A molecular dynamics study of interfaces: from pure liquids to biological membranes
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Chapter 2

Surface tension calculation for liquid-vapour systems*

2.1 Introduction

Alkanes are an important class of molecules that occur in many practical applications. These last few years, many molecular models have been developed to describe the interactions between alkanes [4–9]. In these studies the models have been tested via a comparison with the experimental vapour-liquid coexistence curve. Subsequently, these models have been further validated via a comparison of the simulated and experimental diffusion coefficients [10] and viscosities [11, 12]. Less attention has been given to the surface tension.

In this chapter, we compare the predictions of two different alkane models to obtain some insight in the dependence of the computed surface tension on the details of the intermolecular interactions. We have computed the surface tension for the linear alkanes (n-hexane, n-decane and n-hexadecane) using OPLS [13] and SKS [4] (developed by Smit, Karaborni, and Siepmann) force field models. We have performed the simulations in two temperature ranges. One temperature range is the same as in ref. [14] in which Alejandro and co-workers have computed the surface tension of hexane at coexistence (vapour-liquid) for high temperatures using the SKS and de Pablo [15, 16] models. Our results for the surface tension of the hydrocarbons can be compared with the simulation data of Alejandro and co-workers. This allows us to validate our program and extend their results to other chain lengths and

temperatures. To the best of our knowledge, there is no experimental data available for these systems at coexistence. Therefore, we do not know how accurately these alkane models can predict the surface tension. Experimental data are available at much lower temperatures, at densities higher than the coexistence density. We performed simulations at these conditions to assess the accuracy of the computed surface tensions.

In this chapter, we first describe the models used during our simulations, and then compare the densities and surface tension values predicted by our simulations with previous results and available experimental data. The method implemented for the surface tension calculation is described in the appendix 2.5.

2.2 Models and simulation methodology

2.2.1 Force fields

We calculate the surface tension for liquid/gas systems of the linear alkanes: hexane, decane, hexadecane. Two sets of force fields, SKS and OPLS, are compared.

We use the united-atom representation, which means that every methylene (\(-CH_{2}\)) or methyl (\(-CH_{3}\)) group is modelled as a single interaction site. Three types of potentials are employed: nonbonded interaction, bond bending potentials, and torsion potentials. The nonbonded interactions between united atoms of different molecules and within a molecule (if two atoms are more than four atoms apart) are described with a Lennard-Jones potential. The interactions are truncated and shifted with a cut-off radius \(r_c\):

\[
U(r_{ij}) = \begin{cases} 
U(r_{ij})^{LJ} - u(r_c)^{LJ} & r_{ij} \leq r_c \\
0 & r_{ij} > r_c
\end{cases}
\]  

(2.1)

with

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

(2.2)

where \(r_{ij}\) is the distance between united atoms \(i\) and \(j\), \(r_c\) is the cut-off distance, \(\epsilon\) and \(\sigma\) are Lennard-Jones energy and distance parameters, respectively. The numerical values of these parameters are shown in table 2.1. \(\epsilon_{ij}, \epsilon_i, \epsilon_j\) and \(\sigma_{ij}, \sigma_i, \sigma_j\) are related by \(\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}\) and \(\sigma_{ij} = (\sigma_i + \sigma_j)/2\), respectively.
### 2.2 Models and simulation methodology

<table>
<thead>
<tr>
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<th>$-CH_2-$</th>
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<td>3.93</td>
<td>114</td>
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<td>59.4</td>
<td>3.905</td>
<td>88.1</td>
<td>11.5</td>
</tr>
</tbody>
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Table 2.1: Values of Lennard-Jones parameters and $r_c$ from SKS and OPLS models [4, 17], respectively.

We use the SHAKE algorithm [18] to impose a fixed bond length of 1.53 Å between two connected united atoms. The bond-bending potential [19] is given by:

$$ U^{\text{bend}}(\theta) = \frac{1}{2} k_\theta (\theta - \theta_0)^2, $$

where $\theta$ is the angle between two connected bonds, and $\theta_0$ the equilibrium value of this angle, $k_\theta$ the force constant. We have used $k_\theta = 62500 \text{ K.rad}^{-2}$ for both models, $\theta_0 = 112^\circ$ in the OPLS model and $114^\circ$ in the SKS model.

The torsion potential is defined for the OPLS model [17]:

$$ U^{\text{tors, OPLS}}(\phi) = \sum_{k=0}^{5} c_k \cos^k(\phi), $$

and for the SKS model:

$$ U^{\text{tors, SKS}}(\phi) = 0.5 [c_1 (1 + \cos \phi) + c_2 (1 - \cos 2\phi) + c_3 (1 + \cos 3\phi)], $$

where $\phi$ is the dihedral angle. In the OPLS model, we use $c_0 = 1116 \text{ K}$, $c_1 = 1462 \text{ K}$, $c_2 = -1578 \text{ K}$, $c_3 = -368 \text{ K}$, $c_4 = 3156 \text{ K}$, $c_5 = -3788 \text{ K}$. For the SKS model we use $c_1 = 355 \text{ K}$, $c_2 = -68.19 \text{ K}$ and $c_3 = 791.3 \text{ K}$.

#### 2.2.2 Simulations

Our simulations are performed in an NVT ensemble [20], i.e., with constant number of particles, volume and temperature. The equations of motion are solved using the Verlet Leapfrog integration algorithm [2]. The SHAKE method [18] is used to constrain the bond lengths. Simulations are run with periodic boundary conditions. We have used the DL POLY program [21] for all our simulations.

At high temperatures, we have investigated the system at vapour-liquid coexistence (with liquid and gas densities obtained from Gibbs-ensemble simulations) and at low temperatures the system is defined “off coexistence”
(with experimental liquid densities and vacuum). At coexistence we compare our simulation results with those from Alejandre et al. [14] and at lower temperatures with experimental data [22, 23].

The simulations at coexistence are initiated in the following way. First, we construct a cubic box with molecules placed on a lattice at the estimated liquid density from Gibbs-ensemble computations [4]. For hexane, decane, and hexadecane the simulation cell contains 675, 405, and 300 molecules, respectively. This box is equilibrated during 50,000 time steps with a time step duration $\Delta t = 3fs$. This liquid box is "sandwiched" by two empty cubic simulation cells and these boxes are filled with a few alkane molecules to obtain the vapour coexistence density.

At low temperatures, off coexistence, we initiate the simulation at the liquid density taken from experimental data. At this temperature range, the vapour pressure is so low that the gas boxes contain on average less than one molecule. Therefore, we use for these simulations empty boxes and run a few hundreds steps in order to stabilize the interface. After this equilibration, liquid and gas boxes have approximately the same volume and the box length in $z$ direction exceeds 100 Å.

We accumulate surface tension values every 500 steps during 3 ns. These data are analysed using the block average method [24].

### 2.3 Results and discussion

#### 2.3.1 Liquid densities

Before discussing the results for the surface tension, we compare the simulated liquid densities for the various models with experimental data. An example of a computed density profile of hexane at coexistence using the SKS model is presented in figure 2.1. This plot shows liquid-vapour coexistence. Because of the periodic boundary conditions we obtain two interfaces. From this figure we can compute the coexistence densities of the liquid with reasonable accuracy. Good agreement is found between results from simulations and those from experiments [25]. For the gas density, however, the number of molecules is too small to determine the coexistence gas density accurately. Figure 2.2 shows the coexistence liquid densities for hexane at various temperatures as obtained from our simulations using the SKS model. This figure shows that the Gibbs ensemble results [4] are in reasonable agreement, but not perfect, with the present simulations. Important to note is that the Gibbs ensemble simulations use a truncated potential [4] while in this work a truncated and shifted potential is used. For a simple Lennard-
2.3 Results and discussion

Jones fluid a truncated but not shifted potential has a 10% higher critical temperature (Tc) [26,27]. A similar shift of the critical temperature has been observed here. In figure 2.2, we also compare our results with the MD simulations of Alejandre et al. [14]. Alejandre et al. used a similar method as in the present work to compute the coexistence properties. However, in the work of Alejandre et al. a slightly larger cut off radius (15.8 Å) together with an inhomogeneous tail correction were used compared to Gibbs ensemble simulations [4,28]. This results in a higher $T_c$ and hence a higher coexistence density compared to our simulations. For hexane also the OPLS model gives a good description of the experimental data. Concerning the highest temperature (450 K), the interfaces are too broad to yield an accurate estimation of the liquid density.

For n-decane and n-hexadecane figure 2.2 shows that the SKS model predicts a lower liquid density, compared to the OPLS model which is consistent with the conclusion in ref. [4] that the OPLS model overestimates the critical temperatures for long-chain alkanes.

In figure 2.3, we compare the simulated liquid densities at low temperature (off coexistence), using the SKS model, with the experimental liquid densities. For n-decane and n-hexadecane the agreement with the experimental data is very good, while for n-hexane, the simulations underestimate the liquid densities.
Surface tension calculation for liquid-vapour systems

![Graphs](image)

**Figure 2.2:** Comparison of the liquid coexistence densities ($\rho$), for n-hexane (top), n-decane (centre), and n-hexadecane (bottom), as a function of temperature for the present work, the Gibbs ensemble results [4], the results from previous molecular dynamic simulations [14] and experimental results concerning n-hexane [25].
2.3 Results and discussion

2.3.2 Surface tension estimations

In figure 2.4, the computed surface tension for hexane, decane, and hexadecane at coexistence are shown as a function of the temperature and density. To the best of our knowledge experimental data for these systems have not been published. For hexane we can compare the surface tension as a function of temperature as obtained by our simulations with previous results [14]. The agreement between these two studies is satisfactory; the small differences can be related to the larger cut-off radius used by Alejandre et al. For the OPLS model a similar result is obtained. If we plot the results versus liquid densities the differences between the various models become much smaller.

For decane and hexadecane the differences between simulated surface tension as a function of the temperature of the OPLS and SKS model are larger compared to hexane. Also for these molecules the differences disappear if we plot the surface tension as a function of the densities. This indicates that predicting the correct liquid density is a prerequisite for estimating a reliable value of the surface tension.

Since the SKS model gives a better prediction of general properties at coexistence for the long-chain alkanes [4, 29], we focus on this model for a comparison with experimental data.

Figure 2.3: Density $\rho$ as a function of the temperature for n-hexane (C6), n-decane (C10), and n-hexadecane (C16) from our simulations (SKS model) and from experiments.
Figure 2.4: Surface tension $\gamma$ versus the temperature (left), and density $\rho$ (right). $C_6$ (top), $C_{10}$ (centre) and $C_{16}$ (bottom), at coexistence.
In this chapter we have computed liquid densities and the surface tension of various linear alkanes at various temperatures. For longer alkanes, the computed liquid densities confirm that they are better described by the SKS model than the OPLS model at high temperatures. At lower temperatures, the agreement between experimental and computed densities from the SKS model increases with the length of the linear alkanes.

The density prediction is a major parameter in surface tension calculations. Differences observed between the SKS and OPLS models in the critical temperature and liquid density predictions are cancelled when the predicted surface tension values are plotted as a function of the liquid density. At low temperatures, comparison with experimental data shows that the surface tension is underestimated by approximately 15%.

Our simulations show that to predict the surface tension at a given tem-
For a surface normal to the $z$ axis, the surface tension $\gamma$ is proportional to the integral of the difference between the normal $P_N(z)$ and tangential $P_T(z)$ components of the pressure tensor:

$$\gamma = \frac{1}{2} \int_{-L_z/2}^{+L_z/2} \text{d}z \left[ P_N(z) - P_T(z) \right], \quad (2.6)$$

where $\frac{1}{2}$ is a correction factor when the simulation boxes contain two surfaces. The components of the pressure tensor are obtained as a function of the position along the $z$ axis using the Irving and Kirkwood definition [30, 31]:

$$P_T(z) = \rho(z)k_BT - \frac{1}{A} \left\langle \sum_i \sum_{j<i} \frac{x_{ij}^2 + y_{ij}^2}{2r_{ij}} \frac{dU(r_{ij})}{dr_{ij}} \left| z_{ij} \right| \right\rangle \times \theta \left( \frac{z - z_i}{z_{ij}} \right) \theta \left( \frac{z_{ij}}{z_i - z} \right), \quad (2.7)$$

$$P_N(z) = \rho(z)k_BT - \frac{1}{A} \left\langle \sum_i \sum_{j>i} \frac{z_{ij}^2}{r_{ij}} \frac{dU(r_{ij})}{dr_{ij}} \left| z_{ij} \right| \right\rangle \times \theta \left( \frac{z - z_i}{z_{ij}} \right) \theta \left( \frac{z_{ij}}{z_i - z} \right), \quad (2.8)$$

where $\theta(x)$ is the Heaviside step function.

2.5 Appendix: Surface tension calculation

We have used for this calculation a method described in literature [30, 31].

From the particle coordinates and the forces acting upon particles, we have computed the pressure profile along an axis perpendicular to the surface, and calculated the surface tension (which corresponds to the interfacial tension in the case of an interface). The pressure profile, which cannot yet be measured from experiments, will give an insight on the lateral pressure occurring in a membrane, and can be related to the properties specific to the composition of the membrane. The pressure profile calculation is detailed below.

For a surface normal to the $z$ axis, it is very important to use a model that predicts the density of the liquid phase at the given conditions sufficiently accurately. For example, the SKS model and the OPLS model give very similar results for the surface tension as a function of the liquid density. Therefore, if a given model does not predict the liquid density correctly such a model has very limited value for predicting the surface tension.
where $\rho(z)$ is the atomic density profile along the $z$ direction, $k_B$ is Boltzmann’s constant, $T$ is the temperature, $A = L^2$ is the area of one surface, $x_{ij}$, $y_{ij}$, and $z_{ij}$ are the $x$, $y$, and $z$ components of the distance $r_{ij}$ between atoms $i$ and $j$, respectively, $\langle \cdots \rangle$ denotes the canonical ensemble average, $U_{\text{int}}$ is the potential energy, and $\theta(z)$ is the Heaviside step function. Practically, the components of the pressure tensor are computed by dividing the simulation box into $N$ slabs, parallel to the $xy$ plane, and the contribution of each interaction between atoms $i$ and $j$ (including bond constraint forces from the SHAKE algorithm) is distributed in the involved slabs, i.e., slabs in which the particles $i$ and $j$ reside and slabs in between [32]. The contribution from electrostatic interactions, when taken into account, is computed from a coulombic expression.

It has been acknowledged that the position of the surface of tension $z_s$:

$$z_s = \frac{1}{\gamma} \int_0^{+L_z/2} dz \, z \left[ P_N(z) - P_T(z) \right]$$

(2.9)
cannot be specified exactly, but lies within a correlation length from the surface position [33,34]. In turn, the pressure profile and its location are arbitrarily set by the used definition.