

# Calculation of Interfacial Properties of Binary Mixtures Containing Polar and Non-polar Components

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## ABSTRACT

Carbon dioxide (CO<sub>2</sub>) is a component that has become a central role for the industry nowadays. Not only is this compound of wide use for certain applications (i.e. supercritical extraction processes) but also plays an important role in global warming. Therefore, the understanding of the phenomena related with this molecule is of great importance. Furthermore, the accurate modelling of its mixtures may not only have a positive effect on technical modelling, but also on economical revenue in several applications. This paper focuses on the understanding of phase and interfacial behaviour of CO<sub>2</sub> mixtures. These mixtures may appear in petrochemical processes like the enhanced oil recovery or in carbon capture and storage systems [1]. Recently [2, 3, 4,], a method was suggested to predict the surface tension of non-polar mixtures with help of the density gradient theory [5] in very good agreement with experimental data. The proposed methodology uses a suited equation of state (EOS), namely the polar perturbed chain statistical association fluid theory (PCP-SAFT EOS) [6], for calculation or prediction of the phase behaviour and interfacial properties of a given mixture. This model allows to take into account the quadrupole moment of CO<sub>2</sub>, resulting in improvements for the modelling of properties of pure CO<sub>2</sub> and its mixtures [2, 3, 4]. With help of this theoretical background it is possible to make use of the density gradient theory for prediction of interfacial tension of CO<sub>2</sub> in mixtures. Some examples (CO<sub>2</sub> + methane, CO<sub>2</sub> + benzene and CO<sub>2</sub> + toluene) of these mixtures will then be presented and compared with experimental data from the literature, if available.

## INTRODUCTION

Besides the phase behaviour the interfacial properties play an important role in process design. This is especially true in the field of oil- and gas gathering. In order to reduce the global warming effect carbon dioxide (CO<sub>2</sub>) can be pressed into the oil- or/and gas reservoir. From the economical point of view the interfacial tension between the carbon dioxide and the oil- or/and gas phase, and hence the necessary pressure is essential information for the system. For this reason the modelling of thermodynamic properties of mixtures containing CO<sub>2</sub> are of great interest [7, 8, 9]. Previous works [2, 3, 4] have suggested a method to predict the surface tension of non-polar and polar-non polar mixtures based on the density gradient theory (DGT) [5] in very good agreement with experimental data. In this case, the most important feature of CO<sub>2</sub> is the quadrupole moment. The present paper aims to further application of the theoretical framework for the following CO<sub>2</sub> containing mixtures: CO<sub>2</sub> + methane, CO<sub>2</sub>+ benzene and CO<sub>2</sub> + toluene, where the PCP-SAFT [6] is used.

## THEORY

The density gradient theory was first proposed by van der Waals [10] and further developed from Cahn-Hilliard for pure substances [5] and extended by Poser and Sanchez [11] to binary

mixtures. The core of the theory lies on calculation of the interfacial properties based on bulk-properties of the binary mixture and the surface tension of the pure component.

## DENSITY GRADIENT THEORY

### Pure Components

The DGT [5] describes the thermodynamic properties of a system where an interface exists between two equilibrium phases. On the interface between liquid and gas phases in thermodynamic equilibrium only the density  $\rho$  varies continuously from the bulk liquid density,  $\rho^L$ , to the vapour density,  $\rho^V$ . Assuming that the density gradient is small compared with the reciprocal of the intermolecular distance allows the density  $\rho$  and its derivatives to handle as independent variables. This means that the Helmholtz free energy  $F$  for a system with an interface can be obtained by expanding the Helmholtz free energy  $F$  in a Taylor series about the equilibrium bulk state. Following Cahn and Hilliard [5], the surface tension,  $\sigma$ , for a planar surface reads:

$$\sigma = 2 \int_{\rho^L}^{\rho^V} \sqrt{\kappa \Delta \omega(\rho)} d\rho \quad (1)$$

The interfacial tension is thus proportional to the Helmholtz free energy density,  $\Delta \omega(\rho)$ , of homogeneous fluid. This quantity is also called grand thermodynamic potential. Geometrically,  $\Delta \omega(\rho)$  can be represented as the vertical distance between the curve of  $f_0(\rho)$  versus  $\rho$  and a straight line touching  $f_0(\rho)$  at the vapour and liquid densities,  $\rho^L$  and  $\rho^V$ . Additionally, the influence parameter  $\kappa$  of the pure substance has to be known.

The density profile,  $\rho(z)$  in the direction perpendicular to the interface, is described with help of the following equation:

$$z = z_0 + \int_{\rho^0}^{\rho} \sqrt{\frac{\kappa}{\Delta \omega(\rho)}} d\rho \quad (2)$$

$z_0$  and  $\rho^0$  represent an arbitrarily chosen origin and composition. The  $z$ -origin can be arbitrarily located, for example, at a density of  $(\rho^L + \rho^V)/2$ . A distance  $z$  may be determined for any  $\rho$  lying between the bulk densities by means of numerical evaluation of the integral.

Before any interfacial properties can be computed, it is necessary to find the thermodynamic equilibrium densities between which the interface is formed. The densities of the vapour and the liquid phase can be calculated at a given temperature and pressure. After this, the expressions (Eqs. 1 and 2) permit calculation of surface tensions and density profiles if  $\kappa$  and  $\Delta \omega$  are known. The influence parameter,  $\kappa$ , has a molecular theoretical definition [5] but is not usually calculable. Thus, it is treated as a parameter of the fluid in the same spirit as

the parameter of semi empirical models. Equations of state (PCP-SAFT) will be used to evaluate  $\Delta\omega$  and explained in a further section.

### Binary Mixtures

The first step during the calculation of any interfacial properties is the calculation of the equilibrium of the two phases, between which the interface being considered. Such calculations are carried out by equating the chemical potentials and the pressures in both coexisting phases.

The Cahn - Hilliard Theory [5] describes the thermodynamic properties of a system where an interface exists between two fluid phases. In contrast to systems of pure components, in binary mixtures not only the density but also the composition changes through the interface. In order to take both effects into account we define the partial densities,  $\rho_i$ .

$$\rho_i = X_i \rho \quad (i = A, B) \quad (3)$$

Usually, the thermodynamic quantities of binary systems at constant temperature are functions of density and composition, expressed by mole fraction (e.g. Helmholtz energy  $F(\rho, X_i)$ ). Applying Eq. 3 the thermodynamic functions can be rewritten as functions of both partial densities (e.g.  $F(\rho_A, \rho_B)$ ). Using a similar procedure like Cahn and Hilliard [5], to calculate the interfacial tension of an planar interface, Poser and Sanchez [11] worked out a method that consider the change of two variables  $(\rho_A, \rho_B)$  within the interface. The interfacial tension between two fluid phases in equilibrium reads [11]:

$$\sigma = 2^{1/2} \int_{\rho_B^I}^{\rho_B^{II}} \sqrt{\kappa' \Delta\omega(\rho_A, \rho_B)} d\rho_B \quad (4)$$

The value of  $\kappa'$  results from the influence parameters of the pure components,  $\kappa_i$ . Same as in the case of a pure substance  $\Delta\omega(\rho_A, \rho_B)$  is defined as the grand thermodynamic potential. The limits of integration  $\rho_B^I$  and  $\rho_B^{II}$  are the partial densities in the coexisting phases and can be obtained by Eq. 3.  $\kappa'$  is given by:

$$\kappa' = \kappa_B + 2\kappa_{AB} \left( \frac{d\rho_A}{d\rho_B} \right) + \kappa_A \left( \frac{d\rho_A}{d\rho_B} \right)^2 \quad (5)$$

The  $\kappa_i$ -parameters can be fitted to one experimental surface tension. The parameter  $\kappa_{AB}$  can be calculated using geometrical average of the pure component parameters:

$$\kappa_{AB} = \sqrt{\kappa_A \kappa_B} \quad (6)$$

Eq. 6 allows the prediction of surface tensions of the mixtures based on the surface tension of the pure components. The grand thermodynamic potential  $\Delta\omega(\rho_A, \rho_B)$  is then:

$$\begin{aligned}\Delta\omega(\rho_A, \rho_B) &= (\rho_A + \rho_B)F(\rho_A, \rho_B) - \rho_A\mu_A^I(\rho_A^I, \rho_B^I) - \rho_B\mu_B^I(\rho_A^I, \rho_B^I) + p^{Eq.} \\ &= \rho_A \left( \mu_A(\rho_A, \rho_B) - \mu_A^I(\rho_A^I, \rho_B^I) \right)\end{aligned}\quad (7)$$

The quantity  $p^{Eq.}$  is the equilibrium pressure. The Helmholtz free energy,  $F$ , and the chemical potentials,  $\mu_i$ , can be obtained by an equation of state, if the quantities  $\rho_A$  and  $\rho_B$  are known. Therefore, the calculation of  $\Delta\omega(\rho_A, \rho_B)$  needs the knowledge of  $\rho_A$  to each value of  $\rho_B$  within the interface. This dependence conforms to the density profiles through the interface. The minimisation of the interfacial tension leads to the following system of equations to calculate the densities at each value of  $z$ , the direction perpendicular to the interface [11].

$$\left( \frac{\partial \Delta\omega(\rho_A, \rho_B)}{\partial \rho_A} \right) = \kappa_A \left( \frac{\partial^2 \rho_A}{\partial z^2} \right) + \kappa_{AB} \left( \frac{\partial^2 \rho_B}{\partial z^2} \right) \quad (8)$$

$$\left( \frac{\partial \Delta\omega(\rho_A, \rho_B)}{\partial \rho_B} \right) = \kappa_{AB} \left( \frac{\partial^2 \rho_A}{\partial z^2} \right) + \kappa_B \left( \frac{\partial^2 \rho_B}{\partial z^2} \right) \quad (9)$$

The solution of this system of equations represents the profiles of the partial densities,  $\rho_A(z)$  and  $\rho_B(z)$ , during the interface. The use of the geometrical mixing rule for  $\kappa_{AB}$  (Eq. 6) shows noticeable simplifications [11]. In this case the system of equations (Eqs. 8 and 9) reduce to one algebraic equation:

$$\sqrt{\kappa_B} \left( \frac{\partial \Delta\omega(\rho_A, \rho_B)}{\partial \rho_A} \right) = \sqrt{\kappa_A} \left( \frac{\partial \Delta\omega(\rho_A, \rho_B)}{\partial \rho_B} \right) \quad (10)$$

The application of Eq. 10 in Eqs. 8 and 9 leads to following relation:

$$\sqrt{\kappa_B} \left( \mu_A(\rho_A, \rho_B) - \mu_A^I \right) = \sqrt{\kappa_A} \left( \mu_B(\rho_A, \rho_B) - \mu_B^I \right) \quad (11)$$

This expression shows the combination of the partial densities  $\rho_A$  and  $\rho_B$  in one expression. At constant phase equilibrium temperature Eq. 11 has two variables,  $\rho_A$  and  $\rho_B$ . If the value of  $\rho_B$  is chosen as a sampling point within the interface, to calculate the integral Eq. 4 the corresponding value  $\rho_A$  can estimate in a way, that Eq. 11 is fulfilled. After this, the grand thermodynamic potential  $\Delta\omega(\rho_A, \rho_B)$  can be evaluated with Eq. 7 at every sampling point. The differential ratio in Eq. 4 is then given at each value  $\rho_B$ . During the derivation of Eq. 4 the coordinates transformation from the location space to the density space was used [11]. The integration of this transformation permits the calculation of the density:

$$z = z_0 + \int_{\rho_B(z_0)}^{\rho_B(z)} \sqrt{\frac{\kappa'}{\Delta\omega(\rho_A, \rho_B)}} d\rho_B \quad (12)$$

whereas  $\kappa'$  is given in Eq. 5 and  $z_0$  represents an arbitrarily chosen origin. Another important quantity which can be deriving from the density profiles is the thickness of the interface. This thickness is thermodynamically not exactly defined. In order to specify a physically value the 10/90-rule, given by Lekner and Henderson[12] can be used.

### PCP-SAFT-EOS

The PCP-SAFT-EOS [6] is a further development of the PC-SAFT-EOS [13]. In this model the chain-length dependence of the attractive (dispersive) interactions is also taken into account. A hard-chain fluid serves as a reference for the perturbation theory, differing from spherical molecules as in the original SAFT version. Molecules are conceived as chains composed of spherical segments. The pair potential for the segment of a chain is given by a modified square-well potential. Based on the Wertheim's thermodynamic perturbation theory [14, 15], the attractive interactions are treated as a perturbation of the reference system. The equation of state is given has then an ideal gas contribution (id), a hard-chain contribution (hc), and a perturbation contribution, which accounts for the attractive interactions (disp), a contribution arising from the self- or cross-association of polar molecules (assoc) and additionally a contribution taking polar interactions (polar) into account:

$$f = f^{id} + f^{hc} + f^{disp} + f^{assoc} + f^{polar} \quad (13)$$

For a non- associating substance this EOS contains three pure-component parameters: the segment diameter ( $\sigma$ ), the interaction energy related to the dispersion interaction ( $\varepsilon$ ), and the number of segments ( $m$ ). The parameters can be fitted using vapour pressure and liquid densities. More details can be found in the papers of Gross and Sadowski [13].

The heart of the PCP-SAFT-EOS is the new additional term  $f^{polar}$  in Eq. 13 . In order to derive an expression for this quantity the starting point is the Padé- approximation in terms of the Helmholtz energy:

$$\frac{f^{polar}}{RT} = \frac{f^{quadrupole}}{RT} = \frac{A_2 / RT}{1 - A_3 / A_2} \quad (14)$$

with  $A_2$  and  $A_3$  as the second-order and third-order perturbation terms, respectively. Gross [6] suggested for these terms the following expressions:

$$\begin{aligned} \frac{A_2}{RT} &= -K_{A_2} \eta J_{2,11}^{00} & \frac{A_3}{RT} &= K_{A_3} \eta^2 J_{3,111}^{00} \\ K_{A_2} &= \frac{27}{8} \frac{\varepsilon_1^2 \sigma_1^3 Q_1^{*4}}{m_1 d_1^3 (k_B T)^2} & K_{A_3} &= \frac{81}{4} \frac{\varepsilon_1^3 \sigma_1^6 Q_1^{*6}}{(k_B T)^3 m_1^2 d_1^6} \end{aligned} \quad (15)$$

where  $Q_1^*$  is the reduced quadrupole moment and reads:

$$Q_1^{*2} = \frac{10^{-19} Q_1^2}{k_B m_1 \varepsilon_1 \sigma_1^5} \quad (16)$$

where the quadrupole moment  $Q$  is measured in  $10^{-26} \text{erg}^{1/2} \cdot \text{cm}^{5/2}$  and  $k_B$  is the Boltzmann-constant.

The expression for the calculation of the quantities  $J_{2,11}^{QQ}$  and  $J_{3,111}^{QQ}$  occurring in Eq. 15 can be found in the literature [6].

For the application of the equations of state to mixtures made from the component  $i$  and  $j$  mixing rules must be specified. The perturbation theory of Baker and Henderson makes use of an average radial distribution function and thus treats the segments of a chain as indistinguishable. Within this concept, a rigorous application of the perturbation theory to a mixture is in principle possible. However, the mathematical expressions are not available in analytical form. Therefore, two mixing rules were used for the application of the PCP-SAFT to mixtures, namely:

$$\sigma = \frac{1}{2}(\sigma_i + \sigma_j) \quad \varepsilon = (1 - k_{ij}) \sqrt{\varepsilon_i \varepsilon_j} \quad (17)$$

where  $k_{ij}$  is a binary interaction parameter. The binary interaction parameter will be fitted to phase equilibrium data.

## RESULTS

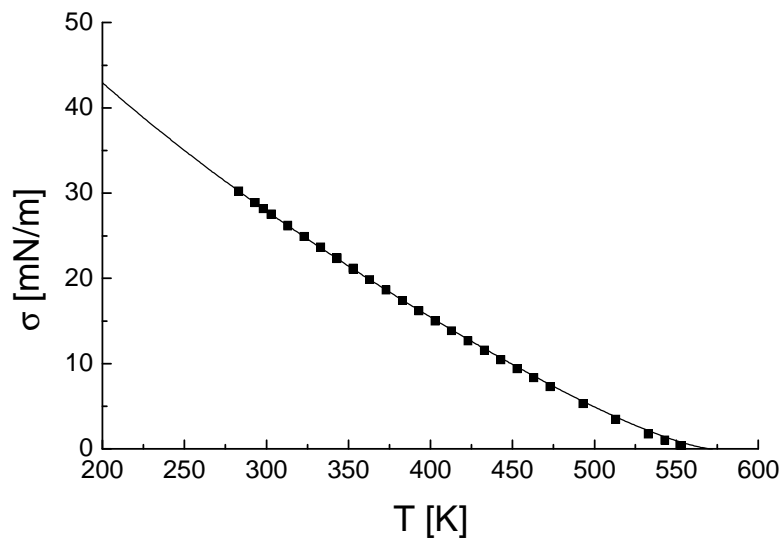
### Pure Components

First the phase equilibrium of the pure substances was calculated and the surface tension was taken from the literature [4]. The fitted influence parameters are listed in Table 1.

**Table 1: Influence parameter  $\kappa$  for components using PCP-SAFT.**

Pure component	$10^{20} \kappa [\text{Jm}^5/\text{mol}^2]$	Source
Methane	1.973	[2]
Benzene	23.989	This work
Toluene	31.890	[2]
Carbon dioxide	2.327	[4]

The influence parameters taken from previous works [2, 4] for the given substances have proved to be able to describe the temperature dependence of the surface tension of pure components. Only in the case of benzene it is necessary to fit this parameter to one single point at one temperature. Results of the surface tension curve with the given influence parameter from Table 1 are shown in Figure 1. The experimental behaviour can be accurately reproduced with help of the DGT using PCP-SAFT EOS.

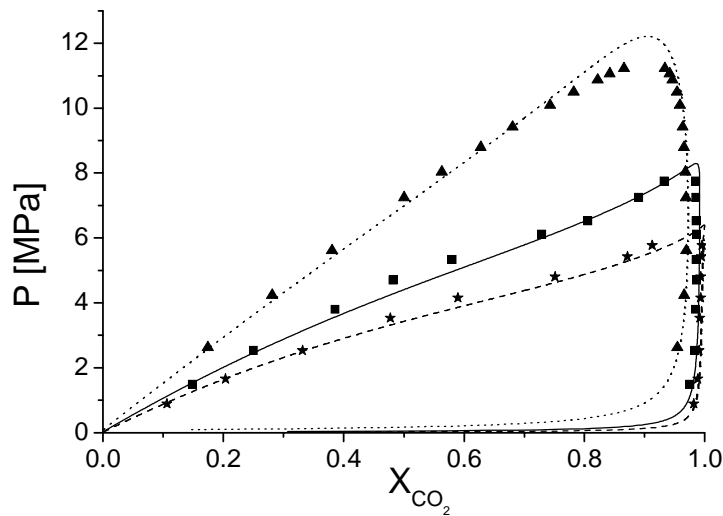


**Figure 1: Experimental (squares [16]) and predicted surface tension (solid line) for benzene using PC-SAFT-EOS with  $\kappa=23.989 \cdot 10^{20}$  [Jm<sup>5</sup>/mol<sup>2</sup>].**

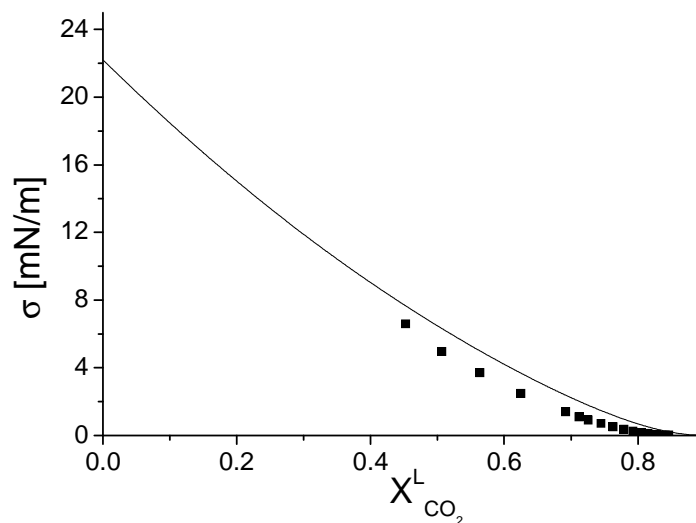
### Binary Mixtures

In order to describe the phase behaviour of a binary mixture the binary interaction parameter  $k_{ij}$  (Eq. 17) has to be specified. This is done via the calculation of the binary phase diagram and comparison with the experimental data given in the literature. Using the fitted  $k_{ij}$  from the phase equilibrium and in combination with the fitted influence parameters of the pure components,  $\kappa_i$ , the interfacial tension of the binary mixture can be predicted.

Previous works [2, 4] have shown the ability of the combination of the DGT with PCP-SAFT to describe and predict CO<sub>2</sub> mixtures with n-alkanes and cycloalkanes; however, no aromatic molecules have been taken into account in the theoretical framework. Figure 2 depicts the vapour-liquid equilibrium for the mixture CO<sub>2</sub> + benzene, at one temperature below and two above the critical temperature of CO<sub>2</sub> and comparisons to data taken from the literature [17, 18]. No binary interaction parameter is needed in this case, showing the predictive power of the equation of state. For a comparison, the previous version without inclusion of polar interactions requires a  $k_{ij}$  value of 0.088 [6]. Gross discussed also a quadrupole moment for benzene and the interaction of the quadrupole moments of CO<sub>2</sub> and benzene. This situation requires a  $k_{ij} = 0.042$  in order to reach agreement with the data measures by Bendale et al. [18]. From these results it can be concluded that the incorporation of the quadrupole moment for CO<sub>2</sub> is sufficient for an accurate description of the VLE for the system CO<sub>2</sub> + benzene.



**Figure 2: Experimental and calculated VLE applying PCP-SAFT with  $k_{ij}=0$  of the system  $\text{CO}_2$  + benzene at  $T=298.15\text{K}$  (stars [17] + broken line), at  $T=313.15\text{K}$  (squares [17] and solid line) and at  $347.25\text{K}$  (triangles [18] and dotted line).**



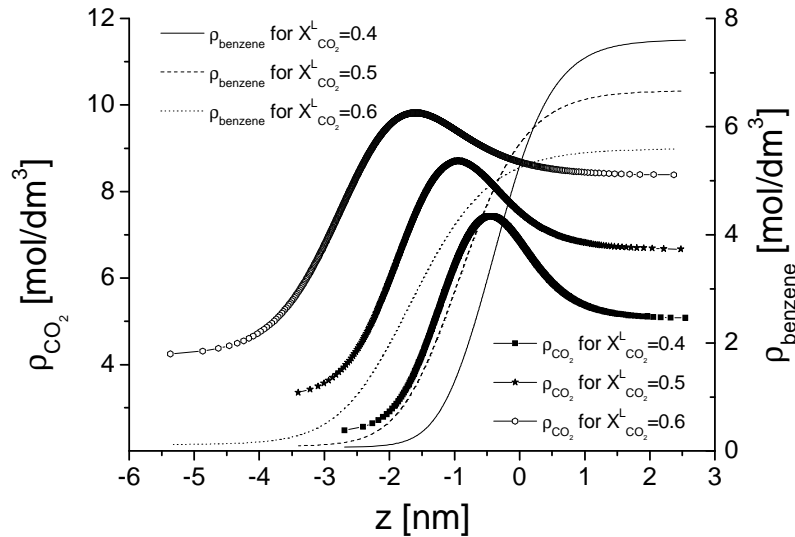
**Figure 3: Experimental (squares [19]) and predicted (solid line) surface tension applying PCP-SAFT with  $k_{ij}=0.0$  of the system  $\text{CO}_2$  + benzene at  $T=344\text{K}$ .**

The next step is the calculation of the surface tension for this system. Figure 3 shows a comparison between experimental data [19] and calculation made with the DGT in combination with PCP-SAFT at 344K. The theoretical framework does a good job in predicting surface tension of these mixtures made from polar and non-polar substances.

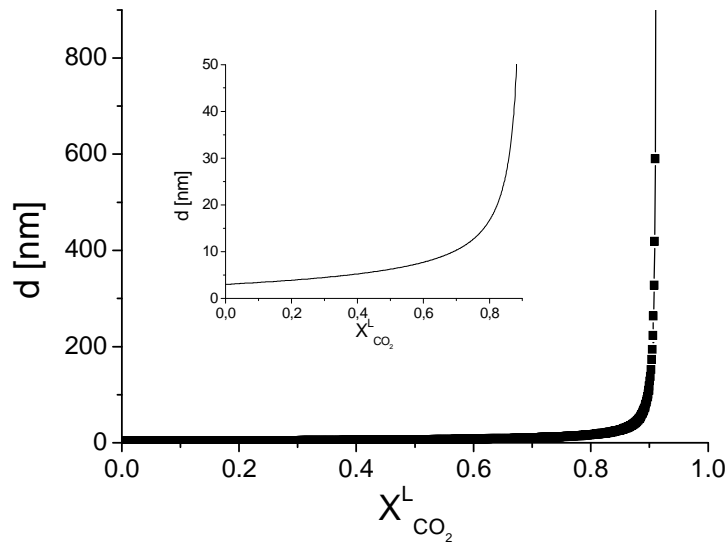
For some applications the question about the density- and the composition gradient within the surface arise. The advantage of the modelling tool lies in the possibility to calculate interfacial properties, like the density profiles of both components within the interface, which are not accessible by experiments. The density profile can be calculated using Eq. 12 . Figure 4 depicts the partial density of both components within the surface at three different liquid



phase bulk-concentrations and at 344K. At 344K CO<sub>2</sub> has a higher vapour pressure than benzene. Because of this, the density profile of CO<sub>2</sub> runs through a maximum in the interface. This phenomenon is called relative enrichment in the interface. The density profile of benzene shows the typical tanh-shape. Relative enrichment can play an important role as hindrance against the mass transfer over the interface.



**Figure 4:** Predicted partial density profiles for the system CO<sub>2</sub> + benzene at T=344K using the density gradient theory with PCP-SAFT-EOS ( $k_{ij}=0$ ).

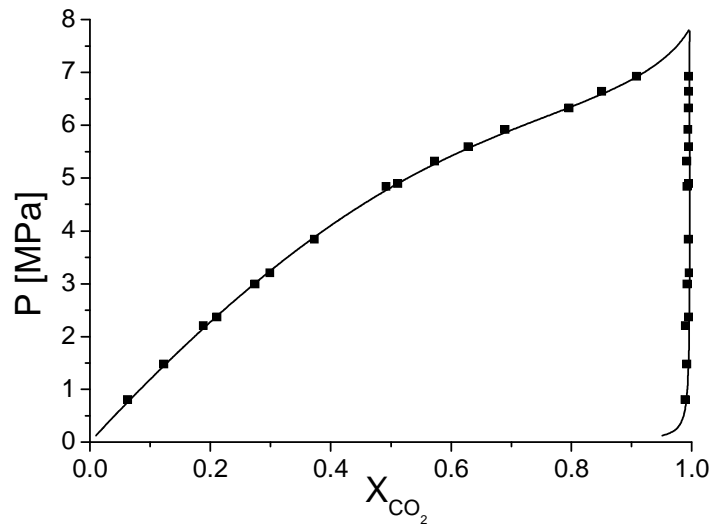


**Figure 5:** Predicted thickness of the interface for the system CO<sub>2</sub> + benzene at T=344K using the density gradient theory with PCP-SAFT-EOS ( $k_{ij}=0$ ).

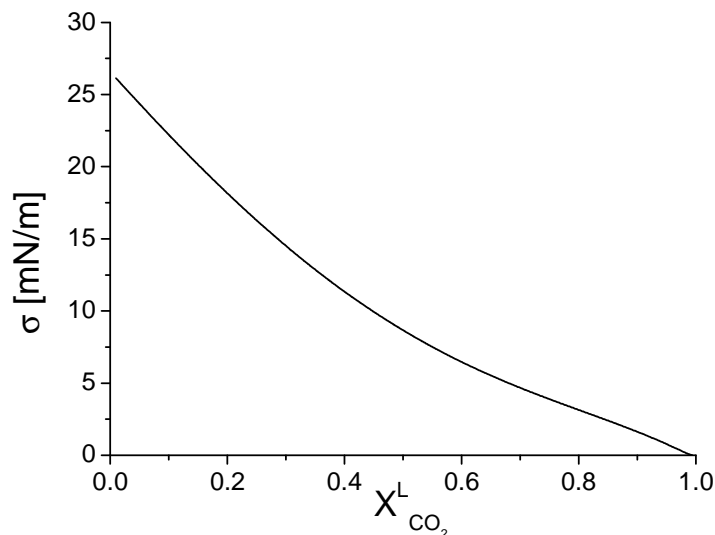
Additionally, the higher CO<sub>2</sub> content in the mixture leads to a broader interface, as shown in Figure 5, because with increasing concentration one approaches the critical point. Per definition, the length of the interface has to become infinite at this point, since there are no two phases anymore.

The DGT has an enormous potential in industrial processes, since it can use properties of the pure components in order to predict interfacial properties of mixtures, where experimental

data may be scarce. We center in this work the prediction of surface tension for two mixtures: CO<sub>2</sub> – methane and CO<sub>2</sub> – toluene. For the last mixture values of the binary interaction parameter  $k_{ij}$  are available in the literature [6]. Figure 6 shows the vapour-liquid equilibrium curve for the system CO<sub>2</sub> + toluene with  $k_{ij}=0.03$ . Agreement between calculated and experimental VLE is excellent, as already stated in previous works from Gross [6]. With help of the VLE data it is now possible to make a prediction of the surface tension of the mixture. This is presented in Figure 7. Experimental data for this mixture is not available in the literature; however, it is possible to say, based on previous analysis of the mixtures, that at least a qualitative and very likely a quantitative agreement with the real surface tension can be expected.

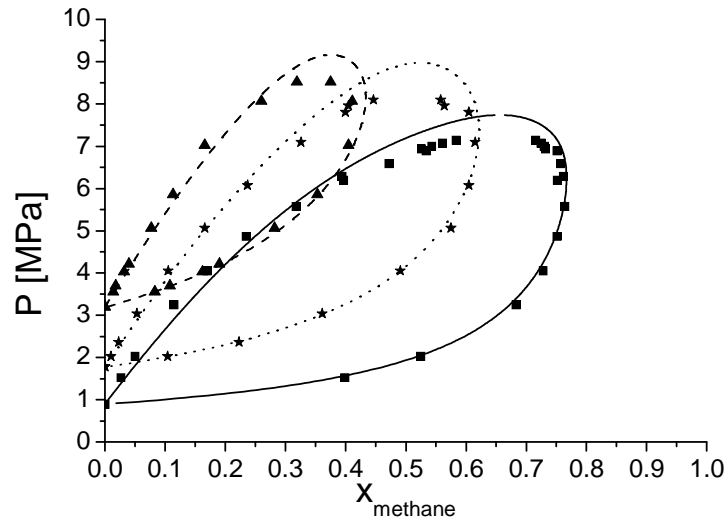


**Figure 6:** Experimental (squares [200]) and calculated (solid line) VLE of the mixture CO<sub>2</sub> + toluene using PCP-SAFT-EOS with  $k_{ij}=0.03$  at 308K.

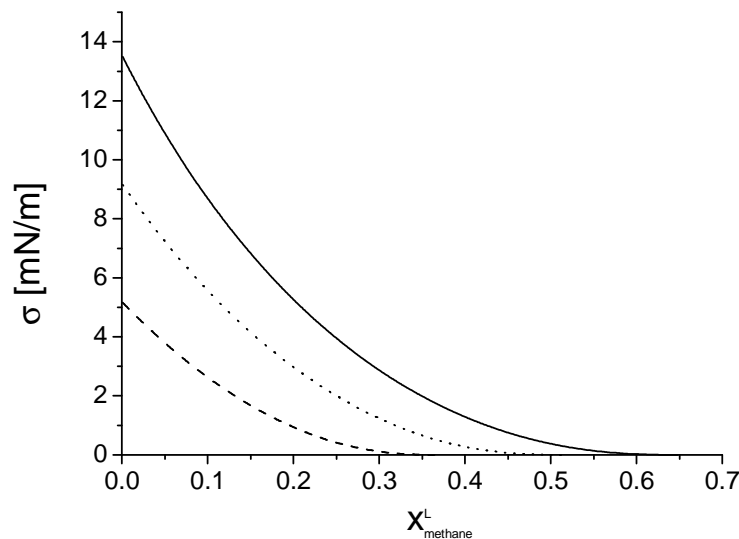


**Figure 7:** Predicted surface tension of the mixture CO<sub>2</sub> + toluene using PCP-SAFT-EOS at 308K.

The mixture CO<sub>2</sub> + methane is of great importance in industrial processes, since it can emulate equilibrium of a mixture of carbon dioxide with natural gas (predominantly methane). Therefore, it is of interest to see predictions of the interfacial properties for this mixture. As usual, it is first needed to know the binary interaction parameter for the system. Figure 8 depicts the calculated VLE data. With help of this we can be able to predict the surface tension of the mixture. Previous works [2] have shown a good agreement for mixtures with n-alkanes. Therefore, it is expected that these predictions may be accurate in describing the behaviour of the surface tension at several temperatures.



**Figure 8: Experimental [21] and calculated vapour-liquid equilibrium of the system CO<sub>2</sub> and methane at different temperatures (squares and solid line T=230 K, stars and dotted line T=250K, triangles and broken line T=270K) using PCP-SAFT with  $k_{ij}=-0.033$ .**



**Figure 9: Predicted surface tension of the system CO<sub>2</sub> and methane at different temperature (solid line: 230K, dotted line: 250K, broken line: 270K) using PCP-SAFT.**

## SUMMARY

In summary, the proposed model is able to predict the interfacial tension of binary mixtures made from CO<sub>2</sub> + benzene close to the experimental data, whereas in our model only the quadrupole moment of CO<sub>2</sub> is taken into account. Unfortunately, for the other two considered mixtures, namely CO<sub>2</sub> + methane and CO<sub>2</sub> + toluene no experimental data are available. Nevertheless, the theoretical framework can be used to predict the surface tension as function of composition, temperature and pressure.

Additionally, the theory gives useful information, like the relative enrichment in the interface, which is not accessible by experiments. This effect occur always if the vapour pressures of the two pure components at the system temperature are strong different. The component having the higher vapor pressure will always enrich in the interface.

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