Coexistence Densities of Methane and Propane by Canonical Molecular Dynamics and Gibbs Ensemble Monte Carlo Simulations

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We present preliminary canonical molecular dynamics (MD) and Gibbs ensemble Monte Carlo (GEMC) results for the vapour–liquid orthobaric densities of methane and propane. Computational advantages and drawbacks of both simulation methods are discussed and future work is outlined on the application of these techniques to the calculation of transport and interfacial properties. n-Alkanes are described through the TraPPE-UA force field. We study the effect of the truncation of interactions in the Lennard–Jones potential on the accuracy of the orthobaric liquid densities for these inhomogeneous systems along the phase diagram. We observed that a cut-off of at least 5.5 times the Lennard–Jones diameter is needed to obtain accurate results for saturated liquid densities.

INTRODUCTION

Molecular simulations are undoubtedly becoming a standard and powerful tool in science and engineering, increasingly providing answers to a broad range of fundamental and industrial problems. Of particular importance in many technological applications in the chemical and petrochemical industries is knowledge of the phase behaviour of hydrocarbons. Since the pioneering work of Siepmann et al. [1], much effort has been devoted in the recent years to the development of accurate force fields for hydrocarbons using molecular simulations. Among the recently proposed models for n-alkanes with the united-atom approach the most accurate ones are: the NERD force field developed by de Pablo and co-workers [2], the TraPPE-UA model proposed by the group of Siepmann [3] and the model proposed by Errington and Panagiotopoulos (which we shall denote EP) [4]. The TraPPE-UA and the NERD models reproduce well the critical parameters and the saturated liquid densities of n-alkanes over a wide range of chain lengths, although they are less accurate for the saturated vapour densities and vapour pressures. On the other hand, the EP model is able to describe more accurately the vapour pressures and critical properties. All these models have been used to predict, with no additional fitting, the phase diagram of binary mixtures of n-alkanes, including short and long chains, finding, in general, good agreement with experimental data.

All the simulations mentioned above were performed using the Gibbs Ensemble Monte Carlo (GEMC) technique, with additional algorithms to improve the sampling of the phase space, or to increase the acceptance probability for insertion/deletion. Due to its simplicity, speed and accuracy in predicting the equilibrium properties of both phases in a single simulation, GEMC [5] has become the standard method to compute phase equilibria properties through molecular simulations. However, it should be mentioned that the molecular dynamics (MD) method was employed long before for phase equilibria predictions of simple fluids, as already reported in the pioneering work of Ladd and Woodcock [6], and on that of Holcomb et al. [7,8], some years later. The simulations were performed putting in physical contact two bulk phases previously equilibrated through NVT MD
simulations. Nevertheless, as Ladd and Woodcock mentioned in their paper, at that time there were severe limitations on running these simulations, i.e. the total number of molecules one could deal with was very small, and also the total simulation time was very limited. Now-a-days, increasing computer power makes direct simulations of the interface by Monte Carlo (MC) or canonical MD increasingly more attractive, since both of the limitations previously mentioned can be overcome. A clear advantage of them over the GEMC method is that they yield microscopic information on the interfacial region and thermodynamic properties such as the surface tension, in addition to phase equilibrium properties in both phases. Moreover, MD can provide dynamical properties in the same simulation run, such as the residence time of molecules at the interface and the self-diffusion coefficient in both phases and at the interface.

A main drawback of these MD and MC approaches is the difficulty to stabilize the interface when the density difference between the coexisting phases is small, as occurs in the near critical region, a consequence of the finite-size effect of the simulations. We should note the GEMC method also deals with the same problems near the critical point. Additionally, MC methods encounter problems when simulating dense systems, where low acceptance probabilities may cause obtaining results to be impractical. Although this limitation has been overcome to a large degree by making use of the configurational-bias techniques, it is still very costly to obtain LLE equilibria of mixtures by MC simulations. On the other hand, as pointed out by Gelb and Müller [9], MD has an advantage when simulating systems at very high densities, since it does not require insertion into the dense phase, and it is particularly suitable for the study of multi-component systems or more complex molecules.

This paper is part of an on-going work in calculating several equilibrium and dynamical properties of some industrial relevant fluids. Our mid-term goal is to employ the MD technique for the computation of thermodynamic and structural properties, which, in addition to providing vapour–liquid equilibrium data, will allow us to simultaneously investigate the dynamics of the interface formation, to compute transport coefficients and to study the structure of the interface, as well as the surface tension. In particular, simulation results for the surface tension will allow a direct comparison and testing of theoretical calculations. Here, as a first step on this work, we check the accuracy and performance of our program on providing the coexistence densities of some fluids, as compared to experimental data.

Accurate results for the vapour–liquid phase equilibria and surface tension of chlorine and hexane were obtained by Alejandre et al. [10] through MD simulations. They outlined the advantages and drawbacks of MD and GEMC methods for chain molecules and addressed the two major difficulties associated with the truncation of interactions in inhomogeneous systems: (1) truncation of the forces in MD results in a shift of the truncated potential used in MC, i.e. the models are, a priori, different, and this has a significant influence in phase equilibrium calculations and (2) truncation of the interactions have a considerable effect on phase equilibrium properties. Both effects were quantified later by Trokhymchuk and Alejandre [11] for the monatomic Lennard-Jones (LJ) fluid. The effect of the potential truncation on the chemical potential and other thermodynamic properties of the LJ fluid has also been addressed in a recent paper by Shi and Johnson [12]. They used the GCMC method combined with histogram reweighting techniques, arriving to similar conclusions as Ref. [11] regarding the influence of the cut-off on the phase equilibria properties.

Transport properties were also computed using MD by Rivera et al. [13] for nitrogen and butane mixtures. They parameterised the NERD force field for nitrogen with the GEMC technique and employed MD simulations to compute diffusion coefficients, surface tension and shear viscosity of the mixture, as a function of the temperature. They approximated the full potential by truncating the interactions at a large cut-off and did not apply long-range corrections to the configurational energy in the MD calculations. The importance of the cut-off value

![Figure 1](image-url)  
**FIGURE 1** Coexistence curve of methane from MD (circles) and GEMC (squares) calculations compared to experimental data [20]. The influence of the cut-off radius is shown at 150 K.
used is seen in Fig. 1 of their paper, where for a value of 4.3 the full potential is not reached, leading to lower saturated liquid densities for pure nitrogen.

In more recent works, Goujon et al. [14,15] investigated vapour–liquid equilibrium properties of n-pentane by direct MC simulations, implementing a method for incorporating long-range corrections in inhomogeneous fluids. Comparison to experimental data showed the importance of the cut-off (and the long-range corrections) in these calculations. Goujon et al. also determined the surface tension of n-pentane as a function of temperature through calculation of the pressure tensor. A conclusion from their work is that the deviations between the calculated surface tension and those obtained from a generalized equation for the surface tension, from the triple point to the critical point, decrease as the cut-off is increased. However, little dependence on the cut-off radius is observed if long-range corrections are applied. They suggested simulations using the MD technique to compare with the thermodynamic equilibrium properties obtained by direct MC simulations.

It is clear that molecular simulations are also very useful to test and refine molecular models in a systematic way, since they provide exact data for a given potential model. However, computational limitations may still affect the accuracy of simulation results for complex systems, as can occur with multi-branched, highly polar, or long polymer molecules, and for multicomponent or multiphase systems. Such limitations are nearly always driven by three factors: system size, truncation of interactions and equilibration time. Nowadays, system size is rarely a factor when dealing with simple systems, since large numbers of small molecules are easily simulated, even on todays PCs. Truncation of the pair potential may or may not be a significant source of error. For example, many pair potentials in the field of biological simulation are parameterised with a cut-off assumed; hence, using a cut-off in calculations with these potentials is only problematic if the cut-off used is different from that used to parameterise the potential. Generally, however, potentials are parameterised using long-range corrections (i.e. essentially no cut-off). In simulating coexistence by MD, the question of a cut-off becomes quite important, since the incorporation of a long-range correction is non-trivial (see, for example, Ref. [16]). A straight solution is to use a cut-off as large as is necessary to ensure the results are essentially independent of cut-off and not attempt to apply a long-range correction for the non-uniform fluid. Trokhymchuk and Alejandre [11] studied the influence of the cut-off on phase equilibrium properties for the LJ fluid from MD simulations. Less is known about the influence of truncation in the case of chain-like molecules such as the alkanes.

While the cut-off used is an important determinant of actual computer time used for simulating a given system (execution time will increase at least linearly and at worst quadratically in the cut-off), for most simulations, the equilibration time—measured as the longest relaxation time in the system—is generally the primary determinant of the computational cost of a simulation. For MD, the time to form and stabilize the interface can be long, especially in the case of large molecules that diffuse slowly and have long internal relaxation times. The time required for collection of statistics is also driven by the longest relaxation time in the system, since to obtain reliable statistical measurements of the properties of interest, typically one must collect averages over several relaxation times.

This work is focused on the prediction of orthobaric densities of methane and propane by both MD and GEMC. We study the influence of the truncation of interactions on the accuracy of coexistence densities, and obtain additional properties, such as density profiles, and the time dependence of selected properties by MD.

**MODEL AND SIMULATION DETAILS**

The TraPPE-UA force field describes n-alkanes as united-atom (UA) cores interacting through a Lennard–Jones 12–6 potential when they belong to different molecules or are separated by more than three bonds within the same molecule,

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

where \( \varepsilon_{ij} \) is the energy parameter of the interaction, \( \sigma_{ij} \) is the Lennard–Jones (LJ) core diameter and \( r_{ij} \) is the distance between interaction sites \( i \) and \( j \). In MD, we truncate interactions using a cut-and-shifted potential, which corresponds to truncated forces. The LJ parameters for the interaction sites of the TraPPE-UA model were fitted by Martin and Siepmann [3] to critical temperatures and saturated liquid densities. They are summarized in Table I. United-atom cores are connected by bonds at an equilibrium distance of 1.54 Å. The TraPPE-UA model also accounts for intramolecular forces, which, apart from the non-bonded LJ interactions, include bond angle bending and the torsion of

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>Interaction potential parameters of the TraPPE-UA model</th>
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<tbody>
<tr>
<td></td>
<td>( \varepsilon/\kappa_0 ) [K]</td>
</tr>
<tr>
<td>CH4</td>
<td>148</td>
</tr>
<tr>
<td>CH3 (n-alkane)</td>
<td>98</td>
</tr>
<tr>
<td>CH2</td>
<td>46</td>
</tr>
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</table>
dihedral angles. Dihedral angles apply for molecules with more than four carbons, i.e. from butane on. Bond angle bending is governed by the harmonic potential

\[ u_{\text{bend}} = \frac{k_{\theta}}{2} (\theta - \theta_0)^2, \]

with the force constant \( k_{\theta}/k_B = 62.500 \text{ K rad}^{-2} \), where \( k_B \) is the Boltzmann’s constant. The equilibrium angle between three consecutive united-atom cores is set to \( 114^\circ \).

In the canonical MD technique we use here, a fixed number of molecules is initially placed in a simple cubic lattice and the fluid then melted to an established liquid density. Once the system is equilibrated, the box is suddenly enlarged in one of its dimensions forming a rectangular parallelepiped, thereby fixing a constant equilibrium global density that lies between the corresponding coexisting densities at the simulation temperature, and thus allowing the interface and the vapour phase to form. Finite size effects play an important role in the MD technique, mainly because of the high energy cost of forming the interfaces. The energy barrier can be sometimes so high that the system does not have enough energy to cross it. Hence, system sizes need to be much larger than those normally used in GEMC simulations. For example, for \( n \)-propane, we could not stabilize the interfaces with less than approximately 2000 molecules. As a guide, the number of molecules \([11]\) should be larger than 1000 and the shortest dimension of the box should measure not less than \( 10\sigma \), even for simple LJ spheres.

We have used the reversible multi-time step RESPA algorithm \([17]\) to integrate the equations of motion with a large time step of 5 fs and a small time step of 0.5 fs. The canonical ensemble is generated by the Nosé-Hoover thermostat. Instead of using a constrained integration algorithm, such as RATTLE \([18]\), we included a bond stretching potential \([19]\)

\[ u_{\text{stretch}} = \frac{k_l}{2} (l - l_0)^2, \]

which is a harmonic function around an equilibrium bond length \( l_0 = 1.54 \text{ Å} \) and with a large spring constant \( k_l/k_B = 452.900 \text{ K m}^{-2} \). This effectively maintains the bonds at the fixed length \( l_0 \) and has a negligible effect on the phase diagram \([19]\). Neighbour lists with a cut-off skin of 0.3\( \sigma \) are used in the calculation of non-bonded forces. The choice of skin width means that the recalulation of the neighbour list takes place only when the maximum displacement inside the interaction cut-off plus the cut-off skin exceeds 0.15\( \sigma \). After 50 000 time steps the box is suddenly enlarged in one Cartesian direction to form a parallelepiped with a side ratio of 2.5, allowing the interface to form. Properties are continuously monitored in block averages of 500 fs. Density profiles are determined by dividing the simulation box into 500 slabs, and calculating the density in each slab with respect to the centre of mass of the system, every 5000 time steps. By monitoring the Hamiltonian and the density profile we can check the equilibration of the interfaces. After equilibrating the system, further averaging for at least 125 000 time steps is performed.

There are two important practical aspects to consider when enlarging the simulation box on these MD simulations. On one hand, the volume of the box should be chosen such that the overall density in the box is close to the line of rectilinear diameters. In this way, liquid and vapour volumes in the box become similar and both vapour–liquid interfaces are almost equally distant between them by the liquid and the vapour sides. On the other hand, and related to the latter, the number of molecules must be large enough to satisfy the condition that the distance between both interfaces is larger than twice the cut-off radius. This avoids the situation in which a molecule simultaneously interacts with others located at both interfaces. Consequently, the larger the cut-off radius is, the larger the number of molecules to be simulated. Table II summarizes the initial conditions for the MD simulations, where the global density in the box is included.

We have also performed GEMC simulations, in combination with the configurational-bias Monte Carlo method (CBMC), to check the computational time needed to reproduce the simulation data published by Martin and Siepmann \([3]\) and to compare to the MD simulation run at equivalent thermodynamic conditions. Since GEMC and CBMC are well established in the literature, only the details concerning our implementation are discussed here. We perform five types of MC moves: swapping of volume and swapping of particles between the two boxes, and three moves related to individual molecules: translation of the centre of mass, rotation about the centre of mass, and change of the internal conformation of the chain by means of a configurational-bias re-growth (for molecules with more than two united-atom cores). Fixed probabilities are set to select the type of move to be attempted: 3 and 34%.

Table II Summary of MD simulation details. Note that \( L_x = L_y \) and \( L_z \) was set to 2.5 \( L_x \).

<table>
<thead>
<tr>
<th>( T ) [K]</th>
<th>( N )</th>
<th>Density [mol/( L )]</th>
<th>( L_z/\sigma_{CC} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>110</td>
<td>2197</td>
<td>11.0</td>
</tr>
<tr>
<td>130</td>
<td>2197</td>
<td>11.0</td>
<td>13.67</td>
</tr>
<tr>
<td>150</td>
<td>2197</td>
<td>11.0</td>
<td>13.67</td>
</tr>
<tr>
<td>170</td>
<td>2197</td>
<td>11.0</td>
<td>13.67</td>
</tr>
<tr>
<td>Propane</td>
<td>200</td>
<td>2197</td>
<td>7.0</td>
</tr>
<tr>
<td>217</td>
<td>2197</td>
<td>6.0</td>
<td>15.80</td>
</tr>
<tr>
<td>249</td>
<td>2197</td>
<td>6.0</td>
<td>15.80</td>
</tr>
<tr>
<td>281</td>
<td>3375</td>
<td>6.0</td>
<td>18.23</td>
</tr>
</tbody>
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for the exchange of volume and the exchange of particles, respectively, and a probability of 21% for each one of the remaining moves. The maximum displacements for the translation, rotation and volume changes are adjusted independently in each box to achieve a 50% acceptance rate. For the modification of the conformation of a molecule with the CBMC technique, a molecule and the number of atoms to be re-grown are randomly selected. The number of trial orientations is equal to 10, while 50 random trial positions were used to increase the molecule exchange acceptance rate when inserting the first interaction site.

In the propane GEMC simulations, we truncated the interactions at 3.5\(\sigma_{CH2}\) and analytic tail corrections were applied. A system size of 400 molecules of propane at 200 K was equilibrated for at least 5000 cycles (one cycle is \(N\) MC moves, where \(N\) is the number of molecules). The production length consisted of 25000 cycles. The run required 39 h of CPU time on a 1.3 GHz PC. A MD simulation at the same temperature with 2197 molecules (sufficient to stabilize the interfaces) and a cut-off \(r_c = 5.5\sigma_{CH4}\), which was run for 750 ps (125000 time steps) after equilibration, needed slightly more than 140 h of CPU time on the same computer, which is equivalent to that used by Goujon et al. [14,15] for the direct simulation of the interface with the NVT MC methodology. We set \(r_c = 5.5\sigma_{CH4}\) to approximate the full potential and to avoid dealing with long-range corrections in inhomogeneous media.

RESULTS AND DISCUSSION

We present here phase coexisting densities of methane and propane obtained by MD and GEMC, focusing on the importance of the cut-off radius used in the simulations. Additional properties for propane calculated from MD simulations, such as the density profiles, time dependence of the density of the centre of mass and the temperature, and the influence of the number of molecules on the density profiles are also presented and discussed here.

As it has already been shown by Trokhymchuk and Alejandre [11], spherically truncated and spherically truncated and shifted potentials do not significantly differ from the full LJ potential when interactions are truncated beyond 5.5\(\sigma\). We have quantified the effect of the cut-off in the vapour–liquid equilibria of methane, modelled as a spherical LJ fluid. Results calculated in this work by MD are shown in Fig. 1, compared to GEMC simulations, also obtained in this work, and to experimental values [20]. Error bars in the simulation data are smaller than the symbol size. We have used three different cut-off values for an intermediate temperature (150 K), \(r_c = 3.0, 4.0\) and \(5.5\sigma_{CH4}\). It is clearly seen from the figure that using a small cut-off radius effectively makes the molecules less attractive and that the larger value (5.5\(\sigma_{CH4}\)) provides an adequate representation of the full potential, giving quantitative agreement with experimental data. For the case of the GEMC simulations, long range corrections are applied (it is straightforward in this case) and, hence, no point is made on the value of the cut-off radius in these simulations.

Figure 2 shows the coexisting densities of propane, a non-spherical molecule. We present MD results for two values of the cut-off, 4.5 and 5.5\(\sigma_{CH4}\), compared to GEMC simulations and to experimental data taken from the literature [20]. As for the case of methane, a clear dependence of the coexisting densities on the potential cut-off is observed. It should be noted that for the MD simulations of propane, a larger number of molecules compared to methane was needed to equilibrate the interface, especially close to the critical point. For instance, for the case of \(T = 281\) K, the stable two-phase equilibrium interface was obtained with 3375 molecules. This is essentially due to the larger fluctuations observed at these conditions. Simulations at lower temperatures needed less molecules and reached equilibrium faster.

The MD simulation results for propane at a cut-off value of 5.5\(\sigma_{CH4}\) are also presented in Table III, compared to GEMC simulation results from this work for the case of \(T = 200\) K, and from the work of Martin and Siepmann [3] for the rest of
the temperatures, and to experimental data [20]. The overall deviation of the MD predicted saturated liquid densities from the experimental values is 2.1%. Relative deviations in the equilibrium vapour densities are very large, mainly because of poor statistics due to the smaller number of molecules in the vapour phase in the simulations. This is more noticeable at low temperatures. A question may remain on how the liquid phase changes by considering a larger cut-off. It is possible that the quantitative agreement with experimental data improves in that case. In fact, a detailed study on the dependency of the cut-off for each member of the \( n \)-alkanes series is needed, in principle, following this approach. As mentioned already, a larger cut-off implies a larger number of molecules in the simulation, making some of them very lengthy, as the chain length increases. However, since for the case of propane the overall deviations from the experimental data is 2.1% (in the range of the experimental error), and it is out of the scope of this work to quantify the exact value of the cut-off for each member following this procedure, we think that a cut-off of 5.5\( \sigma_{\text{CH}_2} \) suffices in this case. If one is interested in obtaining the VLE of the whole series through MD simulations, it is clear than long range corrections can not be avoided in that case.

Once vapour–liquid equilibria for propane was reached, the differences in computing time between MD and GEMC quantified, and the importance of the cut-off value in the absence of long-range corrections evaluated, we calculated density profiles and time dependent properties. As we have mentioned already, a clear advantage of performing MD simulations versus GEMC simulations is the fact that these and other properties can be obtained, including interfacial and transport properties. Figure 3 presents the evolution of the density profile of propane at 217 K. The density in the direction perpendicular to the interfaces planes is plotted versus the value of \( z \), the position along that direction with respect to the position the centre of mass of the whole system. Therefore, although the centre of mass of the system may move, it always lies at \( z = 0 \) in our plots. The density profile at the time step when the box is suddenly enlarged keeping a slab of liquid in its centre surrounded by two void spaces, is shown in Fig. 3a, while Fig. 3b–d shows different times after the enlargement. In this particular case, somewhat unusual, the profile inverts its shape so that the liquid and vapour phases swap their position in the box. A possible explanation

![FIGURE 3 Time evolution of the density profile for propane at 217 K along the longest axis \( z \) of the simulation box. \( z \) is dimensionless. (a) Profile at the time step at which the enlargement of the simulation box takes place; (b) and (c) Transition profiles; (d) Profile at the equilibrium state.](image-url)
could be that the evaporation rate of the molecules from the liquid to the vapour phase initiated by the enlargement of the box is high enough to invert the position of the phases.

Figure 4 shows a snapshot of a particular equilibrium configuration of 2197 propane molecules at 249 K in a $15.80 \times 15.80 \times 39.51 \text{ Å}$ simulation box, as obtained from MD simulations, where the two phases and the interfaces are clearly observed. A significant number of molecules are at the vapour–liquid interface, which becomes more evident at higher temperatures, where the percentage can exceed 50% of the total number of molecules.

The time evolution of the temperature and density at the centre of mass of propane at 249 K are shown in Fig. 5. Three different regimes are observable in these figures: the equilibration of the liquid before the sudden enlargement of the box, the instant at which the enlargement takes place, and the time evolution of the system after it. A study of these properties is useful as a test of when and how fast equilibrium is reached, depending on the thermodynamic conditions and on the simulation parameters.

Additional properties, such as the pressure tensor and from it the surface tension, can be obtained by MD. It would be very interesting to use this technique to investigate the formation of the interface itself, the orientation of the molecules around it, and the transport properties governing these phenomena. The calculation of these properties and their comparison with experimental data will be matter of future work.

CONCLUSIONS

We have presented here some preliminary results on the application of the MD technique to obtain vapour–liquid equilibria properties of some alkanes. The influence of the cut-off radius on the coexisting orthobaric densities of methane and propane was studied by MD and results compared to those obtained by GEMC simulations, and to experimental data. Molecules were modelled according to the TraPPE-UA model for $n$-alkanes. In order to study the influence of the cut-off value on the coexisting densities, no long-range corrections were applied in the MD simulations. MD results showed that a cut-off of at least 5.5 times
the Lennard–Jones diameter is needed to obtain an accuracy of about 2% when compared to experimental saturated liquid densities and to GEMC simulations with effectively infinite range (finite-range cut-off with long-range correction). An alternative approach is to include the long range correction calculations in these inhomogeneous fluids.

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References