Monte Carlo versus molecular dynamics simulations in heterogeneous systems: An application to the n-pentane liquid-vapor interface

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The Monte Carlo (MC) and molecular dynamics (MD) methodologies are now well established for computing equilibrium properties in homogeneous fluids. This is not yet the case for the direct simulation of two-phase systems, which exhibit nonuniformity of the density distribution across the interface. We have performed direct MC and MD simulations of the liquid-gas interface of n-pentane using a standard force-field model. We obtained density and pressure components profiles along the direction normal to the interface that can be very different, depending on the truncation and long range correction strategies. We discuss the influence on predicted properties of different potential truncation schemes implemented in both MC and MD simulations. We show that the MD and MC profiles can be made in agreement by using a Lennard-Jones potential truncated via a polynomial function that makes the first and second derivatives of the potential continuous at the cutoff distance. In this case however, the predicted thermodynamic properties (phase envelope, surface tension) deviate from experiments, because of the changes made in the potential. A further readjustment of the potential parameters is needed if one wants to use this method. We conclude that a straightforward use of bulk phase force fields in MD simulations may lead to some physical inconsistencies when computing interfacial properties.

I. INTRODUCTION

Most of the phenomena in surface science (adhesion, wetting, and lubrication) involve the combination of liquid-liquid, liquid-vapor, and liquid-solid interfaces. Many important fundamental problems in chemistry and biology lead to practical applications in ion separation and extraction, drug delivery, oil recovery, and detergents. They involve ion and charge transfers, adsorption and solvation processes that occur at the vicinity of the liquid-gas interface or between two immiscible liquids. These liquid-liquid interfaces are characterized by specific electrical, structural, and dynamical properties. Due to the difficulties of experimental probes to access the molecular level structure of the interface, direct molecular simulation methods have become powerful techniques to examine the nature of the interface region and to calculate interfacial properties such as the interfacial tension and the interface thickness.

The necessity for the direct molecular simulations to provide reliable properties compared to experiments implies to simulate realistic molecular systems with appropriate energetic descriptions. Molecular simulation technique has been widely used to study the liquid-liquid interfacial properties, the energetic and the mass transfer process. However, the modeling of an oil-water interface often leads to an important difference in polarity between the two phases resulting thus in low mutual solubilities. The interface region can be thus characterized by a high density gradient and a strong asymmetry in the intermolecular interactions. These particularities make the results very sensitive to the nonbonded interaction potential models.

Wipff and co-workers \(^1,2\) have performed molecular dynamics (MD) simulations on the oil-water interface to study the extraction of alkali cations and trivalent lanthanide cations from water to oil phases. The nonbonded interactions are described by a 6–12 pairwise contribution and the electrostatic long range interactions are calculated either using a slightly modified version of the Ewald summation technique or the reaction field method. Recent MD simulations \(^3\) on the water-n-alkanes liquid-liquid interfaces show an excellent agreement between the calculated and experimental surface tension when both electrostatic interactions are handled by the Ewald summation method and two specific contributions from the real and reciprocal space are added in the surface tension calculation. MD simulations \(^4,5\) have been applied successfully to calculate the ion transfer free energy profile across a liquid-liquid interface. This study shows the importance in including explicitly polarization effects into poten-
tial model to make the results closer to the experimental interpretations of the ion transfer mechanism, especially when the two phases differ considerably in polarity. Molecular simulations reported in the literature show that the MD method has been widely applied to liquid-liquid interfaces. We also observe a great variety of methodologies used in the treatment of the repulsion-dispersion potential and long range electrostatic interactions. As a result, it is very difficult to evaluate the influence of each long range interaction potential model on the interfacial properties.

As concerns the liquid-vapor interface, numerous simulations using both direct Monte Carlo (MC) and MD methods have been undertaken. In the literature, there have been an important number of direct simulations of the liquid-vapor interface of a Lennard-Jones fluid but this technique has not been widely applied to molecular systems. Recently, MD simulations of the liquid-vapor interface of a molten salt show that a better agreement between experimental and calculated surface tension values can be found when a full Ewald summation of dispersion interactions and polarization effects are included into the interaction model. These results corroborate what was already observed in a previous study in the case of a liquid-liquid interface.

Since alkanes are the basis of the petrochemical industry, the determination of their phase behavior is of great importance in many technological applications, such as for oil recovery and separation process. For this reason, there have been significant theoretical efforts towards the molecular simulation method and the potential models used for alkanes. In the united atom (UA) model, all CH₃ and CH₂ are treated as neutral interaction sites and the repulsion-dispersion interaction between these sites is only described by means of a Lennard-Jones (LJ) 6–12 potential.

We have shown in previous papers that the direct MC method of simulating liquid-vapor interface of n-alkanes is now well established. The key feature in these systems is the nonuniformity of the density distribution along the direction normal to the interface. This implies that the usual treatments for homogeneous systems may not be applied any longer. The long range corrections to the configurational energy to the pressure components and to the interfacial tension must be carefully applied with the use of truncated potential and forces. We have used the local long range corrections to the configurational energy developed by Guo and Lu within the Metropolis scheme and we have demonstrated that we obtain the thermal equilibrium conditions by calculating the profiles of the configurational temperature along the direction normal to the surface. The equality between the normal and tangential pressures throughout the liquid and vapor phases has been highlighted once two contributions of the long range corrections to the pressure tensor components were included. The coexisting densities and the critical points were in good agreement with the experimental results. We have also calculated the long range corrections to the surface tension using different analytical forms and we have shown that this tail contribution may represent up to 30% of the total value. We have also checked that the dependence of the surface tension with system size and the cutoff radius was cancelled as the long range corrections were taken into account. However, recent works have shown that it was also possible to avoid the inclusion of long range corrections by using the lattice sum method for the dispersion term of the Lennard-Jones potential.

One of the objectives of this work is to calculate the residence time of alkane molecules at the liquid-vapor interface region. This important dynamical property can only be calculated from MD. Before doing this, it is interesting to determine the coexistence curve of an alkane using MD technique, especially as the force field parameters used in MD have been preliminary established from MC calculations. This comparison leads to a quantitative evaluation of the differences between MC and MD on the coexisting densities, critical properties, and interfacial properties.

In principle, these two methods should lead to the same equilibrium properties although they differ in the way of generating the trajectory in the phase space. MC simulation aims to explore the configurational space of a system using the calculation of changes in intermolecular energy whereas MD simulation generates configurations by solving the classical equations of motions using the forces. The differences between MC and MD techniques on inhomogeneous systems have been highlighted for a long time. It was already shown that MC and MD methods yield different coexisting densities in the case of the liquid-vapor coexistence curve of Lennard-Jones fluids. These differences between MC and MD results are explained by the fact that the potential in MC is not differentiable at the cutoff value and that consequently the force used in MD does not correspond to the potential in MC. MC and MD are therefore carried out with different potential models. Making MC and MD consistent requires an investigation on the conditions of the differentiability of the potential function and amounts to address the question of the discontinuity of the potential at the cutoff value. In fact, differentiating a truncated potential with respect to r gives a δ function at the cutoff value, which consequently causes impulses on an atom pair whose separation distance crosses the cutoff. This delta function is not considered as crucial in the simulations of a homogeneous fluid because we may assume that the forces affecting a particle from outside its cutoff sphere will average out. This explains why no significant differences are usually observed between MC and MD simulations for homogeneous systems. In the case of inhomogeneous system, this assumption is no longer valid.

To solve this problem, Trokhymchuk and Alejandre have added a δ function to the force taking thus into account the discontinuous change in the potential at the cut off. They have performed direct simulations of the liquid-vapor interface of a Lennard-Jones fluid and have shown that including this δ function in MD simulations makes the coexistence properties (densities, normal and tangential pressures and surface tension) identical to those calculated in MC simulations with a truncated potential.

We have reinvestigated the conditions under which MC and MD yield similar results concerning the coexistence properties and the thermodynamic equilibria on a molecular system. To do this, we perform MD simulations using different analytical forms for the force (truncated, truncated, and shifted, truncated LJ modified by a cubic spline) and MC
Simulations with the corresponding potential. We will be comparing the MC and MD methods on a molecular system with a vapor-liquid density coexistence curve and surface tension values already established by experiments and by different molecular simulations methods MC (Refs. 23 and 24) and GEMC (Ref. 28). The coexisting densities, the surface tension, and its long range corrections, the normal and tangential pressure components are calculated as a function of the expressions of the potentials and forces used.

We check what it was already observed on the Lennard-Jones fluid liquid-vapor interface. The coexisting densities calculated from MC using a truncated potential and from MD using a truncated force are different. The use of a shifted potential with MC decreases the discrepancy with MD. To obtain a close agreement between MC and MD, we have chosen to remove discontinuities in the energy and the residence time of pentane molecules in the interface region. We conclude in Sec. V, with a short summary of our main results.

II. SIMULATION METHOD
A. Interaction model

The \textit{n}-pentane is modeled as a flexible molecule containing five united atom sites using the TraPPE (Ref. 29) alkane model. The sites \(i\) and \(j\) on different molecules and sites on the same molecule, separated by more than three bonds, interact through a Lennard-Jones potential

\[
u_{ij}(r_{ij}) = 4 \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right],
\]

where \(\epsilon_{ij}\) is the energy parameter of the interaction, \(\sigma_{ij}\) is the Lennard-Jones core diameter, and \(r_{ij}\) is the distance between interaction sites \(i\) and \(j\). The LJ parameters for the interactions between sites of different types are calculated by using the Lorentz-Berthelot mixing rules:

\[
\epsilon_{ij} = (\epsilon_{ii} \epsilon_{jj})^{1/2}, \quad \sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj}).
\]

The interaction sites have the following Lennard-Jones parameters: \(\epsilon_{\text{CH}_3}/k_B = 98\) K and \(\epsilon_{\text{CH}_2}/k_B = 46\) K, where \(k_B\) is Boltzmann’s constant. The size parameters are \(\sigma_{\text{CH}_3} = 3.75\) Å and \(\sigma_{\text{CH}_2} = 3.95\) Å.

The bond distance between two sites is fixed at the separation of 1.54 Å. The bond-angle interactions are harmonic, with

\[
u_{\text{bond}} = \frac{1}{2} k_B (\theta - \theta_0)^2.
\]

where \(\theta\) is the angle between three consecutive united atoms, \(k_B/k_B = 62.500\) K rad \(^{-2}\) is the bending constant, and \(\theta_0 = 114^\circ\) is the equilibrium bond angle.

In pentane, the two torsional potentials are represented by the OPLS potential model

\[
u_{\text{tors}} = c_1 (1 + \cos \phi) + c_2 (1 - \cos 2\phi) + c_3 (1 + \cos 3\phi),
\]

where \(\phi\) is the dihedral angle between four subsequent united atoms, \(c_1/k_B = 355.03\) K, \(c_2/k_B = -68.19\) K, and \(c_3/k_B = 791.32\) K.

B. Methodology

The simulation box is a rectangular parallelepiped box of dimensions \(L_x L_y L_z\) (\(L_x = 30\) Å, \(L_y = 200\) Å) with \(N = 300\) pentane molecules. The periodic boundary conditions are applied in the three directions. MC simulations are performed in the \(NVT\) ensemble. Each cycle consists of \(N\) randomly selected moves with fixed probabilities. The moves are (1) displacement of the center of mass of a random molecule, (2) rotation of a randomly selected molecule around its center of mass, and (3) regrowth of part of a random molecule using the configurational-bias scheme. The relative probabilities for the different types of moves are 0.45 for translations, 0.35 for rotations, and 0.20 for the modification of the conformation. The maximum displacement and maximum rotation are adjusted during the equilibration phase to give an acceptance ration of 0.4. As concerns the translational moves, two different displacements have been chosen randomly with equal probability. The adjustment of these two maximum displacements, during the equilibration phase, give acceptance ratios of 20% and 60%. This specificity for the translational moves improves the sampling of the configurational space of the vapor phase. Further details concerning the specifications of the MC simulations can be found in a previous paper. The MD simulations have been performed in the \(NVT\) ensemble using the Nosé-Hoover thermostat. The first-order equations of motions are integrated using a five-value Gear predictor-corrector procedure with a time step \(\Delta t\) of 2 fs. The C–C bond lengths are constrained to a fixed distance using the Gauss’s principle of least constraint.

The initial configuration has been built by placing the center of mass of \(N\) \textit{n}-pentane molecules on a cubic lattice with random orientations. MC and MD simulations in the \(NPT\) ensemble have been performed on this bulk fluid configuration. The dimension of the resulting box has been increased along the \(z\) axis by placing two empty cells on both sides of the bulk liquid box. A typical MC run consists of 50,000 cycles for equilibration and 100,000 cycles for the production phase. Equilibration in MD is performed over 200,000 steps whereas the acquisition phase is carried out over 10^6 steps. The total simulation time for the production runs is 2 ns. The configurational temperature, the normal and tangential components of the pressure tensor, the surface tension and the coexisting densities are calculated every ten cycles for the MC simulation and every 100 steps for the MD simulation. This means that, in both methods, the calculation of the thermodynamic properties is performed over 10,000
configurations. The statistical errors in these properties are estimated using five blocks averages of 2000 configurations. For the geometry of the system, we expect there a dependence of the thermodynamic properties only in the direction normal to the interface. We have therefore calculated the profiles of the temperature, pressure, and surface tension and its long range correction as a function of \( z \) by splitting the cell into slabs of width \( \delta z \).

**C. Thermal equilibrium**

The configurational temperature \( T_{\text{conf}}(z_k) \) profile along the direction normal to the interface may be expressed as follows:

\[
k_BT_{\text{conf}}(z_k) = \left( \frac{\Sigma_{i=1}^{N} H_k(z_i)F_i^2}{\Sigma_{i=1}^{N} H_k(z_i)\frac{\partial F_i}{\partial r_{ix}} + \frac{\partial F_i}{\partial r_{iy}} + \frac{\partial F_i}{\partial r_{iz}}} \right),
\]

where \( F_i \) is the intermolecular force on molecule \( i \) acting upon the molecular center-of-mass \( r_i \), and \( H_k(z_i) \) is a top-hat function defined such that

\[
H_k(z_i) = \begin{cases} 
1 & \text{for } z_k - \frac{\delta z}{2} < z_i < z_k + \frac{\delta z}{2}, \\
0 & \text{otherwise}.
\end{cases}
\]

The configurational temperature profile can be calculated in both MC and MD simulations and can be compared in MD simulations with the temperature calculated from the molecular momenta, according to the following equation:

\[
k_BT_{z}(z_k) = \left( \frac{\Sigma_{i=1}^{N} H_k(z_i)m_i(v_{i,z} - v_{z})}{\Sigma_{i=1}^{N} H_k(z_i)} \right),
\]

where \( T_z(z_k) \) is the slab temperature in the \( z \) direction, and \( m_i \) and \( (v_{i,z}) \) are the molecular mass and \( z \) component of the velocity of the center of mass of molecule \( i \), respectively.

**D. Mechanical equilibrium**

In the case of an equilibrium planar interface, the Irving-Kirkwood definition (IK) (Refs. 37 and 38) of the pressure tensor leads to the following expression for the \( p_{\alpha\beta} \) component as a function of \( z \). The \( p_{\alpha\beta} \) component is thus composed of an ideal gas contribution \( p_{\alpha\beta}^{\text{kin}} \) and a potential part \( p_{\alpha\beta}^{\text{conf}} \), defined in Eqs. (8a) and (8b), respectively,

\[
p_{\alpha\beta}^{\text{kin}}(z_k) = \langle \rho(z_k)k_BT \rangle I,
\]

\[
\times \left( F_{ij}\rho \frac{1}{|r_{ij}|} \theta \left( \frac{z_k - z_i}{|z_k|} \right) \theta \left( \frac{z_j - z_k}{|z_k|} \right) \right),
\]

where \( \langle \cdots \rangle \) denotes a canonical ensemble average. \( \rho(z_k) \) is the molecular density profile along the \( z \) direction, \( I \) is the unit tensor, and \( T \) is the input temperature. \( \alpha \) and \( \beta \) represent \( x \), \( y \), or \( z \) directions. \( \theta(x) \) is the unit step function defined by \( \theta(x) = 0 \) when \( x < 0 \) and \( \theta(x) = 1 \) when \( x \geq 0 \). \( A \) is the surface area normal to the \( z \) axis. The distance \( |r_{ij}| \) be-
tical uncertainty.

We have also shown that the calculation of the surface tension is very sensitive to the cutoff value and necessitates the addition of long range corrections. Various analytical forms have been compared and the following form is used throughout this work to determine a profile along the direction normal to the interface.

\[ \gamma_{(lrc)}(z_k) = \frac{\pi}{2} \rho(z_k) \frac{V_c}{A} \int_{r_{i-1}}^{r_{i}} dr \int_{r}^{r_{i}} d\Delta z \sum_{i=1}^{n} \left[ \rho(z_i) - \rho(z_{i-1}) \right] \frac{d u_{LJ,m}}{d r} \left[ r^2 - 3(\Delta z)^2 \right], \]  

(12)

where \( \Delta z \) is equal to the difference \( z - z_k \), \( u_{LJ,m} \) is the intermolecular energy between two pentane molecules, and \( r \) is the difference between the two centers of mass. The total long range correction is calculated by summing up all the contributions to the local values of each slab and dividing the result by 2.

III. RESULTS AND DISCUSSIONS

A. MC and MD with truncated models

The aim of this section is to quantify the inconsistencies of the coexisting densities, critical temperature, and surface tensions along the coexistence curve of the \( n \)-pentane between the MC method using a truncated potential and the MD using a truncated force. We are using here for a polyatomic-heterogeneous molecular system the methods previously used for studying a simple LJ system.

Herein, we use a relatively small cutoff (\( r_c = 12 \text{\AA} \)) to maintain an objective of computational efficiency. As concerns the algorithmic specificities of the MC code, we use a truncated potential \( u_{LJ} \) in which we include long range contributions. The long range corrections to the total energy is composed of two terms: the first term depends on the local density and the second one takes into consideration that each slab is surrounded with neighboring slabs with different densities. We have also shown that the calculation of the second part is very cumbersome and that the fact of neglecting this term amounts to overestimate the long range correction of 13%. For computational efficiency, only the first part is considered. The long range correction is then calculated at every change in the position of a molecular center of mass, occurring during the translational and internal configurational moves. This tail correction is obtained by summing up the corresponding local contributions and then implemented in the acceptance rule. For the MD simulations, we use only a truncated and unshifted force and no long range correction is added to the force.

We compare the results for MC and MD at four different temperatures (299 K, 325 K, 350 K, and 375 K). The coexisting densities result from the fit to the molecular density profiles using Eq. (13)

\[ \rho(z_k) = \frac{1}{2} (\rho_l + \rho_v) - \frac{1}{2} (\rho_l - \rho_v) \tanh \left( \frac{2(z_k - z_o)}{d} \right), \]  

(13)

where \( \rho_l \) and \( \rho_v \) are the coexisting densities of the liquid and vapor phases, respectively. \( z_o \) indicates the position of the Gibbs surface and \( d \) represents the interfacial thickness. Figure 1(a) shows the coexisting densities calculated from MC and MD simulations. As should be expected from a force field established from MC simulations, we check in Fig. 1(a) that the phase envelope is better predicted using MC calculations than using MD. We note that the incorporation of the long range corrections into the truncated potential in MC improves the agreement with experiments. However, the magnitude of the differences observed between MC and MD is too important to be explained by only the presence of these long range corrections. In fact, deviations of the liquid and vapor densities from experimental values increases from

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The vapor density (\(\rho_v\)) and liquid density (\(\rho_l\)) are given in g cm\(^{-3}\). The total surface tension \(\gamma_{\text{tot}}\), represents the sum of the \(\gamma\) part calculated from Eq. (11) and of the long range correction contribution defined in Eq. (12). All the surface tension values are reported in mN m\(^{-1}\). The subscript indicates the accuracy of the last decimal (s). The number 0.556\(\pm\)0.010 means 0.556\(\pm\)0.010.

<table>
<thead>
<tr>
<th>(T/K)</th>
<th>(\rho_l)</th>
<th>(\rho_v)</th>
<th>(\gamma_{\text{conf}})</th>
<th>(\gamma)</th>
<th>(\gamma_{\text{tot}})</th>
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</thead>
<tbody>
<tr>
<td>MC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>299</td>
<td>0.609(\pm)0.00023(\pm)5.5, 11.3(\pm)16.8(\pm)5</td>
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</tr>
<tr>
<td>325</td>
<td>0.589(\pm)0.00065(\pm)4.8, 7.7(\pm)12.5(\pm)1</td>
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<tr>
<td>350</td>
<td>0.556(\pm)0.016(\pm)4.1, 6.9(\pm)11.0(\pm)0</td>
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<tr>
<td>375</td>
<td>0.526(\pm)0.024(\pm)3.2, 5.1(\pm)8.3(\pm)4</td>
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<tr>
<td>MD</td>
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<tr>
<td>299</td>
<td>0.584(\pm)0.009(\pm)4.7, 9.1(\pm)13.8(\pm)6</td>
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<tr>
<td>325</td>
<td>0.549(\pm)0.017(\pm)3.8, 6.2(\pm)10.0(\pm)0</td>
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<tr>
<td>350</td>
<td>0.506(\pm)0.035(\pm)3.0, 4.7(\pm)7.7(\pm)4</td>
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<tr>
<td>375</td>
<td>0.453(\pm)0.055(\pm)2.1, 2.9(\pm)5.0(\pm)3</td>
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The average temperature calculated in MD from the momenta matches also very well with the input temperature \(T_{\text{vap}} = 370\pm12\ K\) and \(T_{\text{liq}} = 377\pm5\ K\). We also check that the diagonal elements \(T_{xx}\) and \(T_{yy}\) are equivalent to \(T_{zz}\) within the fluctuations showing thus an equipartition of the kinetic energy in the three directions. The profiles of the off-diagonal elements of the temperature tensor fluctuate about a zero mean value, as expected for a system at thermal equilibrium. From the temperature profiles, we check that both MC and MD correctly sample the canonical ensemble and that the difference in coexisting densities and surface tensions between MC and MD are not due to shifts in the calculated temperature. Moreover, we check that thermal equilibrium of the liquid-vapor interface is obtained in both MC and MD.

From MC and MD simulations, we can draw the following conclusions: first, the MC calculations using the first part of the long range corrections to the configurational energy with a truncated potential and a relatively small cutoff yield coexisting densities and surface tensions in close agreement with the corresponding experimental values. This result is consistent with the fact that the set of LJ parameters of the force field has been developed from MC calculations. Second, the phase diagram of the \(n\)-pentane calculated from the MD method with a truncated force is shifted to the low temperatures. This particularity is in line with what it was observed in previous simulations of the liquid-vapor coexistence curve of LJ fluids.\(^{15,14}\) The fact that the potential function is not differentiable at the cutoff value makes the MC and MD calculations different. Moreover, the differences are slightly increased by the fact that MC uses a potential modified by the presence of long range corrections. Consequently, in what follows, we try to evaluate the importance of the truncation procedures on different potential functions and to analyze the magnitude of the discrepancies between MC and MD when the potential and force equations change accordingly.

### B. MC and MD with truncated and shifted models

We compare, in Fig. 2(a), the density profiles calculated both from MC using a truncated \(u_T\) potential using Eq. (14) without any long range corrections applied to the potential and from MD using a truncated \(f_T\) force according to Eq. (16). We also add for comparison the density profiles resulting from MC using the truncated potential, corrected by long range corrections to the configurational energy and from MD using a truncated and shifted \(u_{T_{c51}}\) potential defined in Eq. (15). We check in Fig. 2(a) and in Table II that the incorporation of long range corrections to the total energy increases the liquid density and decreases the vapor density leading thus to surface tension slightly larger and closer to the experimental value. This particularity, already observed in a previous work,\(^{23}\) confirms that a better prediction of the coexistence properties is observed when the long range corrections are included in the Metropolis scheme. Second, MC calculations with the \(u_{T_{c51}}\) model, where a constant term is present.

### Table I. Simulation results for \(n\)-pentane using MC and MD calculations.

The vapor density (\(\rho_v\)) and liquid density (\(\rho_l\)) are given in g cm\(^{-3}\). The total surface tension \(\gamma_{tot}\), represents the sum of the \(\gamma\) part calculated from Eq. (11) and of the long range correction contribution defined in Eq. (12). All the surface tension values are reported in mN m\(^{-1}\). The subscript indicates the accuracy of the last decimal (s). The number 0.556\(\pm\)0.010 means 0.556\(\pm\)0.010.
TABLE II. Simulation results for n-pentane using MC and MD calculations with different analytical shapes for the potential energy and the force at $T = 325$ K. The vapor density $\rho_v$ and liquid density $\rho_l$ are expressed in g cm$^{-3}$. The total surface tension $\gamma_{tot}$, the $\gamma$ part and its long range corrections are reported in mN m$^{-1}$. The experimental data result from Dortmund Data Bank.$^{42}$ The subscript indicates the accuracy of the last decimal (s). The number 0.589, means 0.589 ± 0.006.

<table>
<thead>
<tr>
<th></th>
<th>$\rho_l$</th>
<th>$\rho_v$</th>
<th>$\gamma_{lrc}$</th>
<th>$\gamma$</th>
<th>$\gamma_{tot}$</th>
</tr>
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<tr>
<td>Expt.</td>
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<td>0.0052</td>
<td>12.3</td>
<td></td>
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<tr>
<td>$T = 328$ K</td>
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<tr>
<td>MC</td>
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<td>0.0065</td>
<td>4.81</td>
<td>7.710</td>
<td>12.510</td>
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<tr>
<td>$u_T + \Sigma u_{lrc}$</td>
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</tr>
<tr>
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<td>0.0192</td>
<td>4.11</td>
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<tr>
<td>$u_{TS1}$</td>
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<tr>
<td>MC</td>
<td>0.520</td>
<td>0.0294</td>
<td>0</td>
<td>3.416</td>
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<td>6.217</td>
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<tr>
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<td>0</td>
<td>8.017</td>
<td>8.017</td>
</tr>
<tr>
<td>MD</td>
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<td>0.0114</td>
<td>0</td>
<td>8.017</td>
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</tbody>
</table>

The study of the components of the pressure tensor is very instructive. As concerns the pressure profiles computed from MD simulations [Fig. 2(b)], we check that the profiles of the ideal $p^{id}$ and kinetic $p^{kin}$ components are equivalent and superimposed in Fig. 2(b) and cannot be distinguished on the scale of the figure. The kinetic part profile calculated from the momentum flux using the method of planes presents local values located on both sides of the profile of the ideal part. The kinetic part calculated both from the Irving-Kirkwood and MOP definitions are shown to be similar within the statistical uncertainties with a noisier profile for the MOP method. The profiles of the potential part of $p_{zz}$ component calculated from these two methods are very close, as it was already shown for MC calculations.$^{24}$ The normal pressure is constant throughout the simulation box. The tangential pressure has also the same value in the liquid and vapor phases and is equal to the normal pressure away from interface regions. The tangential pressure presents two negative peaks at the interfaces showing that the liquid phase is under compression. We also note that the configurations calculated from MD with the $f_T$ force are in mechanical equilibrium, as expected from a method which uses directly the forces to generate the evolution of the system. It means that the profiles of the pressure components need not be corrected by the addition of long range corrections to obtain mechanical equilibrium. On the other hand, these corrections were required to demonstrate the mechanical equilibrium in the case of MC simulations using a truncated potential with its long range corrections incorporated in the Metropolis scheme.$^{24}$ Figure 3(a) displays the profiles of the tangential and

FIG. 2. (a) Density profiles calculated at $T = 325$ K from different truncation procedures and methods. MC, $u_T + \Sigma u_{lrc}$, (—); $u_T$, (○); MC, $u_{TS1}$, (●); MD, $f_T$, (■); (b) normal (—) and tangential (—) pressure profiles calculated from the IK method in MD using a truncated force. (●) normal components (kinetic, potential, and total) parts calculated from the method of planes. $p^{id}$ and $p^{conf}$ indicate the different contributions; the ideal gas contribution is represented by (○) and the kinetic part by (●). The curves in the center of the part (b) correspond to the total pressure expressed as the sum of the ideal and potential parts.
values of the normal and tangential components of the pressure are approximately the same in the vapor phase and in the liquid phase but differ between the two phases, indicating thus that apparently the configurations resulting from MC are not in mechanical equilibrium. In contrast to molecular dynamics method, Monte Carlo generates configurations by calculating the change in energy. The comparison between MC using a truncated potential and a MD using a truncated force is not really pertinent for a two phase system. Actually, the introduction of a cutoff leads to a discontinuity in both the potential energy and the force at \( r_c \). At the cutoff distance, the force and the potential have a finite value which drops suddenly to zero just beyond the cutoff. It means that truncating the force at the cutoff leads to small impulses on atoms \( i \) and \( j \) when the distance \( r_{ij} \) exceeds \( r_c \). To take into account this impulsive correction to the pressure tensor components, we follow the method already used by Trokhymchuk and Alejandre\(^{13} \) which consists to add a \( \delta \) function in the definition of the force as in Eq. (17),

\[
    f_{TC}(r_{ij}) = \begin{cases} 
        -\frac{\partial u_{LJ}}{\partial r_{ij}} & r_{ij} < r_c \\
        \frac{u_{LJ}(r_c)}{\Delta r} & r_c \leq r_{ij} < r_c + \Delta r \\
        0 & r_{ij} \geq r_c + \Delta r 
    \end{cases}
\]

In Eq. (17) \( \Delta r \) is taken equal to 0.05 Å. Figure 3(b) presents the profiles of the normal and tangential components calculated with the \( f_{TC} \) force. The introduction of the \( u_{LJ}(r_c)/\Delta r \) contribution between \( r_c \) and \( r_c + \Delta r \) is sufficient to change significantly the profile of the potential part. In fact, the local values of the \( p_N \) and \( p_T \) components are now the same in the liquid phase and in the vapor phase. The normal component becomes constant throughout the interface. The configurations generated with MC using the \( u_T \) potential are shown to be in mechanical equilibrium on condition that the \( f_{TC} \) force is used in the pressure tensor calculation. The part of the surface tension calculated from the virial expression is equal to 8.6 mN m\(^{-1} \) using the \( f_{TC} \) force whereas it is equal to 7.3 with \( f_T \). As it can be seen in Fig. 3(b), the presence of this impulsive contribution to the pressure makes the peaks of the tangential part throughout the interface regions more negative in agreement with a higher value of the surface tension. In the work of Trokhymchuk and Alejandre,\(^{13} \) it has been reported that MD using the \( f_T \) force corresponds to MC using the \( u_T \) model and MD with the \( f_{TC} \) force to MC using the \( u_{TS1} \) model. Our simulations also show that the best agreement between MC and MD using truncated potential and force is found between MC with \( u_{TS1} \) and MD with \( f_T \). However, a more satisfactory agreement will not be obtained as long as the force is discontinuous at \( r_{ij} = r_c \).

In fact, all the analytical forms of potentials we have used, up to now for this comparison, involve a discontinuity in their derivative with respect to \( r_{ij} \) at the cutoff distance and are not differentiable at the cutoff value.

To avoid a discontinuity of the derivative of the potential, we now add an additional term \((r_{ij} - r_c)(\partial u_{LJ}/\partial r_{ij})_r\) making thus the derivative of the potential zero at the cut off.
The potential and the force are expressed in Eq. (18) and in Eq. (19), respectively. A discontinuity remains in the derivative of the force, not in the force itself.

\[
\begin{align*}
  u_{TS2}(r_{ij}) & = \\
  & = \begin{cases} 
    u_{LJ}(r_{ij}) - u_{LJ}(r_c) - (r_{ij} - r_c) \frac{\partial u_{LJ}}{\partial r_{ij}} & r_{ij} < r_c, \\
    0 & r_{ij} \geq r_c
  \end{cases}, \\
  f_{TS}(r_{ij}) & = \\
  & = \begin{cases} 
    -\frac{\partial u_{LJ}}{\partial r_{ij}} + \left(\frac{\partial u_{LJ}}{\partial r_c}\right) & r_{ij} < r_c, \\
    0 & r_{ij} \geq r_c
  \end{cases}. 
\end{align*}
\]

(18)

(19)

We show in Fig. 4(a) that MC using the \( u_{TS2} \) model and MD using the \( f_{TS} \) yield close density profiles leading to a deviation between the liquid densities of 2% (Table II). Figures 4(b) and 4(c) show that the profiles of the tangential and normal parts of the pressure tensor, calculated both in MC and MD, are similar within statistical fluctuations and that the configurations resulting from the two methods are in mechanical equilibrium. When shifted force or shifted potential are used to calculate surface tension, long range corrections to the surface tension must be included to account for both the long range interactions and the shift. Such long range corrections are approximate\(^{45} \) and not easy to calculate. Consequently, we prefer to compare the surface tension values over the contribution calculated from the virial route in Eq. (11). The calculated values (Table II) can be considered as very close with the standard deviations. We conclude that the truncated and shifted potential \( u_{TS2} \) model and the truncated and shifted \( f_{TS} \) force do lead to the same point in the coexistence curve and that the mechanical and thermal equilibria are respected for MC and MD. We see that taking the derivative of the potential continuous at the cutoff radius is the key to yielding an agreement between both methods.

C. MC and MD with models modified by switching functions

In order to avoid any problems concerning both the discontinuity in the potential and in the gradient of the force at the cutoff radius and the use of the long range corrections, we define consistent potential and force by taking the force and its derivative zero at the cutoff value. To do this, we use the Lennard–Jones potential \( u_{LJ}(r_{ij}) \), modified by a cubic spline\(^{46-48} \) to give the following expressions for the potential and the force:

\[
\begin{align*}
  u_{SP}(r_{ij}) & = \begin{cases} 
    u_{LJ}(r_{ij}) - u_{LJ}(r_c) + a & r_{ij} < r_s, \\
    -\frac{b}{3}(r-r_c)^3 - \frac{c}{4}(r-r_c)^4 & r_s \leq r_{ij} < r_c, \\
    0 & r_{ij} \geq r_c
  \end{cases}, \\
  f_{SP}(r_{ij}) & = \\
  & = \begin{cases} 
    -\frac{\partial u_{LJ}}{\partial r_{ij}} & r_{ij} < r_s, \\
    \frac{b}{3}(r-r_c)^2 + \frac{c}{4}(r-r_c)^3 & r_s \leq r_{ij} < r_c, \\
    0 & r_{ij} \geq r_c
  \end{cases}. 
\end{align*}
\]

(20)

(21)

The parameters \( a, b, \) and \( c \) are calculated by requiring that the first and second derivatives of the \( u_{SP} \) potential be continuous at \( r_s \) and \( r_c \).

\[
c = -\frac{\partial^2 u_{LJ}}{\partial r_{ij}^2}(r_c) \left(\frac{\partial u_{LJ}}{\partial r_{ij}}(r_c)\right)^2 + 2 \left(\frac{\partial u_{LJ}}{\partial r_{ij}}(r_c)\right)^3.
\]

FIG. 4. (a) Density profiles at \( T = 325 \) K calculated in MC (○) using the \( u_{TS2} \) potential model and in MD (■) with the \( f_{TS} \) force; normal (—·—·) and tangential (——,——,——) pressure profiles calculated in both (b) MC, and (c) MD.
changing the potential function obviously amounts to signifi-
cantly deviate the coexisting densities from the experimental
values. The profiles of the tangential and normal components
can be considered as similar for MC [Fig. 5(b)] and MD
[Fig. 5(c)] within statistical fluctuations. We note that the
oscillations of the pressure components calculated in the li-
quid phase are more marked in MC than in MD. From these
pressure profiles, we may deduce the following equalities in
the homogeneous phases \( p_F^v = p_F^l = p_T^v = p_T^l \), where the
superscripts \( v \) and \( l \) refer to the vapor and liquid phases, re-
spectively. The configurations generated using both MC and
MD are in mechanical equilibrium and correspond to the
same point on the phase diagram. The surface tension values
evaluated from the virial part are very close within the stan-
dard deviations calculated from the block averages. No trun-
cation corrections must be added to the surface tension. As
the long range contribution of the surface tension can reach
up to 40% of the total value, it means that the surface tension
calculated with a potential truncated via a cubic spline devi-
ates very much from the experimental value. A calibration of
this potential is thus required to predict accurate surface ten-
vation value and coexisting densities. We also observe that the
increase in the cutoff radius \( r_c = 15 \, \text{Å} \) and \( r_c = 14 \, \text{Å} \)
veys significantly the coexisting densities and the surface
tension values. The profiles of the tangential and normal com-
ponents of the pressure calculated in both (b) MC and (c) MD.

MC simulation using the \( u_{SP} \) potential is compared with
MD simulation using the \( f_{SP} \) force. We take the cutoff radius
\( r_c = 12 \, \text{Å} \) and \( r_s = 11 \, \text{Å} \). As expected, the density profiles,
shown in Fig. 5(a), calculated from MC and MD simulations
match very well. The liquid and vapor densities are identical
within the statistical uncertainties (Table II). However,

\[
\begin{align*}
\frac{\partial^2 u_{LF}}{\partial r_{ij}^2}(r_c) &= -3 \frac{\partial u_{LF}}{\partial r_{ij}}(r_c) \\
&= \frac{b}{(r_s - r_c)^3} - \frac{c}{4} (r_s - r_c)^4.
\end{align*}
\]

An other important result we can extract from this study
is that MD using standard force fields, which have been es-
ablished from MC simulations, cannot predict accurately the
phase diagram and the surface tension of \( n \)-alkanes. Using
such force field, only MC calculations using a truncated poten-
tial can give accurate predictions for both the coexisting
densities and surface tension when a rigorous calculation of
the long range correction to the surface tension is applied.
The implementation of the long range corrections to the con-
figurational energy to the Metropolis scheme slightly in-
creases the coexisting densities. It means that if we wish to
make MC and MD consistent techniques for the prediction of
the phase envelope of alkanes and for the use of long range
corrections, one solution is to use a Lennard-Jones potential
modified by a cubic spline. In this case, a new calibration is
required and the development of new set of potential param-
eters is necessary, making inappropriate the present force
fields of the literature.

D. Structural properties of the \( n \)-pentane chain

Concerning the conformation of the \( n \)-pentane, we cal-
culate the profile along the direction normal to the interface

FIG. 5. (a) Density profiles at \( T = 325 \, \text{K} \) calculated in MC (□) using the \( u_{SP} \)
model and in MD (■) with the corresponding \( f_{SP} \) force. The dashed curve
represents the density profile calculated in MD using a cubic spline with
er a cutoff radius of 15 Å instead of 12 Å; normal (−−−) and tangential
(−−−−) pressure profiles calculated in both (b) MC and (c) MD.
of the end-to-end distance of the molecule for MC and MD. These profiles are indistinguishable between MC and MD and do not depend on the truncation procedures. Further oscillations around the mean value are observed in the vapor phase. The mean value of the end-to-end distance calculated from the different slabs is 4.78 ± 0.03 Å for MC and 4.79 ± 0.03 Å for MD at T = 299 K. This same average distance decreases up to 4.72 ± 0.01 Å for MC and MD when the temperature is increased at 375 K. The comparison of the conformation shows that MC and MD lead to the same average structure of the n-pentane and to the same evolution of the structure as a function of temperature.

E. Dynamical properties of the liquid-vapor interface

To precisely investigate the sampling of the system along the z direction, we calculate the percentage of molecules which were found at least once inside the liquid and vapor phases over the 10,000 saved configurations. This percentage increases from 58% to 80% for MC and from 67% to 97% for MD as the temperature is increased from 299 K to 375 K. These percentages show that the sampling of the liquid-vapor system in the z direction is almost equally performed by MC and MD. The implementation of the algorithm allowing to use randomly two different magnitudes for the displacements makes the MC method competitive compared to MD for the moves of the molecules along the direction normal to the interface. One of the advantages of MD is the possibility of studying the dynamical properties at the interface, as for example, the residence time of pentane molecules in the interfacial region. The mean residence time is calculated from the correlation function \( r(t) \) defined as

\[
r(t) = \frac{\langle P_j(t,t_1; t^*) \rangle_f}{\langle P_j(0,t_1; t^*) \rangle_f},
\]

(23)

where \( P_j(t,t_1; t^*) \) is the Heaviside unit step function which is equal to 1 if the pentane molecule \( j \) lies within the interface region at both time \( t \) and \( t + t^* \), and in the interim does not leave the interfacial zone for any continuous period longer than \( t^* \). Otherwise, the unit step function is equal to zero. This function gives a probability for a pentane molecule to stay in the interface region during time \( t \). The parameter \( t^* \) is introduced to take into account molecules which leave the interface temporarily, but for a time period shorter than \( t^* \). The calculations are carried out using different values of \( t^* \) within the range 0.6–10 ps. The time correlation function \( r(t) \) can be fitted to a second-order exponential decay:

\[
r(t) = A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right).
\]

(24)

In Eq. (24), the first term corresponds to an escape of the molecules located close to the border of the interface at a time about \( \tau_1 \) ps. The second term describes a persistence of the molecules in the interface and \( \tau_2 \) corresponds to the residence time of pentane molecules at the liquid-vapor interface. Roughly, the fitted parameters \( A_1 \) and \( A_2 \) can be interpreted as the percentage of molecules involved in both processes. We calculate the residence time of the molecules in the interface region by delimiting the interface region with two \( z \) positions. Each position is given within a fluctuation of ±3 Å, which is taken into account in the calculation of \( r(t) \). The residence time \( \tau_2 \) in the interface region at \( T = 325 \) K increases from 22 ps to 46 ps as \( t^* \) is increasing from 0.6 ps to 10 ps. Although the choice of \( t^* \) is somewhat arbitrary, it can be seen that \( \tau_2 \) is weakly dependent on the value of \( t^* \). More exactly, between 0.6 ps and 2 ps, \( \tau_2 \) is insensitive to the value of \( t^* \) whereas values of \( t^* \) varying from 2 to 20 ps affect significantly the residence time values. The \( r(t) \) curves calculated using a value of \( t^* \) of 2 ps at the interface region are displayed in Figure 6 for \( T = 325 \) K and \( T = 350 \) K. This value of 2 ps has been already used in previous works but with different systems. In addition, it is not clear that such a value of 2 ps is the most appropriate for the liquid-vapor interface system. Because of the dependence of \( t^* \) on \( T \), it is difficult to extract a correlation between \( T \) and \( \tau_2 \). When \( t^* \) is fixed to 2 ps, we find a value of \( \tau_2 \) equal to 27 ps and 33 ps for \( T = 325 \) K and \( T = 350 \) K, respectively. It means that the variation of \( \tau_2 \) with the temperature is much less marked than that of \( \tau_2 \) with the parameter \( t^* \). Less than 30% (\( A_1 \)) of the pentane molecules are located close to the border to the interface and leave this zone at a time of about 3 ps (\( \tau_1 \)). This work represents the attempt to calculate the residence time of molecules at the interface region. A previous work has calculated the residence time of water molecule at the liquid-vapor interface and the authors have found a residence time of the order of 2 ps. From the calculation of the residence time of \( n \)-pentane molecules, we can only say that the residence time in the interface region ranges roughly from 20 to 50 ps.

IV. CONCLUSIONS

This work lies within the framework of direct molecular simulations of interfaces. As we have shown in the beginning of this paper, there is a great variety of direct simulations in the liquid-liquid and liquid-vapor interfaces, differing in their methodologies, energetic potential models (electrostatic contributions, polarization effects, and truncation procedures), and the technique used (MC and MD). This diversity results in important difficulties to discriminate between the different
We have established an efficient methodology for the determination of the coexistence properties and surface tension of the n-pentane using the MC approach. When dealing with neutral molecules such as alkanes, we need not to take into account the way of describing the electrostatic and polarization contributions. Consideration must be only given to the way the nonbonded Lennard-Jones interactions are truncated. In addition, the study of the dynamical properties of the molecules at the interface region requires to make MC and MD results in agreement.

In this paper, we have performed various comparisons between MC and MD results on the basis of the values of coexisting densities and surface tension. We have shown that the MC simulations combining both the use of a truncated potential and the incorporation of the long range corrections to the configurational energy with the use of a moderate cut-off radius provide a good agreement between the calculated properties and the corresponding experimental values. Using force fields which have preliminary been established for alkanes from MC, it is expected that the direct MC calculations predicts much better than MD the phase coexistence properties and surface tension of alkanes. We have quantified the differences between the MD calculations using a truncated force and MC calculations using a truncated potential. This result is in line with what it was already observed in previous simulations involving MC and MD techniques of the LJ fluid liquid-vapor interface. These discrepancies are due to the fact that the potential function is not differentiable at the cutoff value, which therefore makes that the force in MD does not correspond to the potential in MC. However, we note that shifting the potential in MC improves the agreement with MD.

A satisfactory agreement between MC and MD can be obtained by using a shifted-force potential for which the derivative of the potential is continuous at the cutoff radius. To obtain a close agreement between MC and MD and avoid any long range interactions, we suggest changing the LJ potential by the addition of a polynomial function making thus any long range interactions, we suggest changing the LJ potential by the addition of a polynomial function making thus the force in MD does not correspond to the potential in MC. However, we note that shifting the potential in MC improves the agreement with MD.

Concerning the structural properties of pentane, no difference has been found on the end-to-end distance between MC and MD and the potential models. In addition, we have shown that the two methods predict the same evolution of the end-to-end distance as a function of the temperature. One of our objectives was to calculate the residence time of the n-pentane molecules at the liquid-vapor interface. To do so, we have developed a specific algorithm and established a computational procedure. The residence time of the pentane molecules at the liquid-vapor interface ranges approximately from 20 ps to 50 ps.

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