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On the study of the vapor-liquid interface of associating fluids with classical density functional theory

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Abstract

Classical density functional theory (DFT) is applied to study the vapor-liquid interface of associating fluids. Our classical DFT implementation uses a Helmholtz free energy functional that reduces to the perturbed-chain statistical associating fluid theory (PC-SAFT) equation of state in the bulk limit. We apply a new association functional presented in one of our previous works based on the weighted density approximation to calculate the interfacial tension of associating fluids and compare them with the most used association functionals from literature. It is found that classical DFT with the three association functionals and the current molecular parameters of PC-SAFT is not able to predict satisfactorily the interfacial tension of alkanols. Therefore, the experimental interfacial tension of alkanols and some associating fluids is included in the determination of the pure molecular parameters of PC-SAFT. With this approach the determination of interfacial tension of pure associating fluids can be greatly improved with the new parameters but at the expense of slightly higher deviations in the vapor pressure. The new parameters are tested for the determination of vapor-liquid equilibria (VLE) and the prediction of interfacial tension of binary mixtures containing at least one associating compound. Good agreement is found between experimental data of VLE and interfacial tension of the binary mixtures and the three association functionals. Furthermore, we discuss about

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the limitations and capabilities of the current classical DFT implementation in the study of the vapor-liquid interface of associating fluids.

**Keywords:** Classical density functional theory, associating fluids, interfacial tension

### 1. Introduction

Understanding the microscopic structure of fluids is of great importance for both science and industry as it gives valuable insight on how particle interactions influence the macroscopic properties of fluids. One area of considerable interest in development is the study of inhomogeneous fluids, which concern systems where the microscopic particle density varies along the spacial coordinates due to the effect of an external potential. Examples of these systems are the fluid-fluid and fluid-solid interfaces. Close to these interfaces, the local particle density deviates from its bulk value giving origin to properties such as interfacial tension or adsorption, for fluid-fluid and solid-fluid interfaces. These properties are of great interest especially to the chemical, biochemical and petroleum industries as many chemical and physical process comprise surface phenomena.[1] In addition, many of these processes involve the use of complex fluids capable of forming hydrogen bonds. The associating interactions, such as hydrogen bonding, play an important role in the study of interfaces as they considerable contribute to the microscopic structure of fluids in the determination of interfacial tension, adsorption, capillary condensation and evaporation, and many other self-assembly properties like nucleation, micelle formation and colloid stability characteristic of the behavior of surfactants.[2][3][4]

One powerful tool to study inhomogeneous fluids with an unified framework is the classical density functional theory (DFT). Classical DFT is able to bridge the rigorous concepts used in molecular simulations with the versatile and capable equations of state used to study the behavior of bulk fluids.[1] In this manner classical DFT brings together the best of two worlds, as it is possible to implement bulk theories and already parameterized models in the study of...
complex systems in different geometries with great accuracy and a degree of predictability regularly only achieved with molecular simulations. One of the clear advantages of classical DFT over other theories used in the study of inhomogeneous fluids such as gradient theories for the determination of interfacial tension,\[5, 6, 7, 8\] or the multicomponent potential theory of adsorption for the determination of adsorption isotherms, \[9, 10, 11\] is that classical DFT is able to tackle both different phenomena under the same framework with an adequate definition of an external potential.\[12\] The cornerstone of a classical DFT implementation is the definition of the inhomogeneous Helmholtz free energy functional, which contains the complete information about the interactions between the particles of the fluids. Hence, the reliability of classical DFT will depend on how the Helmholtz free energy functional is capable of representing the nature of the particle interactions from a microscopic point of view in the study of the macroscopic properties of the inhomogeneous systems.

As stated previously, the Helmholtz free energy functional is one of the most important aspects in a classical DFT implementation as it is responsible of describing the microscopical behavior of particles in an inhomogeneous system, therefore, it is not strange that research is focused mostly in developing free energy functionals for the study of different types of fluids, e.g. single particles, chain molecules, associating fluids, among others. To carry out this task, several of the classical DFT implementations are based on the Thermodynamic Perturbation Theory (TPT) of Wertheim, \[13, 14, 15, 16\] which by means of a reference state, usually the hard sphere, additional particle interactions are accounted for by perturbations that contribute to the total Helmholtz free energy of the uniform fluid. An example is the Statistical Association Fluid Theory (SAFT) equation of state.\[17, 18\] In order to make use of bulk theories in the development of the Helmholtz free energy functional the concept of weighted densities is introduced, which implies the calculation of an \textit{averaged} density over a volume usually related to the actual range of interaction of the particles. The use of averaged densities in the approximation of the inhomogeneous free energy functional is known as the Weighted Density Approximation (WDA).\[19, 20, 21\]
Even though WDA is widely used in the development of classical DFT functionals due to its proven success, simpler approximations such as the local density approximation (LDA) have also been used in the study of inhomogeneous fluids but only offering semiquantitative results.\[1\]

Probably the most successful and used functional in classical DFT implementations is the modified fundamental measure theory (FMT) for the study of inhomogeneous hard sphere systems simultaneously developed by Yu and Wu,\[22\] and Roth et al.\[23\] The modified FMT, from now on called only FMT, is an improved version of the original FMT developed by Rosenfeld.\[24\] It makes use of six weighted densities that account for the fundamental measures of hard spheres. For bulk fluids, the functional reduces to the hard spheres equation of state developed in parallel by Boublík\[25\] and Mansoori-Carnahan-Starling-Leland.\[26\] Starting from FMT for inhomogeneous hard spheres, different contributions to the Helmholtz free energy functional have been developed. For polymeric fluids, or chain molecules, Yu and Wu\[27\] developed a chain functional by combining Wertheim’s first order TPT1 for chain connectivity with weighted densities defined in FMT, explicitly taking into account the distributions of the individual segments of the chain molecules. Later, Tripathi and Chapman\[28\] introduced a new chain functional that was obtained by evaluating Wertheim’s TPT1 for inhomogeneous associating fluids in the limit of complete association in order to form chains between the segments. With this implementation the result is the density distribution of chain molecules, making possible to avoid the determination of the distribution of the individual segments, thus considerably reducing the complexity and calculation time required. Additionally, the chain functional developed by Tripathi and Chapman\[28\] allows the use of non-integer values for the number of segments $m$ usually used as a molecular parameter, which made it suitable for classical DFT implementations based on SAFT EoS and some of its variants. In the investigation of associating fluids, the first developed functionals correspond to the work of Segura et al.\[29\][30][31] They used two different approaches to account for association. In the first approach the inhomogeneous form of Wertheim’s TPT1 with the local density was used. For
the second approach they used a density-dependent WDA together with the bulk version of Wertheim’s TPT1, obtaining good agreement with molecular simulation of associating hard spheres and mixtures, especially with this second approach. Later, Yu and Wu\cite{32} introduced an association functional (aFMT) similar to the second approach of Segura et al.\cite{29} but using the weighted densities defined in FMT, obtaining superior performance. Then, Bymaster and Chapman\cite{4} took the first approach of Segura et al.\cite{29} and improved it to introduce the association functional iSAFT by taking into account a weighted density only in the approximation of the cavity correlation function of the inhomogeneous fluid, obtaining better agreement than the previous functionals when compared to molecular simulations. Recently, Camacho et al.\cite{33} introduced a new association functional (aWDA) purely based in the bulk expression of Wertheim’s TPT1 for associating fluids and a WDA approach. In addition, they carried out a thorough comparison of the performance of the association functionals aFMT, iSAFT and aWDA against molecular simulations and found excellent agreement for fluids with one, two and four association sites confined in slit-like pores under a wide range of conditions. Even though the results with the three functionals are equally good for many of the cases studied, aFMT and aWDA offer a better compromise in terms of computational time opposite to iSAFT.

In the previous paragraph we gave a succinct introduction about the hard sphere, chain and association functionals that form the backbone of a large number of classical DFT works developed for a wide range of applications, including calculation of fluid-fluid and fluid-solid interfacial properties such as interfacial tension, adsorption, solvation, phase behavior in porous media, particle self-assembly, etc. On the other hand, functionals for dispersive interactions follow a different path as they are what really differentiate many of the classical DFT implementations. Pertinent examples comprise the works of the perturbed-chain statistical association fluid theory (PC-SAFT),\cite{34,35,36,37,38,39,40,41,42} where they use WDA together with the bulk reduced free energy density expression for dispersive interactions directly from
the equation of state. Implementations that make use of the mean field approximation (MFA)\textsuperscript{43} to treat dispersion forces include several studies with interfacial-SAFT functionals\textsuperscript{44, 46, 47, 48}. SAFT with potential of variable range (SAFT-VR)\textsuperscript{49, 50, 3, 51, 52, 53} and SAFT-\(\gamma\).\textsuperscript{56, 57, 58}

Likewise, many classical DFT implementations are based on the work of Yu and Wu\textsuperscript{32, 27} for chain and association functionals, on which the dispersive interactions are approximated with the quadratic density expansion and mean spherical approximation.\textsuperscript{59, 2, 60, 61, 62}

In this work we focus our attention to the study on the calculation of the interfacial tension of the vapor-liquid interface of associating fluids with a classical DFT implementation based on the PC-SAFT equation of state. It has been proven in previous works\textsuperscript{39, 38, 8, 40, 41} that classical DFT and PC-SAFT are able to correlate the interfacial tension of pure non-associating compounds with great accuracy with the current molecular parameters of PC-SAFT.\textsuperscript{63} Furthermore, the prediction of interfacial tension of mixtures of these compounds with only information of the bulk vapor-liquid equilibrium (VLE) have shown excellent results, positioning classical DFT as a valuable predictive tool in the calculation of interfacial properties in comparison with other theories. However, Mairhofer and Gross\textsuperscript{8} showed that classical DFT and PC-SAFT produce relatively large deviations at low temperatures in the calculation of interfacial tension of normal alkanols with the current molecular parameters of these associating compounds.\textsuperscript{64} In their work they concluded that these deviations may be attributed to an inadequate description of the orientation of molecules at the interface due to hydrogen bonding, especially for the larger alkanols. Similar results for alkanols were obtained also by Gloor \textit{et al.}\textsuperscript{51} with a classical DFT implementation based on SAFT-VR, where the interfacial tension calculated with the molecular parameters for SAFT-VR obtained with regressions of pure VLE experimental data was not satisfactory. To overcome this issue, they included experimental data of interfacial tension in the determination of the molecular parameters obtaining good agreement for this property. Nonetheless, they did not quantify the effect of the new parameters in the determination of
the vapor pressure and equilibrium liquid density. Fu and Wu\cite{2} on the other hand, studied the vapor-liquid interface and interfacial tension of associating compounds, including alkanols from methanol to pentanol. They obtained the molecular parameters by regressing calculated values of vapor pressure, liquid density and interfacial tension to experimental data. The results obtained show good agreement with experiments only in a narrow temperature range for each of the compounds.

Given the state of the current results of interfacial tension for associating fluids and classical DFT, in this work we make a comparison of the performance of the two most used association functionals, aFMT developed by Yu and Wu\cite{32} and the association functional from iSAFT developed by Bymaster and Chapman,\cite{4} together with a new approach based on Wertheim’s TPT1 association term and the weighted density approximation introduced in one of our previous works.\cite{33} In the first part we evaluate the interfacial tension of associating fluids with the current molecular parameters for the PC-SAFT equation of state obtained from experimental data of vapor pressure and liquid density.\cite{63, 64} Subsequently, we propose a new set of parameters which include the interfacial tension during the regression and make an assessment of the impact they have in vapor pressure, liquid density and in the VLE of binary mixtures in comparison with the original parameters. In the last section of the calculations we use our classical DFT implementation to assess the performance of the predictive capabilities for the determination of the interfacial tension of binary mixtures of non-associating and associating fluids.

2. Classical density functional theory

The classical DFT formalism defines the grand potential as a functional of the particle density distribution of an inhomogeneous system at fixed temperature $T$, volume $V$, and the chemical potential of each species $\mu_{b,t}$ in the system at bulk conditions \cite{12}. The grand potential functional for a free interface, which
is the case of the vapor-liquid interface, is given by

$$
\Omega[\rho(r)] = F[\rho(r)] - \sum_{i}^{n} \mu_{b,i} \int \rho_i(r) dr
$$

(1)

where the vector $$\rho(r) = \{\rho_1(r), \rho_2(r), ..., \rho_n(r)\}$$ represents the local densities of all components $$n$$, $$\mu_{b,i}$$ is the chemical potential of component $$i$$ in the bulk phase. The Helmholtz free energy functional, which is represented with $$F[\rho(r)]$$, contains all the information of the particle interactions and can be separated into an ideal and residual part. The ideal term is known exactly [12], whereas the residual part based on the PC-SAFT equation of state can be approximated as

$$
F_{\text{res}}[\rho(r)] = F_{\text{hs}}[\rho(r)] + F_{\text{hc}}[\rho(r)] + F_{\text{at}}[\rho(r)] + F_{\text{as}}[\rho(r)]
$$

(2)

The superscripts hs, hc, at, and as represent the contributions to the free energy functional due to hard sphere exclusion, chain formation, dispersive interactions and association of the molecules. In this work for $$F_{\text{hs}}$$ we use the modified fundamental measure theory (FMT) [22, 65]. For the $$F_{\text{hc}}$$ contribution we use the thermodynamic perturbation theory (TPT) chain functional [28]. For dispersive interactions $$F_{\text{at}}$$ we use WDA and the bulk expression from PC-SAFT. The contribution due to association follows the functionals aFMT [32], iSAFT [4], and aWDA [33]. For more details of the non-associating functionals as implemented here we refer to our previous work [41]. The determination of the interfacial tension requires the minimization of the grand potential functional to obtain the equilibrium particle density $$\rho^*(r)$$ [12]. The later is found with the solution of the Euler-Lagrange equation obtained with the functional derivative of $$\Omega[\rho(r)]$$ for each species $$j$$

$$
\rho_j(r) = \exp \left( \frac{\mu_j}{k_B T} - \frac{\delta F_{\text{res}}[\rho_j]}{\delta \rho_j(r)} \right)
$$

(3)

Several methods for the solution of Eq. (3) have been reviewed elsewhere [38]. Once the equilibrium density profile is found with the minimization of the grand potential, the interfacial tension can be calculated

$$
\gamma = \Omega[\rho^*(z)] + P \int_{0}^{H} dz
$$

(4)
where $f[p^*(z)]$ is the total free energy density of the inhomogeneous system evaluated with the equilibrium density profile as function of the axis perpendicular to the planar interface, and $P$ is the equilibrium pressure of the two phases.

2.1. Association functionals

The functional $aFMT$ [32] is given by

$$F^\text{as} = k_B T \int \Phi^\text{as}(\{n_\alpha(r)\}) \, dr$$

(5)

The free energy density $\Phi^\text{as}$ is a function of the weighted densities $n_\alpha(r)$, three scalar $\alpha = 0, 2, 3$ and one vector $\alpha = V2$. Details of $n_\alpha(r)$ compatible with PC-SAFT can be found in Refs. [34] and [39]. Therefore, the free energy density due to association is expressed as

$$\Phi^\text{as} = \sum_i n_{0i}(r) \zeta_i(r) \sum_{A_i} \left( \ln \chi_{A_i}(\{n_\alpha(r)\}) - \frac{\chi_{A_i}(\{n_\alpha(r)\})}{2} + 1 \right)$$

(6)

Where $n_{0i}$ is a weighted density, $\zeta_i$ is a correction factor function of a scalar and vector weighted densities, $m_i$ is the segment number of component $i$ and $\chi_{A_i}$ is the fraction of non-bonded particles at site $A_i$. The first summation is carried out over all components $n$, and the second summation over all sites of component $i$ available for bonding. The fraction of non-bonded particles is given by

$$\chi_{A_i}(\{n_\alpha(r)\}) = \left( 1 + \sum_j n_{0j}(r) \zeta_j(r) \sum_{B_j} \chi_{B_j}(\{n_\alpha(r)\}) \Delta^{A_iB_j}(\{n_\alpha(r)\}) \right)^{-1}$$

(7)

where $\Delta^{A_iB_j} = \kappa^{A_iB_j} \sigma^{3}_{ij}(\exp(\varepsilon^{A_iB_j}/k_BT) - 1) g^{ij}_0(\{n_\alpha(r)\})$ is the association strength related to sites $A_i$ and $B_j$. The association strength is a function of the bonding energy $\varepsilon^{A_iB_j}$ and the volume available for bonding given by $\kappa^{A_iB_j}$ which are unique for each fluid. Moreover, $g^{ij}_0(\{n_\alpha(r)\})$ is the radial correlation function evaluated at contact from FMT [32]. The mixture parameters are obtained with $\sigma_{ij} = 0.5(\sigma_i + \sigma_j)$, $\kappa^{A_iB_j} = (\kappa^{A_iB_i} \cdot \kappa^{A_jB_j})^{1/2}$ and $\varepsilon^{A_iB_j} =$
The iSAFT functional \[4\] is given by

\[
F_{\text{as}}[\rho(r)] = k_B T \int \sum_i^n \rho_i \sum_{A_i} \left( \ln \chi_{A_i}(r) - \frac{\chi_{A_i}(r)}{2} + \frac{1}{2} \right) dr
\]  

(8)

A compatible form\[38\] for the fraction of non-bonded particles is given by

\[
\chi_{A_i}(\rho(r)) = \left( 1 + \frac{1}{2} \sum_j^n \int_{|r-r'|<\sigma_{ij}} \rho_j(r') \sum_{B_j} \chi_{B_j}(r') \Delta^{A_i,B_j}(r,r') \right)^{-1}
\]  

(9)

Where the association strength is \[
\Delta^{A_i,B_j}(\rho(r)) = \kappa^{A_i,B_j} \sigma_{ij}^3 \left( \exp \left( \frac{\epsilon^{A_i,B_j}}{k_B T} \right) - 1 \right) \sigma_{ij} \]  

(10)

And the cavity correlation function is calculated with the local value of the weighted density as given by Eq. (10).

The implicit equations for \(\chi_{A_i}\) must be solved prior to the calculation of the interfacial properties of the associating fluid. For the three methods, we use a simple successive substitution approach with a combining factor to avoid divergence.

Where the association strength is \[
\Delta^{A_i,B_j}(\rho(r)) = \kappa^{A_i,B_j} \sigma_{ij}^3 \left( \exp \left( \frac{\epsilon^{A_i,B_j}}{k_B T} \right) - 1 \right) \sigma_{ij} \]  

(11)

The fraction of particles not bonded at site \(A_i\) is

\[
\chi_{A_i}(\bar{\rho}(r)) = \left( 1 + \sum_j^n \bar{\rho}_j(r) \sum_{B_j} \chi_{B_j}(\bar{\rho}(r)) \Delta^{A_i,B_j}(\bar{\rho}(r)) \right)^{-1}
\]  

(12)

We define the association strength as \[
\Delta^{A_i,B_j}(\bar{\rho}(r)) = \kappa^{A_i,B_j} \sigma_{ij}^3 \left( \exp \left( \frac{\epsilon^{A_i,B_j}}{k_B T} \right) - 1 \right) \sigma_{ij} \]  

(13)

And the cavity correlation function is calculated with the local value of the weighted density as given by Eq. (10).
3. Results and discussion

In this section we present the results for the interfacial tension of associating fluids obtained with the three functionals introduced previously. All calculations are compared to experimental data or correlations obtained from literature. The results are organized in three parts. In the first part we show results with the original molecular parameters for PC-SAFT which are normally fitted to experimental data of vapor pressure and equilibrium liquid density of pure compounds. In the second part, pure component parameters of PC-SAFT are optimized by including liquid densities, vapor pressures and the interfacial tension of the vapor-liquid interface. We make comparisons of the results obtained with the new parameters to those using the original parameters in the calculation of vapor pressures, liquid densities and interfacial tension. In the last part we further test the performance of the new optimized parameters in correlating VLE of binary systems and predictions of interfacial tension of binary mixtures.

In the following results, calculations are compared to experimental data using the relative absolute average deviation (AAD %), obtained with

\[
\text{AAD} \% = \frac{1}{n_{\text{exp}}} \sum_{i} \left| \frac{X_{i}^{\text{exp}} - X_{i}^{\text{cal}}}{X_{i}^{\text{exp}}} \right| \times 100\% \quad (14)
\]

Where \(X_{i}\) represents a data point of the property of interest, either experimental (exp) or calculated (cal).

3.1. Original parameters

One of the main advantages of classical DFT over other theories used in the study of the vapor-liquid interface is that it is not required to fit additional parameters for the calculation of the interfacial tension for pure compounds or mixtures, e.g. density gradient theories usually require the determination of an influence parameter. Therefore, only five molecular parameters of PC-SAFT for associating fluids and binary interaction parameters for mixtures are needed. These parameters are commonly fitted to experimental data of pressure and liquid density at vapor-liquid equilibrium conditions of the pure compounds,
whereas the binary interaction parameters are obtained by fitting the VLE of the binary mixtures. Table 1 shows molecular parameters for PC-SAFT found in literature used for the study of associating fluids.[63, 66, 67, 68, 69, 8, 40]

Firstly, we focus our attention to the series of normal alkanols from methanol to 1-nonanol. In Fig. 1, the selected experimental data of the interfacial tension of alkanols are plotted as function of temperature[70]. These data are selected as used by Somayajulu[71] to develop a series of correlations that have been reported to be very accurate[72] and they are extensively used by other works[73, 34, 74, 8], including NIST.[75] Comparison of these data sets with other experimental results found in literature for some of the alkanols are shown in the Supporting Information. From Fig. 1 it can be seen that for a given temperature the interfacial tension increases as the chain length of alkanol increases from ethanol to 1-nonanol. Methanol on the other hand, shows an interfacial tension almost identical to ethanol, and in some cases the interfacial tension of methanol is higher than ethanol according to the experimental data. The fact that for these two components the interfacial tension is almost identical reflects that the effect of associative interactions are predominant in these two molecules, neglecting in some degree the additional methylene group in the ethanol molecule. Surprisingly, the similarities between the experimental interfacial tension of methanol and ethanol are in agreement with the results found by Luck[76] in the experimental study of the fraction of non-bonded species for these two compounds, which also show almost identical values for both components. Similarities in the association strength of methanol and ethanol based on the fraction of non-bonded species data has motivated studies about the performance of association theories and equations of state,[77, 78, 79] however, as there are not more experimental data sets available for comparison, conclusions based only in one data set must be made with caution. Although the trend of the experimental data of interfacial tension and the fraction of non-bonded species is almost identical for methanol and ethanol, other properties such as the dielectric constant[80], or the formation of azeotropic mixtures only for the ethanol-water system, still give evidence of the clear differences between the
Table 1: PC-SAFT molecular parameters fitted to vapor pressure and equilibrium liquid density only.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m</th>
<th>σ (Å)</th>
<th>ε/k_B (K)</th>
<th>ε^AB/k_B (K)</th>
<th>κ^AB</th>
<th>Scheme</th>
<th>AAD %</th>
<th>( P )</th>
<th>( \rho_L )</th>
<th>( \gamma )_aFMT</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1.8824</td>
<td>3.0023</td>
<td>181.77</td>
<td>2738.03</td>
<td>0.054664</td>
<td>2B</td>
<td>1.33</td>
<td>0.52</td>
<td>11.53</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.6351</td>
<td>3.0577</td>
<td>191.90</td>
<td>2574.01</td>
<td>0.041290</td>
<td>2B</td>
<td>0.35</td>
<td>0.17</td>
<td>18.23</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>1-Propanol</td>
<td>2.9997</td>
<td>3.2522</td>
<td>233.40</td>
<td>2276.80</td>
<td>0.015268</td>
<td>2B</td>
<td>0.92</td>
<td>1.17</td>
<td>34.66</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1-Butanol</td>
<td>2.7515</td>
<td>3.6139</td>
<td>259.59</td>
<td>2544.60</td>
<td>0.006692</td>
<td>2B</td>
<td>1.98</td>
<td>0.76</td>
<td>32.16</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>3.6260</td>
<td>3.4508</td>
<td>247.28</td>
<td>2252.10</td>
<td>0.010319</td>
<td>2B</td>
<td>0.92</td>
<td>0.17</td>
<td>18.23</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>3.5146</td>
<td>3.6735</td>
<td>262.32</td>
<td>2538.90</td>
<td>0.005747</td>
<td>2B</td>
<td>2.28</td>
<td>0.53</td>
<td>20.19</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1-Heptanol</td>
<td>4.3985</td>
<td>3.5450</td>
<td>253.46</td>
<td>2878.50</td>
<td>0.001155</td>
<td>2B</td>
<td>3.19</td>
<td>1.97</td>
<td>13.75</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1-Octanol</td>
<td>4.3555</td>
<td>3.7145</td>
<td>262.74</td>
<td>2754.80</td>
<td>0.002197</td>
<td>2B</td>
<td>3.94</td>
<td>0.53</td>
<td>11.83</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1-Nonanol</td>
<td>4.6839</td>
<td>3.7292</td>
<td>263.64</td>
<td>2941.90</td>
<td>0.001427</td>
<td>2B</td>
<td>2.06</td>
<td>1.16</td>
<td>11.75</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>2.0</td>
<td>2.3449</td>
<td>171.67</td>
<td>1704.06</td>
<td>0.304800</td>
<td>4C</td>
<td>1.51</td>
<td>1.61</td>
<td>7.88</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>1.5026</td>
<td>3.7014</td>
<td>286.12</td>
<td>5248.62</td>
<td>0.006660</td>
<td>1A</td>
<td>0.27</td>
<td>0.09</td>
<td>11.20</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>DEA</td>
<td>5.2731</td>
<td>2.9785</td>
<td>276.77</td>
<td>1419.67</td>
<td>0.072550</td>
<td>4C</td>
<td>0.89</td>
<td>0.47</td>
<td>32.47</td>
<td>( TW^{c} )</td>
<td></td>
</tr>
</tbody>
</table>

\( ^{a} \) For alkanols the vapor pressure and liquid density are taken from Ref. 82, and interfacial tension from Ref. 70. All experimental data for water is taken from Ref. 75. Experimental data of vapor pressure and liquid density for acetic acid is taken from DIPPR correlations[82], and for DEA data comes from Ref. 83, 84. \( ^{b} \) For all compounds AAD % is calculated in the temperature range from 275 K to \( 0.85T_c \). \( ^{c} \) This work.

The deviations of the prediction of interfacial tension of some alkanols using the original PC-SAFT molecular parameters are shown in Table 1. For the sake of clarity, the deviations shown are obtained only with aFMT as the other two association functionals give virtually the same values. AAD % is calculated in the temperature range from 275 K to \( 0.9T_c \). For all compounds studied here, Rather large deviations are found for the predicted interfacial tension of alkanols, increasing from methanol (~ 11.5 %) to 1-propanol (~ 35 %), and then decreasing until 1-nonanol (~ 11.7 %). This behavior has been reported also by Mairhofer and Gross[8] with a classical DFT implementation based on PC-SAFT with the iSAFT association functional. In their work, they discussed that one of the probable reasons of these rather large deviations may be attributed to an
Figure 1: Experimental data sets of interfacial tension for the series of normal alkanols from methanol to 1-nonanol as a function of temperature. Data was originally obtained by Efremov and Yu (1966) and compiled in Ref. [70]. Symbols represent the actual experimental data and lines are guides to the eye.
inadequate description by classical DFT of the highly directional orientation of molecules at the vapor-liquid interface due to hydrogen bonding. In other words, the hydroxyl group of the 1-alkanol molecules is preferably oriented towards the high density zones as there are more association sites available for bonding and this behavior is expected to be more pronounced in the short alkanols \[77\]. However, it is also observed that this conclusion is only supported by the results obtained from 1-propanol to 1-nonanol as the deviations for methanol are interestingly lower than ethanol and 1-propanol.

Based on the similarities of the experimental interfacial tension between methanol and ethanol, and also using the monomer fraction data as support\[76\], it is conceivable to assume that the properties of these molecules are mainly dominated by hydrogen bonding. Therefore, an additional explanation introduced here is that the competition between association and the other contributions to the Helmholtz free energy is not been represented accurately by classical DFT and the three association functionals. This behavior can be observed especially at temperatures lower than 400 K as seen in Fig. 2 for ethanol. Comparison of the results obtained with classic DFT and experiments of the remaining alkanols with the original molecular parameters appearing in Table 1 are shown in the Supporting Information in Figs. SI-5 to SI-9.

An example of the competition between contributions to the Helmholtz free energy functional was studied by Segura \textit{et al.} \[29\,30\] and Yu and Wu \[32\] while developing the first versions of iSAFT and aFMT. More recently, Camacho \textit{et al.}\[33\] took on these works and compared both association functionals together with the lately proposed aWDA. In those studies, they evaluated the behavior of hard spheres and associative spheres close to hard walls and observed that, depending on the conditions the systems where either dominated by repulsive or associative interactions. In conditions where both repulsive and associative interactions have equivalent weights on the system’s particle density, deviations between classical DFT and molecular simulation were larger. Even though Segura \textit{et al.}\[29\], Yu and Wu \[32\] and Camacho \textit{et al.}\[33\] only took into account hard sphere exclusion and associative interactions, a similar behavior could be
observed here where the competition between hard spheres, chain formation, dispersion and association apparently is not being represented accurately in the vapor-liquid interface. For methanol, association could be considered the dominating contribution and it shows the lowest deviations. On the other hand, ethanol shows larger deviations than methanol while still having an equivalent interfacial tension and similar associative interactions judging from information of the monomer fractions.[76] We consider this an indication of an inadequate description of the competition between the contributions to the free energy introduced by the additional methylene group in ethanol. Subsequently, 1-propanol shows even larger deviations than methanol and ethanol with only an additional methylene group than the later. Accordingly, it may be considered possible that the relation between the contributions to the Helmholtz free energy is not being described accurately by the classical DFT implementation. On the other hand, for the heavier alkanols it is expected that dispersion forces and chain formation become more predominant in the contribution to the surface energy by increasing the interfacial tension at higher molecular weights.[85] This effect that can be observed from 1-propanol to 1-nonanol as the deviations moderately decrease.

The molecular parameters for water shown in Table 1 were taken from the work of Liang et al.[81]. In their work, they tested several sets of parameters for water against different bulk properties. The set chosen for this work was determined by taking into account the liquid-liquid equilibrium (LLE) of water and alkanes, and gave the best overall results according to their findings. More recently, Mairhofer and Gross[38] tested several sets of molecular parameters for water in interfacial tension calculations and also found that the set with the lowest overall deviation of bulk properties and interfacial tension was the one from Liang et al.[81] Fig. 3 shows the interfacial tension of water calculated with the three association functionals compared to experimental data.[75] The results show good agreement with experimental data and are also in agreement with other implementations of classical DFT and PC-SAFT.[38, 40] All three functionals overpredict the interfacial tension at temperatures close to the crit-
Figure 2: Interfacial tension of ethanol calculated with classical DFT using three different association functionals compared to experimental data [70]. The PC-SAFT molecular parameters of the pure compounds are shown in Table I.

The interfacial tension of acetic acid and diethanolamine (DEA) was also investigated. The PC-SAFT parameters are shown in Table I where the association scheme used for acetic acid is 1A and for DEA is 4C. The results for acetic acid are plotted in Fig. SI-10a in Supporting Information, where it can be seen that all functionals show good agreement with the experimental data in the whole temperature range. For this case, aFMT shows the larger deviations (AAD % = 11.2), aWDA (AAD % = 7.5) and iSAFT shows the...
Figure 3: Interfacial tension of water calculated with the three association functionals and compared to reference data from the International Association for the Properties of Water and Steam given by NIST [75].

lowest (AAD % = 3.2). For the case of DEA, new parameters were determined in this work by fitting experimental data of vapor pressure and liquid densities only [83, 84]. In Fig. SI-10b in Supporting Information, the deviations obtained with the three functionals are considerable large in comparison with the other compounds, showing values of AAD% larger than 30 % with all functionals.

It is surprising that the three models predict the interfacial tension of DEA very close to that of water despite the large differences in the segment number and dispersive energy parameters between water and DEA, \( m_w = 2.0 \) and \( \varepsilon_w/k_B = 171.7 \) for water, against \( m_{DEA} = 5.3 \) and \( \varepsilon_{DEA}/k_B = 276.8 \) for DEA. The later implies a considerable difference of the particle interactions due to dispersion forces, which apparently are not taken into account by the models.

3.2. New PC-SAFT parameters

Given the results shown in the previous section, we propose a correlation of a new set of pure component parameters for alkanols and DEA in order to
improve the calculated interfacial tension of these associating fluids. Although the prediction of interfacial tension of acetic acid show good agreement with experimental data, we also included this compound in the study in order to investigate the effect of a new set of parameters. Oppositely, it was decided to keep the current parameters of water as they have been already optimized to accurately reproduce other bulk properties and also produce acceptable results for interfacial tension with the three functionals. To obtain the new sets of molecular parameters the calculated vapor pressure, liquid density and interfacial tension of the vapor-liquid interface are regressed to experimental data with an optimization procedure in the temperature range $275-0.9T_c$. The objective function used during the optimization is

$$\text{Obj} = \sum_{i}^{m_{\text{set}}} \sum_{j}^{n_{p,i}} \left( \frac{X_{ij}^{\text{exp}} - X_{ij}^{\text{cal}}}{X_{ij}^{\text{exp}}} \right)^2$$

Where $m_{\text{set}}$ is the type of experimental data set, i.e. vapor pressure, liquid density or interfacial tension, and $\alpha_i$ correspond to the weight assigned to each of the data sets which for this work we treat it as $\alpha_i = 1$ for the three properties. Moreover, $n_{p,i}$ is the total number of experimental points in set $i$, with $X_{ij}^{\text{exp}}$ and $X_{ij}^{\text{cal}}$ as the experimental and calculated property $j$ of set $i$ to be fitted.

Preliminary results showed that the inclusion of interfacial tension during the regression of the molecular parameters for PC-SAFT improved the results for interfacial tension but also increased the deviation of the correlation of vapor pressure. Therefore, for many of the associating fluids studied, the inclusion of the interfacial tension greatly decreased the accuracy of the calculated vapor pressure. To overcome this issue, one approach could be to give different weights to the three properties, however, it was decided to fixed the value of the segment number $m_i$ and only regress the four additional parameters, i.e. $\sigma_i$, $\epsilon_i$, $\kappa_{A,B_j}$, and $\epsilon_{A,B_j}$. In this way, several minimizations are carried out by fixing the segment number and the deviations for the vapor pressure, liquid density and interfacial tension are recorded as shown in Fig. 4 where the deviations as a function of the segment number for the determination of the parameters of
Table 2: Molecular parameters of some associating fluids for PC-SAFT determined with vapor pressure, liquid density and interfacial tension for each of the three association functionals.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m</th>
<th>(\sigma) (Å)</th>
<th>(\varepsilon/k_B) (K)</th>
<th>(\varepsilon^{AB}/k_B) (K)</th>
<th>(\kappa^{AB}) (K)</th>
<th>Scheme</th>
<th>Functional</th>
<th>(\text{AAD}^a) %</th>
<th>(\rho^2)</th>
<th>(\gamma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>1.20</td>
<td>3.5170</td>
<td>189.48</td>
<td>3020.57</td>
<td>0.02765</td>
<td>2B</td>
<td>aFMT</td>
<td>1.67</td>
<td>0.16</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>1.20</td>
<td>3.5127</td>
<td>188.59</td>
<td>3038.96</td>
<td>0.02675</td>
<td>2B</td>
<td>aWDA</td>
<td>1.15</td>
<td>0.20</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>3.4299</td>
<td>194.69</td>
<td>2965.86</td>
<td>0.02752</td>
<td>2B</td>
<td>iSAFT</td>
<td>0.92</td>
<td>0.28</td>
<td>3.1</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.70</td>
<td>3.5458</td>
<td>199.43</td>
<td>3103.77</td>
<td>0.01577</td>
<td>2B</td>
<td>aFMT</td>
<td>1.89</td>
<td>0.28</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>1.70</td>
<td>3.5406</td>
<td>197.56</td>
<td>3124.86</td>
<td>0.01562</td>
<td>2B</td>
<td>aWDA</td>
<td>1.84</td>
<td>0.30</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>1.80</td>
<td>3.4825</td>
<td>200.88</td>
<td>3052.25</td>
<td>0.01604</td>
<td>2B</td>
<td>iSAFT</td>
<td>1.54</td>
<td>0.27</td>
<td>2.0</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>1.62</td>
<td>3.6087</td>
<td>270.82</td>
<td>5648.0</td>
<td>0.004997</td>
<td>1A</td>
<td>aFMT</td>
<td>0.60</td>
<td>1.86</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>1.56</td>
<td>3.6410</td>
<td>275.80</td>
<td>5802.5</td>
<td>0.003337</td>
<td>1A</td>
<td>aWDA</td>
<td>0.59</td>
<td>0.68</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>1.52</td>
<td>3.6859</td>
<td>282.47</td>
<td>5503.0</td>
<td>0.004724</td>
<td>1A</td>
<td>iSAFT</td>
<td>0.39</td>
<td>0.32</td>
<td>1.5</td>
</tr>
</tbody>
</table>

*a* Experimental data is the same as shown in Table 1.

ethanol and 1-propanol are shown as an example. For ethanol, it can be seen that there is a limit where both the deviations of vapor pressure and liquid density reach a minimum, whereas the deviation for the interfacial tension of ethanol increases with increasing \(m\). In addition, 1-propanol shows a similar trend but the lowest deviations are shifted towards larger values of \(m\) and generally showing larger deviations than those for ethanol. These results imply that any expected reduction for the deviation of interfacial tension may be achieved at the expense of deviation for both vapor pressure and liquid density. Accordingly, we manually selected the set of parameters for each of the associating components that satisfy that deviations on vapor pressure should not be greater than the deviations of interfacial tension, and that the deviation of interfacial tension should be maximum \(\sim 5\%\). For the cases where the second condition could not be met, we selected the set of parameter with deviations of maximum \(\sim 5\%\) in vapor pressures. This procedure was motivated by the one implemented by Liang et al.\cite{81} when obtaining the parameters of water used here.

Results of the new regressed parameters for methanol, ethanol and acetic acid are shown in Table 2 where optimizations with each of the three functionals were carried out and the corresponding deviations of vapor pressure, liquid density and interfacial tension are also shown. With the exception of the as-
Figure 4: Absolute average deviations of vapor pressure, liquid density and interfacial tension of ethanol (solid line) and 1-propanol (dashed-line) with different sets of pure compound parameters for PC-SAFT and aWDA as a function of the segment number $m$. Lines are guides to the eye.
sociation volume between the functionals, all molecular parameters shown in Table 2 are almost identical for the three functionals not exceeding a difference of more than ~5%. In general, the lowest deviations were obtained with the iSAFT functional for the three parameters only with a few exceptions in the liquid density. The deviations of interfacial tension of these three compounds are greatly reduced while keeping the deviations of vapor pressure well below 2%, and the liquid densities were not greatly affected with the largest deviation found of 1.86% for acetic acid and aFMT. The comparison between experimental data and the calculated vapor pressure and liquid densities with the different parameters in Supporting Information.

Table 3 shows the results and deviations of the new parameters for the larger alkanols from 1-propanol to 1-nonanol and DEA. As opposed to Table 2 in Table 3, we present parameters for each of the compounds that can be used by either of the association functionals because during the optimization, the resulting molecular parameters and deviations of vapor pressure and liquid density between the functionals were virtually identical, only changing the performance of interfacial tension. Therefore, each compound has the vapor pressure and liquid density deviations calculated with the PC-SAFT equation of state, and three deviations for interfacial tension with each of the functionals. It is worth mentioning that as described in the theory, in the bulk limit all functionals reduce to the same reduced free energy density of PC-SAFT. Ideally, the new molecular parameters for alkanols are selected so the deviations of interfacial tension are not larger than 5%. However, from 1-propanol to 1-nonanol, it was not possible to obtain values lower than 5% without compromising larger deviations in vapor pressure. Hence, the set of parameters selected were those with vapor pressure deviations lower than interfacial tension. In the case of liquid density, deviations obtained with the new parameters are found to be in the same order of magnitude as the original parameters only for 1-propanol, 1-butanol and 1-pentanol, whereas for the heavier alkanols larger deviations between 2−5% are found. For DEA, results of interfacial tension improved considerably in comparison with the original parameters while maintaining a
Table 3: Molecular parameters of some associating fluids for PC-SAFT determined with vapor pressure, liquid density and interfacial tension for any of the association functionals studied.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m</th>
<th>σ (Å)</th>
<th>ε/kB (K)</th>
<th>ε^AB/kB (K)</th>
<th>κ^AB</th>
<th>Scheme</th>
<th>( P_{\text{sat}} )</th>
<th>( \rho )</th>
<th>( \gamma_{\text{aFMT}} )</th>
<th>( \gamma_{\text{aWDA}} )</th>
<th>( \gamma_{\text{iSAFT}} )</th>
<th>AAD* %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Propanol</td>
<td>2.00</td>
<td>3.6961</td>
<td>215.81</td>
<td>3153.53</td>
<td>0.011746</td>
<td>2B</td>
<td>3.6</td>
<td>3.3</td>
<td>6.6</td>
<td>5.4</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>1-Butanol</td>
<td>2.80</td>
<td>3.5346</td>
<td>212.76</td>
<td>2911.96</td>
<td>0.022259</td>
<td>2B</td>
<td>5.6</td>
<td>0.91</td>
<td>8.5</td>
<td>7.5</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>3.20</td>
<td>3.5904</td>
<td>220.15</td>
<td>2767.87</td>
<td>0.029676</td>
<td>2B</td>
<td>5.8</td>
<td>0.72</td>
<td>8.5</td>
<td>7.8</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>3.00</td>
<td>3.9255</td>
<td>253.05</td>
<td>2900.37</td>
<td>0.009405</td>
<td>2B</td>
<td>6.5</td>
<td>4.8</td>
<td>11.2</td>
<td>11.5</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>1-Heptanol</td>
<td>3.10</td>
<td>4.0069</td>
<td>262.91</td>
<td>3204.03</td>
<td>0.005923</td>
<td>2B</td>
<td>5.4</td>
<td>2.4</td>
<td>9.2</td>
<td>9.9</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>1-Octanol</td>
<td>3.10</td>
<td>4.2773</td>
<td>294.73</td>
<td>3005.07</td>
<td>0.003432</td>
<td>2B</td>
<td>5.8</td>
<td>4.8</td>
<td>7.5</td>
<td>8.2</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>1-Nonanol</td>
<td>3.70</td>
<td>4.0947</td>
<td>273.90</td>
<td>3122.29</td>
<td>0.005410</td>
<td>2B</td>
<td>4.2</td>
<td>3.8</td>
<td>11.2</td>
<td>11.6</td>
<td>11.2</td>
<td></td>
</tr>
<tr>
<td>DEA</td>
<td>6.90</td>
<td>2.6611</td>
<td>194.05</td>
<td>1901.24</td>
<td>0.424855</td>
<td>4C</td>
<td>3.4</td>
<td>1.1</td>
<td>4.3</td>
<td>3.6</td>
<td>3.5</td>
<td></td>
</tr>
</tbody>
</table>

* Experimental data is the same as shown in Table 1

deviation in vapor pressure lower than 3.5 % and slightly larger deviations for the liquid density. The comparison of vapor pressure and liquid density obtained with the new parameters and the original parameters for the compounds shown in Table 3 are included in the Supporting Information.

In addition to vapor pressure and liquid density, deviations for the calculated interfacial tension with the new parameters are shown in Tables 2 and 3. In comparison to the previous sets of parameters, the correlation for interfacial tension is greatly improved. The inclusion of the interfacial tension during the parameter estimation procedure enhances the results for the calculation of interfacial tension but as mentioned before it comes at the cost of larger deviation for the vapor pressure. As a result of the latter, the interfacial tension of the larger alkanols, i.e. 1-heptanol to 1-nonanol, does not show a considerable improvement over the original parameters as the error of the vapor pressure notably exceeds the 5 % mark. The three functionals perform very similarly for the alkanols as depicted in Fig. 5, where the deviations of interfacial tension are plotted versus the carbon number of each of the alkanol for the three functionals. It can be seen that aWDA and iSAFT show lower deviations for methanol to 1-pentanol, performing almost identically. On the other hand, from 1-hexanol to 1-nonanol aFMT and iSAFT show lower deviations with very close values. Namely, it may be considered that there is a proportional increase in
the deviations of the interfacial tension of alkanols with increasing alkanol carbon number from ethanol to 1-hexanol. We recall that with increasing chain length the ordering caused by hydrogen bonding at the interface becomes more difficult, accordingly it would be expected that the deviations decrease if the association functionals were solely the cause of the deviations observed. Moreover, for 1-nonanol we observe that the deviations, ranging between $8 - 12\%$, show almost no improvement from the previous parameters which makes difficult to recommend the use of the new parameter set for this compounds.

Results of the calculated interfacial tension of ethanol are plotted in Fig. 6, where it can be seen that the description of the interfacial tension agree very well with the experimental results in the whole temperature range, and it is considerably improved in comparison to the original parameters. The performance of the three functionals is rather similar, but iSAFT shows slightly better correlations followed by aWDA and aFMT. An example of the results obtained
for the larger alkanols is the interfacial tension of hexanol, which is shown in Fig. 7. In comparison to ethanol, the three functionals perform almost identically for 1-hexanol, with larger deviations at low temperatures and only good quantitative agreement at temperatures larger than ~ 450 K. Similar results are obtained for methanol, 1-propanol and 1-octanol which are included in the Supporting Information.

With the addition of these findings to our previous discussion about the competition of the different contributions to the Helmholtz free energy it is possible to support that difficulties for classical DFT in the description of the vapor-liquid interface of associating compounds arise when the competition between the different contributions is more pronounced. Strictly speaking, deviations increase with increasing molecular weight for the series of alkanols, which translates to a predominant effect from, for example, dispersion and chain formation relative to association. Furthermore, deviations for the individual components are concentrated at low temperatures where association interactions are greater.
and compete with the other contributions, e.g. dispersion and chain formation. Finally, with evidence of good agreement between the calculated interfacial tension and experiments for methanol, ethanol and 1-propanol it is possible to justify that the association functionals alone are not responsible for the deviations obtained in the results of the larger alkanols.

The calculated interfacial tension of acetic acid with the new parameters is shown in Fig. 8. The results with the three functionals agree very well with the experimental data and show better performance than the previous parameters with no great increase in deviations of vapor pressure and liquid density. The iSAFT functional performs better than the other two functionals, followed by aWDA and then aFMT. In our previous work we found that iSAFT generally shows better performance in the determination of the density distribution of confined associating hard spheres with one association site, similar to the scheme used for acetic acid. In contrast to the larger alkanols, it was possible to find an adequate set of parameters with deviations in vapor pressure and liquid density.
lower than 2%. In Fig. 9 the calculated interfacial tension of DEA is compared to experimental data showing slight deviations at lower and higher temperatures as shown in the figure. However, the large deviations obtained with the original parameters could be greatly reduced with a slight increase in deviations for vapor pressure and liquid density.

3.3. Vapor-liquid interface of binary systems

3.3.1. Mixtures with one associating compound

In this section we extend our analysis of the new parameters into the study of VLE of binary mixtures and predictions of interfacial tension of these mixtures. For all cases, to obtain accurate representations of the VLE of binary mixtures a binary interaction parameter is used according to the following combining rule for the energy parameter of the dispersion term in PC-SAFT [63, 81]

$$
\varepsilon_{ij} = (\varepsilon_{ii} \cdot \varepsilon_{jj})^{1/2}(1 - k_{ij})
$$

(16)
Figure 9: Interfacial tension of DEA calculated with aFMT, aWDA and iSAFT using the same new molecular parameters shown in Table 3. Symbols represent experimental data[70].

Where $\varepsilon_{ij}$ represents the binary energy parameter between components $i$ and $j$, and $\varepsilon_{ii}$ and $\varepsilon_{jj}$ are the energy parameters of the individual compounds. The binary interaction parameter $k_{ij}$ is determined by fitting experimental VLE pressure or temperature of the binary mixture as a function of the composition of one of the components. Individual $k_{ij}$ are obtained for each parameter set (original and optimized) with the experimental VLE data of the binary mixture. For all the cases, the experimental VLE data are selected to be the closest as possible to the conditions of the experimental interfacial tension of the binary mixture. Once we have defined all $k_{ij}$, the predictions of interfacial tension of mixtures are carried out with classical DFT and the three association functionals: aFMT, aWDA and iSAFT, and subsequently compared to experimental data. VLE results are obtained with a bubble point calculation for either constant pressure or temperature. In all figures, results with the original parameters are included unless otherwise stated, they are represented with a dotted-black line for both VLE and interfacial tension. Furthermore, for the sake of clarity
the calculation of interfacial tension with the original parameters is only done
with aFMT and included as reference to compare with the performance of the
new parameters.

Fig. 10a shows the results for VLE of the mixture ethanol-hexane at three
temperatures in the range 298.15 – 333.15 K. The original parameters for
ethanol are shown in Table 1 and the three sets of optimized parameters for
interfacial tension are shown in Table 2 for each of the association function-
als, whereas the molecular parameters of hexane are taken from Gross and
Sadowski. The new sets perform very well in comparison with the original pa-
rameters at the three temperatures with slightly larger deviations in the bubble
pressure, which is expected from the increase in deviations found for the vapor
pressure of pure compounds introduced by the new parameters. Furthermore,
the new sets for each of the association functionals give almost identical VLE
results of vapor pressure for the mixture. Similarly, values of the binary interac-
tion parameters obtained with the new sets are almost identical with relatively
small positive values $k_{ij}^{aFMT} = 0.024130$, $k_{ij}^{WDA} = 0.021781$, $k_{ij}^{iSAFT} = 0.023488$,
whereas the original set give a larger value of $k_{ij}^{Original} = 0.037655$.

The prediction of interfacial tension of the mixture ethanol-hexane has been
extensively studied as it has proven to be a difficult test for theories used
for the study of the vapor-liquid interface, including density gradient theory
(DGT) and classical DFT. Results obtained in this work for the interfacial tension of the ethanol-hexane mixture are shown in Fig. 10b. The
dotted-black line shows the performance of the original parameters with aFMT
in the prediction of the interfacial tension of ethanol-hexane, which agrees with
previously published works with classical DFT and PC-SAFT using both aFMT
and iSAFT. At ethanol concentrations lower than $x_{Ethanol} < 0.8$ the in-
terfacial tension shows good agreement with experimental data. On the other
hand, at high ethanol concentration the deviation between results and experi-
ments increases, which is expected because, as shown in previous sections, the
interfacial tension of pure ethanol is greatly overpredicted with the original pa-
rameters. With the new parameters for ethanol, this problem is overcome as the
interfacial tension of pure ethanol is captured considerably better. The results for the three functionals are almost identical, showing a slight underprediction at low concentrations of ethanol. However, the agreement at high ethanol concentration \( x_{\text{Ethanol}} > 0.8 \) is greatly improved in comparison with the previous parameters.

The density distribution of ethanol-hexane as a function of the spatial coordinate parallel to the interface is plotted in Fig. 11. The results are plotted at 298.15 K for a composition of \( x_{\text{Ethanol}} = 0.78 \) and the three association functionals. The density profiles of ethanol are shown in blue (top), and for hexane are shown in red; the different line-styles correspond to each of the functionals. The liquid side of the interface correspond to the larger density values, whereas the lower densities correspond to the vapor phase. As seen in the VLE results in Fig. 10, the three set of parameter for ethanol give almost identical results for bubble pressure and vapor composition of the binary mixture, which can also be appreciated for the liquid density on the left side of the interface. Even though the values of interfacial tension are similar at low ethanol concentration for all the functionals, at \( x_{\text{Ethanol}} = 0.88 \) the interfacial tension of the mixture show slight differences, which can also be observed in the different density profiles. The density distribution of hexane in red shows enrichment at the interface predicted by the three functionals. Differently, for ethanol aFMT and aWDA predict a monotonic transition as the density transitions from liquid to vapor, whereas iSAFT shows minor enrichment of ethanol at about \( z \sim 60 \) Å. The behavior of the density distribution at the interface for ethanol-hexane is in agreement with results reported with classical DFT based on PC-SAFT with iSAFT as the association functional.[8]

Another mixture of a non-associating and associating components is shown in Fig. 12 for ethanol and benzene. The VLE of the mixture at 298.15 K is shown in panel Fig. 12a for the different molecular parameters. It can be seen that the vapor pressure obtained with the new parameters is slightly overpredicted in comparison with the original parameters. The resulting \( k_{ij} \) with the original parameters is \( k_{ij}^{\text{Original}} = 0.023418 \), whereas for the new parameters negative
Figure 10: Results for the binary mixture ethanol-hexane, (a) VLE results with original and new molecular parameters for PC-SAFT (lines are on top of each other). The resulting binary interactions parameters are $k_{ij}^{\text{Original}} = 0.037655$ (black-dotted), $k_{ij}^{\text{aFMT}} = 0.024130$ (red-dashed), $k_{ij}^{\text{aWDA}} = 0.021781$ (blue-solid), $k_{ij}^{\text{iSAFT}} = 0.023488$ (green-dashed-dotted) for the experimental data shown in symbols.[86] (b) Interfacial tension prediction for the binary mixture calculated with the three association functionals and classical DFT; squares are the experimental data.[88]
Figure 11: Density distribution of the system ethanol (blue) and hexane (red) at $x_{\text{Ethanol}} = 0.78$ and $T = 298.15$ K calculated with classical DFT and association functionals aFMT (dashed), aWDA (solid) and iSAFT (dashed-dotted). Molecular parameters of PC-SAFT are shown in Table 2 with $k_{ij}$ values shown in Fig. 10.
but smaller values were obtained $k_{ij}^{\text{aFMT}} = -0.006992$, $k_{ij}^{\text{aWDA}} = -0.007542$ and $k_{ij}^{\text{iSAFT}} = -0.001903$. In general, the new sets of parameters show good agreement with experimental results for the vapor pressure of the mixture, including an adequate representation of the azeotropic composition $x_{\text{Ethanol}} \sim 0.35$. Fig. 12b shows the predictions for interfacial tension; the new parameters perform remarkably better than the originals due to the fact that the interfacial tension of the pure compound is well captured. Similar to the previous results for the mixture with hexane, the three functionals give practically identical results with the exception of aFMT that shows slightly larger deviations for the interfacial tension of pure ethanol. At low concentration of ethanol ($x_{\text{Ethanol}} < 0.32$), however, classical DFT underpredicts the interfacial tension of the mixture showing a steep decrease close to pure benzene. Moreover, the interfacial tension of pure ethanol is overpredicted by the three functionals which negatively impacts the prediction of the interfacial tension of the mixture at high ethanol concentration.

The VLE and interfacial tension of the mixture for acetic acid-benzene are shown in Fig. 13. Fig. 13a the binary VLE is compared with the new and original sets of parameters, where excellent agreement with the experimental data is found with all sets. For this mixture the binary interaction parameters for the different sets are very similar, $k_{ij}^{\text{Original}} = 0.031353$ for the original set and for the new set we get $k_{ij}^{\text{aFMT}} = 0.034107$, $k_{ij}^{\text{aWDA}} = 0.034021$ and $k_{ij}^{\text{iSAFT}} = 0.032519$, which is expected based on the similarities between the sets. The results obtained with the new parameters are almost identical to the original set due to the fact that the original parameters already gave good predictions for the interfacial tension of acetic acid. In addition, Fig. 13b shows the comparison of interfacial tension for the binary mixture at 298.15 K with data digitalized from Ref. 6. There is good agreement between experiments and the predicted interfacial tension with aWDA and iSAFT, whereas the performance of aFMT is affected by a relatively large overprediction of the interfacial tension of pure acetic acid.
Figure 12: Binary mixture ethanol-benzene; (a) VLE results calculated with different parameters (lines are on top of each other): \( k^{\text{Original}}_{ij} = 0.023418 \) (black-dotted), \( k^{\text{aFMT}}_{ij} = -0.006992 \) (red-dashed), \( k^{\text{aWDA}}_{ij} = -0.007542 \) (blue-solid), \( k^{\text{iSAFT}}_{ij} = -0.001903 \) (green-dashed-dotted) and experiments.\(^{[89]}\) (b) Prediction of interfacial tension with classical DFT compared to experimental data digitalized from Ref.\(^{[6]}\) (squares).
Figure 13: Binary mixture of acetic acid and benzene; (a) VLE calculation with $k_{ij}^{\text{Original}} = 0.03135$ (black-dotted), $k_{ij}^{\text{aFMT}} = 0.03411$ (red-dashed), $k_{ij}^{\text{aWDA}} = 0.03402$ (blue-solid), $k_{ij}^{\text{iSAFT}} = 0.03252$ (green-dashed-dotted) compared to experimental data at constant pressure.\cite{90,91} (b) Prediction of the interfacial tension of acetic acid-benzene at 298.15 K calculated with classical DFT and three association functional compared to experimental data digitalized from Ref.\cite{6}
3.3.2. Mixtures of two associating compounds

We present results for VLE and interfacial tension predictions of binary mixtures of two associating compounds, i.e. DEA (4C), methanol (2B), acetic acid (1A) and ethanol (2B) with water (4C). Even though the VLE of these mixtures is mainly determined by hydrogen bonding between the components, they represent an adequate test for the new sets of parameters as at low water concentration the organic part of the tested compounds play an important effect in the results VLE behavior. Similar to the previous section, the $k_{ij}$ of the component-pair is first determined by fitting it to experimental data of the VLE. For the case of DEA, as shown in Table 3, we obtained only one set of parameters that can be used for any of the three functionals, i.e. see Table 3. Fig. SI-18 in Supporting Information presents results for the VLE of DEA with water calculated with the old and new molecular parameters for PC-SAFT at a constant pressure of 0.067 bar compared to experimental data.\[92\] Both sets of parameters are able to correlate with great accuracy the equilibrium temperature and vapor composition of the mixture with relatively low values of the binary interaction parameter, for the old parameters $k_{ij} = -0.0079$ and for the new parameters $k_{ij} = 0.0107$. It is worth noting that the new parameters have a positive value for $k_{ij}$ opposite to the negative value obtained with the old parameters. According to the mixing rule used for dispersive interactions, this may indicate that the component-pair does not appear to have the same level affinity as with the old parameters. It is worth mentioning that the pure parameters of DEA were obtained exclusively with vapor pressure and liquid density data and have not been tested with other properties. We did not include parameters for DEA from other works\[40, 69\] for comparisons as it was found that they did not correlate accurate enough the vapor pressure or liquid densities compared to the experimental data used in this work.\[92\]

We recall that for methanol, acetic acid and ethanol three different sets for each compound were obtained as given in Table 2, one for each functional. Therefore, results for these mixtures include comparisons between the original
parameters and calculated results with the three different sets of new parameters corresponding to each of the association functionals. The VLE results for the mixture methanol-water are presented in Fig. SI-19 in Supporting Information, where it can be observed that the performance of the old and new parameters is virtually identical and in very good agreement with the experimental data.\[93\] In addition, the values of the binary interaction parameters are very close, with \( k_{ij} = -0.0300 \) for the original set and with \( k_{ij}^{\text{FMT}} = -0.0285, k_{ij}^{\text{WDA}} = -0.0285 \) and \( k_{ij}^{\text{SAFT}} = -0.0247 \) for the new parameters optimized for interfacial tension. The fact that the new sets of parameters perform similarly as the old set is a good indication of the reliability of the new parameters in describing various thermodynamic properties besides improving only the interfacial tension.

Fig. SI-20 in Supporting Information displays the VLE of acetic acid and water at two different pressures.\[94\] For this mixture, the new sets of parameters for acetic acid with the three associating functionals perform almost identical as lines on the figure are on top of each other. The binary interaction parameters for the new sets are all negative with values \( k_{ij}^{\text{FMT}} = -0.0285, k_{ij}^{\text{WDA}} = -0.0285 \) and \( k_{ij}^{\text{SAFT}} = -0.0247 \), whereas the for the new set we get a positive value \( k_{ij}^o = 0.0139 \). In terms of performance, the new parameters have slightly better agreement with the experimental data, however, all sets show considerable deviations in the bubble temperature and vapor composition of this mixture, especially at high concentrations of acetic acid. Particularly, mixtures of acetic acid with different compounds have resulted challenging for thermodynamic models as acetic acid is capable of forming dimers in the liquid and vapor phase. The later may indicate that the association scheme 1A is the most suitable to model the associating interactions for this molecule, however, many equations states that account for this type of interactions struggle with finding an adequate association scheme and the corresponding molecular parameters that work for many systems.\[91, 68, 95, 96\]

For the case of ethanol-water, presented in Fig. SI-21 in Supporting Information, it is evident that the original parameters give better agreement to the experimental data as the deviations introduced in the vapor pressure by the new
parameters clearly affect the description of the mixture VLE as the vapor pressure of pure ethanol is lightly underpredicted. Similarly, results show that the pressure of azeotropes, with an ethanol concentration of about $x_{\text{Ethanol}} = 0.9$ for the three temperatures, is also underpredicted with the new parameters. The new sets of parameters for the three functionals perform rather similar with very close values for the binary interaction parameters, $k_{ij} = 0.0087$ for aFMT, $k_{ij} = 0.0107$ for aWDA and $k_{ij} = 0.0106$ for iSAFT, whereas for the original set we get a negative value of $k_{ij} = -0.00785$.

Once we have determined all the $k_{ij}$ values of the binary systems we proceed to the prediction of the interfacial tension between the liquid and vapor phases of these systems. First, the results for DEA and water are displayed in Fig. 14, where it can be seen that the new molecular parameters greatly improve the prediction of interfacial tension for the mixture, where the results with the original parameters are shown with aFMT only for the sake of comparison. Both aFMT and aWDA give almost identical results for the pure compounds, and in general both overpredict the interfacial tension of the mixture in the whole concentration range especially at high DEA concentration. On the other hand, iSAFT underpredicts the interfacial tension at low DEA concentration, which may be attributed to the fact that it underpredicts the interfacial tension of pure water for about 5 mN/m at this temperature. These results may be improved if new parameters of water are obtained for iSAFT because it appears that most of the deviations are caused by the deviations in the results for pure water. However, a similar behavior was found for this mixture by Wang et al.\cite{40}, where it can be seen that iSAFT with a different model for water is able to reduce the deviations in the interfacial tension but still with a slight underprediction. The density profile of the vapor-liquid interface of the system DEA-water is shown in Fig. 15 at a concentration of $x_{\text{DEA}} = 0.208$, and only calculated with the new parameters. The density distribution of DEA predicted by the three functional have similar behavior displaying slight enrichment at the interface. For the distribution of water molecules, aFMT predicts a monotonic decrease whereas iSAFT shows considerable enrichment and aWDA somewhat
between the two.

Results for the interfacial tension of methanol and water are presented in Fig. 16. The behavior of this mixture is similar to DEA and Water, with a large interfacial tension for water that monotonically decreases with increasing concentration of methanol. Both aFMT and aWDA show and excellent agreement for the interfacial tension of the pure compounds, but slight deviations in the middle concentrations of the mixtures. iSAFT, on the other hand, shows better agreement at concentrations of methanol of about $x_{\text{methanol}} = 0.2$ that may be cause for the performance of the water parameters used in this work. Additionally, Fig. 17 displays the density distribution of methanol and water at the interface with a methanol concentration of $x_{\text{Methanol}} = 0.208$. For the density profile of water molecules, we observe again enrichment predicted only by aWDA and iSAFT. Similarly, methanol is adsorbed at the interface considerably increasing that local density larger than its bulk liquid partial density. It is worth noting that oscillations characteristic of a high level of packing of
Figure 15: Density distribution of the system DEA-water at $x_{\text{DEA}} = 0.208$ and $T = 298.15$ K calculated with classical DFT and the association functionals aFMT, aWDA and iSAFT. Red lines with the larger liquid densities at the left are for water, and blue lines with the lower liquid densities are for DEA.
particles it is observed in the density profile of methanol for both aWDA and iSAFT, which is not predicted at all by aFMT. This effect may be a result of the large enrichment found for water, as it acts as an external potential applied to the methanol molecules. Given the chain functional used by our classical DFT implementation, we are not able to distinguish between different segments that conform molecules in the PC-SAFT model, and it is not possible to compare the distribution between the organic and associating parts of the alkanol molecule against water molecules, similar to the work carried by Ballal and Chapman [98]. Furthermore, by comparing the density profiles at the interface of methanol and water obtained with the three association functionals against molecular simulations from the work of Partay et al. [99], it can be observed that at low methanol concentration ($\leq 0.3$), both methanol and water show enrichment at the interface. These results are in agreement with the density profiles obtained with aWDA and iSAFT, and additional molecular simulations from Safaei and Maghari [100]. Moreover, in a different work carried out by Biscay et al. [74], they present only the density profile of methanol for the same system. They found that at low methanol concentration, the density profiles of methanol in the mixtures are in agreement with our results and the simulations carried out by Partay et al. [99].

Figs. [18] and [19] show the interfacial tension of the water mixtures with acetic acid and ethanol in comparison to experimental data and the different sets of parameters. For the two mixtures, aFMT and aWDA fail to capture accurately the experimental data in the middle concentrations of the two mixtures showing deviations from 2.5 to approximately 5 mN/m, even though the results for the pure compounds agree very well with the experimental data. The interfacial tension results obtained for iSAFT show an interesting inflection point at about $x_{\text{Acetic Acid}} = 0.4$, where at lower concentrations the agreement with the experiments is excellent. At a closer inspection of the convergence results we observed that in fact the change in slope is due to a divergence problem found for this system in the approximate range of $0.2 < x_{\text{Acetic Acid}} < 0.4$. Similar trend is found in the system ethanol and water shown in Fig. [19] where for this case
Figure 16: Prediction of the interfacial tension of the mixture methanol-water calculated with classical DFT and PC-SAFT compared to experiments [101].

Figure 17: Density distribution of the system methanol-water at $x_{\text{Methanol}} = 0.208$ and $T = 298.15$ K calculated with classical DFT and association functionals aFMT, aWDA and iSAFT. The molecular parameters of PC-SAFT are shown in Table 2.
Figure 18: Interfacial tension of the mixture acetic acid-water calculated with aFMT, aWDA and iSAFT with the new parameters and compared to the old parameters with aFMT. Symbols are experimental data [97]. Results for iSAFT are converged to a minimum error of $10^{-6}$ based on Eq. [17].

Both aWDA and iSAFT showed a divergent behavior during the minimization of the grand potential. For the sake of comparison, the results shown for both systems are converged to a maximum error of approximately $10^{-5}$ calculated as the euclidian norm of $g^k(\rho^k)$, which is obtained by rearranging Eq. [3] at iteration $k$

$$g^k(\rho^k) = \exp\left(\beta \mu_j - \beta \frac{\delta F_{\text{res}}[\rho^k]}{\delta \rho_j(z)} - \rho^k_j(z)\right)$$

(17)

The density distributions of the binaries of ethanol and acetic acid with water are shown in Figs. [21] and [20] at 298.15 K. The compositions of water for the two mixtures are close to $x_{\text{water}} = 0.8$. This value of concentration is chosen as it is similar to the value at which the molecular simulation results of Partay et al. [99] and Safaei and Maghari [100] show enrichment at the interface for both water and methanol. For the distribution of water molecules in both
mixtures, aFMT predicts a smooth transition from the liquid density to the vapor density at the interface. On the other hand, aWDA and iSAFT show a pronounced layering behavior in the density profiles of acetic acid and ethanol. In other words, both components of the mixture show a considerable degree of enrichment at the interface followed by slight depletion that then reaches the corresponding equilibrium value of the liquid density. However, it is relevant to point out that this behavior produces instabilities in the iterative procedure and calculations for the two mixtures shown in Figs. 21 and 20 are converged to a maximum of $10^{-5}$ according to Eq. 17. After this point the evolution of the iterative procedure leads to a divergent behavior in the density distribution which considerably affects the value of the interfacial tension. An example of the evolution of the error based on the euclidian norm as shown in Eq. 17 can be found in Supporting Information. Ballal and Chapman [98] carried out a thorough analysis with classical DFT of the vapor-liquid interface between water.
and alkanols and in their findings they did not report any convergence problems. However, in their predictions of the density distributions of the mixture ethanol-water they also observed a slightly oscillatory behavior. Molecular dynamics simulations of the mixture ethanol-water carried out by Tarek and coworkers [102] predict enrichment of both substances at the interface, similar to the results obtained by Partay et al. [99] for methanol-water, and closer to the results predicted by aWDA and iSAFT.

The layering structure present in the vapor-liquid interface calculated with classical DFT has been studied before elsewhere, and it has been related to the properties of the radial distribution function. [103, 104, 105] The oscillatory behavior typical of fluid structuring is caused because the density distribution of the particles in the vapor side of the interface act as an external potential. [48] At this condition, it has been proven that the layering reach the bulk liquid density
Figure 21: Density distribution of the system ethanol-water at $x_{\text{Ethanol}} = 0.208$ and $T = 298.15$ K calculated with classical DFT and association functionals aFMT, aWDA and iSAFT. The molecular parameters of PC-SAFT are shown in Table 2 with $k_{ij} = 0.0107$. Results for iSAFT and aWDA are converged to a minimum error of $10^{-5}$ based on Eq. [17].
in either an exponentially damped oscillation or with monotonic decay, similar to how the radial distribution function decays at infinite distance. There has been an effort in connecting this behavior with capillary waves phenomena and theories, including classical DFT. It is worth mentioning that Fisher and Widom established a principle named the Fisher-Widom line that described the limits of asymptotic decay of the radial distribution function, that later has been also satisfactorily applied to the decay of the density profile of an inhomogeneous fluid. Even though it is not possible to directly connect this behavior with our results as some of our calculations did not find a stable solution, it may be probable that the weighted density approach followed by iSAFT and aWDA in the calculation of the cavity correlation function, which for aFMT is done with the weighted densities of FMT, may be cause for the divergence behavior in the iteration procedure and a more adequate technique than Piccard iterations could be applied to overcome this issues.

4. Conclusions

A classical DFT implementation based on the PC-SAFT equation of state is used to study the vapor-liquid interface of associating fluids and mixtures. The study is carried out with the calculation of the interfacial tension from the equilibrium density profiles obtained with the minimization of the grand potential functional as defined in classical DFT. Three association functionals are used in this study, two from literature and one implemented here using Wertheim’s thermodynamic perturbation theory of first order together with the weighted density approximations as a way to approximate the bulk expression into the study of inhomogeneous systems.

We use the well-established compound-specific molecular parameters of PC-SAFT of associating fluids that are obtained by fitting vapor pressure and liquid densities of bulk vapor-liquid equilibria. These parameters, together with the classical DFT and the three functionals are used to predict the interfacial tension of alkanols and other associating compounds. We found that the current
parameters for PC-SAFT drastically overpredict the interfacial tension of alkanols from methanol to 1-nonanol at temperatures lower than 400−450 K. Good agreement was found in the interfacial tension for water and acetic acid, whereas diethanolamine (DEA) showed deviations greater than 30%. In addition, by using the interfacial tension during the determination of the molecular parameters of PC-SAFT it was possible to reduce the deviations in the interfacial tension of alkanols, especially for methanol, ethanol and 1-propanol. For the larger alkanols, deviations of interfacial tension in the range of 10% were found even at the expense of larger deviations in the vapor pressure of the pure compounds. Additionally, the interfacial tension of acetic acid and DEA were also improved with the new parameters.

We use the new optimized parameters to predict the interfacial tension of mixtures of associating compounds. For such a task, the VLE of the binary systems must be determined together with the binary interaction parameters for each of the systems. The results indicated that the new parameters have an almost identical performance to the original parameters even though the deviations in vapor pressure are slightly larger. One of the exceptions is the VLE of the system ethanol and water that showed slight underprediction of the vapor pressure of the binary mixture and also for pure ethanol. For all binary mixtures tested, the agreement with experimental data of the predictions of interfacial tension is excellent. The introduction of interfacial tension in the determination of the molecular parameters of PC-SAFT improves the correlation of interfacial tension of the pure compounds as expected. It was observed that most of the errors for mixtures with the original parameters are attributed to the lack of accuracy in the calculation of the interfacial tension of the pure compounds. Therefore, by improving the latter the prediction for the mixtures also improved.

Even though the values of interfacial tension for mixtures agree very well with experimental results, differences in the description of the density distribution of the vapor-liquid interface were found for the three functionals. The density profiles that best matched molecular simulation results of alkanols and water were obtained with aWDA and iSAFT. In other words,
molecular simulations predict enrichment of both water and the alkanols at low alkanol concentration, followed by a slight depletion as the profile reaches the bulk value of the liquid density. For the case of aFMT, enrichment is only found in the density distribution of the alkanols. This difference between the functionals may be attributed to the use of the weighted density approximation in the description of the pair correlation function if the inhomogeneous fluids used to calculate the association strength. aFMT also makes use of weighted densities, but the approach implemented in the calculation of the pair correlation function is based on the fundamental measure theory. However, limitations were found for aWDA and iSAFT as it is the case that for some of the binary mixtures of two associating compounds, it was not possible to find a stable solution during the minimization of the grand potential functional, as oscillations in the liquid side of the interface would not decay to the bulk density values. Therefore, further inspection of the weighted density approximation in the calculation of the cavity correlation function may be subject of future works.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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