Vapor-Liquid Interfacial Properties of the System Cyclohexane + CO₂: Experiments, Molecular Simulation and Density Gradient Theory

Simon Stephan*, Stefan Becker, Kai Langenbach, Hans Hasse

Laboratory of Engineering Thermodynamics (LTD), TU Kaiserslautern, Erwin-Schrödinger-Straße 44, 67663 Kaiserslautern, Germany

Abstract

Properties of the vapor-liquid interface of the binary mixture cyclohexane + CO₂ as well as for the two pure substances are reported. The data were obtained from pendant drop experiments (Exp), molecular dynamics (MD) simulation, and density gradient theory (DGT) in combination with the PCP-SAFT equation of state. The following interfacial properties were studied: surface tension (Exp, MD, DGT), relative adsorption (Exp, MD, DGT), enrichment (MD, DGT), and interfacial thickness (MD, DGT). The measurements were carried out at temperatures between 303.15 K and 373.15 K and pressures up to 6 MPa. Furthermore, bulk VLE properties were computed by MD and PCP-SAFT and compared to experimental data from the literature. Data from experiment, MD, and DGT were found to be in good agreement throughout.

Keywords: Interfacial properties, cyclohexane + CO₂, Experiment, Molecular dynamics, Density gradient theory

*Corresponding author

Email address: simon.stephan@mv.uni-kl.de (Simon Stephan)

1. Introduction

Information on interfacial properties is important in many fields of chemical and process engineering. While there is plenty of information on the surface tension of pure substances [1–3], much less data is available for mixtures. Also, information on other interfacial properties than the surface tension is rare for mixtures. For example, the adsorption of components at interfaces and the nanoscopic arrangement of that surface excess at the interface, i.e. the enrichment, is not yet fully understood.

In the present work, therefore different interfacial properties of the binary system cyclohexane + CO₂ were studied both by experiments and simulations. Also some data on the pure substances are reported. Table 1 gives an overview of the available experimental data on the surface tension of pure cyclohexane and pure CO₂ as well as their binary mixture. To the best of our knowledge, no information on the nanoscopic properties at the vapor-liquid interface of the system cyclohexane + CO₂ is available in the literature. Data on the surface tension of the mixture is still scarce.

The mixture was furthermore chosen for two reasons: first, a significant enrichment of the CO₂ at the interface was to be expected according to the experiences from studies of similar systems [4–7]. Second, for both pure substances cyclohexane and CO₂ and their mixture, accurate and validated force field and PCP-SAFT EOS models for the description of the vapor-liquid equilibrium are available in the literature [8–12], such that the main focus of the present work could be laid on the interfacial properties.

While interfaces are treated as two dimensional objects on a macroscopic level, it is found that the density changes continuously at the interface on an atomistic scale. There are presently no experimental methods that yield information on such density profiles across fluid interfaces and thereby on the arrangement of the surface excess and the interfacial thickness. However, such data can be obtained from molecular simulations based on classical force fields on the one side and density gradient theory (DGT) combined with an equation of state (EOS) or density functional theory (DFT) on the other side [2, 3].

Interesting phenomena have been observed in the nanoscopic interfacial region of binary and multicomponent mixtures, such as maxima in the density profiles of the low-boiling component at the interface [13–16]. The density of low-boiling components at such maxima can be several times higher than the bulk densities. This phenomenon is referred to as *enrichment* and is closely related to the relative adsorption. The enrichment of components at the vapor-liquid interface of mixtures

has recently received particular attention as it is suspected to influence the mass transfer across the interface [4, 7, 17–19], which is of fundamental importance for fluid separation processes. Also, the relation between the relative adsorption and the enrichment (both describe the surface excess) and their relation to the molecular interactions is not yet fully understood [4, 20].

Table 1: Literature overview of experimental data of the system cyclohexane + carbon dioxide as well as the pure components.

author	T / K	p / MPa
Cyclohexane + carbon dioxide		
VLE		
<i>Al-Sahhaf et al.</i> [97]	333.15	1.08 - 8.17
<i>Dymond</i> [166]	304.23	0.1
<i>Esmelindro et al.</i> [98]	303, 333	4.59 - 9.81
<i>Kaminishi et al.</i> [167]	303.15	1.09 - 5.81
<i>Mukhopadhyay & Srinivas</i> [169]	366	10.2 - 11.97
<i>Shibata & Sandler</i> [134]	366.5 - 410.9	1.75 - 12.8
<i>Yang et al.</i> [99]	333.15	3.46 - 8.6
<i>Zhang & Zheng</i> [168]	303.15	0.97 - 6.66
<i>Nagarajan & Robinson</i> [108]	344.26	6.8 - 11
<i>Krichevskii & Sorina</i> [135]	473.15 - 483.15	1.3 - 13
Surface tension		
<i>Nagarajan & Robinson</i> [108]	344.3	6.87 - 10.96
<i>Yang et al.</i> [109]	308.15, 323.15, 333.15	3.6 - 9.6
Cyclohexane		
Surface tension		
<i>Azizian & Bashavard</i> [136]	293.15 - 323.15	
<i>Azizian et al.</i> [137]	293.15 - 313.15	
<i>Campbell & Anand</i> [138]	298.15 - 323.15	
<i>Clever and Chase</i> [139]	298.15 - 308.15	
<i>Gómez-Díaz et al.</i> [140]	298.15 - 323.15	

<i>Grafe</i> [142]	295.15 - 306.15
<i>Hückel & Harder</i> [141]	279.55 - 349.95
<i>Hennaut-Roland & Lek</i> [143]	288.15 - 303.15
<i>Jain & Singh</i> [144]	298.16 - 308.16
<i>Kahl et al.</i> [63]	287.81 - 327.88
<i>Kahl et al.</i> [64]	279.33 - 337.93
<i>Kaur et al.</i> [145]	298.15 - 308.15
<i>Konobeev & Lyapin</i> [146]	293.15 - 353.85
<i>Lakomy & Lehar</i> [147]	298.15
<i>Lam & Benson</i> [148]	293.15 - 303.15
<i>Mc Lure et al.</i> [149]	303.2
<i>Moll</i> [150]	293.15
<i>Ramakrishna & Patel</i> [151]	308.15
<i>Romero et al.</i> [152]	283.15 - 313.15
<i>Rusanov et al.</i> [153]	293.15 - 323.15
<i>Siskova & Secova</i> [154]	293.15 - 313.15
<i>Suri & Ramakrishna</i> [155]	293.15 - 303.15
<i>Trieschmann</i> [156]	295.15
<i>Villares et al.</i> [157]	298.15 - 313.15
<i>Vogel</i> [158]	293.95 - 316.75
<i>Wang et al.</i> [159]	288.15 - 328.15
<i>Wright & Akhtar</i> [160]	303.15
<i>Wright & Akhtar</i> [162]	303.15
<i>Zvereva & Smirnova</i> [161]	303.15
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Carbon dioxide	
Surface tension	
<i>Muratov & Skripov</i> [163]	216.55 - 302
<i>Anonymous</i> [164]	298.15
<i>Rathjien & Straub</i> [165]	273.15 - 304.14
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There are basically two approaches for developing a better understanding of the phenomena

at fluid interfaces. On the one side, studies on simple model systems can be carried out. We have recently systematically studied binary mixtures of Lennard-Jones fluids and have examined the influence of the variation of parameters, which describe the molecular interactions on the interfacial properties [4, 16, 17, 21]. Similar studies have also been carried out by multiple other groups, e.g. Refs. [13–15, 22–33]. The second approach is to study real systems, both by experiments and simulation. Unfortunately, only the surface tension is directly accessible by experiments and the relative adsorption indirectly [2, 34, 35], while other properties, like the enrichment and interfacial thickness, are not as readily accessible. However, the composition and orientation of molecules at fluid interfaces can be examined by radiation scattering methods, cf. [36–40].

The models used in both MD and DGT can be calibrated using experimental data to predict the density profiles at vapor-liquid interfaces. The models should not only represent the interfacial properties well, but also the bulk VLE properties. Theoretical studies on nanoscopic interfacial properties of real mixtures have been for example reported in Refs. [5–7, 18, 20, 41–55].

In the present work we have followed the second route and studied the mixture of cyclohexane + CO₂. As in Refs. [20, 56], the present study was carried out using several methods: pendant drop experiments, molecular dynamics (MD) simulation, and density gradient theory (DGT) calculations in combination with the PCP-SAFT equation of state [11, 12, 57–59]. We report surface tension and relative adsorption data obtained from all three methods, whereas nanoscopic density profiles at the interface, the enrichment of CO₂ at the interface, and the interfacial thickness were only investigated by MD and DGT. The experiments were carried out at temperatures between 303 K and 373 K in intervals of 10 K. MD and DGT calculations were carried out at 303 K, 333 K, and 363 K. The employed methods are described in Section 2 and the results are reported and discussed in Section 3. Conclusions are drawn in Section 4.

2. Methods

2.1. Pendant Drop Experiments

2.1.1. Chemicals and Sample Preparation

Details of all materials (CAS Number, supplier, purity) used for the experiments are listed in Table 2. Carbon dioxide was used without further purification. Cyclohexane was degassed by vacuum distillation. The samples of the mixture were prepared as described by *Becker et al.* [20].

Table 2: Chemicals that were used in the present work.

	CAS number	supplier	purity (mole fraction)
cyclohexane (C ₆ H ₁₂)	110-82-7	Merck KGaA, Germany	0.998
carbon dioxide (CO ₂)	124-38-9	Air Liquide, France	0.99995

2.1.2. Measurements and Experimental Setup

The pendant drop method [60–62] was used for the determination of the surface tension of pure cyclohexane and its binary mixture with CO₂. Due to the low critical temperature of CO₂, no measurements with pure CO₂ were carried out. The method is based on the mechanical equilibrium of a drop pending at a capillary tube, which is governed by gravitational forces and the surface tension. The surface tension γ is determined from

$$\gamma = \frac{\Delta\rho g z}{A}, \quad (1)$$

where $\Delta\rho = \rho' - \rho''$ is the density difference between the liquid and the vapor phase, g is the gravitational constant, z is the height coordinate of the drop as measured from the apex, and A is a geometric factor characterizing the shape of the drop [61, 62]. The latter was obtained from a photographic examination of the pending droplet.

The pendant drop measurements were carried out with a custom-built apparatus as introduced in a previous publication of our group [20]. The procedure was the same as described therein. The measurements yield data on the surface tension as a function of temperature and pressure [20]. The mole fraction of CO₂ in the liquid phase x'_{CO_2} at a given temperature and pressure is subsequently determined with the PCP-SAFT EOS, such that the experimental data can be related to the liquid phase composition. It is shown in the results section and the Appendix that the PCP-SAFT EOS gives a good description of the bulk properties of the mixture cyclohexane + CO₂.

As discussed in Ref. [20], the main contribution to the uncertainty of the surface tension determined from Eq. (1) stems from the density difference $\Delta\rho$. Any error in $\Delta\rho$ will result in a similar error in γ , cf. Eq. (1). In the present work, $\Delta\rho$ was calculated from the PCP-SAFT EOS. It is shown in the Appendix that the numbers for $\Delta\rho$ obtained in this way are in good agreement with available experimental data. Nevertheless, the resulting uncertainty of the surface tension that stems from the uncertainty in $\Delta\rho$ is up to 3%, cf. Appendix B. The random uncertainty of the measurement method was estimated from repeated measurements of the surface tension of pure cyclohexane. Hence, the statistical error was computed from three times the standard deviation of five independent data points. This random uncertainty of the measurement method is less than 1.1% and the total uncertainty in the experimental data on the surface tension of the binary mixture is better than 4.1%.

2.1.3. Determination of the Relative Adsorption from the Experimental Data on the Surface Tension

The relative adsorption $\Gamma_2^{(1)}$ of a component 2 with reference to the second component 1 in a binary mixture can be obtained from the Gibbs adsorption equation [35], which yields for the relative adsorption of CO_2 at the vapor-liquid interface $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ in a mixture of CO_2 with cyclohexane (C_6H_{12})

$$\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})} = - \left(\frac{\partial \gamma}{\partial \mu_{\text{CO}_2}} \right)_T, \quad (2)$$

where μ_{CO_2} is the chemical potential of CO_2 in the equilibrated phases.

Different ways have been established in the literature to describe the chemical potential in Eq. (2) to obtain the relative adsorption, e.g. with activity coefficient models [63, 64], equations of state [20], or an ideal gas phase assumption [34, 56]. The PCP-SAFT EOS is used here for the determination of the chemical potential. The chemical potential of CO_2 μ_{CO_2} was therefor computed from the PCP-SAFT EOS at every state point (characterized by (T, p)) at which the surface tension was measured. A value of the chemical potential μ_{CO_2} was subsequently assigned to each value of the surface tension obtained from the pendant drop experiment. For each isotherm, a polynomial curve was fitted to the data points $(\gamma, \mu_{\text{CO}_2})$, which is then used to compute the derivative in Eq. (2). The adsorption data $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ obtained in this way are referred to as experimental data in the following.

2.2. Molecular Models and Simulation Method

Molecular dynamics simulations were carried out with the program *ls1 mardyn* [65], the force fields were taken from the MolMod database [8]. The molecular model for CO_2 was that of *Merker et al.* [9]. It consists of three Lennard-Jones sites, representing each atom and a point quadrupole

in the center of mass representing the polarity of the molecule. The cyclohexane model was taken from *Merker et al.* [10] and consists of six Lennard-Jones sites (one for each methylene group). The molecular models of both substances are rigid. It has been shown that thermodynamic properties of low molecular weight molecules can be described well by rigid models, cf. [66–68].

The potential energy of the molecular models is given by

$$U = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \left\{ \sum_{a=1}^{n_i^{\text{LJ}}} \sum_{b=1}^{n_j^{\text{LJ}}} 4\varepsilon_{ijab} \left[\left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^{12} - \left(\frac{\sigma_{ijab}}{r_{ijab}} \right)^6 \right] + \sum_{c=1}^{n_i^e} \sum_{d=1}^{n_j^e} \frac{1}{4\pi\varepsilon_0} \left[\frac{Q_{ic}Q_{jd}}{r_{ijcd}^5} \cdot f(\omega_i, \omega_j) \right] \right\}, \quad (3)$$

where ε_{ijab} and σ_{ijab} are the Lennard-Jones energy and size parameter, r_{ijab} and r_{ijcd} are site-site distances, Q_{ic} and Q_{jd} are the magnitude of the electrostatic interactions, i.e. the point quadrupole moments, and $f(\omega_i, \omega_j)$ are dimensionless angle-dependent expressions representing the orientation ω_i, ω_j of the point multipoles [69]. The indices i and j indicate the molecules, the indices a, b, c, d the interaction sites of a molecule.

The modified Lorentz-Berthelot combination rules [70, 71] were employed for describing the dispersive/ repulsive interactions between unlike particles:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad (4)$$

$$\varepsilon_{ij} = \xi_{ij} \sqrt{\varepsilon_{ii} \varepsilon_{jj}}, \quad (5)$$

where the index ii and jj indicate the interaction of two particles of the same type and the index ij the cross interaction between different particle types. Eq. (4) and (5) were also employed for the modeling of the cross interactions using the PCP-SAFT EOS; see the following section for details. The binary interaction parameter $\xi_{\text{CO}_2, \text{C}_6\text{H}_{12}}^{\text{MD}} = 0.95$ was used in the present work for the MD simulations. It was fitted by *Merker et al.* [10] to experimental data of the Henry’s law constant of the mixture cyclohexane + CO_2 .

The molecular force field models of the pure components which were employed in the present work were parametrized to reproduce the saturated liquid density, the vapor pressure, and the enthalpy of vaporization [9, 10]. The absolute average deviations between the calculated values by the molecular simulation and experimental data are 0.3%, 3.7%, and 0.9% for cyclohexane [10] and 0.4%, 1.8%, and 8.1% for carbon dioxide [9]. The surface tension was not considered in the parametrization of the molecular models. For other pure fluid force field models developed with a similar parametrization

Table 3: Overview of models used in the present work. The column MD indicates the employed force fields, the column PCP-SAFT the respective EOS models. The column κ_{DGT} reports the DGT influence parameter used. The first and second lines give the pure component models, the third line the cross interaction.

	Force field	PCP-SAFT	DGT influence parameter κ
cyclohexane	<i>Merker et al.</i> [10]	<i>Gross & Sadowski</i> [11]	<i>Niño-Amézquita</i> [94]
CO ₂	<i>Merker et al.</i> [9]	<i>Gross</i> [12]	<i>Niño-Amézquita</i> [95]
cyclohexane + CO ₂	<i>Merker et al.</i> [10]	this work	Eq. (8)

strategy the surface tension agrees with experimental data within 20%, whereat the MD results often overestimate the experimental data [7, 20, 72–78].

In the molecular simulations of the vapor-liquid interfaces, systems were studied in which a liquid phase is arranged as a slab in the middle of the simulation volume with a vapor phase on each side. Periodic boundary conditions were applied in all directions. The coordinate z is perpendicular to the interfaces. The elongation of the simulation box normal to the interface was 30 nm and the thickness of the liquid slab in the middle of the simulation box was 15 nm. The elongation in the directions parallel to the interfaces was at least 6 nm. The simulations were performed in the NVT ensemble with $N = 32,000$ particles. The equation of motion was solved by a leapfrog integrator [79] with a time step of $\Delta t = 2$ fs. The initial densities and compositions in the simulations were taken from the PCP-SAFT EOS to ensure fast equilibration.

For all simulations carried out in the present work, the cutoff radius was set to 17.5 Å with a center-of-mass cutoff scheme. A slab-based long range correction scheme was employed to incorporate the long-range Lennard-Jones interactions [80, 81].

The equilibration was executed for 750,000 time steps. The production was conducted for 4,000,000 time steps for the pure substances, and 8,000,000 for the mixture. Density and pressure profiles were computed in block averages of 500,000 time steps during the production phase. From each block average, the vapor pressure p , the saturated liquid and vapor density ρ' and ρ'' , respectively, and the saturated vapor and liquid phase mole fractions x'_i and x''_i were calculated as an average in the respective phase – excluding the area close to the interface, where the first derivative of the density with respect to the z -coordinate significantly deviates from zero.

The surface tension in the MD simulations was calculated from the deviation between the normal and the tangential diagonal components of the pressure tensor [82, 83] in the pressure profiles, i.e.

by the mechanical route

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} (p_N - p_T) dz, \quad (6)$$

where p_N is the normal pressure given by the z -component of the diagonal of the pressure tensor and p_T is the tangential pressure, which was determined by averaging over the x - and y -components of the diagonal of the pressure tensor. The statistical uncertainties of the surface tension γ and the bulk VLE properties ($p, \rho', \rho'', x'_i, x''_i$) were estimated to be three times the standard deviation of all sampled block averages.

2.3. Density Gradient Theory + PCP-SAFT EOS

2.3.1. Density Gradient Theory

Density gradient theory [84, 85] is a widely used method for computing the surface tension of both pure substances [6, 46, 86, 87] and mixtures [42, 43, 49, 51, 53, 54, 88–90]. Also, nanoscopic interfacial properties can be obtained from DGT, namely the density profiles across the interface. To model fluid interfaces, DGT requires a model of the Helmholtz energy of the bulk fluid and the so-called influence parameter κ that describes the influence of the density gradient on the Helmholtz energy. For a comprehensive introduction of DGT we refer the reader to Refs. [2, 86, 91].

Table 4: Pure component parameters used in the present work in the PCP-SAFT + DGT calculations.

component	m	$\sigma / \text{\AA}$	$\varepsilon/k_B / \text{K}$	$Q / \text{D}\text{\AA}$	$10^{20} \kappa_{\text{DGT}} / \text{Jm}^5 \text{mol}^{-2}$
cyclohexane	2.5303	3.8499	278.11	-	34.07
carbon dioxide	1.5131	3.1869	163.33	4.4	2.327

The Helmholtz energy of the heterogeneous system is expanded in DGT in a Taylor series in the derivatives of the component densities with respect to the spatial coordinate normal to the interface $\nabla^m \boldsymbol{\rho}$, $m = 1, 2, \dots$ and truncated after the square gradient term. For a planar interface of a binary mixture, the Helmholtz energy density $a = A/V$ can be written as

$$a[\boldsymbol{\rho}] = a_0(\boldsymbol{\rho}) + \sum_{i=1}^2 \sum_{j=1}^2 1/2 \kappa_{ij} \nabla \rho_i \cdot \nabla \rho_j, \quad (7)$$

where $a_0(\boldsymbol{\rho})$ is the Helmholtz energy per volume of a hypothetical homogeneous system at the local composition and $\boldsymbol{\rho}$ indicates the vector of the number densities. κ_{ij} is the influence parameter, for the pure substances (if $i = j$) and the cross interaction (if $i \neq j$).

The cross-interaction influence parameter was assumed here to be the geometric mean of the pure substance influence parameters [51, 92]

$$\kappa_{ij} = \sqrt{\kappa_i \kappa_j}. \quad (8)$$

In a previous work of our group, it was shown that this assumption leads to almost perfect agreement between results from DGT and computer experiment for different Lennard-Jones mixtures with various types of phase behavior [4, 93] in the entire composition range. The influence parameters of the pure components cyclohexane and carbon dioxide were adopted from the literature [94, 95], cf. Table 4.

The stabilized DGT algorithm proposed by *Mu et al.* [88] was employed to obtain the equilibrium density profiles $\rho_i(z)$ of both components connecting the bulk phases, which is numerically robust and avoids choosing a reference component, which has numerical pitfalls [96]. The domain length was set to 12 nm with a spatial discretization of 0.02 nm.

The surface tension γ was calculated from

$$\gamma = \int \sum_{i=1}^2 \sum_{j=1}^2 \kappa_{ij} \nabla \rho_i \cdot \nabla \rho_j \, dz. \quad (9)$$

2.3.2. PCP-SAFT Equation of State

The PCP-SAFT equation of state [11, 12], which is an extension of the original SAFT EOS of *Chapman et al.* [57–59], was used in this work for describing the Helmholtz energy in DGT. It was also used for the computation of phase equilibria of the studied systems, the density differences $\Delta\rho$ used in the pendant drop method (cf. Eq. (1)), and the calculation of the chemical potential of CO₂ in the mixture (cf. Eq. (2)). The details of the EOS are described elsewhere [11, 12].

For non-associating components, as the ones that are studied here, the PCP-SAFT EOS has four pure component parameters: the segment number m , the segment diameter σ , the segment dispersion energy ε , and the quadrupole moment Q . The pure component parameters for cyclohexane and CO₂ were taken from the literature [11, 12] and are summarized in Table 4. Carbon dioxide was modeled as a component with a quadrupole moment. Cyclohexane was described with the dispersion and chain term, cf. Table 4. The pure component models were adjusted in Refs. [11, 12] such as to yield a good description of the saturated liquid density and the vapor pressure [11, 12].

The modified combination rules of Lorentz and Berthelot presented in Eq. (4) and (5) were also used in the PCP-SAFT equation of state. The binary interaction parameter $\xi_{\text{CO}_2, \text{C}_6\text{H}_{12}}^{\text{EOS}} = 0.945$

was fitted in the present work to experimental data [97–99] of the vapor-liquid equilibrium at $T = 333.15$ K.

2.4. Interfacial Properties obtained from Density Profiles

Molecular simulations and density gradient theory yield the component density profiles $\rho_i(z)$ across the vapor-liquid interface on a nanoscopic scale. On the basis of the density profiles of both pure components, the relative adsorption can be computed by the symmetric interface segregation according to *Telo da Gama and Evans* [14, 100]. For CO_2 in the binary mixture with C_6H_{12} this leads to:

$$\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})} = -(\rho'_{\text{CO}_2} - \rho''_{\text{CO}_2}) \int_{-\infty}^{\infty} \left[\frac{\rho_{\text{C}_6\text{H}_{12}}(z) - \rho'_{\text{C}_6\text{H}_{12}}}{\rho'_{\text{C}_6\text{H}_{12}} - \rho''_{\text{C}_6\text{H}_{12}}} - \frac{\rho_{\text{CO}_2}(z) - \rho'_{\text{CO}_2}}{\rho'_{\text{CO}_2} - \rho''_{\text{CO}_2}} \right] dz, \quad (10)$$

where ρ'_i and ρ''_i are the component densities at saturation in the bulk liquid and bulk vapor phase, respectively.

The interfacial excess at the surface can also be characterized by the interfacial enrichment E_{CO_2} , which is defined according to *Becker et al.* [20] as the ratio of the maximum local component density of CO_2 in the interfacial region and the larger of the component densities of CO_2 in the two bulk phases

$$E_{\text{CO}_2} = \frac{\max(\rho_{\text{CO}_2}(z))}{\max(\rho'_{\text{CO}_2}, \rho''_{\text{CO}_2})}. \quad (11)$$

Since the relative adsorption and the enrichment both describe the surface excess, they are closely linked, but they do not contain the same information [4, 16, 20]. Adsorption may occur although no enrichment is present ($E_{\text{CO}_2} = 1$) – if the two component density profiles are shifted relative to each other [4]. But an enrichment will generally result in a positive relative adsorption of the low-boiling component. By definition, the enrichment assumes values equal to or larger than unity. In binary mixtures, an enrichment $E_i > 1$ is only observed for the low-boiling component. At least, no contrary evidence has been reported yet – to the best of the author’s knowledge.

The thickness of the vapor-liquid interface is characterized in this work by the 90-10% definition for the effective interfacial thickness L_{10}^{90} according to *Lekner and Henderson* [101], which is the distance between the points where the total local density $\rho_{\text{tot}}(z) = \rho_{\text{CO}_2}(z) + \rho_{\text{C}_6\text{H}_{12}}(z)$ reaches 10% and 90% of the total bulk number densities, respectively:

$$\begin{aligned} L_{10}^{90} &= z(\rho_{90}^{\text{tot}}) - z(\rho_{10}^{\text{tot}}), \\ \rho_{10}^{\text{tot}} &= \rho''_{\text{tot}} + 0.1(\rho'_{\text{tot}} - \rho''_{\text{tot}}), \\ \rho_{90}^{\text{tot}} &= \rho''_{\text{tot}} + 0.9(\rho'_{\text{tot}} - \rho''_{\text{tot}}). \end{aligned} \quad (12)$$

For both MD and DGT, the origin on the z -axis of the interfacial profiles was chosen here such that $\rho_{\text{tot}}(z) = 0$ at $\rho_{\text{tot}} = \rho''_{\text{tot}} + 0.5(\rho'_{\text{tot}} - \rho''_{\text{tot}})$.

For the MD results, the enrichment E_{CO_2} , the relative adsorption $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$, and the interfacial thickness L_{10}^{90} were calculated from each block averaged density profile. The reported value was computed from the mean of the block averages; the statistical uncertainty was estimated to be three times the standard deviation of all sampled block averages.

3. Results and Discussion

First, the results for the pure components are discussed (vapor-liquid equilibrium and interfacial properties) and subsequently the results for the binary mixture. The numeric values of all results from this work (pendant drop experiment, MD, and DGT) are reported in the supplementary material.

3.1. Results for the Pure Substances

3.1.1. Bulk Properties

Fig. 1 shows the vapor-liquid equilibrium of the two pure substances cyclohexane and carbon dioxide. Both the vapor pressure and the saturated densities from both components are shown. The results from the molecular models (MD force field and PCP-SAFT model) are compared with correlations of experimental data from *Span and Wagner* [102, 103]. These correlations are reported to agree with experimental data within the following range [102, 103]: the absolute average deviation for cyclohexane is at least 0.2% for the vapor pressure and 0.3% for the saturated liquid density [102]; and for carbon dioxide 0.006% for the vapor pressure, 0.01% for the saturated liquid density, and 0.01% for the saturated vapor density [103]. It is known that the critical pressure is not represented well by the reference EOS of cyclohexane [102], cf. Fig. 1.

The results obtained from the MD force fields and the PCP-SAFT models agree excellently with the reference correlations. The absolute average deviations of the PCP-SAFT models and experimental data are: for cyclohexane: 0.5% for the vapor pressure and 3.1% for the saturated liquid density [11] and for carbon dioxide: 0.3% for the vapor pressure and 1.3% for the saturated liquid density [12], excluding the region in the vicinity of the critical point.

The molecular simulation results from this work are in excellent agreement with results reported in the literature for the same force fields [9, 10, 104, 105], i.e. the results agree within their statistical uncertainties. The agreement of the results obtained with the force fields for the two pure substances with experimental data has been studied before: for carbon dioxide, the deviations were reported to be below 1.8% for the vapor pressure and 0.4% for the saturated liquid density [9], for cyclohexane the corresponding numbers are 3% for the vapor pressure and 0.4% for the saturated liquid density [10]. This is confirmed by the results from the present work.

The three dashed lines in the plot of Fig. 1 (top) indicate the three temperatures that were investigated by all three methods (experiment, MD, and DGT) for the binary mixture of cyclohexane + CO₂: 303.15 K, 333.15 K, and 363.15 K. The experimental value of the critical temperature of cyclohexane is $T_c^{\text{C}_6\text{H}_{12}} = 553.8 \text{ K}$ [106]. Hence, the temperatures of the binary mixture investigated with

Figure 1: Vapor pressure curves (top) and saturated densities (bottom) of the pure substances cyclohexane (black) and carbon dioxide (blue). The solid lines are the results from the PCP-SAFT EOS. The dashed lines are the correlations of the experimental data [102, 103]. All symbols are MD results: open symbols represent data from this work, filled squares data from *Merker et al.* [10], and filled triangles data from *Werth et al.* [104, 105]. The vertical dashed lines in the upper plot indicate the three temperatures (303.15 K, 333.15 K, and 363.15 K) for which data of the binary mixture was taken with all three methods (experiments, MD, and DGT) in the present work.

all three methods correspond to reduced temperatures of approximately $T/T_c^{\text{C}_6\text{H}_{12}} = 0.55, 0.6, 0.65$.

The experimental critical temperature of CO_2 is 304.2 K [1]. The lowest investigated temperature 303.15 K is thereby slightly below the critical temperature of CO_2 . The critical temperature of the molecular force field model was estimated to be 304 K [9]; for the PCP-SAFT model [12] that number is 304.99 K.

3.1.2. Interfacial Properties

Fig. 2 shows the surface tension (top) and interfacial thickness (bottom) of the vapor-liquid interface of the pure substances cyclohexane and CO_2 . For the surface tension, data from experiment,

MD, and DGT are compared, whereas for the thickness only results from the theoretical methods MD and DGT can be compared. As explained above, no experimental data for the surface tension of pure carbon dioxide was taken in the present work. The surface tension from both cyclohexane and CO_2 decreases with increasing temperature and becomes zero at the critical point. The interfacial thickness, on the other hand, increases monotonously and has a pole at the critical point.

Figure 2: Surface tension (top) and interfacial thickness (bottom) of the pure substances cyclohexane (black) and carbon dioxide (blue). Crosses are experimental data from the literature: Refs. [63, 64, 136–162] for cyclohexane and Refs. [163–165] for CO_2 . The solid lines are the results from DGT (this work). Open symbols are results from this work: open diamonds are results from the pendant drop experiment which were only carried out for cyclohexane; open circles are MD results. Filled triangles are results from *Werth et al.* [7, 104, 105].

The experimental results for the surface tension of cyclohexane from the present work agree with corresponding results from the literature (cf. Table 2) within their scattering.

The surface tension obtained from DGT agrees excellently with experimental data, for both cyclohexane and CO_2 , since such data was used for the parametrization of the DGT influence parameter

κ [94, 95]. For both substances, the molecular dynamics simulation results systematically overestimate the surface tension, which has already been reported by *Werth et al.* [7, 104, 105] for both employed force fields. These deviations might be related to the parameterization strategy employed for the force field development (see Section 2.2), i.e. the surface tension was not considered during the parametrization. However, the results for the surface tension obtained in the present work agree very well with MD results from the literature [7, 104, 105].

For the interfacial thickness, the results obtained from MD and DGT agree qualitatively well. Nevertheless, for most temperatures, the MD results exceed those from DGT, which is likely due to the fluctuations, which are present in MD but not in DGT [107].

3.2. Results for the Mixture Cyclohexane + Carbon Dioxide

3.2.1. Bulk Properties

Fig. 3 shows isothermal $p-x$ phase diagrams of the binary mixture cyclohexane + CO₂ at 303.15 K, 333.15 K, and 363.15 K. Experimental data from the literature (cf. Table 1) are compared with molecular simulation data from this work and the PCP-SAFT EOS. As discussed above, CO₂ is still subcritical at $T = 303.15$ K, which is described correctly by the EOS.

Overall, EOS and MD results agree well with the experimental data. For both theoretical methods, the agreement with the experimental data is better for the dew line than for the bubble line. At 303.15 K, the molecular simulation results agree excellently with the experimental bubble line data while the PCP-SAFT EOS results show some deviations, whereas at 333.15 K, these trends are inverted: the EOS agrees very well with experimental bubble line data while the MD simulation results show some deviations. The good agreement of the results from the EOS model with the experimental data at 333.15 K is due to the fact that it was used for the fitting of $\xi_{\text{CO}_2, \text{C}_6\text{H}_{12}}^{\text{EOS}}$. For both temperatures where CO₂ is supercritical, the PCP-SAFT EOS overestimates the critical pressure, as it is usually observed for classical EOS. The PCP-SAFT EOS yields an absolute average deviation for the equilibrium pressure from the available experimental data at the three studied temperatures of 5.2%.

3.2.2. Surface Tension

The surface tension for the binary system cyclohexane + CO₂ was determined with the pendant drop method at eight temperatures between 303.15 K and 373.15 K in intervals of 10 K and pressures up to 6 MPa. The numeric values of all experimental data is reported in the supplementary material.

Figure 3: Vapor-liquid equilibrium of the system cyclohexane + CO₂ at three temperatures. The solid lines are PCP-SAFT results and the open circles are MD simulation results obtained in this work; the crosses indicate experimental data from the literature: 303.15 K (Refs. [98, 166–168]), 333.15 K (Refs. [97–99]), and 363.15 K (Refs. [169, 170]).

DGT and MD calculations were only carried out at three temperatures (303.15 K, 333.15 K, and 363.15 K), cf. Fig. 1.

Fig. 4 shows results for the surface tension obtained in this work for the temperatures 303.15 K, 333.15 K, and 363.15 K. Results from all three employed methods (pendant drop experiment, MD, and DGT) are shown. Experimental data on the surface tension in the system cyclohexane + CO₂ has been reported previously by *Nagarajan & Robinson* [108] and *Yang et al.* [109]. Their data is compared to results from the present work in the Appendix. The data from *Nagarajan & Robinson* [108] is found to be in good agreement with our results, whereas the data of *Yang et al.* [109] systematically deviates from our results.

Figure 4: Surface tension of the system cyclohexane + CO₂ as a function of the liquid phase mole fraction of carbon dioxide x'_{CO_2} at three temperatures (indicated by the color). The lines are DGT results, circles are MD results, and diamonds are results from the pendant drop experiments. For $T = 303.15$ K and $x'_{\text{CO}_2} = 1$ mol mol⁻¹, the DGT yields $\gamma_{\text{DGT}} = 0.0983$ mN m⁻¹.

The surface tension of the binary mixture decreases with increasing liquid phase mole fraction of carbon dioxide x'_{CO_2} and with increasing temperature. For high concentrations of CO₂, the surface tension of the binary mixture exhibits an interesting feature: above the critical temperature of CO₂, the surface tension isotherms have a convex shape close to the critical point, as it is observed in many systems of the type solvent + supercritical solute. However, for the subcritical isotherm at 303.15 K, the surface tension of the mixture exhibits a concave shape at high CO₂ concentrations x'_{CO_2} . This behavior is described well by both molecular simulations and DGT.

The DGT surface tension results agree very well with the experimental data from the present work. The absolute average deviation is approximately 1.8% for the data shown in Fig. 4, which confirms the assumption of using a geometric mixing for the influence parameter, cf. Eq. (8). The molecular simulation results systematically overestimate the surface tension of the binary mixture obtained from DGT by approximately 13% in the entire temperature and composition range, which is due to the deviations already present in the pure substances surface tension, cf. Fig. 2.

3.2.3. Nanoscopic Interfacial Properties

Nanoscopic interfacial properties were studied with MD and DGT. Fig. 5 shows the density profiles in the vapor-liquid interface obtained from MD and DGT at three state points at high CO₂ concentrations and temperature of 303.15 K, 333.15 K, and 363.15 K. In all cases, starting

in the bulk vapor phase, the component density of cyclohexane $\rho_{\text{C}_6\text{H}_{12}}(z)$ increases monotonously towards the liquid bulk phase, whereas the component density of carbon dioxide $\rho_{\text{CO}_2}(z)$ exhibits a distinct maximum in the interfacial region, i.e. there is an enrichment. Such an enrichment of low-boiling components at vapor-liquid interfaces has been reported many times in the literature, e.g. [4, 5, 7, 13–15, 17, 18, 20, 21, 23–31, 33, 43–45, 47, 48, 52, 54, 73, 88, 89, 92, 94, 110–132].

Figure 5: Component density profiles of cyclohexane and CO_2 at the vapor-liquid interface of their binary mixture. Each plot shows one state point. Symbols are MD simulation results, lines are DGT results. Diamonds and solid lines represent CO_2 ; circles and dashed lines are cyclohexane.

Overall, the results from MD and DGT show excellent agreement. However, small differences may be pointed out. Since the liquid phase composition was prescribed for the calculations shown in Fig. 5, the densities from MD and DGT + PCP-SAFT match very well in the liquid bulk phase. The minor differences for the gas phase simply stem from differences in the description of the bulk VLE data (cf. Fig. 3).

The MD simulations predict a slightly larger interfacial width compared to the results from DGT. This is due to the fluctuations of the interface, which are present in MD, whereas in DGT the surface

is always perfectly flat – as already discussed for the pure substances, cf. Fig. 2. Considering the fact that both methods are independent predictions for the mixture, the density profiles obtained from both methods agree remarkably well.

The adsorption of carbon dioxide increases with decreasing temperature, which agrees well with findings from the literature for similar systems [13, 16, 20]. The interfacial thickness, on the other hand, decreases with decreasing temperature.

It has been shown in a recent work of our group that the difference of the bulk density of the low-boiling component $\Delta\rho_{\text{CO}_2} = \rho'_{\text{CO}_2} - \rho''_{\text{CO}_2}$ has an important influence on the enrichment [16]. According to [16], $\Delta\rho_{\text{CO}_2} \approx 0$ favors an enrichment, since the relative adsorption (cf. Eq. (10)) must always result in an enrichment in that case. For the binary mixture cyclohexane + CO₂ investigated in the present work, $\Delta\rho_{\text{CO}_2} > 0$ holds in the entire considered temperature range.

Fig. 6 shows the density profiles obtained from DGT in the entire composition range at the three temperatures 303.15 K, 333.15 K, and 363.15 K. The corresponding plots for the MD results are shown in the supplementary material. The state points depicted in Fig. 6 are the same as for the MD results in the supplementary material. For all state points, the agreement between the MD and the DGT results is similar to that found for the examples shown in Fig. 5.

For all state points, the high-boiling component cyclohexane exhibits a monotonous transition from the vapor to the liquid bulk phase and the low-boiling component CO₂ exhibits a maximum at the interface. The interfacial width increases with increasing mole fraction x'_{CO_2} and with increasing temperature. The adsorption of CO₂ increases with x'_{CO_2} but decreases with increasing temperature.

The position of the density maximum z_{max} exhibits an interesting behavior with varying x'_{CO_2} : at $T = 363.15$ K, the position of the maximum in the CO₂ density profile is found at approximately $z_{\text{max}} = 0$ for all studied x'_{CO_2} . On the contrary, at 333.15 K and 303.15 K, starting at low concentrations of CO₂, the maximum moves towards the liquid bulk phase, i.e. $z_{\text{max}} > 0$, with increasing x'_{CO_2} . This is an indication for a decreasing adsorption with increasing x'_{CO_2} . Evidently, this finding is linked to our choice of the definition of $z = 0$, cf. Section 2.4.

Fig. 7 - top shows results for the relative adsorption of CO₂ at the vapor-liquid interface $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$. The relative adsorption $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ computed from the nanoscopic density profiles (MD and DGT) via the symmetric interface segregation presented in Eq. (10) is compared to the results obtained from the macroscopic relation given by the Gibbs adsorption equation (2). The latter are referred to as 'experimental results'.

Overall, the results obtained from both routes (nanoscopic and macroscopic) agree very well,

Figure 6: Density profiles of cyclohexane and CO₂ at the vapor-liquid interface of binary mixtures of these components for three temperatures: 303.15 K (bottom), 333.15 K (middle), and 363.15 K (top) and different compositions of the bulk liquid phase (indicated by the colors). Results from DGT. Dashed lines are CO₂; solid lines are cyclohexane.

Figure 7: Relative adsorption (top) and enrichment (middle) of CO_2 at the vapor-liquid interface and its thickness (bottom) as a function of the liquid phase mole fraction x'_{CO_2} in the system cyclohexane + CO_2 . Results for three temperatures (indicated by the color). The lines are DGT results, circles are MD results, and diamonds are results from the pendant drop experiment (only available for $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$). The MD and DGT results were calculated from the density profiles via Eq. (10); the experimental results were calculated from the macroscopic definition Eq. (2).

both qualitatively and quantitatively. The relative adsorption of CO_2 at the vapor-liquid interface is found to be up to $12 \mu\text{mol m}^{-2}$, which is in the range of results reported in the literature for similar systems [20, 56, 100].

Starting at infinite dilution of CO_2 in the liquid phase, $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ first increases linearly with increasing x'_{CO_2} , passes through a maximum and drops down to zero towards the critical point. The relative adsorption of CO_2 at the interface increases with decreasing temperature, as discussed for the density profiles in Fig. 6.

As the density profiles obtained from MD and DGT agree very well (cf. Fig. 5), the relative adsorption computed by the integral in Eq. (10) agree also well. However, the MD results are slightly above those from DGT in the linear regime of $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}(x'_{\text{CO}_2})$, whereas they are below those from DGT in the concave regime. However, there is a high statistical uncertainty of the MD results at high x'_{CO_2} . The DGT and the experimental results agree excellently, especially for moderate values of x'_{CO_2} .

The enrichment of CO_2 at the vapor-liquid interface of the binary mixture as obtained from MD and DGT is shown in Fig. 7 - middle. The enrichment of CO_2 is highest at infinite dilution and decreases to unity with increasing x'_{CO_2} . Furthermore, the enrichment decreases with increasing temperature.

The results for the enrichment obtained from MD and DGT agree very well, especially at low x'_{CO_2} . At high x'_{CO_2} , the enrichment predicted by DGT exceeds that predicted by MD.

The fact that the behavior of $E_{\text{CO}_2}(T, x'_{\text{CO}_2})$ resembles that of the surface tension, cf. Fig. 4, may well be a coincidence, since differing behavior of $E_{\text{CO}_2}(T, x'_{\text{CO}_2})$ and $\gamma(T, x'_{\text{CO}_2})$ has been reported for other mixture types, cf. [4, 124].

The surface excess of CO_2 at the interface is characterized here by the relative adsorption $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ and the enrichment E_{CO_2} . The temperature dependency of $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ and E_{CO_2} are similar: both decrease with increasing temperature. However, the composition dependency of $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ and E_{CO_2} differs strongly: at infinite dilution, the relative adsorption is $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})} = 0$ by definition, whereas the enrichment E_{CO_2} is highest at infinite dilution of CO_2 . With increasing x'_{CO_2} , $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ increases until a maximum is reached and then decreases, whereas E_{CO_2} decreases monotonously. This supports the findings from previous work [4, 20], that $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ and E_{CO_2} contain different information even though both describe the surface excess of the low-boiling component.

The results for the interfacial thickness L_{10}^0 of the vapor-liquid interface as defined by Eq. (12) are shown in Fig. 7 - bottom. As for the enrichment, results are only available from the theoretical

methods MD and DGT.

Adding CO₂ to cyclohexane at constant temperature first leads to a moderate increase of the interfacial thickness, followed by a steep increase as the critical point is approached. Hence, the composition dependency of L_{10}^{90} for the binary mixture is similar to the temperature dependency of L_{10}^{90} of the pure components. The interfacial thickness of the binary mixture also increases with increasing temperature.

For the lowest investigated temperature 303.15 K, the interfacial thickness obtained from DGT shows an unexpected anomaly that is, however, not found in the results from MD: the curve $L_{10}^{90}(x'_{\text{CO}_2})$ has a wiggle in the region of low x'_{CO_2} before the continuous increase of L_{10}^{90} sets in. These calculations were confirmed using the reference density DGT method. The maximum/ minimum of the interfacial thickness might be due to the specific phase behavior at 303.15 K (CO₂ is supercritical and cyclohexane is close to its triple point). The mathematical form of the PCP-SAFT equation is known to yield artifacts in the metastable and unstable region at low temperatures [133]. This might be related to the anomaly that was observed here in the DGT results. Apart from this difference, the results from MD and DGT agree qualitatively well, but the molecular simulations yield a larger interfacial thickness for most state points as discussed already for the pure substances.

4. Conclusions

Interfacial properties of the mixture cyclohexane + CO₂ were studied by experiment, molecular dynamics simulations, and density gradient theory in combination with the PCP-SAFT equation of state. Properties that can be determined in experiments were investigated with all three methods (surface tension and relative adsorption). Furthermore, using MD and DGT, the density profiles of the components at the interface were determined and used for calculating the enrichment and the interfacial thickness, which cannot be measured experimentally. The experimental surface tension data obtained from the pendant drop method agrees well with experimental data from the literature for pure cyclohexane. For mixtures of cyclohexane with CO₂, two sets of data were available, which, however, do not agree. The present data confirms that of *Nagarajan & Robinson* [108]. The results for the surface tension of the mixture obtained from DGT + PCP-SAFT agrees very well with the experimental data. The model was adjusted to bulk VLE data of the mixture as well as to pure component data, which included surface tension data. The molecular models of cyclohexane and carbon dioxide that were used for the MD simulations describe the VLE data of the pure components and the mixture (to which they were adjusted) well. The results for the surface tension, which was not used in the adjustment, are systematically too high by about 10 - 15% for both the pure components and the mixture. Similar findings have been reported before by *Werth et al.* [72, 104] for a large number of systems. However, the temperature and composition dependency of the surface tension is predicted well by the MD simulations.

The surface excess of carbon dioxide at the vapor-liquid interface was quantified using the relative adsorption $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ and the enrichment E_{CO_2} . The experimental data for the relative adsorption was obtained from the experimental data for the surface tension in the Gibbs adsorption equation and the chemical potential from the PCP-SAFT EOS, whereas the data for the relative adsorption from MD and DGT were determined from the nanoscopic density profiles at the vapor-liquid interface. The results for the relative adsorption of CO₂ obtained from the macroscopic and nanoscopic route agree very well.

As the enrichment of CO₂ at the interface is not accessible by experiment, it was determined by MD and DGT only. The predictions of the enrichment from both methods are in excellent agreement. Even though $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ and E_{CO_2} characterize the surface excess of the low-boiling component, both properties show important differences: starting at infinite dilution of CO₂ in cyclohexane, the relative adsorption $\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$ increases with increasing mole fraction of CO₂ in the liquid phase x'_{CO_2} , passes

through a maximum and decreases to zero at the critical point. The enrichment E_{CO_2} , on the other hand, is highest at infinite dilution of CO_2 and monotonously decreases with increasing x'_{CO_2} .

The detailed study of the system cyclohexane and CO_2 that was carried out here shows that interfacial properties of mixtures can be predicted well both by MD and DGT if models are used that are suitably parameterized using pure component data and bulk VLE mixture data. However, no mixture data on interfacial properties was needed for the parameterization.

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Appendix A – Comparison of Experimental Mixture Surface Tension Data with Data from the Literature

The surface tension results obtained in the present work for the mixture cyclohexane + CO₂ are compared to the available data from the literature in Fig. 8. Surface tension data of mixtures of cyclohexane and CO₂ is available at four temperatures in the literature [108, 109], cf. the four plots in Fig. 8. At three of those four temperatures experiments were also carried out in the present work. The surface tension at all four temperatures was computed by DGT as described in the main body of the article and compared with the literature data.

For $T \cong 344$ K, the surface tension results from the present work and the data of *Nagarajan & Robinson* [108] agree well. The surface tension data reported by *Yang et al.* [109] shows significant systematic deviations from the results obtained in the present work.

Appendix B – Saturated Densities in the Binary Mixture of Cyclohexane + CO₂

The density difference of the saturated phases $\Delta\rho = \rho' - \rho''$ of the binary mixture cyclohexane + CO₂ is shown in Fig. 9. Results from the PCP-SAFT EOS are compared with experimental data from the literature (cf. Table 1). Experimental data is available in Refs. [108, 134, 135] for five temperatures. The results obtained from the PCP-SAFT EOS agree very well with the experimental data from *Nagarajan & Robinson* [108] and *Shibata & Sandler* [134] – except in the vicinity of the critical point. The data from *Krichevskii & Sorina* [135] deviates significantly from the PCP-SAFT results in the entire composition range. The absolute average deviation from the results of Refs. [108, 134] and the PCP-SAFT EOS are better than 3% – when the direct vicinity of the critical point is excluded.

Figure 8: Comparison of experimental data for the surface tension of the system cyclohexane + CO₂ from the literature with results from the present work. All available literature data are shown: (*) *Nagarajan & Robinson* [108] and (+) *Yang et al.* [109]. The lines are results from DGT obtained in the present work, (◇) are experimental results from the present work. In the upper panel, the temperatures are: 343.15 K for (◇); and 344.23 K for both (*) and DGT.

Figure 9: Difference between the saturated liquid and vapor density $\Delta\rho = \rho' - \rho''$ of the binary mixture cyclohexane + CO_2 . Experimental data from the literature (symbols) is compared with results obtained from the PCP-SAFT EOS (lines). Experimental data are from *Nagaraajan & Robinson* [108] (* 344.3 K), *Shibata & Sandler* [134] ($\triangleleft$ 366.5 K and $\triangleright$ 410.9 K), and *Krichevskii & Sorina* [135] (+ 473.15 K and $\times$ 483.15 K).

Nomenclature

Abbreviations

CO ₂	carbon dioxide
DGT	density gradient theory
C ₆ H ₁₂	cyclohexane
EOS	equation of state
LJ	Lennard-Jones
MD	molecular dynamics
PCP-SAFT	polar perturbed chain statistical associating fluid theory

Latin symbols

A	Helmholtz energy (J);
a	Helmholtz energy per particle $a = A/V$ (J m ⁻³);
A	geometric factor (1);
E_{CO_2}	enrichment of carbon dioxide (1);
g	acceleration constant (m s ⁻²)
k_{B}	Boltzmann constant (J K ⁻¹)
L_{10}^{90}	interfacial thickness (nm)
m	segment number in the PCP-SAFT equation of state (1)
N	number of particles (1)
p	pressure (Pa)
Q	quadrupole moment (C m ²)
r	site-site distance (m)
R	radius of curvature (m)
S	interfacial area (m ²)
t	time (s)
T	temperature (K)
U	internal energy (J)
x	mole fraction (1)
y, z	length coordinate (m)

Greek symbols

γ	surface tension (N m^{-1})
$\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})}$	relative adsorption of carbon dioxide with respect to cyclohexane (mol m^{-2})
$\Delta\rho$	difference between the saturated liquid phase and vapor phase mass density (kg m^{-3})
ε	dispersion energy
ε_0	vacuum permittivity
κ_{ij}	DGT influence parameter ($\text{mol}^2 \text{J}^{-1} \text{m}^{-5}$)
μ_i	chemical potential of component i (J mol^{-1})
ξ	binary interaction parameter in the Berthelot combination rule (5)
ρ	mass density (kg m^{-3}) or molar density (mol m^{-3})
$\underline{\rho}$	vector of the molar component densities (mol m^{-3})
σ	molecular size parameter
ω	orientation angle

Superscripts

bulk	bulk phase
red	reduced
pure	pure component
'	liquid bulk phase at saturation
"	vapor bulk phase at saturation

Subscripts

a, b, c, d	interaction site
c	critical
i, j	component
N	normal
ref	reference
T	tangential
tot	total

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SUPPLEMENTARY MATERIAL

Vapor-Liquid Interfacial Properties of the System Cyclohexane + CO₂: Experiments, Molecular Simulation and Density Gradient Theory

Simon Stephan, Stefan Becker, Kai Langenbach and Hans Hasse*

Laboratory of Engineering Thermodynamics (LTD), TU Kaiserslautern,
Erwin-Schrödinger-Straße 44, 67663 Kaiserslautern, Germany

*simon.stephan@mv.uni-kl.de

The supplementary material for the publication *Vapor-Liquid Interfacial Properties of the System Cyclohexane + CO₂: Experiments, Molecular Simulation and Density Gradient Theory* contains

- the numeric values of the experimental surface tension measurements, cf. Table 1,
- the numeric values (results from MD and EOS) of the phase equilibria for the pure substances and the mixture of cyclohexane and CO₂, cf. Table 2 - 3 for the pure substances and Table 4 - 6 for the binary mixture results at three temperatures,
- the numeric values of the interfacial properties obtained from MD and DGT; Tables 7 and 8 report the pure substance interfacial properties; Tables 9 - 11 the mixture interfacial properties,
- the density profiles obtained from MD simulation of the binary mixture cyclohexane+CO₂ at three temperatures (Fig. 1).

Table 1: Experimental data of the surface tension of the binary mixture cyclohexane + CO₂ obtained with the pendant drop apparatus. Absolute uncertainties U are $U(T) = 0.1$ K, $U(p) = 0.0025$ MPa for $p > 2.5$ MPa and $U(p) = 0.01$ MPa for $p < 2.5$ MPa. The relative uncertainty of the surface tension is $u(\gamma) = 0.041 \gamma$.

T / K	p / MPa	γ / mN m ⁻¹	T / K	p / MPa	γ / mN m ⁻¹
303.15	0.573	21.63	343.15	0.526	17.79
	1.028	20.30		1.034	16.83
	2.014	17.40		2.065	14.93
	3.001	14.02		3.138	12.77
	4.032	10.21		4.093	11.13
	4.998	6.35		5.089	9.27
	5.991	2.59		5.974	7.61
313.15	0.529	20.72	353.15	0.539	16.87
	1.031	19.50		1.036	16.04
	2.106	16.68		2.083	14.22
	3.066	13.76		3.099	12.48
	4.065	11.01		4.109	10.74
	5.06	7.90		5.079	9.23
	6.47	3.13		6.028	7.63
323.15	0.561	19.74	363.15	0.584	16.06
	1.055	18.72		1.063	15.15
	2.065	16.35		2.078	13.59
	3.098	13.72		3.129	11.96
	4.106	11.26		4.126	10.40
	5.099	8.70		5.133	8.86
	6.107	6.10		6.027	7.57
333.15	0.512	19.07	373.15	0.583	14.83
	1.044	17.82		1.023	14.24
	2.122	15.56		2.076	12.78
	3.132	13.31		3.162	11.25
	4.131	11.09		4.129	9.85
	5.114	9.06		5.081	8.60
	6.053	7.07		5.954	7.49

Table 2: MD and PCP-SAFT results for the vapor-liquid equilibrium of cyclohexane. The columns are from left to right: the temperature, the vapor pressure, saturated liquid and vapor density. The number in the parentheses indicates the statistical uncertainty in the last decimal digit.

T / K	p / MPa		$\rho' / \text{mol l}^{-1}$		$\rho'' / \text{mol l}^{-1}$	
	MD	EOS	MD	EOS	MD	EOS
280	0.00524(4)	0.0054	9.349(34)	9.2530	0.0023(4)	0.0023
290	0.009(1)	0.0089	9.239(30)	9.1465	0.0039(7)	0.0037
303.15	0.0185(26)	0.0163	9.101(89)	9.0062	0.0075(16)	0.0065
313.15	0.0286(17)	0.0246	8.991(82)	8.8989	0.0112(21)	0.0096
323.15	0.0343(22)	0.0362	8.874(88)	8.7907	0.0131(29)	0.0137
333.15	0.0495(28)	0.0517	8.767(92)	8.6813	0.0185(33)	0.0190
343.15	0.0904(43)	0.0722	8.654(88)	8.5704	0.0334(41)	0.0259
353.15	0.1096(67)	0.0985	8.54(10)	8.4577	0.0392(43)	0.0347
363.15	0.1367(84)	0.1319	8.404(75)	8.3427	0.0476(44)	0.0455
373.15	0.1783(52)	0.1735	8.291(75)	8.2252	0.0615(55)	0.0588
390	0.278(9)	0.2657	8.075(27)	8.0200	0.0929(43)	0.0878
410	0.429(11)	0.4189	7.818(30)	7.7620	0.1402(65)	0.1356
430	0.650(11)	0.6309	7.536(34)	7.4838	0.211(10)	0.2020
450	0.945(11)	0.9143	7.227(42)	7.1790	0.308(18)	0.2929
470	1.327(18)	1.2829	6.882(59)	6.8381	0.440(34)	0.4171
490	1.812(14)	1.7517	6.494(98)	6.4465	0.629(71)	0.5882
510	2.438(11)	2.3374	5.91(31)	5.9783	0.995(276)	0.8309
530	3.155(27)	3.0593	5.33(35)	5.3783	1.435(348)	1.1991

Table 3: MD and PCP-SAFT results for the vapor-liquid equilibrium of CO₂. The columns are from left to right: the temperature, the vapor pressure, saturated liquid and vapor density. The number in the parentheses indicates the statistical uncertainty in the last decimal digit.

T / K	p / MPa		ρ' / mol l ⁻¹		ρ'' / mol l ⁻¹	
	MD	EOS	MD	EOS	MD	EOS
220	0.396(15)	0.607	26.60(17)	26.457	0.23(2)	0.360
230	0.864(24)	0.898	25.58(10)	25.685	0.56(10)	0.524
240	1.221(63)	1.282	24.51(16)	24.852	0.71(3)	0.743
250	1.89(12)	1.779	23.65(51)	23.939	1.13(7)	1.035
260	2.32(16)	2.407	22.83(21)	22.911	1.39(6)	1.423
270	3.20(16)	3.187	21.47(15)	21.718	2.02(12)	1.947
280	4.25(8)	4.144	20.18(23)	20.263	2.83(17)	2.681
290	5.08(19)	5.306	18.65(48)	18.327	3.48(21)	3.792

Table 4: MD and PCP-SAFT results for the vapor-liquid equilibrium of the binary mixture cyclohexane + CO₂ at $T = 303.15$ K. The columns are from left to right: the liquid phase concentration, the vapor phase concentration, the coexistence pressure, the liquid phase density, and the vapor phase density. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The given liquid phase composition holds for both the EOS and MD; for the EOS exactly and for MD with the reported uncertainty.

$x'_{\text{CO}_2}/\text{mol mol}^{-1}$	$x''_{\text{CO}_2}/\text{mol mol}^{-1}$		p / MPa		$\rho' / \text{mol l}^{-1}$		$\rho'' / \text{mol l}^{-1}$	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.0380(8)	0.9672(21)	0.9611	0.559(5)	0.4473	9.283(40)	9.196	0.228(6)	0.182
0.0618(14)	0.9777(16)	0.9745	0.906(11)	0.7120	9.411(48)	9.319	0.376(6)	0.294
0.0893(25)	0.9835(13)	0.9812	1.248(14)	1.0092	9.558(54)	9.465	0.527(8)	0.423
0.1711(21)	0.9893(6)	0.9883	2.213(21)	1.8511	10.02(9)	9.928	0.986(14)	0.815
0.2021(24)	0.9902(8)	0.9894	2.595(26)	2.1513	10.20(13)	10.115	1.182(15)	0.965
0.2526(35)	0.9909(9)	0.9906	3.097(24)	2.6163	10.53(17)	10.434	1.459(26)	1.211
0.3070(53)	0.9916(7)	0.9913	3.570(45)	3.0831	10.89(25)	10.801	1.739(21)	1.477
0.3655(50)	0.9915(4)	0.9918	4.033(33)	3.5423	11.29(38)	11.223	2.036(34)	1.761
0.4302(45)	0.9918(7)	0.9921	4.463(28)	3.9975	11.78(57)	11.727	2.341(43)	2.069
0.5039(46)	0.9914(10)	0.9923	4.868(42)	4.4477	12.38(72)	12.352	2.659(42)	2.408
0.5849(71)	0.9915(8)	0.9924	5.240(62)	4.8625	13.11(76)	13.107	2.983(72)	2.758
0.6711(44)	0.9912(6)	0.9924	5.487(53)	5.2253	13.91(84)	13.988	3.238(62)	3.105
0.7746(29)	0.9914(10)	0.9925	5.824(50)	5.6030	14.95(61)	15.119	3.625(85)	3.521
0.8692(14)	0.9911(7)	0.9929	6.164(55)	5.9897	15.84(28)	16.061	4.074(11)	4.030

Table 5: MD and PCP-SAFT results for the vapor-liquid equilibrium of the binary mixture cyclohexane + CO₂ at $T = 333.15$ K. The columns are from left to right: the liquid phase concentration, the vapor phase concentration, the coexistence pressure, the liquid phase density, and the vapor phase density. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The given liquid phase composition holds for both the EOS and MD; for the EOS exactly and for MD with the reported uncertainty.

$x'_{\text{CO}_2}/\text{mol mol}^{-1}$	$x''_{\text{CO}_2}/\text{mol mol}^{-1}$		p / MPa		$\rho' / \text{mol l}^{-1}$		$\rho'' / \text{mol l}^{-1}$	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.0351(9)	0.9145(41)	0.9022	0.7039(87)	0.5694	8.928(36)	8.845	0.262(5)	0.212
0.0607(9)	0.9464(24)	0.9381	1.1717(83)	0.9436	9.046(40)	8.968	0.444(8)	0.356
0.0980(16)	0.9624(15)	0.9578	1.7852(87)	1.4835	9.233(48)	9.153	0.691(10)	0.572
0.1369(24)	0.9702(8)	0.9669	2.439(23)	2.0388	9.433(66)	9.354	0.968(13)	0.805
0.1770(17)	0.9740(11)	0.9720	3.149(15)	2.6035	9.648(73)	9.569	1.287(18)	1.055
0.2201(18)	0.9762(12)	0.9752	3.907(19)	3.1991	9.89(12)	9.811	1.654(18)	1.336
0.3324(38)	0.9785(11)	0.9788	5.365(37)	4.6910	10.54(24)	10.493	2.447(32)	2.130
0.3993(48)	0.9799(8)	0.9792	6.090(34)	5.5303	10.99(33)	10.938	2.893(49)	2.655
0.4648(50)	0.9774(11)	0.9790	6.971(51)	6.3094	11.39(53)	11.399	3.537(63)	3.215
0.5592(74)	0.9764(17)	0.9775	7.798(70)	7.3493	12.01(66)	12.103	4.238(93)	4.121
0.6392(59)	0.9729(14)	0.9752	8.546(72)	8.1479	12.56(79)	12.712	5.06(16)	5.014
0.7332(25)	0.9687(16)	0.9706	9.196(46)	8.9922	13.01(84)	13.358	6.01(34)	6.303

Table 6: MD and PCP-SAFT results for the vapor-liquid equilibrium of the binary mixture cyclohexane + CO₂ at $T = 363.15$ K. The columns are from left to right: the liquid phase concentration, the vapor phase concentration, the coexistence pressure, the liquid phase density, and the vapor phase density. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The given liquid phase composition holds for both the EOS and MD; for the EOS exactly and for MD with the reported uncertainty.

$x'_{\text{CO}_2}/\text{mol mol}^{-1}$	$x''_{\text{CO}_2}/\text{mol mol}^{-1}$		p / MPa		$\rho' / \text{mol l}^{-1}$		$\rho'' / \text{mol l}^{-1}$	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.0306(5)	0.8158(47)	0.7906	0.835(8)	0.6792	8.544(32)	8.474	0.288(6)	0.234
0.0479(8)	0.8688(30)	0.8513	1.210(11)	0.9900	8.621(39)	8.550	0.421(7)	0.343
0.0817(14)	0.9124(26)	0.9014	1.954(15)	1.5965	8.777(44)	8.702	0.692(10)	0.564
0.1454(24)	0.9434(25)	0.9347	3.286(34)	2.7419	9.068(71)	9.000	1.206(20)	1.006
0.1743(19)	0.9484(15)	0.9416	3.914(15)	3.2623	9.212(84)	9.141	1.466(25)	1.220
0.2188(24)	0.9506(15)	0.9484	4.858(25)	4.0623	9.42(11)	9.365	1.879(33)	1.566
0.2682(24)	0.9545(14)	0.9526	5.790(26)	4.9486	9.66(15)	9.624	2.313(36)	1.979
0.3068(32)	0.9536(14)	0.9544	6.598(36)	5.6392	9.85(21)	9.832	2.722(44)	2.325
0.3648(44)	0.9551(11)	0.9553	7.576(49)	6.6740	10.16(30)	10.157	3.248(56)	2.893
0.4279(51)	0.9533(25)	0.9545	8.680(49)	7.7873	10.46(45)	10.521	3.933(80)	3.586
0.5002(46)	0.9487(14)	0.9512	9.797(46)	9.0453	10.81(61)	10.946	4.68(22)	4.508
0.5859(59)	0.9415(23)	0.9431	10.865(76)	10.4977	11.15(90)	11.433	5.66(31)	5.837
0.6665(44)	0.9304(227)	0.9289	11.825(74)	11.7944	11.4(10)	11.811	6.73(47)	7.384

Table 7: MD, DGT, and experimental results for the vapor-liquid interfacial properties of cyclohexane. The columns are from left to right: the temperature, the surface tension, and the interfacial thickness. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. For the experimental data, the absolute uncertainty for the temperature U is $U(T) = 0.1$ K and the relative uncertainty of the surface tension is $u(\gamma) = 0.035 \gamma$.

T / K	γ / mN m ⁻¹			L_{10}^{90} / nm	
	MD	DGT	Exp	MD	DGT
280	28.72(37)	26.69	-	0.693(1)	0.80
290	27.64(15)	25.44	-	0.736(1)	0.82
303.15	25.78(13)	23.83	23.26	0.743(16)	0.85
313.15	24.69(23)	22.63	22.19	0.815(16)	0.87
323.15	23.69(15)	21.45	21.11	0.859(16)	0.90
333.15	22.78(21)	20.29	20.05	0.844(22)	0.92
343.15	21.06(25)	19.14	18.85	0.953(25)	0.95
353.15	19.81(15)	18.02	17.83	0.981(20)	0.98
363.15	18.53(19)	16.91	16.77	1.032(30)	1.01
373.15	17.47(15)	15.82	15.63	1.111(20)	1.05
390	15.66(18)	14.01	-	1.205(16)	1.11
410	13.19(15)	11.93	-	1.313(20)	1.21
430	11.18(15)	9.92	-	1.487(20)	1.32
450	9.07(10)	7.98	-	1.696(16)	1.47
470	7.08(9)	6.13	-	1.912(16)	1.66
490	5.08(17)	4.39	-	2.237(32)	1.94
510	3.20(12)	2.78	-	2.540(82)	2.36
530	1.76(11)	1.38	-	3.08(16)	3.14

Table 8: MD and DGT results for the vapor-liquid interfacial properties of CO₂. The columns are from left to right: the temperature, the surface tension, and the interfacial thickness. The number in the parentheses indicates the statistical uncertainty in the last decimal digit.

T / K	$\gamma / \text{mN m}^{-1}$		L_{10}^{90} / nm	
	MD	DGT	MD	DGT
220	20.32(69)	15.66	0.81(2)	0.73
230	15.75(60)	13.42	1.09(8)	0.80
240	13.48(47)	11.24	1.14(4)	0.87
250	11.3(14)	9.13	1.49(25)	0.97
260	9.06(36)	7.10	1.43(4)	1.10
270	7.8(17)	5.16	1.75(12)	1.27
280	4.7(11)	3.34	2.14(23)	1.56
290	2.77(41)	1.70	2.58(48)	2.10

Table 9: MD and DGT results for the vapor-liquid interfacial properties of the binary mixture cyclohexane + CO₂ at $T = 303.15$ K. The columns are from left to right: the liquid phase concentration, the surface tension, the relative adsorption of CO₂ at the interface, the interfacial thickness, and the enrichment of CO₂. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The given liquid phase composition holds for both the EOS and MD; for the EOS exactly and for MD with the reported uncertainty.

$x'_{\text{CO}_2}/\text{mol mol}^{-1}$	$\gamma / \text{mN m}^{-1}$		$\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})} / \mu\text{mol m}^{-2}$		L_{10}^{90} / nm		E_{CO_2}	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.0380(8)	24.24(17)	22.43	0.65(2)	0.57281011	0.83(1)	0.89	2.66(8)	2.68
0.0618(14)	23.26(29)	21.56	1.12(5)	0.94766042	0.87(1)	0.90	2.70(11)	2.64
0.0893(25)	22.24(22)	20.56	1.56(9)	1.39117202	0.90(2)	0.90	2.56(11)	2.60
0.1711(21)	18.95(23)	17.69	3.12(12)	2.79745698	0.96(2)	0.87	2.38(6)	2.46
0.2021(24)	17.80(15)	16.64	3.81(11)	3.36052806	0.98(2)	0.83	2.32(3)	2.40
0.2526(35)	16.08(12)	14.98	4.77(24)	4.30661582	1.00(3)	0.79	2.19(6)	2.29
0.3070(53)	14.28(14)	13.29	5.97(18)	5.36025348	1.03(2)	0.77	2.07(7)	2.17
0.3655(50)	12.41(16)	11.58	7.22(24)	6.51843965	1.11(3)	0.81	1.91(4)	2.03
0.4302(45)	10.56(16)	9.86	8.20(22)	7.81381184	1.23(2)	0.85	1.71(3)	1.87
0.5039(46)	8.74(19)	8.12	9.37(31)	9.27075818	1.28(3)	0.92	1.55(3)	1.68
0.5849(71)	7.23(13)	6.49	10.04(43)	10.7579958	1.46(3)	1.04	1.36(3)	1.49
0.6711(44)	5.83(18)	5.06	9.9(6)	11.9794891	1.61(3)	1.21	1.20(2)	1.30
0.7746(29)	4.22(24)	3.62	11.0(12)	12.3953079	2.02(8)	1.50	1.07(1)	1.12
0.8692(14)	3.00(16)	2.35	10.4(15)	11.2818141	2.30(9)	1.94	1.01(1)	1.01

Table 10: MD and DGT results for the vapor-liquid interfacial properties of the binary mixture cyclohexane + CO₂ at $T = 333.15$ K. The columns are from left to right: the liquid phase concentration, the surface tension, the relative adsorption of CO₂ at the interface, the interfacial thickness, and the enrichment of CO₂. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The given liquid phase composition holds for both the EOS and MD; for the EOS exactly and for MD with the reported uncertainty.

$x'_{\text{CO}_2} / \text{mol mol}^{-1}$	$\gamma / \text{mN m}^{-1}$		$\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})} / \mu\text{mol m}^{-2}$		L_{10}^{90} / nm		E_{CO_2}	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.0351(9)	20.85(19)	19.11	0.49(3)	0.43	0.96(3)	0.96	2.31(8)	2.32
0.0607(9)	19.77(28)	18.25	0.85(4)	0.76	1.00(3)	0.98	2.28(6)	2.28
0.0980(16)	18.56(23)	17.03	1.41(7)	1.24	1.04(3)	1.00	2.20(7)	2.21
0.1369(24)	17.01(35)	15.77	1.95(7)	1.76	1.10(2)	1.02	2.12(5)	2.15
0.1770(17)	15.60(23)	14.49	2.58(6)	2.30	1.13(3)	1.02	2.07(3)	2.08
0.2201(18)	14.08(28)	13.15	3.41(8)	2.90	1.19(2)	1.02	2.00(2)	2.00
0.3324(38)	10.65(27)	9.86	4.73(19)	4.52	1.34(3)	1.04	1.70(3)	1.80
0.3993(48)	9.19(49)	8.05	5.8(2)	5.49	1.39(3)	1.08	1.60(3)	1.67
0.4648(50)	6.88(28)	6.42	6.3(4)	6.44	1.61(6)	1.19	1.45(3)	1.54
0.5592(74)	5.1(16)	4.34	6.6(5)	7.72	1.90(6)	1.44	1.26(3)	1.37
0.6392(59)	3.47(30)	2.84	7.5(7)	8.61	2.33(8)	1.83	1.15(1)	1.23
0.7332(25)	2.12(80)	1.43	5.3(11)	9.03	3.08(20)	2.64	1.04(1)	1.10

Table 11: MD and DGT results for the vapor-liquid interfacial properties of the binary mixture cyclohexane + CO₂ at $T = 363.15$ K. The columns are from left to right: the liquid phase concentration, the surface tension, the relative adsorption of CO₂ at the interface, the interfacial thickness, and the enrichment of CO₂. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The given liquid phase composition holds for both the EOS and MD; for the EOS exactly and for MD with the reported uncertainty.

$x'_{\text{CO}_2}/\text{mol mol}^{-1}$	$\gamma / \text{mN m}^{-1}$		$\Gamma_{\text{CO}_2}^{(\text{C}_6\text{H}_{12})} / \mu\text{mol m}^{-2}$		L_{10}^{90} / nm		E_{CO_2}	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.0306(5)	17.52(29)	15.98	0.36(3)	0.31	1.10(2)	1.06	2.08(6)	2.05
0.0479(8)	17.01(24)	15.46	0.53(3)	0.49	1.13(2)	1.06	2.03(7)	2.02
0.0817(14)	15.84(39)	14.44	0.94(3)	0.84	1.19(3)	1.10	1.98(4)	1.97
0.1454(24)	13.79(30)	12.57	1.75(10)	1.51	1.28(3)	1.15	1.88(4)	1.87
0.1743(19)	12.84(23)	11.74	1.95(9)	1.82	1.33(2)	1.17	1.82(3)	1.83
0.2188(24)	11.22(28)	10.48	2.69(8)	2.29	1.40(2)	1.21	1.77(3)	1.76
0.2682(24)	9.67(51)	9.13	2.99(16)	2.81	1.50(3)	1.25	1.66(3)	1.68
0.3068(32)	8.59(31)	8.11	3.18(16)	3.22	1.61(3)	1.29	1.56(3)	1.63
0.3648(44)	7.16(40)	6.64	3.75(15)	3.81	1.71(4)	1.37	1.48(2)	1.54
0.4279(51)	5.54(33)	5.14	4.01(28)	4.40	1.91(5)	1.50	1.36(2)	1.44
0.5002(46)	4.12(81)	3.59	2.38(34)	4.96	2.19(6)	1.75	1.21(2)	1.33
0.5859(59)	2.69(35)	2.02	2.96(58)	5.29	2.6(1)	2.29	1.11(1)	1.21
0.6665(44)	1.65(29)	0.90	1.55(61)	4.92	2.9(2)	3.29	1.04(1)	1.11

Figure 1: Density profiles of the binary mixture cyclohexane + CO_2 at three different temperatures: 303.15 K (bottom), 333.15 K (middle), and 363.15 K (top) and different composition. Results from MD. Dashed lines are CO_2 ; solid lines are cyclohexane. The color indicates the liquid phase composition.