phase diagram of methane with $R_c=2.5\sigma$ produced by applying the long range corrections, is compared with the results obtained by $R_c=5.5\sigma$ and $R_c=2.5\sigma$ without considering long range corrections. The results are also compared with the experimental data from NIST[26]. As is expected, without application of the long range correction contributions, poor results are produced by $R_c=2.5\sigma$ while the results obtained by $R_c=2.5\sigma$ when the long range correction terms are applied is in rather good agreement with experimental data. In the case of simulations with cut-off radius equal to 5.5σ, the average absolute deviation (AAD) of calculated liquid densities from the experimental values is 1.81%, while liquid densities are predicted with AAD equal to 1.33% with the application of long range corrections for cut-off radius $R_c=2.5\sigma$. The AAD in the prediction of vapor phase densities is 1.79% with small cut off distance and using long range corrections, while the vapor densities with $R_c=5.5\sigma$ without the application of long range corrections show AAD value equal to 15.23%. This observation shows that the corrections applied to the truncated forces of interactions have improved the prediction of the potential function model for smaller values of cut-off distance.
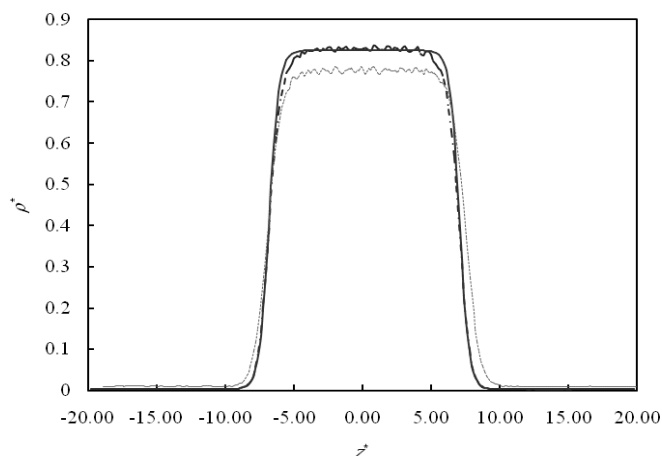
Figure 1. Density profiles for T^*=0.72, (dotted line) with Rc=2.5σ, (Dashed-dotted line) with Rc=5.5σ and (solid line) is the fitting curve to density data with Rc=5.5σ.

Table 2. Vapor-liquid densities and surface tension values obtained from simulations with two cut-off values in comparison with experimental data.

| T^*	Experimental			Rc=5.5σ			Rc=2.5σ		
	ρ_l^*	ρ_v^*	γ^*	ρ_l^*	ρ_v^*	γ^*	ρ_l^*	ρ_v^*	γ^*
0.7	0.845	0.002	1.045	0.833	0.002	1.065	0.784	0.007	0.654
0.72	0.837	0.002	0.994	0.825	0.003	0.977	0.774	0.009	0.572
0.8	0.804	0.006	0.798	0.790	0.007	0.839	0.727	0.020	0.397
0.9	0.758	0.014	0.575	0.743	0.017	0.630	0.665	0.047	0.222
0.92	0.748	0.016	0.534	0.732	0.018	0.565	0.649	0.052	0.221
1	0.705	0.029	0.379	0.689	0.033	0.420	0.566	0.093	0.109
1.127	0.623	0.066	0.172	0.611	0.071	0.220	-	-	-
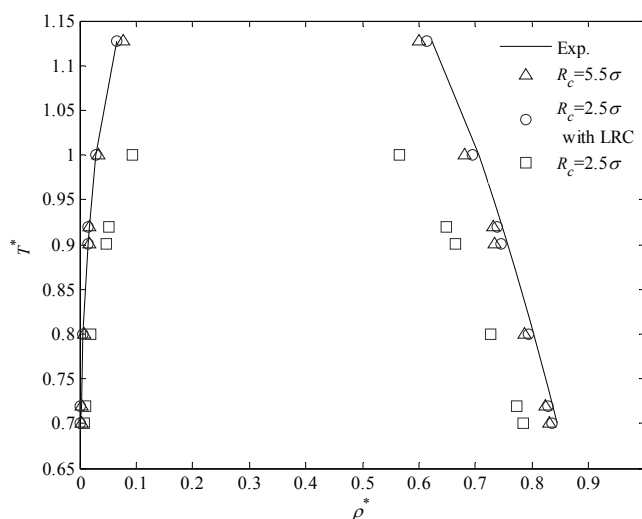
Figure 2. Vapor−liquid coexistence curve of methane, the solid line corresponds to the experimental data [26], (triangles) simulation results by R_c=5.5σ, (squares) simulation results with R_c=2.5σ, (circles) simulation results with R_c=2.5σ including long range corrections.

We should mention that one of the important sources of error is the Lennard-Jones potential function model. Lennard-Jones potential function is an approximate model for describing the complex nature of intermolecular interactions. However, since in this work we are dealing only with simulations of methane molecules we have used this model.Our main goal is to introduce a methodology for applying long range corrections. For more complex molecules, more sophisticated potential models are needed.

Another observation in Fig. 2 is that at reduced temperatures larger than about 0.9, more pronounced deviations of the liquid and vapor densities from experimental data have occurred for $R_c=2.5\sigma$ without long range correction contributions. However, application of the long range correction terms to the simulation runs with $R_c=2.5\sigma$ has resulted in accurate predictions in this region. Another advantage of the method implied in this work

is that the time required for the simulation runs is reduced averagely by a factor of 5 for the runs with $R_c=2.5\sigma$ by applying the long range correction contributions, in comparison with the runs with $R_c=5.5\sigma$ without application of the long range correction terms.

The average values of the normal pressure in the vapor phase are reported as a measure of the vapor pressure. The obtained values for vapor pressure at different temperatures are represented as a Clausius-Clapeyron plot in Fig. 3. The results show good agreement with the experimental data[26], which is a consequence of applying the long range correction effects. As it is also observed in Fig. 3, the obtained vapor pressures by $R_c=5.5\sigma$ have considerable deviations from experimental data at lower temperatures, while the vapor pressure values produced by $R_c=2.5\sigma$ with the proposed long range correction terms shows small deviations from experimental data.
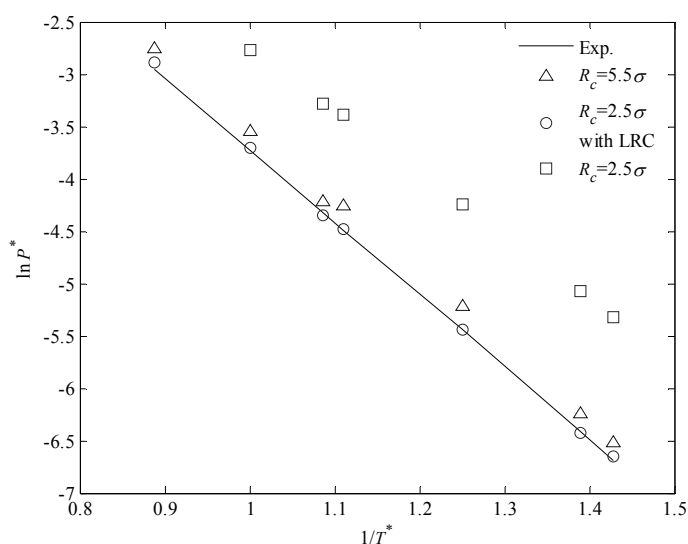

Figure 3. The vapor pressure presented as a Clausius-Clapeyron plot. (solid line) experimental data [26], (triangles) results of the simulations with $R_c=5.5\sigma$, (squares) results of the simulations with $R_c=2.5\sigma$, (circles) results of the simulations with $R_c=2.5\sigma$ considering long range correction terms.

In order to investigate the dependence of the coexisting densities on the value of the cut-off distance, more simulations with R_c=5.5σ, 4.4σ, and 3.3σ were performed in the same range of reduced temperature mentioned in Table 2, using the long range correction terms. For illustration, the density profiles at three values of T^*=0.92, 1 and 1.127 are shown in Fig. 4.

The figure shows that utilizing the proposed method has produced the same results for different cut-off radii values within the fluctuations. The results also indicate that we do not need to perform simulations with large values of cut-off radius to ensure accuracy and stability of phase equilibrium.


(a)

(b)

(c)
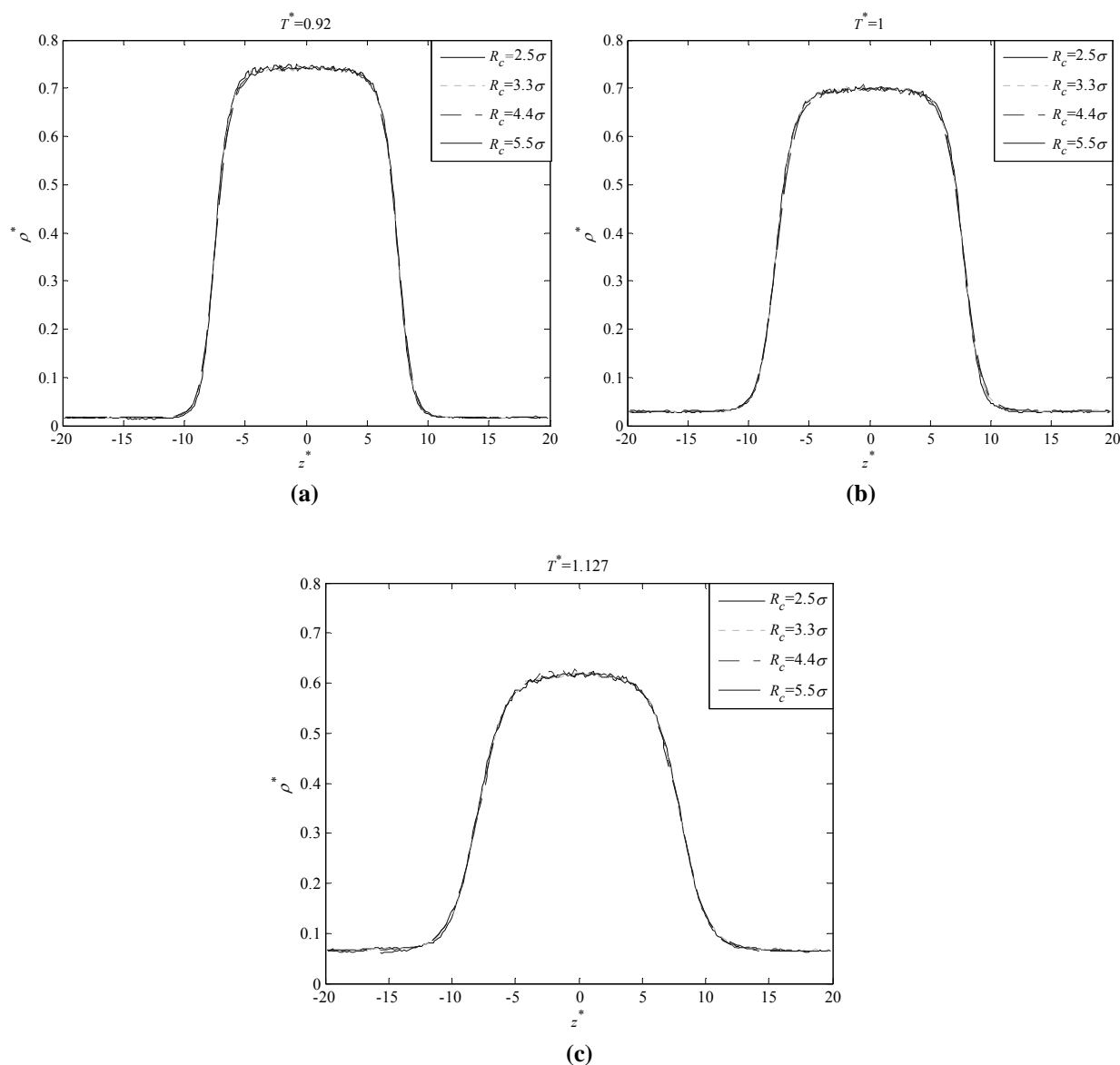
Figure 4. Density profiles for T^*=0.92, T^*=1, T^*=1.127 with different values for cut–off radius: (solid line) with R_c=2.5σ, (dotted line) R_c=3.3σ, (dashed-dotted line) R_c=4.4σ, (dashed line) R_c=5.5σ. All the curves are drawn by applying the long range correction terms.

In Fig. 5 it is shown that at T^*=1.127 the liquid and vapor densities obtained with R_c=2.5σ without the application of long range correction terms are not distinguishable. This observation is another unfavorable effect of the truncated interaction forces, especially at high temperatures. It is also observed that the application of the long range correction-contributions has corrected the profile at the same cut-off distance and temperature.

In this work, instead of adding the long range correction terms to the forces for each molecule located at position z, we have implemented them to each slab. In other words, all the molecules in a slab are considered to have the same position in the z-direction. In this way, the computational time for evaluation of the long range correction effects has not increased considerably. The simulation run time at R_c=2.5σ including long range correction terms increased less than 0.7% compared with the computational time without considering long range correction terms with the same cut-off distance.

A plot of the surface tension against temperature at two values of cut-off radii (2.5σ and 5.5σ)without using long range correction expressions, and atR_c=2.5σ with the addition of the long range correction contributions is presented in Fig. 6. The calculated uncertainties, using the block average method for simulations with small cut-off distance including long range corrections was about 0.0281. The values of the surface tension with smaller cut-off radius have large deviations from experimental data but the long range correction contributions have significantly reduced the error. The figure shows that the simulation results including long range correction with R_c=2.5σ are comparable with the experimental values from NIST [26] within the experimental error.
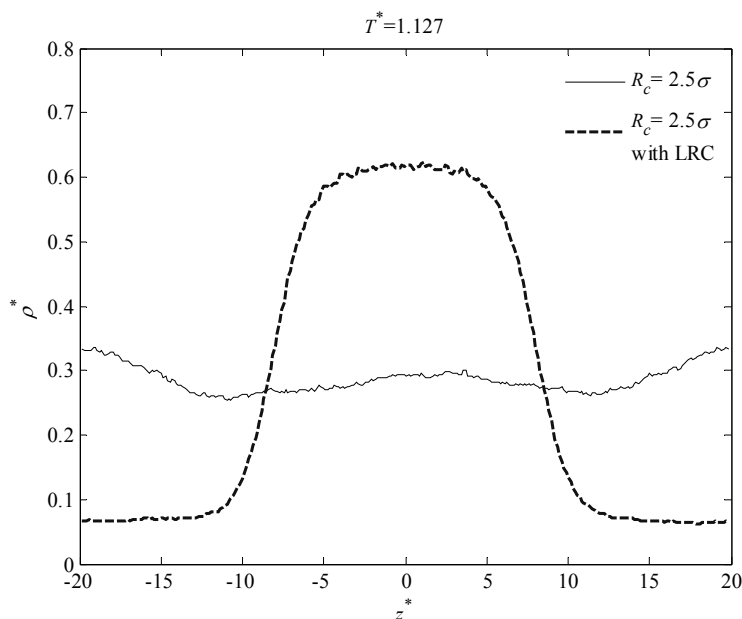
Figure 5. The density profiles at T^*=1.127 obtained with R_c=2.5σ, (solid line) obtained without long range correction contributions, (dashed line) obtained using long range correction contributions.
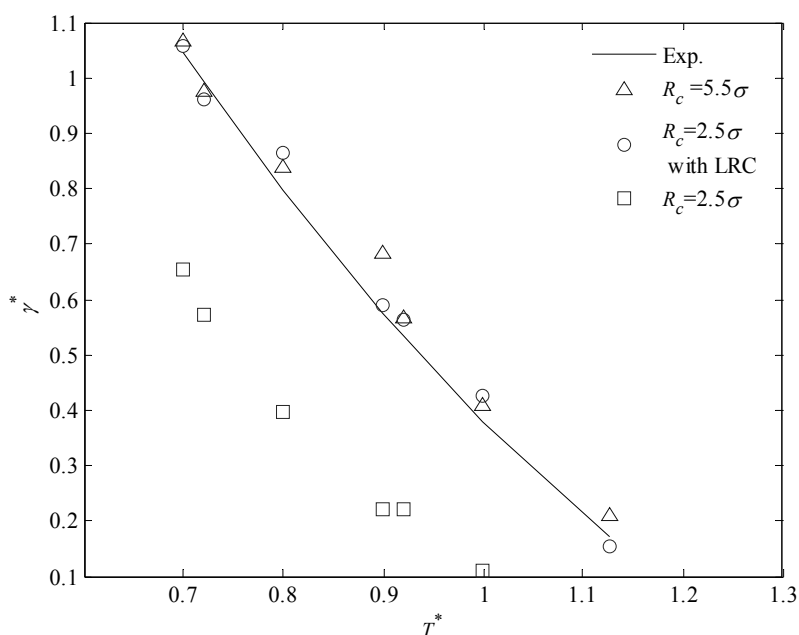
Figure 6. Calculated values of surface tension as a function of temperature, (solid line) represents experimental data [26], (triangles) simulation results with R_c=5.5σ, (squares) simulation results with R_c=2.5σ, (circles), simulation results with R_c=2.5σ, considering long range corrections.

The normal and tangential pressure profiles at T^*=0.72 along the direction perpendicular to interfaces is presented in Fig. 7. The difference between the normal and tangential pressures is also illustrated in this figure. As it is expected, the normal pressure profile obtained with R_c=5.5σ is constant along the z-direction. Also, the values of the normal and tangential pressures are equal in the two coexisting phases, which is an indication of phase equilibrium.It is also observed that in calculating surface tension from Eq. (5), the difference between the normal and tangential components of pressures tensor are pronounced only at the interface.

Applying long range corrections with small cut-off radius has resulted into two noticeable peaks in both the interfaces, however, the conditions of phase equilibrium does still exist. The occurrence of the

negative peaks is a consequence of the distribution of density in the interface.

5. Conclusions

The effects of truncation of intermolecular forces in inhomogeneous systems are treated in this study. Our case study deals with the vapor-liquid equilibrium of methane. Methane molecules were considered to interact via Lennard-Jones potential and the long range correction contributions were added to the expression of forces of interaction between molecules.

We obtained the coexisting densities and surface tension of methane at seven values of reduced temperature with R_c=2.5σ, with higher accuracy compared to the corresponding results obtained with R_c=5.5σ without implementing long range correction contributions. Another advantage of the

method is the reduction of simulation run times. The time required for the simulations with $R_c=2.5\sigma$, applying the method introduced in this work, is 5 times lower than the time required with $R_c=5.5\sigma$ without the application of the corrections.

The suggested approach can also be used for other intermolecular attraction models and in simulations of liquid-liquid equilibrium of two immiscible liquids.

$R_c=5.5\sigma$

(a)

$R_c=2.5\sigma$ with LRC

(b)
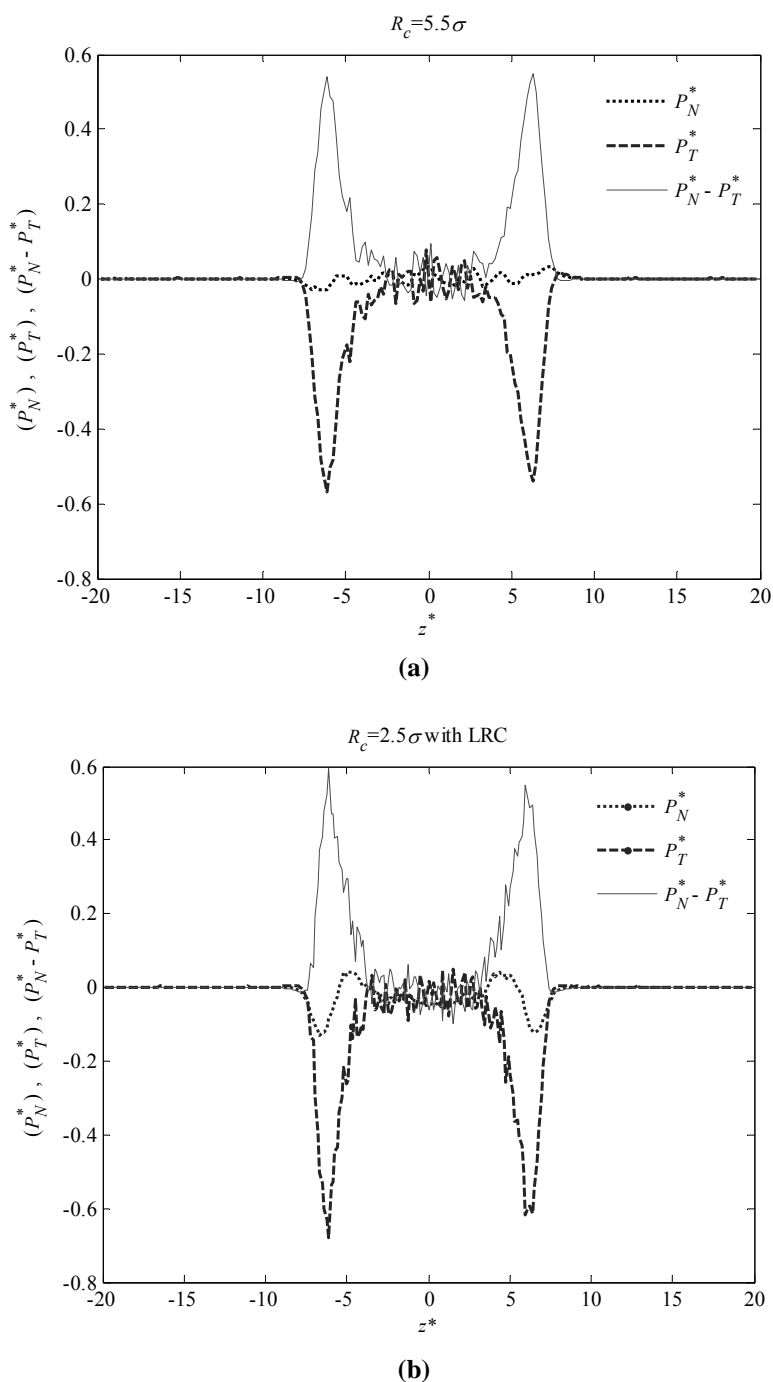
Figure 7. The normal and tangential pressure profiles at $T^*=0.72$. The figure 7(a) is the result of simulation with $R_c=5.5\sigma$ and the figure 7(b) is obtained from simulation with $R_c=2.5\sigma$ and applying long range corrections.

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