Vapour-liquid phase equilibria and interfacial properties of fatty acid methyl esters from molecular dynamics simulations

Esther Feria, Jesús Algaba, José Manuel Míguez, Andrés Mejía, Paula Gómez-Álvarez, and Felipe J. Blas

We have determined the phase equilibria and interfacial properties of methyl esters homologous series (from methyl acetate to methyl heptanoate) from direct simulation of the vapour-liquid interface. Methyl esters are modelled using the united atom approach in combination with the TraPPE force fields for alkanes, alkenes, carbon dioxide, ethers, and carboxylic acids in a transferable way. This allows to take into account explicitly both dispersive and coulombic interactions, as well as the repulsive Pauli-exclusion interactions. Simulations are performed in the NVT or canonical ensemble using molecular dynamics. Vapour-liquid surface tension is determined using the virial route, i.e., evaluating the normal and tangential components of the pressure tensor along the simulation box. We have also calculated density profiles, coexistence densities, vapour pressures, surface entropies and enthalpies, and interfacial thickness as functions of temperature, as well as the normal boiling temperatures and the critical temperatures, densities, and pressures for each member of the series. Special attention is paid to the comparison between experimental data taken from the literature and our results obtained from molecular dynamic simulations. We also analyze the effect of increasing the molecular weight of the methyl esters (at fixed temperature) on all the properties considered, with special emphasis on phase equilibria envelopes and surface tension. The TraPPE force fields transferred from other molecules and chemical families are able to predict very accurately the experimental vapour-liquid phase envelopes of methyl esters. We also compare the results obtained from simulations for the surface tension with experimental data taken from the literature. To our knowledge, this is the first time that vapour-liquid phase equilibria and interfacial properties, and particularly surface tension, of the methyl esters homologous series are obtained from computer simulation.

1 Introduction

Current environmental regulations and energy directives recommend and promote to increase, at least 10%, the use of renewable fuels for transport by 2020, and also to dramatically reduce the transportation emission levels by 2030\(^1\). These initiatives have been motivated to reduce greenhouse gas emissions, where transportation contributes 34% of the total emissions. One of the most groundbreaking alternatives to accomplish these targets is to replace (partially or totally) the fossil-fuels based by biofuels (fuels produced from natural renewable sources), where one of the most recently emerging biofuels is the biodiesel. Biodiesel are considered the third (or fourth) generation of biofuels\(^2\) due to they are renewable, biodegradable, non-toxic, produces less carbon dioxide than fossil fuels, and also they can replace the petroleum diesel and be used either in their neat form or blended with fossil diesel inside of the compression ignition engines without any extensive engine modification. In general terms, biodiesel can be obtained from a group of mono-alkyl esters\(^3\) that, depending on the alcohol (methanol or ethanol) used for the trans-esterification process, become Fatty Acid Methyl Esters (FAMEs) or Fatty Acid Ethyl Esters (FAEEs), respectively. From a technical viewpoint, the use of FAMEs as a fuel is more developed than FAEEs\(^4,5\) for efficient use.

Despite the novel use of FAMEs as diesel fuel, systematic research concerning the characterization of interfacial properties...
facial tensions reported in DEHEMA to methyl heptanoate), the available experimental data for interfacial tension of pure and mixtures with FAMEs is very limited. For the case of pure short chain FAMEs (i.e., from methyl acetate to methyl heptanoate), the available experimental data for interfacial tensions reported in DEHEMA and Landolt-Börnstein databases and also the DIPPR and NIST correlations, only cover a narrow temperature range (273 K to 360 K). Theoretical models, such as the Square Gradient Theory, need the experimental data of interfacial tensions to fit their parameters and use them as a model to predict the other interfacial properties. For the case of mixtures, the scenario is even worse, especially for the case of mixtures of hydrocarbons or aromatics with FAMEs, where interfacial properties are unexplored and only very few sparse data can be found. The only exception is the case of water + FAMEs mixtures, where both experimental determinations and theoretical modeling have been carried out by one of us. Therefore, considering the environmental regulations and energy directives, it is necessary to carry out systematically exploration of the interfacial behavior of the compounds involved in the biodiesel production. These properties are the key requirement for their future use as a fuel, as well as for environmental issues, such as the removal of contaminants from water and for groundwater remediation. Consequently, this work has focused on the determination of some selected interfacial properties for the case of pure short-chain FAMEs from methyl acetate to methyl heptanoate.

Due to the lack of predictive theories, molecular dynamics (MD) simulations can be used as a predictive tools to explore both bulk properties (i.e., coexistence density curve, $T - \rho$, vapour pressure or Clausius-Clapeyron curve, $P - T$) and interfacial properties (e.g., interfacial concentration of species, the interfacial thickness, the superficial enthalpy and entropy, and surface or interfacial tension) from low temperature to near the critical point.

In the last decades, computer simulation has become an essential tool for modelling and predicting thermodynamic properties, including phase equilibria and interfacial properties, of complex systems of fundamental and applied interest. In particular, during the last twenty years, a remarkable progress has been made in the development of new force fields for describing complex molecules from a molecular perspective. Perhaps, the most relevant example of this kind of force fields is the transferable parameters for phase equilibria (TraPPE) approach of Siepmann and coworkers, that allows to determine with high accuracy thermodynamic and structural properties of complex molecules. The key idea behind the TraPPE models is transferability, i.e., to predict the behaviour of a given molecule or set of molecules only from the knowledge of molecular parameters for particular chemical groups taken unchanged from other systems, regardless of the atomic makeup of the rest of the molecule. This strategy allows to truly predict the thermodynamic and other structural and dynamical properties without the need of adjustments to experimental data of the system under study.

In work, we use the united-atoms (UA) version of the Transferable Parameters for Phase Equilibria approach (TraPPE-UA) to predict the phase behaviour and interfacial properties of FAMEs. As it is mentioned in the previous paragraph, it would be possible to obtain new molecular parameter values according to the TraPPE-UA force fields by fitting to experimental vapour-liquid phase equilibria. However, following Kamath et al., it is also possible to use the parameter values from the TraPPE-UA database for chemical groups that describe different molecules, including alkane and alkenes, carbon dioxide, ethers, and carboxylic acids, and transfer them to predict the phase equilibria and interfacial properties of the first members of the methyl esters chemical family. The main goal of this work is to use the transferable molecular parameters of the TraPPE-UA force field to predict the phase equilibria and interfacial properties of the first members of linear methyl esters using MD simulation. In particular, we use the direct coexistence technique in the NVT or canonical ensemble. The results obtained from MD simulation are with experimental data taken from the literature to critically assess the models ability. To our knowledge, this is the first time that the vapour-liquid interfacial properties, and particularly the surface tension, of the first members of the methyl esters chemical family are determined from computer simulations.

The organization of this paper starts with the description of molecular models in Section 2. In the next section, Section 3, simulation details are provided and explained briefly. In Section 4, the main results of interfacial properties are presented and discussed. Finally, the main conclusions are summarized in the last section.

2 Molecular models

As we have mentioned, methyl esters have been modeled following the united-atom approach. In all cases, the force fields use the Lennard-Jones and Coulomb potentials to describe the non-bonded interactions,

$$U(r_{ij}) = 4\varepsilon_{ij} \left[ \frac{\sigma_{ij}}{r_{ij}} \right]^{12} - \frac{\sigma_{ij}}{r_{ij}} \left[ \frac{\sigma_{ij}}{r_{ij}} \right]^{6} + \frac{q_i q_j}{4\pi \varepsilon_{0} r_{ij}}$$

where $r_{ij}$ is the distance between interacting sites $i$ and $j$, $\sigma_{ij}$ and $\varepsilon_{ij}$ are the diameter and well depth associated to the LJ intermolecular potential, $q_i$ and $q_j$ are the partial charges on interacting sites $i$ and $j$, and $\varepsilon_0$ the permittivity of vacuum. All the LJ parameters for unlike interactions are obtained using the Lorentz-Berthelot combining rules.

According to the TraPPE-UA philosophy, molecular parameters are taken from existing parametrizations and combined to form the molecules of interest, as it has been explained in the previous section. Molecular parameters for non-bonded interactions for the carbonyl chemical group (C=O) are taken from molecular parameters of two different molecules: The parameters of the carbonyl oxygen are taken from the oxygen parameters of the carbon dioxide model proposed by Potoff and Siepmann, and the parameters of the carbonyl carbon are taken from the carbon parameters of the carboxylic acids models proposed by Kamath et al. The molecular parameters involved in the methoxy (or terminal methyl group bonded to the ether oxygen, $-O-\text{CH}_3$), i.e., the ether oxygen and the methyl group $\text{CH}_3$ (sp$^3$), are taken from...
the work of Stubbs et al.\textsuperscript{20} The molecular parameters of methyl (CH$_3$ not bonded to the oxygen ether) and methylene (–CH$_2$– not bonded to the carbon –C– atom) groups are taken from the TraPPE-UA parameter values of alkanes proposed by Martin and Siepmann\textsuperscript{21}. It is interesting to mention that Maerzke et al.\textsuperscript{22} considered TraPPE force field for acrylates and metacrylates that share some of the same united atoms as the FAMEs studied in this work. However, these substances contain conjugated double bonds. In our work, we consider methyl esters that do not contain this kind of bonds, and due to that to use the TraPPE molecular parameters of Kamath et al.\textsuperscript{19} and Stubbs et al.\textsuperscript{20}. All the molecular parameters used in this work to describe the non-bonded interactions, including the partial charges values for electrostatic interactions of all the chemical groups, are summarized in Table 1.

### Table 1: Bond length values for the TraPPE-UA force field corresponding to methyl-esters (from methyl acetate to methyl heptanoate). All values are taken from the TraPPE webpage\textsuperscript{16}.

<table>
<thead>
<tr>
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<tr>
<td>C = O</td>
<td>1.200</td>
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<td>C – CH$_3$</td>
<td>1.344</td>
</tr>
<tr>
<td>CH$_3$ – C</td>
<td>1.410</td>
</tr>
<tr>
<td>CH$_2$ – C</td>
<td>1.520</td>
</tr>
<tr>
<td>CH – CH$_x$</td>
<td>1.540</td>
</tr>
</tbody>
</table>

As in the case of the LJ parameters and partial charges, bond lengths, bending, and torsional force field parameters characterizing the bonded interactions are obtained from the TraPPE-UA values of different chemical groups. Tables 2, 3, and 4 collect all the parameter values used in this work. Note that according to the usual TraPPE-UA force field approach, the bond length between different chemical groups are fixed.

### 3 Simulation details

All MD simulations are carried out in conditions at which the vaporeliquid interface is present, following the standard methodology\textsuperscript{23,24} for all models studied. In particular, simulations are performed in the NVT canonical ensemble using GROMACS (version 4.6.1)\textsuperscript{25} at a fixed temperature $T$, in a parallelepipedic simulation cell of constant volume $V = L_x \times L_y \times L_z$, where $L_x$, $L_y$, and $L_z$ are the dimensions of the simulation box. We use periodic boundary conditions in all three directions.

### Table 2: Bond length values for the TraPPE-UA force field corresponding to methyl-esters (from methyl acetate to methyl heptanoate). All values are taken from the TraPPE webpage\textsuperscript{16}.

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A homogeneous liquid system is first equilibrated in a parallelepiped simulation box. The dimensions of the box are $L_x = L_y = 3.9$ nm for the case of methyl acetate and $L_x = L_y = 3.95$ nm for the rest of methyl esters. For the lengths of the simulation boxes along the $z$-axis we have used the following sizes: $L_z = 11$ nm (methyl acetate), $L_z = 13$ nm (methyl propionate), $L_z = 16$ mm (methyl butyrate), $L_z = 19$ nm (methyl valerate), $L_z = 20$ nm (methyl hexanoate), and $L_z = 23$ nm (methyl heptanoate). We consider $N = 1100$ molecules for all the methyl esters studied in this work. After equilibration of these bulk-liquid systems, the box is expanded along the $z$ direction leaving the liquid phase slab at the center. The final overall dimensions of the vapour-liquid-vapour configuration box are therefore $L_x = L_y = 3.9$ nm and $L_z = 33$ nm for the case of methyl acetate, and $L_x = L_y = 3.95$ nm and $L_z = 39$, 48, 57, 60, and 69 nm for the methyl propionate, methyl butyrate, methyl valerate, methyl hexanoate, and methyl heptanoate, respectively.

In order to reduce the truncation and system size effects involved in the phase equilibrium and interfacial properties calculations, the cut-off radius ($r_c$) has been taken equal to a value of $5\sigma$ ($r_c = 1.95$ nm for methyl acetate and $1.975$ nm for the rest of methyl esters). It has been shown by several authors\textsuperscript{26–28} that such a value provides a reasonable description for the interfacial properties. Long-range interactions are determined using three-dimensional Ewald technique with a convergence parameter of 0.1 Å$^{-1}$ and a maximum value for the reciprocal lattice equal to 31 is used.

We have used the Verlet leapfrog\textsuperscript{29} algorithm with a time step of 0.001 ps. It is important to note in this case that the time step value chosen has been necessary to sample correctly the torsional potentials of esters models. A Nosé-Hoover thermostat\textsuperscript{30} with large time constant equal to 1.0 ps has been used. Simulations of the homogeneous liquid systems are equilibrated during 5 ns. After this, the vapour-liquid-vapour systems are also equilibrated during 5 ns. After the systems reach equilibrium, the properties of the coexisting vapour and liquid phases are obtained as appropriate averages during 20 ns. In order to estimate errors on the variables computed, the sub-blocks average method has been applied.\textsuperscript{31} In such approach, the production period is divided into $M$ independent blocks. The statistical error is then deduced from the standard deviation of the average $\bar{\sigma}/\sqrt{M}$, where $\bar{\sigma}$ is the variance of the block averages and $M$ has been fixed in this work to $M = 10$.

The equilibrium vapour pressure, $P$, and interfacial tension, $\gamma$,
are obtained from the diagonal components of the pressure tensor. The vapour pressure corresponds to the normal component, \( P = P_z \), of the pressure tensor, while the interfacial tension is obtained using the mechanical route as:

\[
\gamma = \frac{L_z}{2} \left[ P_{zz}(z) - \frac{P_{xx}(z) + P_{yy}(z)}{2} \right]
\]

In Eq. (2), the additional factor 1/2 comes from having two interfaces in the system, and \( L_z \) is the size of the simulation box in the \( z \) direction, defined along the longitudinal dimension across the interface.

The experimental determination of the critical state of FAMEs is extremely difficult due to their thermal instability. One alternative way to calculate the critical coordinates, i.e., critical pressure, \( P_c \), temperature, \( T_c \), and density, \( \rho_c \), is to use the vapour-liquid equilibrium MD results together the scaling law given by:

\[
\rho_L - \rho_V = A (T - T_c)^\beta
\]

and the corresponding law of rectilinear diameters

\[
\frac{\rho_L + \rho_V}{2} = \rho_c + B (T - T_c)
\]

\( \beta \) is the corresponding critical exponent, with a universal value of \( \beta = 0.325 \), and \( A, B, T_c \) and \( \rho_c \) are four unknown constants obtained fitting to the simulation results. \( \rho_L \) and \( \rho_V \) are the liquid and vapour coexistence densities at the corresponding temperature \( T_c \), respectively. Critical temperature, \( T_c \), and density, \( \rho_c \), can be easily obtained from Eqs. (3) and (4).

An independent way to calculate \( T_c \) is to apply an alternative scaling law using interfacial information from the system. Following this route, \( \gamma \) is related to \( T_c \) by the following expression:

\[
\gamma = \gamma_0 \left( 1 - T/T_c \right)^\mu
\]

where \( \gamma_0 \) is the so-called “zero-temperature” surface tension and \( \mu \) is the corresponding critical exponent. Here, we fix \( \mu \) to the universal value \( \mu = 1.258 \) as obtained from renormalization-group theory. Once again, the unknown constants, \( \gamma_0 \) and \( T_c \), are found by fitting the interfacial tension data with temperature.

The critical pressure can be estimated from an extrapolation of the Clausius-Clapeyron relation to the critical temperature obtained from Eq. (3) or Eq. (5):

\[
\ln P = C_1 + \frac{C_2}{T}
\]

where \( C_1 \) and \( C_2 \) are correlation parameters. The value of \( P_c \) is obtained using Eq. (6) at \( T = T_c \). The critical temperature value, \( T_c \), used in the previous equation is obtained from Eq. (3).

The surface entropy (\( \Delta s^T \)) and surface enthalpy (\( \Delta h^T \)) change of surface formation can be also determined using the temperature dependence of the surface tension from the following derivative expressions:

\[
\Delta s^T = -\frac{\partial \gamma}{\partial T} \bigg|_p
\]

\[
\Delta h^T = \gamma + T \Delta s^T
\]

Finally, an interesting property that can be obtained from the calculation of density profiles is the interfacial width along the vapour-liquid equilibrium. Implicitly this property is defined by fitting the curves from the original mean field van der Waals theory, described in the previous sections. We focus on the interfacial properties, such as density profiles, interfacial thickness, surface entropy and enthalpy, and surface tension. We also examine the temperature dependence of these properties, and compare our results for the different models with experimental data taken from the literature.
We analyze the thermodynamic and interfacial behavior of all the FAMEs at different temperatures using the same methodology that in our previous works.\textsuperscript{41–47} Density profiles are calculated by dividing the system in 200 slabs along the $z$ direction. The molecular density profiles, $\rho_i(z)$, are obtained by assigning the position of each united atom center, $z_i$, to the corresponding slab and constructing the molecular density from mass balance considerations. The bulk vapour and liquid densities in each system are calculated by averaging $\rho_i(z)$ over appropriate regions sufficiently removed from the interfacial region. In addition to that, the final bulk vapour density value, at each temperature and chain length, is obtained after averaging the density profiles on both sides of the liquid film.

We show in Fig. 1 the density profiles $\rho(z)$ for the six methyl esters considered in this work, from methyl acetate up to methyl heptanoate, at different temperatures as modelled using the TraPPE-UA models. For the sake of clarity, we only present one half of the profiles corresponding to one of the interfaces. Also for convenience, all density profiles have been shifted to place $z_0$ at the origin.

As can be seen, liquid density decreases and vapour density increases as the temperature is increased in all cases as expected. The slope of each density profile, in absolute value, along the interfacial region becomes smaller as the temperature approaches the critical point for each system. According to the near-critical scaling laws\textsuperscript{33}, the interfacial thickness must diverge as the temperature approaches the critical temperature. The results presented in Fig. 1 corroborate this behaviour.

From the density profiles depicted in the previous Figure, it is possible to obtain the vapour-liquid phase envelopes of the different FAMEs studied in this work. Results corresponding to the vapour and liquid coexistence densities, at different temperatures, are presented in Table 5. Fig. 2 shows the phase diagrams of all the systems considered as obtained from MD computer simulations. Experimental data taken from the literature\textsuperscript{11} is also included for comparison. In general, computer simulation is able to predict very accurately the vapour and liquid densities in the whole range of temperatures considered, from near the triple-point to the critical temperature. Very small differences between simulation and experimental data for the liquid branch of the phase envelope can be seen at low temperatures in the case of methyl acetate, methyl propionate, and methyl butyrate.

In addition to the vapour and liquid coexistence densities, we have also determined the coordinates of the critical points of all the FAMEs for the MD simulation results using the scaling laws given by Eqs. (3) and (4). In particular, we follow the methodology explained in the previous section. As in the case of the vapour and liquid coexistence densities, we compare our results obtained from the analysis described above with experimental data taken from the literature\textsuperscript{11}. The critical temperatures and densities of all the FAMEs obtained from MD simulations are presented in Table 6. Comparison between simulation and experimental critical coordinates can also be observed in Fig. 2. Agreement between simulation and experiments is excellent in all cases. Computer simulation results overestimate the experimental values less than a 3% (2.7% is the case of methyl hexanoate and 0.7% in the case of methyl butyrate). Differences between experiment and simulation could be due to finite-size scaling effects that occur during simulations when the system is close to the critical state. These effects can be taken into account explicitly using advanced simulation techniques, such as the Finite-Size Scaling procedure of Binder\textsuperscript{48}. However, this kind of analysis is out of the scope of this work. Critical densities of the homologous chemical family is also accurately predicted by the TraPPE-UA models of FAMEs. Deviation between simulation and experiments for $\rho_v$ is always below 2%, except in the case of methyl valerate (5.9%). In all cases, critical densities are slightly overestimated as expected.

We have also determined the normal boiling temperature of each methyl ester. This has been done using Eq. (6) and evaluating the pressure at $P = 101325$ Pa. Predictions from simulation are shown in Table 6. Comparison between values taken from the literature and prediction obtained from simulation show a good agreement between both results. As can be seen, in most cases the deviation is $\approx 2.2 - 3.8\%$, except in the case of methyl hexanoate, in which deviation is 4.69%, approximately.
Vapour pressure of FAMEs is also calculated from MD simulation. Since we are simulating planar vapour-liquid interfaces, the system is inhomogeneous. Consequently, the pressure is no longer a scalar magnitude but a tensorial quantity. In this case, the normal component of the pressure tensor (acting perpendicularly to the planar interface) is equal to the vapour pressure of the system. The results obtained from computer simulations are shown in Table 5. We have also presented the vapour pressure, as functions of temperature, of all the FAMEs studied in this work in Figure 3. Prediction obtained from computer simulations provide, in general, a good description of the vapour pressure curves, particularly for methyl acetate, methyl propionate, and methyl heptanoate. As can be seen in Figure 3, in the case of methyl butyrate, methyl valerate, and methyl hexanoate, MD simulation results overestimate the vapour pressure at mid and high temperatures. We have also represented the vapour pressure data in a Clausius-Clapeyron plot (Figure 4). TraPPE-UA models are able to predict very accurately the vapour pressure of all the FAMEs, from methyl acetate up to methyl heptanoate, at low temperatures.

One of the main goals of this work is to predict the interfacial properties of FAMEs. Figure 5 displays the variation of the interfacial thickness, \( d \), as a function of temperature obtained using Eq. (9) for each FAME. From this Figure it is possible to observe that \( d \) increases with increasing temperature. This means that the interfacial region becomes wider as the temperature is increased. At low temperatures, the density profiles show sharp interfaces, which can be identified with low values of interfacial thickness. An increase of the temperature results in a wider interfacial region as the system approaches the critical point, and consequently, the interfacial thickness increases. As \( T \rightarrow T_c \), the interfacial thickness diverges as the liquid and vapour phases become identical.
The surface entropy, $\Delta s^\gamma$, that can obtained from the temperature derivative of the surface tension according to Eq. (7), is an useful magnitude in studies involving surfaces in which temperature, and also surface tension, is non-uniform, leading to the well-known Bénard-Marangoni convection phenomena. Fig. 6 shows the surface entropy change of surface formation for FAMEs as a function of temperature. $\Delta s^\gamma$ is obtained from MD computer simulations of the interfacial tension in combination with Eq. (7). $\Delta s^\gamma$ varies linearly with $T$ for all the methyl esters considered here and slightly decreases with increasing temperature. This behaviour is related with the slight curvature of the surface tension as a function of temperature (see below). In addition to that, for a fixed temperature, $\Delta s^\gamma$ exhibits its largest values for short methyl esters and gets smaller as the molecular weight of the FAME increases. This indicates that curvature of surface tension, as a function of temperature, is larger for short methyl esters than for long FAMEs. Interestingly, as the temperature increases, differences between $\Delta s^\gamma$ for FAMEs becomes smaller, showing that curvature of surface tension, at high temperature, is similar for all methyl esters. This is a clear indication of the universal behaviour of $\gamma = \gamma(T)$ for different members of the homologous series as the system approaches the critical region.

![Fig. 5](image1.png)

**Fig. 5** 10–90 interfacial thickness $d$ as a function of the temperature for methyl esters (from methyl acetate to methyl heptanoate). The symbols correspond to the values obtained from density profiles obtained from MD NVT simulations and the dashed curves are included as a guide to the eye. The meaning of the symbols is the same as in Fig. 2.

![Fig. 6](image2.png)

**Fig. 6** Surface entropy of methyl esters (from methyl acetate to methyl heptanoate) as obtained from the combination of the MD NVT simulation results and Eq. (7). The meaning of the symbols is the same as in Fig. 2.

![Fig. 7](image3.png)

**Fig. 7** Surface enthalpy of methyl esters (from methyl acetate to methyl heptanoate) as obtained from the combination of the MD NVT simulation results and Eq. (8). The meaning of the symbols is the same as in Fig. 2.

It is possible to obtain the surface enthalpy, $\Delta h^\gamma$, as a function of temperature, for the FAMEs studied in this work. As in the case of the surface entropy, $\Delta h^\gamma$ can be determined from MD simulation data of the interfacial tension using Eq. (8). According to this, surface enthalpy is computed directly from surface tension values and the numerical derivative of $\gamma(T)$ with respect to the temperature. Fig. 7 shows $\Delta h^\gamma$, as a function of temperature, of the methyl esters. As can be seen, this property decreases with temperature, as expected. A nearly linear behaviour is observed for the shortest FAMEs. However, the $\Delta h^\gamma - T$ plots show a certain curvature as the molecular weight is increased. At fixed temperature, the surface enthalpy decreases as the lengths of the methyl esters are increased. Although this is true at low and mid temperatures, this trend seems to change as $T$ is high.

Finally, we consider the vapour-liquid interfacial tension of methyl esters, from methyl acetate up to methyl heptanoate. Fig. 8 shows the surface tension, as a function of temperature, as obtained from MD simulations using the virial or mechanical route. According to this, the surface tension is calculated using Eq. (2), i.e., as the difference between the normal and tangential macroscopic components of the pressure tensor. We have also included experimental data taken from the literature in order to compare the predictions from the TraPPE-UA molecular models. Simulation results obtained in this work show an excellent agreement with experimental data in the temperature range at which experimental data is available ($T \lesssim 360$K). Simulation results obtained from the use of TraPPE-UA models for methyl esters seem to slightly overestimate the surface tension at low temperatures for methyl acetate, methyl propionate, and methyl butyrate. For longer molecules, agreement between simulation and experimen-
tal data is excellent.

As in the case of the vapour-liquid phase envelopes, we have also fit the simulation data using the well-known Guggenheim's scaling law for the surface tension as a function of temperature according to Eq. (5) \cite{38,39}. This allows to obtain the critical temperature of each methyl ester and compare these values with the experimental critical values. Table 6 includes the values found in this work. It is interesting to compare the critical values obtained from Eqs. (3)-(4) and (5). As can be seen, critical temperatures determined using surface tension values and vapor and liquid coexistence densities are different. A priori, one expects that both values should be the same. However, one should take into account the following points: (1) Strictly speaking, the scaling laws given by Eqs. (3) and (5) are only valid in the asymptotic limit $T \rightarrow T_c$; in this work, as it is usual in the literature \cite{41,42,44,50,51}, we have used data corresponding to states located at $T$ far away from $T_c$ (data corresponding to temperatures from around a 30 – 40% below the critical temperature up to near the critical point). (2) The estimation of the critical coordinates depends critically on the size of the system; here we use only 1100 molecules, which in our opinion, it is not enough to avoid the finite-size effects of the systems under study \cite{52}. (3) The location of the critical coordinates depends also critically on the cutoff distance used during the simulation, and if tail corrections are applied or not. This is especially important if we are using two different kind of properties (density and surface tension values) to obtain the critical temperature since they are affected by the truncation of the intermolecular potential in a different way, as it probably happens in this work. (4) Finally, the goal of the this work is not to obtain accurate values of critical temperatures and densities of methyl esters but to check if TraPPE force field is able to predict, in a transferable manner, the phase equilibria and interfacial properties of methyl esters. We think a procedure similar to that followed by Dinpajooh et al. \cite{52}, finite-size scaling \cite{53} or mixed-field theory using the Binder cumulant parameter \cite{54} methodologies, is the correct approach to be followed if accurate estimations of critical points are needed. Unfortunately, this is out of the scope of this work.

It is interesting to mention that experimental data taken from the literature \cite{11} is only available at low temperatures, from 300 up to 360 K, approximately. The reason for which there is no experimental data at higher temperatures is that methyl esters become unstable as temperature is higher; generating micro bubbles in the tensiometer and densimeter, making impossible to measure this property accurately. Fortunately, this is not the case for computer simulations. Our study allows to obtain the surface tension of all the methyl esters analyzed in this work up to 450 – 550 K, depending on the critical temperature of each substance. It is important to recall that the simulated surface tension values in this work are, to the best of our knowledge, reported for the first time. This is particularly important in this case since there is none experimental data at temperatures above 360 K for non of the FAMEs studied, as just commented. The excellent agreement found, not only for surface tension at low temperatures, but also for vapour-liquid coexistence densities and vapour pressures in wide ranges of temperatures, makes the TraPPE-UA models proposed and used in this work excellent candidates for predicting the phase equilibria and interfacial properties of FAMEs. Simulation data presented in this work could be used, not only for theoretical modelling of these compounds, but also for the design and use of new chemical processes involving FAMEs as future and alternative diesel fuels, as well as for environmental issues, including the removal of contaminants from water and for groundwater remediation.

## 5 Conclusion

We have studied the phase equilibria and interfacial properties of methyl esters homologous series (from methyl acetate to methyl heptanoate) using the TraPPE force fields for different molecules and chemical families in a transferable way. In particular, we use the direct coexistence technique, in combination with MD NVT simulations, to study inhomogeneous systems of pure esters containing two vapour-liquid interfaces.

We examine the vapour-liquid surface tension using the virial route, i.e., calculating the normal and tangential components of the pressure tensor. We have also determined density profiles, coexistence densities, vapour pressures, surface entropies and enthalpies, interfacial thickness, and critical temperature, density, and pressure as functions of temperature for all the methyl esters.
considered. Predictions from the MD simulation for vapour-liquid coexistence densities and vapour pressures are compared with experimental data taken from the literature. These three properties are predicted remarkably well by the TraPPE models. This is particularly important since the molecular parameters of the TraPPE force fields are taken in a transferable way from other molecules and chemical families without need of adjustment.

We also predict the behaviour of interfacial thickness, surface entropy, and surface enthalpy, as functions of temperatures, and consider the effect of increasing the molecular weight of the homologous family. Particularly interesting are the results for the surface tension of methyl esters. The TraPPE models and the molecular parameters transferred from other molecules and chemical families are able to predict very accurately the surface tension of all the methyl esters studied in this work at low temperatures. Although experimental data is only available at temperatures below 360K, computer simulations allows us to provide surface tension up to the pure critical points of each substance. This is an important result since this is the first time the vapour-liquid surface tension of methyl esters is determined in the literature at these conditions. In fact, this is the first computer simulation work devoted to the prediction of the vapour-liquid equilibria and interfacial properties of the homologous series.

6 Acknowledgement

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References

the MD NVT coexistence densities using Eqs. (3) and (4), and the analysis of the MD NVT tension data using Eq. (5), respectively. Critical densities,
boiling temperatures of methyl esters (from methyl acetate to methyl heptanoate). Critical temperatures,
Table 6

Table 5 Liquid density $\rho_l$, vapour density $\rho_v$, vapour pressure $P$, compressibility factor $Z$, and surface tension $\gamma$ at different temperatures, as obtained
from MD NVT simulations for methyl esters (from methyl acetate to methyl heptanoate). The errors are estimated as explained in the text.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\rho_l$ (kg/m$^3$)</th>
<th>$\rho_v$ (kg/m$^3$)</th>
<th>$P$ (MPa)</th>
<th>$Z$</th>
<th>$\gamma$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>897(3)</td>
<td>1.2(1)</td>
<td>0.041(3)</td>
<td>1.06 (1)</td>
<td>-</td>
</tr>
<tr>
<td>325</td>
<td>867(3)</td>
<td>3.3(2)</td>
<td>0.114(7)</td>
<td>0.946(2)</td>
<td>22.3(3)</td>
</tr>
<tr>
<td>350</td>
<td>835(3)</td>
<td>6.5(3)</td>
<td>0.231(8)</td>
<td>0.90(1)</td>
<td>18.4(2)</td>
</tr>
<tr>
<td>375</td>
<td>800(4)</td>
<td>10.7(5)</td>
<td>0.42(1)</td>
<td>0.93(2)</td>
<td>15.4(3)</td>
</tr>
<tr>
<td>400</td>
<td>763(3)</td>
<td>20.0(6)</td>
<td>0.78(1)</td>
<td>0.86(1)</td>
<td>12.0(4)</td>
</tr>
<tr>
<td>425</td>
<td>722(8)</td>
<td>32.0(7)</td>
<td>1.26(2)</td>
<td>0.821(7)</td>
<td>9.0(3)</td>
</tr>
<tr>
<td>450</td>
<td>679(4)</td>
<td>51(1)</td>
<td>1.92(1)</td>
<td>0.75(1)</td>
<td>6.4(2)</td>
</tr>
</tbody>
</table>

Table 6 Experimental ($T_a^{c\rho}, \rho_c^{c\rho}, P_c^{c\rho}, \gamma_c^{c\rho}$, and $T_b^{c\gamma}$) and predicted ($T_a^c, T_b^c, \rho_l^c, P_l^c$, and $T_b^c$) critical temperatures, densities, and pressures and normal boiling temperatures of methyl esters (from methyl acetate to methyl heptanoate). Critical temperatures, $T_a^c$ and $T_b^c$, are obtained from the analysis of the MD NVT coexistence densities using Eqs. (3) and (4), and the analysis of the MD NVT tension data using Eq. (5), respectively. Critical densities, $\rho_l^c$, are also obtained from the analysis of the MD NVT coexistence densities using Eq. (4). Critical pressures, $P_l^c$, are obtained using Eq. (6) evaluating the temperature $T_b^c$ as obtained from Eq. (3). Normal boiling temperatures are obtained using Eq. (6) evaluating the pressure $P = 101325$ Pa.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_a^{c\rho}$ (K)</th>
<th>$T_a^c$ (K)</th>
<th>$T_b^c$ (K)</th>
<th>$\rho_l^c$ (kg/m$^3$)</th>
<th>$\rho_l$ (kg/m$^3$)</th>
<th>$P_l^c$ (MPa)</th>
<th>$P_l$ (MPa)</th>
<th>$T_b^{c\gamma}$ (MPa)</th>
<th>$\gamma$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl acetate</td>
<td>510.0</td>
<td>523.9</td>
<td>525.14</td>
<td>324.0</td>
<td>321.0</td>
<td>4.692</td>
<td>6.127</td>
<td>322.63</td>
<td>330.09</td>
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<tr>
<td>Methyl propionate</td>
<td>531.5</td>
<td>543.1</td>
<td>550.38</td>
<td>310.0</td>
<td>310.0</td>
<td>3.986</td>
<td>4.302</td>
<td>340.10</td>
<td>352.44</td>
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<tr>
<td>Methyl butyrate</td>
<td>554.5</td>
<td>558.8</td>
<td>571.65</td>
<td>304.0</td>
<td>300.0</td>
<td>3.464</td>
<td>3.538</td>
<td>359.35</td>
<td>373.60</td>
</tr>
<tr>
<td>Methyl valerate</td>
<td>566.9</td>
<td>558.0</td>
<td>589.80</td>
<td>272.0</td>
<td>288.0</td>
<td>3.090</td>
<td>3.564</td>
<td>388.09</td>
<td>400.65</td>
</tr>
<tr>
<td>Methyl hexanoate</td>
<td>602.6</td>
<td>618.4</td>
<td>597.46</td>
<td>283.0</td>
<td>288.0</td>
<td>2.797</td>
<td>3.487</td>
<td>407.72</td>
<td>427.81</td>
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<tr>
<td>Methyl heptanoate</td>
<td>628.0</td>
<td>644.1</td>
<td>635.28</td>
<td>278.0</td>
<td>278.0</td>
<td>2.543</td>
<td>3.630</td>
<td>435.71</td>
<td>446.15</td>
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</table>