

Examination of Inconsistencies in the Physical Modeling of Vapor-Liquid Interfaces of Strongly Non-Ideal Mixtures

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Abstract

The accurate modeling of fluid interfaces is crucial in numerous scientific and engineering applications. Different physical models such as molecular simulation (MS), density functional theory (DFT), and density gradient theory (DGT) are usually employed for this purpose. However, recent findings have highlighted discrepancies in interfacial structure predictions, particularly for strongly non-ideal azeotropic systems [Fluid Phase Equilib. 564 (2023) 113596]. Specifically, DGT was observed to produce spurious interfacial profiles that deviated significantly from those obtained from MS. This study systematically investigates these inconsistencies by performing a comparative in depth analysis of MS, DFT, and DGT for eight binary alkane + alcohol azeotropic systems. The unusual topology of the interfacial structure is confirmed by

all three methods, although important quantitative differences are observed. Possible reasons for these inconsistencies are discussed.

1 Introduction

The vapor-liquid interfacial properties of mixtures hold significant importance in various engineering applications as well as in nature. While interfaces are regarded as two-dimensional boundary objects at the macroscopic scale, an interfacial region exists at the atomistic scale where the density changes continuously between the bulk phase values. There is a wealth of experimental data on the surface tension of pure substances, and some experimental data are also available for mixtures. However, there is a scarcity of experimental data on the structure of mixtures of molecular substances, with available data pertaining only to special ionic systems and orientational dependencies.¹⁻⁷ Experiments on the structure of fluid interfaces are challenging due to the fast temporal and small scale spatial fluctuations of the interface. Consequently, there is an absence of experimental data on density and pressure profiles at fluid interfaces. Thus, physical methods have played an essential role in predicting and understanding the structure of fluid interfaces over the past decades.⁸⁻¹² Understanding the structure of fluid interfaces is not only intriguing from a fundamental epistemic perspective but is also relevant for technical applications, as it influences transport processes at interfaces. The enrichment of components at vapor-liquid interfaces of mixtures has, for many years, been suspected to impact mass transfer across the interface.¹³⁻²¹

In particular, three computational methods have become the workhorses for studying fluid interfaces at the atomistic length scale, namely, molecular simulations (MS)^{22,23} based on classical force fields, and density gradient theory (DGT) or density functional theory (DFT) in conjunction with an equation of state (EOS).^{24,25} All three approaches generally exhibit strong predictive capabilities, in the sense that they require very few adjustable parameters. Among these three methods (MS, DFT, and DGT), molecular simulations is typically regarded as the "gold standard" and taken as a reference as, in essence, they resolve numerically the statistical mechanics formulations. In this sense, MS are often referred to as 'computer experiments', suggesting that the results serve a similar function to laboratory experiments. DGT and DFT are hybrid theoretical models that rely on the description of

the density variation across an interface. Between them, DFT can be viewed as physically more rigorous compared to DGT, as DFT incorporates information on the local structure of the fluid particles, whereas DGT relies solely on a mean-field picture. For all three methods, adjustments to parameters are typically not made when predicting the interfacial structure. In most cases, only bulk phase properties are employed for parametrization, such as vapor pressure and saturated density data. In some instances, particularly with DGT, data on the surface tension is employed for model parametrization. In any case, the results regarding the interfacial structure are predictions generated by all three methods.

Especially for mixtures, the structure of fluid interfaces can comprise complex and intriguing features,^{8,24,26} i.e. the density profiles can exhibit non-monotonic shapes. It should be noted that different structure features of fluid mixture interfaces have been observed for vapor-liquid, liquid-liquid, and vapor-liquid-liquid interfaces as well as multi-component mixtures.^{27–34} This work is restricted to vapor-liquid interfaces of binary mixtures of molecular fluids. Two main types of non-monotonicity and underlying physical effects have been described in the literature: (1) oscillatory layering structures – OLS, which occurs on the liquid side of vapor-liquid interfaces and decay into the liquid bulk phase (which can also exist for pure components);^{15,35–39} (2) enrichment of components at the interface,^{8,17,26,40–44} which usually is a single maximum (and/or possibly minimum) in the interface. In general, the two non-monotonicity effects (1) and (2) may be present simultaneously and be superimposed, cf. Refs. for examples.^{15,37,45} The peak height of the enrichment is usually significantly larger than that of the OLS. The OLS is a prolongation of the radial distribution function in the liquid bulk at the interface. The vapor-liquid interface effectively acts as an external field, resulting in a layering of molecules on the liquid side of the interface (analogue to the adsorption layering structure observed at solid-fluid interfaces). The OLS can be captured by DFT and molecular simulations, but is not captured in DGT^{35,46} due to the assumptions incorporated in the theory. Moreover, the OLS sampled from molecular simulations are strongly affected by surface wave fluctuations,^{35,47} which decreases the amplitude of the

layering structure. While the OLS can be clearly ascribed to the liquid side of the interface, the enrichment is mostly located approximately in the center of the interface. The enrichment structure effect is closely related to wetting transitions in the vicinity of a three-phase VLLE,^{31,48–50} i.e. approaching the VLLE line through a VL two-phase region, the enrichment increases and can be interpreted as a precursor of the second liquid phase that forms at the interface under the influence of the gradients. Thus, the enrichment structure can be interpreted as a pre-wetting layer. Nevertheless, enrichment at vapor-liquid interfaces in such systems is also found at thermodynamic conditions (temperature and pressure) far away from the three-phase line. Due to the relation between VLLE and the enrichment structure effect, strong enrichment is usually observed for strongly non-ideal systems that form both a LLE and VLLE at some conditions, e.g. heteroazeotropic systems. Strong enrichment has also been observed for low-boiling azeotropic systems. Moreover, azeotropic systems show the special feature that the component exhibiting the enrichment at the interface changes – depending on the composition.^{30,51} In general, the thermodynamic topology of binary mixtures is complex and rich, cf. global phase diagrams and the corresponding binary system’s phase diagrams.^{52–54} Thus, a complex topology for the structure of fluid interfaces can also be expected. Nevertheless, no general theory and framework for the topology of physically possible structures – especially regarding the enrichment – of fluid interfaces has been established yet. The relation between the topology of the (bulk) phase behavior and the topology of the interfacial structure is of particular interest since the enrichment structure effect is directly related to the phase behavior.

Many studies in the literature reported on vapor-liquid interface structures of binary mixtures where either: (a) both component density profiles exhibit a monotonic transition between the bulk phases; (b) one of the component density profiles exhibits a distinct enrichment maximum. In practically all these cases, the results from different methods – mostly MS, DFT, and DGT – are qualitatively in agreement regarding the structure topology. Some studies reported more complex enrichment structures at interfaces,^{37,55–58} namely

a maximum in the density profile followed by a minimum upon approaching the liquid phase. These predictions were solely reported by DGT so far. In a recent work of our group,²⁶ we have critically discussed this structure type – which we refer to as ‘type iv’ structure (see schematic in Ref.²⁶) – by comparing predictions from DGT with those from MS and found the results to be inconsistent. This was studied using a single binary system (cyclohexane + 1-butanol)²⁶ at a single temperature. The DGT results showed the unusual combined maximum/ minimum structure, whereas the MS results showed the expected single enrichment maximum. We hypothesized that the DGT results comprise artifacts due to strong gradients in the interface present in the strongly non-ideal azeotropic system.²⁶

Pure alcohols are known to form clusters in bulk phases on the molecular level, which is a result of the strong association due to the hydrogen bonding nature of their hydroxyl (OH) groups.^{59–61} This has been studied by experiments and models. These clusters range from tree-like branched structures to cyclic structures.⁶⁰ For example, in liquid mixtures of ethanol with water or alkanes, both cluster formation and micro-heterogeneous mixing with segregated domains have been observed.⁶¹ Using conventional density functional theory, *Balanay et al.* investigated pure ethanol and mixtures of ethanol with cyclohexane and hexane in bulk phases.⁶² They found that cyclic clusters of ethanol molecules are thermodynamically more favorable than chain-shaped clusters. Moreover, cyclic tetramers and pentamers were preferred over larger clusters, dimers, and cyclic trimers. Additionally, their experimental results indicated that the presence of monomers is unlikely. The relation of the clustering of alcohols in bulk phases to the structure of fluid-fluid interface is not well understood today. Some experimental and computational studies have shown that hydrogen bonding molecules, such as alcohols, exhibit a surface activity at fluid interfaces; that is, they tend to orient themselves relative to the interface and form clusters.^{63–66} Most of these studies focus on (water + alcohol) systems, where MD simulations revealed an increase in ethanol–ethanol hydrogen bonding at the interface compared to the liquid bulk phase.⁶⁴ Furthermore, an enrichment of alcohol molecules at the interface was observed in such systems^{63,64} – followed

possibly by an alcohol depletion layer on the liquid side. The latter is, however, somewhat inconclusive due to the relatively small number of particles (from today’s standpoint) used in the simulations reported in Refs.^{63,64}

Thus, there are several open questions regarding the equilibrium structure of vapor-liquid interfaces of strongly non-ideal mixtures – in particular those with hydrogen bonding.

In this work, we re-examine aforementioned seeming inconsistencies between predictions of MS, DFT, and DGT in more detail by applying all three methods for systematically studying multiple binary systems. In total, eight binary systems were studied that consist of a cyclic alkane in equilibrium with an alcohol. The systems were selected based on their similarities with systems for which contested DGT results have been reported in the literature.^{26,37,55–58} All systems are strongly non-ideal azeotropic with weak unlike interactions. Two systems (cyclohexane + ethanol and cyclohexane + 2-propanol) were studied using all three methods. The other six systems were studied using DFT and DGT. Additionally, the temperature dependency was studied by considering three temperature values. For the DGT calculations, different equation of state models were employed for elucidating their influence on the topology of the structure of the interface. Also different numerical algorithms were employed. The results of this comprehensive approach provide in depth insights in the inconsistencies of the results from the three physical modeling methods. The focus of this work is on the nanoscopic interfacial structure. Nevertheless, also macroscopic interfacial properties are studied such as the surface tension and the relative adsorption.

This paper is structured as follows: First, the employed computational methods and models are introduced. Also, the definitions for the observables characterizing the structure of the interface are given. Then, the results are presented and discussed. In the main body of this work, the results for the binary systems cyclohexane + ethanol and cyclohexane + 2-propanol (studied by MD, DFT, and DGT) are presented. The results for the systems cyclohexane + 1-propanol, 1-butanol as well as methylcyclohexane + ethanol, 2-propanol, 1-propanol, 1-butanol (only studied by DFT and DGT) are presented in the Supplementary

Information.

2 Methods

2.1 Studied Systems and Conditions

In this work, 8 highly non-ideal binary mixtures were investigated by MD, DFT, and DGT, cf. Table 1. The systems cyclohexane + ethanol and cyclohexane + 2-propanol were studied using all three methods and four different equations of state (EOS) in combination with the DGT, namely the PCP-SAFT, SAFT-VR Mie, sCPA, and Peng-Robinson EOS. Details of the EOS are given elsewhere.^{67–73} Three different temperatures were considered (293.15 K, 303.15 K, and 313.15 K) throughout.

2.2 Molecular Simulation

Molecular dynamics (MD) simulations were conducted using the program *ls1 mardyn*.⁷⁴ MD simulations were performed for the pure components cyclohexane, ethanol, and 2-propanol, as well as the binary mixtures cyclohexane + ethanol and cyclohexane + 2-propanol. The force fields were sourced from the MolMod database.^{75,76} For cyclohexane, the force field described by *Merker et al.*⁷⁷ was employed, comprising six Lennard-Jones sites to represent the CH₂ groups. For ethanol, the force field proposed by *Schnabel et al.*⁷⁸ was utilized, which consists of three Lennard-Jones sites representing the two CH_x groups and the O-atom, along with three charges reflecting the polarity of the molecule. For 2-propanol, the force field proposed by *Muñoz-Muñoz et al.*⁷⁹ was utilized, which consists of four Lennard-Jones sites representing the three CH_x groups and the O-atom, along with three charges reflecting the polarity of the molecule. The molecular models are rigid, which is a reasonable assumption for small molecules.^{80–82}

The potential energy of the systems can be written as

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

where ε_{ijab} and σ_{ijab} are the Lennard-Jones energy and size parameter, r_{ijab} and r_{ijcd} are site-site distances, and q_{ic} and q_{jd} are the point charges. Here, the indices i and j indicate interacting molecules and the indices a, b, c, d the different interaction sites of a molecule.

To describe the dispersive interactions between unlike particles, the modified Lorentz-Berthelot combination rules^{83,84} were employed:

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

$$\varepsilon_{ij} = \xi_{ij} \sqrt{\varepsilon_{ii}\varepsilon_{jj}}, \quad (3)$$

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. The binary interaction parameter ξ_{ij} for the system cyclohexane + ethanol was adjusted to available phase equilibrium data in the investigated temperature range and is $\xi_{\text{cyc,EtOH}}^{\text{MD}} = 1.04$. The binary interaction parameter in the system cyclohexane + 2-propanol was adjusted to $\xi_{\text{cyc,2-Propanol}}^{\text{MD}} = 1.02$.

To determine the vapor-liquid interfacial density profiles and properties, MD simulations with coexisting phases were conducted using *ls1 mardyn*.⁷⁴ In these simulations, a liquid phase slab in the center of the simulation volume coexists with two vapor phases on either side. Periodic boundary conditions were applied in all directions. The elongation of the simulation box normal to the interface was 60 nm and the thickness of the liquid slab was 30 nm. The elongation in the directions parallel to the interfaces was at least 10 nm. The simulations were performed in the canonical ensemble with $N = 16,000$ particles for the pure substances, and $N = 32,000$ particles for the mixtures. The equations of motion were solved using a leapfrog integrator⁸⁵ with a time step of $\Delta t = 2$ fs. The initial densities

and compositions in the simulations were derived from the PCP-SAFT EOS to ensure rapid equilibration.

Thermodynamic properties are quite sensitive to the truncation of the intermolecular potential and long-range corrections.^{86–89} For all simulations conducted in this work, the cut-off radius was established at 17.5 Å using a center-of-mass cut-off scheme. A slab-based long-range correction scheme was employed to incorporate the long-range Lennard-Jones interactions and to account for the system’s inhomogeneity.^{90,91}

Three replica simulations were conducted for each state to improve the signal-to-noise ratio in the results for the component density profiles. For each simulation run, an equilibration for at least 2,000,000 time steps was carried out, followed by a production phase of at least 5,000,000 time steps. Density and pressure profiles were computed in block averages of 500,000 time steps during the production phase for $N = 600$ bins, each with a width of $\Delta z = 0.1$ nm. Thus, the reported density profiles are averaged over surface fluctuations. From each block average, the equilibrium densities ρ' and ρ'' , mole fractions x'_i and x''_i , and vapor pressure p 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 was calculated from the deviation between the normal component p_N (z -direction) and the tangential components p_T (averaged over x - and y -direction) of the pressure tensor^{92,93}

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} (p_N - p_T) \, dz. \quad (4)$$

The statistical uncertainty was estimated as three times the standard deviation of all sampled block averages.

2.3 Density Gradient and Density Functional Theory in Combination with Equations of State

Both density gradient theory (DGT) and density functional theory (DFT) are methods to extend fluid theories (i.e. molecular-based EOS) to inhomogeneous states and, thus, are suitable to model the surface tension based on the component density profiles at interfaces. The basis of both approaches is the minimization of the grand potential Ω with regard to the equilibrium density profiles across the interface.

The grand potential of an inhomogeneous binary mixture (in absence of an external field) can be written as

$$\Omega[\underline{\rho}(\underline{r})] = A[\underline{\rho}(\underline{r})] - \sum_{i=1}^2 \int \mu_{i,\text{bulk}} \rho_i(\underline{r}) \, d\underline{r}, \quad (5)$$

where both the grand potential Ω and Helmholtz energy A are functions of the vector of the component densities $\underline{\rho}$ at the position vector $\underline{r}$. Other functional dependencies, such as T, V, n_i , or μ_i are omitted. The variables ρ_i and $\mu_{i,\text{bulk}}$ indicate the component density and the bulk phase chemical potential of component i .

At equilibrium, the grand potential with respect to the component density profiles $\rho_i(\underline{r})$ is minimized, i.e.

$$\frac{\delta\Omega[\underline{\rho}(\underline{r})]}{\delta\rho_i(\underline{r})} = 0 \quad \forall \quad i. \quad (6)$$

The fundamentals of DGT and DFT can be written as Eqs. (5) and (6) and, thus, share a similar physical picture. Yet, they differ in modeling details, physical assumptions and simplifications, and predictive capabilities. Notably, DGT requires an additional pure-component parameter. In this work, the PCP-SAFT^{68,69} EOS was employed for both methods. For DGT, additionally the SAFT-VR Mie,⁷⁰ sCPA,^{71,72} and Peng-Robinson⁷³ EOS were used.

2.3.1 Equations of State

The EOS models used within this work are formulated as fundamental Helmholtz energy A functions with respect to density and temperature. The Helmholtz energy of a system can be described as the sum of an ideal gas contribution A_{ig} and a configurational contribution A_{config} , i.e.

$$A = A_{\text{ig}} + A_{\text{config}} . \quad (7)$$

For the calculation of e.g. phase equilibria and interfacial properties, the reduced configurational Helmholtz energy per particle $\tilde{a}_{\text{config}} = \frac{A_{\text{config}}}{Nk_{\text{B}}T}$ can favorably be used for the derivation of thermodynamic properties, where $\tilde{a}_{\text{config}}$ can be formulated as a sum of contributions, i.e. of repulsive (rep), dispersive (disp), chain, polar, and associating (assoc) interactions and can be represented by

$$\tilde{a}_{\text{config}} = \tilde{a}_{\text{rep}} + \tilde{a}_{\text{disp}} + \tilde{a}_{\text{chain}} + \tilde{a}_{\text{polar}} + \tilde{a}_{\text{assoc}} , \quad (8)$$

for a system containing N molecules at a given temperature T , and using the Boltzmann constant k_{B} .

Within this work, binary mixtures consisting of one non-associating, non-polar component and one associating, polar component were investigated. Due to these molecular differences, the employed molecular EOS models differ. As such, each component comprises contributions due to repulsive and dispersive interactions, but not due e.g. polar or associating contributions to $\tilde{a}_{\text{config}}$, cf. Table 2-5. For all associating molecules investigated, the association type '2B' was used, i.e. using one electron-donor and -acceptor site on each molecule.

In total, four EOS were investigated within this work, namely the PCP-SAFT^{68,69} EOS, the SAFT-VR Mie⁷⁰ EOS, the sCPA^{71,72} EOS, and the Peng-Robinson⁷³ EOS. The SAFT based EOS employ similar parameters, i.e. the chain length m , the segment diameter σ , the

segment interaction energy ε , the association volume κ_{AB} , and association energy ε_{AB} . However, the PCP-SAFT EOS additionally includes the dipole moment μ , and the SAFT-VR Mie EOS allows for variation of the repulsive λ_r and attractive λ_a exponent. In contrast, the Peng-Robinson EOS does not explicitly consider association or polar interactions. All substances, regardless of their complexity, are characterized by the attraction parameter a_{VDW} , the co-volume parameter b_{VDW} , and the acentric factor ω . For the substances investigated within this work, the parameters are adjusted to critical and vapor pressure data retrieved from the NIST Chemistry WebBook⁹⁴ database, cf. Table. 5. The sCPA EOS combines the simplicity of a cubic EOS and the association term from the Wertheim theory.⁹⁵ The model employs the parameter for the energy term (m), pseudo critical temperature (T_{cm}), pseudo critical pressure (p_{cm}), association volume (κ_{AB}), and association energy (ε_{AB}). The pure component parameters (excluding the PR parameters) were taken from the literature and are given in Tables 2-5.

As for the molecular simulation, binary interaction parameters were used for the modified combination rules of Lorentz and Berthelot (cf. Eqs. (2) and (3)). These interaction parameters were fitted within this work to experimental phase equilibrium data in the considered temperature range and are listed in Table 6. For binary mixtures investigated in this work, corresponding phase diagrams including experimental literature VLE data and EOS calculations are either shown in the main body of this work or in the Supplementary Information.

2.3.2 Density Gradient Theory

Density gradient theory^{96,97} is a widely employed method for calculating the surface tension – especially in chemical engineering – of both pure substances^{57,98–100} and mixtures.^{101–106} Moreover, DGT enables the prediction of nanoscopic interfacial properties, such as density profiles across the interface. To model fluid interfaces, DGT requires a Helmholtz energy model for the bulk phase as well as the pure component influence parameter κ_{DGT} , which

characterizes the impact of density gradients on the Helmholtz energy. A comprehensive introduction to DGT can be found in Refs.^{24,98,107}

In DGT, the Helmholtz energy of a heterogeneous system is expanded as a Taylor series in terms of the derivatives of the component densities with respect to the spatial coordinate normal to the interface. This expansion is truncated after the second-order (square gradient) term. For a planar interface of a binary mixture, the Helmholtz energy density, $a = A/V$, can be written as

$$a[\underline{\rho}] = a_0(\underline{\rho}) + \sum_{i=1}^2 \sum_{j=1}^2 1/2 \kappa_{ij} \nabla \rho_i \cdot \nabla \rho_j. \quad (9)$$

Here, $a_0(\underline{\rho})$ represents the Helmholtz energy per unit volume of a hypothetical homogeneous system at the local composition and $\underline{\rho}$ denotes the vector of number densities. The parameters κ_{ij} are the influence parameters, which account for the impact of density gradients on the Helmholtz energy – for pure components (if $i = j$) and the cross-interaction (if $i \neq j$). The pure component influence parameters were fitted in this work using experimental surface tension data from the literature.^{108–122}

The numeric values for κ_{ii} obtained from the fits are reported in Table 2. The cross-interaction influence parameters were computed from the pure substance influence parameters using

$$\kappa_{ij} = (1 - \beta_{ij}) \sqrt{\kappa_{ii} \kappa_{jj}}. \quad (10)$$

For $\beta_{ij} = 0$, Eq. (10) reduces to the geometric combining rule, which is a widely used assumption in DGT.^{105,123,124} Alternatively, β_{ij} can be used as an additional fitting parameter, which influences the impact of the density gradients on the Helmholtz energy. In previous works of our group, it was shown that the assumption $\beta_{ij} = 0$ leads to good quantitative agreement between predictions from DGT and computer experiments for different model fluids^{14,125} and real substances^{44,126,127} in the entire composition range – including for highly non-ideal mixtures and mixtures with supercritical components. In this work, we have used

the predictive version of DGT using $\beta_{ij} = 0$ as well as versions $\beta_{ij} \neq 0$. For the latter, we have systematically varied β_{ij} for studying its influence on the structure of the interface (cf. Supplementary Information).

We employed two numeric algorithms for solving the DGT equation to obtain the equilibrium density profiles $\rho_i(z)$ of both components connecting the bulk phases, namely the stabilized DGT (sDGT) algorithm proposed by *Mu et al.*¹⁰¹ and the classical reference fluid DGT (RF-DGT) algorithm. For the bulk of the calculations, the sDGT algorithm was used. For comparison, the RF-DGT algorithm was used for selected states. The results for the latter are presented in the Supplementary Information. The results from the two algorithms are in agreement. The domain size was in all cases 12 nm. For the sDGT calculations, a spatial discretization of 0.007 nm was used. The convergence behavior of the sDGT approach is shown in more detail in the Supplementary Information.

The surface tension γ was calculated from the equilibrium density profiles using

$$\gamma = \int \sum_{i=1}^2 \sum_{j=1}^2 \kappa_{ij} \nabla \rho_i \cdot \nabla \rho_j \, dz. \quad (11)$$

2.3.3 Density Functional Theory

In DFT, the Helmholtz energy of the heterogeneous system is developed as the sum of Helmholtz energy functionals, which can be written as sum of individual terms

$$A[\underline{\rho}] = A_{\text{ig}}[\underline{\rho}] + A_{\text{rep}}[\underline{\rho}] + A_{\text{disp}}[\underline{\rho}] + A_{\text{chain}}[\underline{\rho}] + A_{\text{polar}}[\underline{\rho}] + A_{\text{assoc}}[\underline{\rho}], \quad (12)$$

in which the subscripts denote the ideal gas (ig), repulsive (rep), dispersive (disp), chain (chain), polar (polar), and association (assoc) contributions. From Eqs. (5)-(6), the surface tension γ of the planar interface of a binary mixture can be computed as

$$\gamma = \int (a[\underline{\rho}] + p_{\text{bulk}} - \sum_{i=1}^2 \mu_i \rho_i(z)) \, dz, \quad (13)$$

where p_{bulk} is the bulk phase pressure, μ_i the chemical potential of the component i , and the Helmholtz energy density $a[\underline{\rho}]$, which is related to the total Helmholtz energy as

$$A[\underline{\rho}] = S \int a[\underline{\rho}(z)] \, dz, \quad (14)$$

where S is the surface area of the interface. For all DFT calculations, the domain length was 15 nm with a spatial discretization of 0.004 nm (grid size of 4096). For the DFT calculations, the same parameters are employed as for the PCP-SAFT + DGT approach (cf. Table 2), with the exception of the κ_{DGT} parameter, which is not required within the DFT framework. Hence, DGT uses an adjustable pure component parameter, whereas the DFT model is predictive for both pure components and mixtures.

In accordance to the PCP-SAFT EOS, the functional terms used in Eq. (12) reduce to the corresponding EOS contributions for homogeneous phases.^{128,129} Similar to DGT, both the surface tension and density profiles are obtained, from which other interfacial properties are calculated (see below). For an in-depth introduction into DFT, the reader is referred elsewhere.^{25,128,130} For DFT calculations, the software FeO_s¹³¹ was used.

2.4 Interfacial Properties obtained from Density Profiles

Molecular simulations, DGT, and DFT yield component density profiles $\rho_i(z)$ within the interfacial region. In this work, we use the classical profile analysis, where the local density is sampled in the computer experiments in bins normal to the interface. Thus, the MD profiles are sampled in a fixed coordinate system, which also corresponds to the profiles obtained from DGT and DFT. In general, also a moving coordinate system can be used for analyzing the structure of the interface, which has in particular been employed for analyzing MD results.^{132–137} However, MD results represented in this coordinate system are difficult to compare with the results from the employed theories – especially the DGT results. Therefore, we use the classical fixed coordinate system density profiles.

From the density profiles, the relative adsorption and enrichment can be computed (both of which characterize surface excess^{14,43}). To determine the relative adsorption, the symmetric interface segregation definition proposed by *Telo da Gama and Evans*^{36,41} was employed. Thereby, the relative adsorption of component i with respect to component j is computed as

$$\Gamma_i^{(j)} = -(\rho'_i - \rho''_i) \int_{-\infty}^{\infty} \left[\frac{\rho_j(z) - \rho'_j}{\rho'_j - \rho''_j} - \frac{\rho_i(z) - \rho'_i}{\rho'_i - \rho''_i} \right] dz, \quad (15)$$

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

The interfacial excess at the surface can also be characterized by the interfacial enrichment E_i , which is defined according to *Becker et al.*⁴³ as the ratio of the maximum local component density within the interfacial region to the higher of the two bulk phase component densities

$$E_i = \frac{\max(\rho_i(z))}{\max(\rho'_i, \rho''_i)}. \quad (16)$$

Both relative adsorption and enrichment quantify the surface excess, but they convey different information.^{14,26,43,138} The relative adsorption is an integral measure for the interfacial composition and quantifies the number of adsorbed molecules per unit area at the interface and is a rigorous thermodynamic quantity. The enrichment E_i , on the other hand, is a simple geometric quantity and has no direct thermodynamic roots. Relative adsorption $\Gamma_i^{(j)} \neq 0$ can occur without enrichment ($E_i = 1$) if the component density profiles are mutually shifted.^{14,30} Conversely, enrichment of a component i ($E_i > 1$) typically leads to positive relative adsorption of that component. It should be noted, that the definition of the enrichment E_i was designed to characterize fluid interface structures with a single maximum.

The thickness of the vapor-liquid interface is characterized in this work by the 90-10% definition for the effective interfacial thickness t according to *Lekner and Henderson*,¹³⁹ which is the distance between the points where the total local density $\rho_{\text{tot}}(z) = \rho_i(z) + \rho_j(z)$

reaches 10% and 90% of the total bulk number densities, respectively:

$$\begin{aligned}
t &= z(\rho_{90}^{\text{tot}}) - z(\rho_{10}^{\text{tot}}), \\
\rho_{10}^{\text{tot}} &= \rho_{\text{tot}}'' + 0.1(\rho_{\text{tot}}' - \rho_{\text{tot}}''), \\
\rho_{90}^{\text{tot}} &= \rho_{\text{tot}}'' + 0.9(\rho_{\text{tot}}' - \rho_{\text{tot}}'').
\end{aligned} \tag{17}$$

For all results, the origin on the z -axis of the interfacial profiles was chosen here such that $z(\rho_{50}^{\text{tot}}) = 0$ at $\rho_{50}^{\text{tot}} = \rho_{\text{tot}}'' + 0.5(\rho_{\text{tot}}' - \rho_{\text{tot}}'')$.

For the MD results, the enrichment E_i , the relative adsorption $\Gamma_i^{(j)}$, and the interfacial thickness t were calculated from each block averaged density profile. The reported values represent the mean of all block averages with statistical uncertainty estimated as three times the standard deviation of the sampled block averages.

3 Results and Discussion

In the main body of this work, the results for the two binary systems cyclohexane + ethanol and cyclohexane + 2-propanol are presented. The results for the other six systems as well as the numeric values of the simulation results and density profiles are provided in the Supplementary Information.

3.1 Phase Equilibria

Fig. 1 presents the isothermal p - x phase diagrams of the two systems cyclohexane + ethanol and cyclohexane + 2-propanol. Available experimental data from the literature are compared with MD results and EOS results from this work (data for cyclohexane + 2-propanol are presented at 298.15 K, as no experimental data were available in the literature for the other investigated temperatures). Both mixtures exhibit a low-boiling azeotrope at the considered temperature at a mole fraction of cyclohexane of approximately $x'_{\text{cyc}} = 0.66 \text{ mol mol}^{-1}$ and

$x'_{\text{cyc}} = 0.76 \text{ mol mol}^{-1}$ for the mixtures with ethanol and 2-propanol, respectively. For all EOS as well as the MD results, the binary interaction parameter was adjusted. The result of that fit yields a good agreement – except in the case of the PR EOS. The PR EOS is not capable to capture the complex phase behavior of the strongly non-ideal mixtures accurately. The comparison of the EOS phase equilibria obtained from the adjusted binary interaction parameters for the other six mixtures is presented in the Supplementary Information. While there is an overall very good agreement, the predicted isothermal p - x phase diagrams show some differences in regards to their azeotropic composition and pressure (see Supplementary Information for details).

Fig. 2 shows the p - T projection of the phase behavior for the systems cyclohexane + ethanol and cyclohexane + 2-propanol in the temperature range investigated in this work up to the critical points. The p - T projection were computed using the PCP-SAFT EOS. For reference, the triple point temperature of cyclohexane is $T^{\text{TP}} \approx 280 \text{ K}$,⁹⁴ which is slightly below the lowest investigated temperature. Both systems exhibit a similar behavior, i.e. the critical line connects the two pure component critical points and exhibit a temperature minima. Both mixtures comprise a Bancroft point, i.e. the pure substance vapor pressure curves intersect (slightly below 350 K for cyclohexane + ethanol and slightly above 350 K for cyclohexane + 2-propanol). Positive azeotropy ends at an upper critical end point (CAEP) near the pure alcohol critical point. The p - T projections for the other six systems are provided in the Supplementary Information. The overall topology of these projections is similar, however two main differences exist: (a) the azeotropic lines of some of the methylcyclohexane mixtures end on the pure alcohol rather than at the critical line, (b) the mixture methylcyclohexane + ethanol exhibits a heteroazeotropic end point at $T \approx 284 \text{ K}$, indicating the transition to a vapor-liquid-liquid equilibria at lower temperatures. For both mixtures containing 1-butanol, the azeotropic line lies near the vapor pressure curve of either cyclohexane or methylcyclohexane at low temperatures, resulting in very narrow two-phase regions near the pure cyclohexane or methylcyclohexane in the p - x phase diagrams (see Supplementary

Information). For all eight systems, the mole fraction of the alcohol at the azeotropic line increases as a function of the temperature.

3.2 Interfacial Properties

3.2.1 Comparison of MD, DFT, and DGT Results

Fig. 3 shows the density profile results from the three methods MD, DFT, and DGT for the systems cyclohexane + ethanol and cyclohexane + 2-propanol at $T = 303.15$ K. For both DFT and DGT, the PCP-SAFT EOS was used. The results require a careful discussion. On the first view, there are important differences between the three data sets. A detailed evaluation, however, shows that basic features of the topology reoccur in the results from all three methods. Note that the z -axis has different scaling for the MD results and the theory results DFT and DGT.

In the molecular simulations, strong clustering is observed in the bulk phases and in the vicinity of the interface – see evaluation reported in the Supplementary Information. Even at low concentrations of the alcohol, most alcohol molecules are part of cluster structures. As becomes evident from Fig. 3 for both ethanol and 2-propanol, a noticeable enrichment of the alcohol is observed near the interface from the MS results. The molecule architecture of the alcohol evidently influences this clustering structure, which can also be seen in differences in the component density profiles, as the MS results for the two systems (cyclohexane + ethanol and cyclohexane + 2-propanol) differ to some extent quantitatively. For both DFT and DGT, however, the results for the two systems are very similar. Within the MD simulations, an enrichment layer of about $5 \text{ \AA}$ is observed for the system cyclohexane + ethanol – which is similar to the thickness of enrichment layers observed in the literature.^{44,126,127} Also, the enrichment heights in the MD results in the system cyclohexane + ethanol is similar to what was reported in the literature.^{44,126} For the system cyclohexane + 2-propanol, on the other hand, a significant accumulation of cyclohexane is observed in the MS results for low concentrations of cyclohexane in the liquid phase x'_{cyc} . In particular, this accumulation is

located mostly on the liquid side of the interface and has a large thickness of about 80 Å. This large, i.e. thick, cyclohexane layer is possibly a third interfacial effect (in addition to the OLS and the enrichment effect). This thick cyclohexane layer observed at the interface is possibly a result of a bulk phase cluster formation, which has a preferential residency at the interface. This hypothesis is supported by the fact that the cyclohexane density profiles in the cyclohexane + 2-propanol system at low x'_{cyc} exhibit a 'kink' at about $z = +10$ Å. This kink is possibly the result of two superimposing accumulation effects, namely the actual 'enrichment' with a thickness of about 5 Å and the residence of a cyclohexane cluster with a thickness of about 80 Å close to the interface.

In both systems shown in Fig. 3, the MD results yield a decaying enrichment height with increasing x'_{cyc} , i.e. a monotonic cyclohexane density profile at $x'_{\text{cyc}} \rightarrow 1$ mol mol⁻¹. For the associating component (for both ethanol and 2-propanol), on the other hand, a small enrichment is observed in the entire composition range in the MD results. Moreover, in the MD results for both systems, elements of a minimum in the density profiles after the enrichment peak is observed: For the system cyclohexane + 2-propanol, such a minimum is obscured by the cyclohexane cluster residing at the interface. In the system cyclohexane + ethanol, clear elements of a minimum are observed in the cyclohexane density profiles at low x'_{cyc} . In general, this could be a result of an OLS and thereby a structural effect. The thickness of this minimum is approximately 11 Å, which is larger than the size of a cyclohexane molecule (≈ 4 Å), indicating that this is not a simple case of an OLS. As it coincides with a maximum in the ethanol density profile, this is an indication for a structural layering of cyclohexane - ethanol - cyclohexane at the interface. However, the minimum could also be related to the enrichment and a thermodynamic effect. While these observations provide qualitative evidence of local enrichment and depletion effects, they do not unambiguously reveal the microscopic origins of these structures. More rigorous characterization – such as interface-resolved pair distribution functions, molecular orientation profiles, or clustering metrics – could offer further insight; however, such analyses are beyond the scope of the present work.

In summary, the MD density profile results show a (minor) enrichment of cyclohexane, followed by a (minor) depletion of cyclohexane, and a (minor) enrichment of the associating component. Additionally, an accumulation of cyclohexane at the interface can be observed in the system cyclohexane + 2-propanol for small mole fractions of cyclohexane.

For DFT, the results for the two systems cyclohexane + ethanol and cyclohexane + 2-propanol are similar: A strong enrichment of cyclohexane at the interface is observed, which decreases with increasing x'_{cyc} , which is consistent with the expectations that the overall low-boiling component shows enrichment and its concentration dependency at the interface.⁸ The DFT results comprise two more subtle elements: (a) a very small enrichment and depletion of the associating component; (b) a minimum in the cyclohexane density profiles after the enrichment peak. (a) is practically not visible in Fig. 3, but shown in detail in the Supplementary Information; (b) can be barely seen in Fig. 3 and is also presented in detail in the Supplementary Information. No significant OLS is observed in the DFT results, which is probably primarily due to the employed functional as well as the moderately high temperature (with respect to the triple point of cyclohexane being at $T^{\text{TP}} \approx 280 \text{ K}$ ⁹⁴). In summary, the DFT density profile results show a (significant) enrichment of cyclohexane, followed by a (minor) depletion of cyclohexane, and a (very small) enrichment of the associating component. This is qualitatively in agreement with the interface topology obtained from the computer experiments – despite the fact that the quantitative elements differ significantly. Nevertheless, the cluster formation of the alcohol molecule forming the large structure in the cyclohexane + 2-propanol MD results is not captured by the PCP-SAFT mean field bulk phase model.

Also for DGT, the results for the two systems cyclohexane + ethanol and cyclohexane + 2-propanol are similar. A strong enrichment of cyclohexane is observed for low x'_{cyc} values, which decreases with increasing x'_{cyc} . Additionally, a depletion is observed in the cyclohexane density profiles behind the enrichment peak. Moreover, an enrichment of the associating component at the interface is observed. Hence, *the overall topology of the DGT*

density profile results is similar to what is obtained from MS and DFT – despite the fact that there are enormous quantitative differences among the results from the three methods. In particular, the depletion in the cyclohexane profiles behind the enrichment peak is very prominent in the DGT results. Similarly, the enrichment of the associating component at high x'_{cyc} values in the DGT results is very strong. An intriguing feature in the DGT density profiles are the extreme gradients present in the interface – becoming almost vertically. These extreme gradients highlight a fundamental limitation of the square-gradient approximation inherent to DGT, which assumes that density gradients remain small relative to the reciprocal of the intermolecular distance. Under strongly non-ideal conditions, this approximation may no longer be valid, potentially requiring higher-order terms or non-local theories. In a similar context, *Liang et al.*⁵⁸ identified potential pitfalls associated with the DGT geometric-mean combining rule for the cross-interaction influence parameter for mixtures exhibiting a 'type iv' behavior, for which *Mairhofer & Gross*⁵⁵ found that by adjusting β_{ij} the shape of the density profiles changed and steep gradients were largely mitigated, which is not the case for the mixtures studied within this work (cf. Supplementary Information).

For the MD results, we speculated above that the minimum depletion behind the enrichment peak might be an OLS. This question can be revisited in the light of the findings from the DGT results, which also exhibit such a depletion – yet, to a much more prominent extent. In the DGT results, the depletion cannot be an OLS since no local fluid structure information is comprised in the DGT model. Hence, the depletion is likely a thermodynamic effect, i.e. related to the behavior of the Helmholtz energy in the metastable and unstable region in the strongly non-ideal azeotropic systems. Therefore, also the depletion observed in the MD results is possibly a thermodynamic effect.

In our earlier work, we speculated that the 'type iv' structure obtained from DGT is artificial.²⁶ This statement has to be put into the perspective of the more detailed analysis carried out in this work, i.e. also the MD and DFT results exhibit features of a 'type iv' structure – albeit to a very faint degree in parts. Based on the MD results taken as a reference, the

DGT significantly overestimates the structure regarding the enrichment of the associating component and the depletion of cyclohexane. Additionally, the DFT results deviate quantitatively from both the DGT and MD results. Several potential reasons may explain the quantitative differences among the results from the three methods, particularly the extreme features observed in DGT: The employed EOS might lead to the extreme structures; the large gradients at the DGT interface may conflict with the assumptions of the square gradient approximation; the assumptions applied for the DGT influence parametrization, namely being temperature and density independent and predicted by a geometric combination rule for the mixture; and the finding of a local minimum of free energy in DGT, among others. For the MD results, cluster formation of molecules within the liquid bulk phase and at the interface is observed (cf. Supplementary Information), which is not captured by the mean-field approaches. In this work, we employed different EOS in DGT to elucidate their influence on structural topology and also examined the effect of temperature on the intriguing structure obtained from DGT. Also, the effect of the combination rule for the DGT influence parameter as well as different DGT algorithms were studied. Moreover, the macroscopic interfacial properties predicted from the three methods were compared to shed some light on the above hypothesis.

Fig. 4 shows the results for the aggregated interfacial properties surface tension, relative adsorption, and enrichment of both components at the interface, and interfacial thickness. Results are presented for the system cyclohexane + ethanol at $T = 303.15$ K (and $T = 293.15$ and 313.15 K; the temperature dependency being discussed below). In Fig. 4, results are presented for MD, DFT, DGT, and experimental data – the latter being only available for γ at $T = 303.15$ K. For DGT, results from different EOS are shown, which are discussed in detail below. Here, the focus is on the comparison of the MD, DGT+PCP-SAFT, and DFT+PCP-SAFT results as well as the experimental data at $T = 303.15$ K for γ , $\Gamma_{\text{cyc}}^{(\text{EtOH})}$, $\Gamma_{\text{EtOH}}^{(\text{cyc})}$, E_{cyc} , E_{EtOH} , t , which corresponds to the density profiles depicted in Fig. 3: Important qualitative and quantitative differences are observed between these data sets. For the surface tension,

the MD data systematically overestimates the experimental data. Such systematic deviations are often observed in the literature.^{140,141} Also, DGT+PCP-SAFT and DFT+PCP-SAFT do not accurately predict the experimental surface tension. Thus, based on the validation with the experimental data, the accuracy of the computational methods cannot be clearly discerned. For the relative adsorption, the trends of the MD and DGT+PCP-SAFT results are in reasonable agreement, namely mostly negative values of $\Gamma_{\text{cyc}}^{(\text{EtOH})}$ and mostly positive values for $\Gamma_{\text{EtOH}}^{(\text{cyc})}$ (for values of x'_{cyc} larger than 0.2 mol mol⁻¹). This indicates that the alcohol molecules adsorb at the interface, which can visually be confirmed by screenshots of the MD simulations (see Supplementary Information). The adsorption of the alcohol and desorption of cyclohexane is (for the MD results) primarily due to the the relative shift of the component density profiles. The DFT+PCP-SAFT results, on the other hand, yield an opposing trend for the relative adsorption, i.e. a maximum in $\Gamma_{\text{cyc}}^{(\text{EtOH})}(x'_{\text{cyc}})$. For the enrichment E_{cyc} and E_{EtOH} , the predictions from the three methods MD, DGT+PCP-SAFT, and DFT+PCP-SAFT agree qualitatively, i.e. they decrease with decreasing mole fraction of the other component. For the interfacial thickness, on the other hand, significant qualitative deviations between the results from the three methods are observed. Overall, the important qualitative differences in the results for $\Gamma_{\text{cyc}}^{(\text{EtOH})}(x'_{\text{cyc}})$, $\Gamma_{\text{cyc}}^{(\text{cyc})}(x'_{\text{EtOH}})$, and $t(x'_{\text{cyc}})$ reflect the quantitative differences in the density profile results from the different methods.

For the validation of the computational methods employed in this work, some experimental surface tension data are available in the literature, i.e. for the system cyclohexane + ethanol at $T = 303.15$ K,¹⁴² cf. Fig. 4. The experimental surface tension data exhibits a relatively linear transition between the two pure component values. The experimental surface tension data, from Ref.¹⁴² for the cyclohexane + ethanol mixture (Fig. 4, top-middle), lies between the results of PCP-SAFT + DGT, SAFT-VR Mie + DGT, and sCPA EOS + DGT and those of PCP-SAFT EOS + DFT. The Peng-Robinson EOS + DGT results exhibits kink. The MD results overestimate the experimental data from Ref.¹⁴² At infinite dilution states, the DGT results are in agreement with the experimental data, which is not surprising

since the pure component influence parameters were fitted to experimental surface tension data. While the experimental surface tension data has an approximately linear behavior, the DGT (and DFT results) exhibit a distinct surface tension minimum in the mixture.

3.2.2 Influence of EOS on Interfacial Structure predicted by DGT

Fig. 5 shows the density profiles derived from DGT calculations using different EOS models for the system cyclohexane + ethanol at $T = 303.15$ K. Results are presented for the entire composition range in Fig. 5. Additionally, Fig. 6 provides a direct comparison of the density profiles for two selected states. The outcomes for the aggregated interfacial properties computed from these density profiles, are shown in Fig. 3. The corresponding results for the system cyclohexane + 2-propanol are included in the Supplementary Information. For the DGT calculations, the peculiar structural topology (characterized by an enrichment peak followed by a depletion in the cyclohexane density profiles and a corresponding increase in the alcohol component) is observed for all four EOS models, except in the vicinity of pure cyclohexane, where the behavior changes to a monotonic increase (see Supplementary Information for details). Nonetheless, some quantitative variations are noted. While the Peng-Robinson EOS + DGT density profiles show a reasonable behavior (cf. Fig. 5), the corresponding surface tension and relative adsorption results (cf. Fig. 4) exhibit unrealistic kinks in their composition dependency. The dubious behavior in the interfacial properties occurs as the minimum in the component density profile of cyclohexane vanishes with an increasing cyclohexane concentration in the liquid phase for concentrations at about $x'_{\text{cyc}} = 0.7$ mol mol⁻¹ for the temperature $T = 303.15$ K (cf. Fig. 5 - bottom right). For $x'_{\text{cyc}} > 0.7$ mol mol⁻¹ the density profile of cyclohexane transitions to a monotonic increase (cf. Supplementary Information). This behavior exhibits a temperature dependence, as discussed below. This is unsurprising, given that the Peng-Robinson EOS encompasses a vastly simplifying physical model for the examined systems. The density profile results from the PCP-SAFT EOS and SAFT-VR Mie EOS DGT calculations are strikingly similar, displaying extreme

gradients at the interface, as seen in Fig. 5. In both instances, these extreme gradients are positioned between the enrichment peak and the depletion dip, which interestingly occurs approximately at the center of the interface at $z \approx 0$. Practically vertical density profiles are observed for both components at this location. With the sCPA + DGT results, the density profiles do not exhibit such extreme gradients. However, the overall behavior of the aggregated interfacial properties γ , $\Gamma_{\text{cyc}}^{(\text{EtOH})}$, $\Gamma_{\text{EtOH}}^{(\text{cyc})}$, E_{cyc} , E_{EtOH} , and t obtained from sCPA + DGT, cf. in Fig. 5, is similar to the results obtained from the other EOS.

The direct comparison of the results from different EOS in Fig. 6 provides further insights. The peak height and depth for the cyclohexane profiles are similar. The same holds true for the enrichment peak height of the alcohol component (ethanol in this case). Additionally, Fig. 6 shows the profile of the total density. Interestingly, the total density profile also exhibits prominent non-monotonic behavior in most cases. The same observation is made for the cyclohexane + 2-propanol system presented in the Supplementary Information. A non-monotonic total density is unusual for vapor-liquid interfaces, yet it has been noted before for liquid-liquid interfaces.^{27,31} In the systems studied in this work, the non-monotonicity of the total density profile is most pronounced for states with high cyclohexane concentration. To a lesser extent, this non-monotonic behavior is also present in the MD total density profiles at high mole fractions of cyclohexane. This non-monotonicity seems to result from the strong enrichment of the alcohol component at the interface, as seen in Fig. 6-right and the Supplementary Information. In contrast, the DFT results show only a very weak maximum in the total density profiles at low mole fractions of cyclohexane, where the largest enrichment of cyclohexane is observed (cf. Supplementary Information).

3.2.3 Influence of Temperature on Interfacial Structure predicted by DGT

For most interfacial structure features, an increasing temperature yields a diminishing of the structure due to the increased thermal motion. Fig. 7 shows the density profiles calculated using the DGT with the PCP-SAFT EOS at temperatures of 293.15 K, 303.15 K, and 313.15

K across the entire composition range. Results are shown for the systems cyclohexane + ethanol and cyclohexane + 2-propanol. In all depicted cases, the overall same interface structure topology is obtained. With increasing temperature, the enrichment peak height for both the cyclohexane and the alcohol component decreases – as expected. This is confirmed by the results for the enrichment E_i depicted in Fig. 4. With increasing temperature, also the depletion dip decreases. Similarly, the relative adsorption decreases with increasing temperature, cf. Fig. 4. Moreover, the surface tension decreases with increasing temperature, cf. Fig. 4. The interfacial thickness, on the other hand, does not vary significantly in the studied temperature range. These trends are in line with experience from more simple systems.^{31,44,126,127}

For the cubic EOS, an interesting effect is observed for the surface tension. For the Peng-Robinson EOS, a kink for the surface tension is obtained, which is located near the azeotropic composition of $x'_{\text{cyc}} = 0.66 \text{ mol mol}^{-1}$. The extent of this kink and its composition location exhibit depends on the temperature: The kink becomes less pronounced with increasing temperatures. Also for the sCPA EOS, a kink in the surface tension isotherm is observed at lower temperatures. Interestingly, for the sCPA EOS, this effect occurs at $x'_{\text{cyc}} \approx 0.9 \text{ mol mol}^{-1}$. As outlined above, these kinks are probably a result of the cyclohexane density profiles transitioning from a 'type iv' profile behavior to a monotonic transition between the bulk phase densities with an increasing cyclohexane concentration in the liquid phase (see Supplementary Information for details).

4 Conclusions

In a previous work by our group,²⁶ we highlighted severe open questions regarding the structure of vapor-liquid interfaces in strongly non-ideal azeotropic mixtures. In particular, we questioned whether a so-called 'type iv' structure truly exists. Since experiments measuring fluid interface density profiles are unfeasible, we depend on theoretical computational meth-

ods to uncover what exists in reality. Therefore, understanding possible differences among independent theoretical methods is crucial. For strongly non-ideal azeotropic systems, the outcomes from various computational methods have not been conclusive so far. This work unravels some obscurities – yet, leaving several open questions.

Specifically, we addressed these inconsistencies by analyzing eight mixtures using three theoretical methods, namely molecular dynamics simulations, density functional theory, and density gradient theory. Despite notable quantitative variations, the three theoretical approaches reveal a fundamentally similar structure at the interface. This shared topology is characterized by an accumulation of both constituent components at the interfacial region, a phenomenon that diminishes as the mole fraction of the enriching component increases. Concurrently, a discernible reduction in the density of the globally more volatile, non-associating component is observed within the azeotropic mixture’s interfacial profile. However, a direct comparison of the results obtained from MD, DFT, and DGT is intricate and open to interpretation, stemming from diverse physical phenomena inherent in these systems. These include the thermodynamic effect of component enrichment at the interface, the organization of molecules into oscillatory layer structures at the interface, the clustering of molecules within the bulk phases with a potential affinity for the interface, and the complex interplay of intermolecular forces, encompassing both association and strong dissimilar interactions. For a future work, a detailed structural analysis of interface-resolved distribution functions, molecular orientation profiles, and clustering metrics would be interesting.

While the type iv structure is consistently evident across the results from all three methods, significant quantitative divergences persist. The MD results indicate only a marginal increase in the density profiles of both components at the interface and a very subtle depletion of the non-associating component. In contrast, DFT calculations predict a relatively pronounced enrichment of the non-associating component and a minor depletion, yet the enrichment of the associating component is numerically almost negligible. DGT results, on the other hand, exhibit all three effects in a more pronounced manner – the enrichment of both

components as well as the depletion of the non-associating component. Taking the computer experiment results as reference, the DFT results underestimate both the enrichment of the associating component and the depletion of the non-associating component. The underlying reasons for these substantial quantitative discrepancies among the three methods remain largely unclear. Potential explanations include the simplification of neglecting the density dependence of the influence parameter, the application of the geometric combination rule for mixture influence parameters, the inherent limitations of the square gradient approximation within the Taylor series expansion, and the DGT solver possibly converging to a local minimum of the Helmholtz free energy.

The observed substantial quantitative differences in the density profiles obtained from the three methods consequently lead to severe qualitative variations in the aggregated interfacial properties, such as the relative adsorption. After several decades of successful physical modeling of fluid interfaces, it is surprising that these obscure structures have not been studied and understood well today. Despite a comprehensive evaluation in this work, several fundamental questions remain open that are to be addressed in future work.

Data Availability

The data supporting this article have been included as part of the Supplementary Information.

Author Contributions

Florian Fleckenstein: Writing – Original Draft Preparation, Visualization, Methodology, Formal analysis, Data Curation. **Max Wagner:** Visualization, Formal analysis, Data Curation. **Thomas Bernet:** Data Curation. **Erich A. Müller:** Resources, Writing – Review & Editing. **Simon Stephan:** Conceptualization, Funding Acquisition, Supervision, Writing – Original Draft Preparation.

Conflicts of Interest

There are no conflicts of interest to declare.

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Supporting Information Available

The Supplementary Information contains the results and additional density profiles for all studied binary systems. Additionally, the numeric values for all MD results and component density profiles of all methods and systems are reported.

Tables & Figures

Table 1: Studied binary systems and methods employed.

component 1	component 2	employed methods
cyclohexane +	ethanol	MD, DFT(PCP-SAFT), DGT(all)
	2-propanol	MD, DFT(PCP-SAFT), DGT(all)
	1-propanol	DFT(PCP-SAFT), DGT(PCP-SAFT)
	1-butanol	DFT(PCP-SAFT), DGT(PCP-SAFT)
methylcyclohexane +	ethanol	DFT(PCP-SAFT), DGT(PCP-SAFT)
	2-propanol	DFT(PCP-SAFT), DGT(PCP-SAFT)
	1-propanol	DFT(PCP-SAFT), DGT(PCP-SAFT)
	1-butanol	DFT(PCP-SAFT), DGT(PCP-SAFT)
all: PCP-SAFT, SAFT-VR Mie, sCPA, PR		

Table 2: PCP-SAFT^{68,143} + DGT pure component parameters. For all associating molecules, the association type '2B' is used.

component	m	σ / Å	ε/k_B / K	μ / D	κ_{AB}	ε_{AB}/k_B / K	$10^{20} \kappa_{DGT}$ / Jm ⁵ mol ⁻²
cyclohexane ⁶⁸	2.5303	3.8499	278.11	-	-	-	34.07 ¹⁴⁴
methylcyclohexane ⁶⁸	2.6637	3.9993	282.33	-	-	-	42.74*
ethanol ¹⁴³	2.4382	3.1477	191.31	1.7	0.03481	2599.8	5.77*
2-propanol ¹⁴³	2.6850	3.3800	212.32	1.7	0.01552	2485.3	9.00*
1-propanol ¹⁴³	2.8428	3.2928	225.70	1.7	0.01934	2377.7	8.53*
1-butanol ¹⁴³	2.9636	3.5015	243.62	1.7	0.01293	2426.9	13.45*

* fitted within this work.

Table 3: SAFT-VR Mie^{70,145,146} + DGT pure component parameters. For all associating molecules, the association type '2B' is used.

component	m	σ / Å	ε/k_B / K	κ_{AB}	ε_{AB}/k_B / K	λ_r	λ_a	$10^{20} \kappa_{DGT}$ / Jm ⁵ mol ⁻²
cyclohexane ¹⁴⁵	1.8592	4.3660	349.99	-	-	18.447	5.3693	31.19*
ethanol ⁷⁰	1.9600	3.4914	168.15	0.34558	2833.7	7.6134	6	4.81*
2-propanol ¹⁴⁶	2.5794	3.4405	208.00	0.3519	2690.76	10.274	6	8.31*

* fitted within this work.

Table 4: sCPA⁹⁵ + DGT pure component parameters. For all associating molecules, the association type '2B' is used.

component	m	T_{cm} / K	p_{cm} / bar	κ_{AB}	ε_{AB}/k_B / K	$10^{20} \kappa_{DGT}$ / Jm ⁵ mol ⁻²
cyclohexane ⁹⁵	0.7558	564.78	45.015	-	-	35.08*
ethanol ⁹⁵	0.6746	463.34	68.005	0.0080	2589.7043	5.40*
2-propanol ⁹⁵	0.8432	449.76	50.544	0.0091	2525.7195	10.29*

* fitted within this work.

Table 5: Peng-Robinson⁷³ + DGT pure component parameters.

component	ω	$10^3 a_{VDW}$ / Jm ³ mol ⁻²	$10^6 b_{VDW}$ / m ³ mol ⁻¹	$10^{20} \kappa_{DGT}$ / Jm ⁵ mol ⁻²
cyclohexane	0.2076*	2383.6*	88.050*	32.76*
ethanol	0.6815*	1325.7*	52.776*	5.09*
2-propanol	0.6558*	1671.3*	67.195*	8.56*

* fitted within this work.

Table 6: PCP-SAFT, SAFT-VR Mie, sCPA, and Peng-Robinson binary interaction parameter $\xi_{cyc,j}$ of cyclohexane mixed with different components j .

component j	PCP-SAFT	SAFT-VR Mie	sCPA	Peng-Robinson
ethanol	0.9735	1.0190	0.9602	0.9495
2-propanol	0.9831	0.9965	0.9735	0.9210
1-propanol	0.9788	-	-	-
1-butanol	0.9859	-	-	-

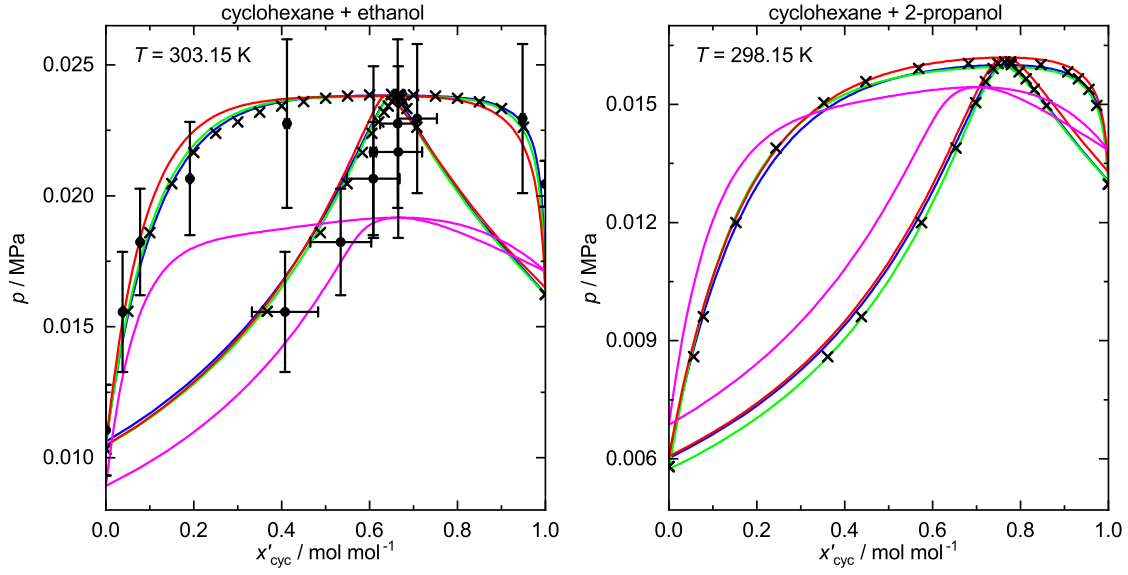


Figure 1: $p - x$ phase diagrams of the binary mixtures cyclohexane + ethanol at $T = 303.15$ K (left) and cyclohexane + 2-propanol at $T = 298.15$ K (right). The solid lines are the results from the PCP-SAFT (blue), SAFT-VR Mie (green), sCPA (red), Peng-Robinson (magenta), and MD (black dots). The crosses are experimental data from *Nagai and Ishii*¹⁴⁷ (left) and *Haase & Tillmann*¹⁴⁸ (right).

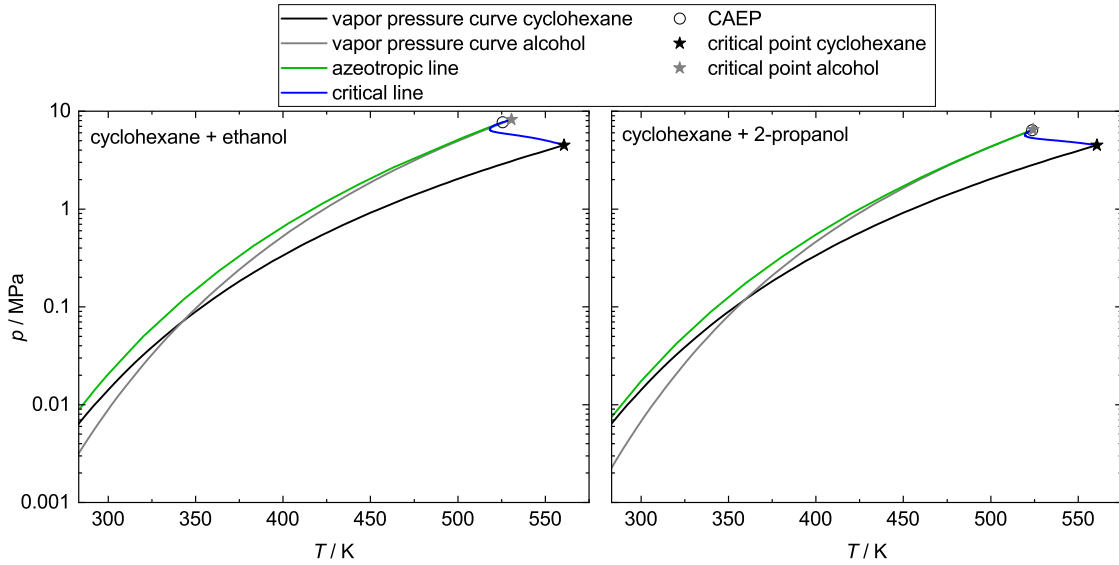


Figure 2: $p - T$ projections of the binary mixtures cyclohexane + ethanol (left) and cyclohexane + 2-propanol (right). Shown are results for the PCP-SAFT EOS. Solid black and gray lines are the vapor pressure curves of the pure components; solid green and blue lines are the azeotropic and critical line respectively; the circle represents the critical azeotropic end point (CAEP) and the stars the critical point of the pure components.

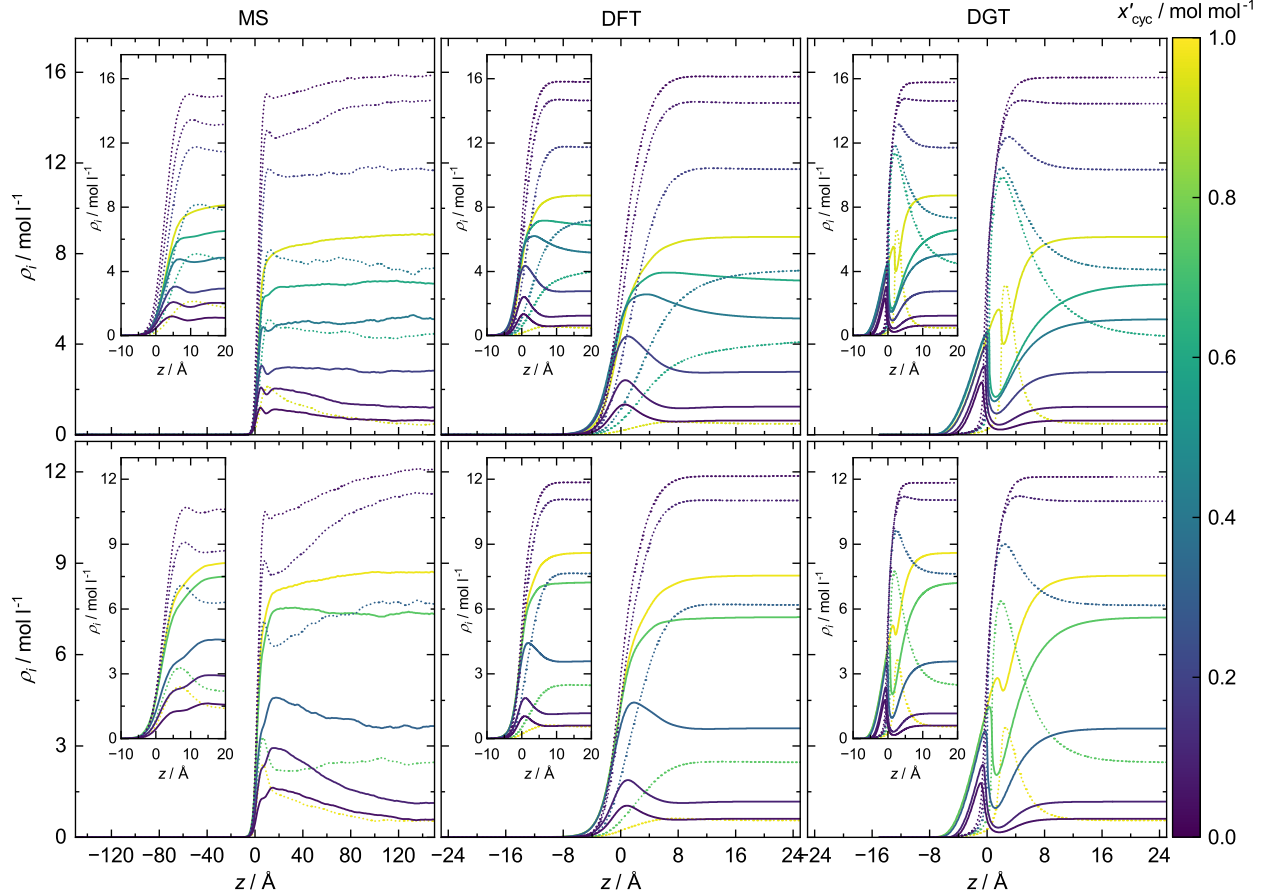


Figure 3: Density profiles of the binary mixture of cyclohexane + ethanol (top) and cyclohexane + 2-propanol (bottom) at $T = 303.15$ K. The liquid phase mole fraction of cyclohexane is color coded. Results from MS (left), PCP-SAFT EOS + DFT (middle), and + PCP-SAFT EOS + DGT (right). The dotted lines indicate ethanol (top) and 2-propanol (bottom); the solid lines cyclohexane. The depicted concentrations are $x'_{\text{cyc}} = 0.038, 0.078, 0.191, 0.412, 0.609, 0.948$ mol mol⁻¹ for cyclohexane + ethanol and $x'_{\text{cyc}} = 0.049, 0.095, 0.319, 0.745, 0.939$ mol mol⁻¹ for cyclohexane + 2-propanol.

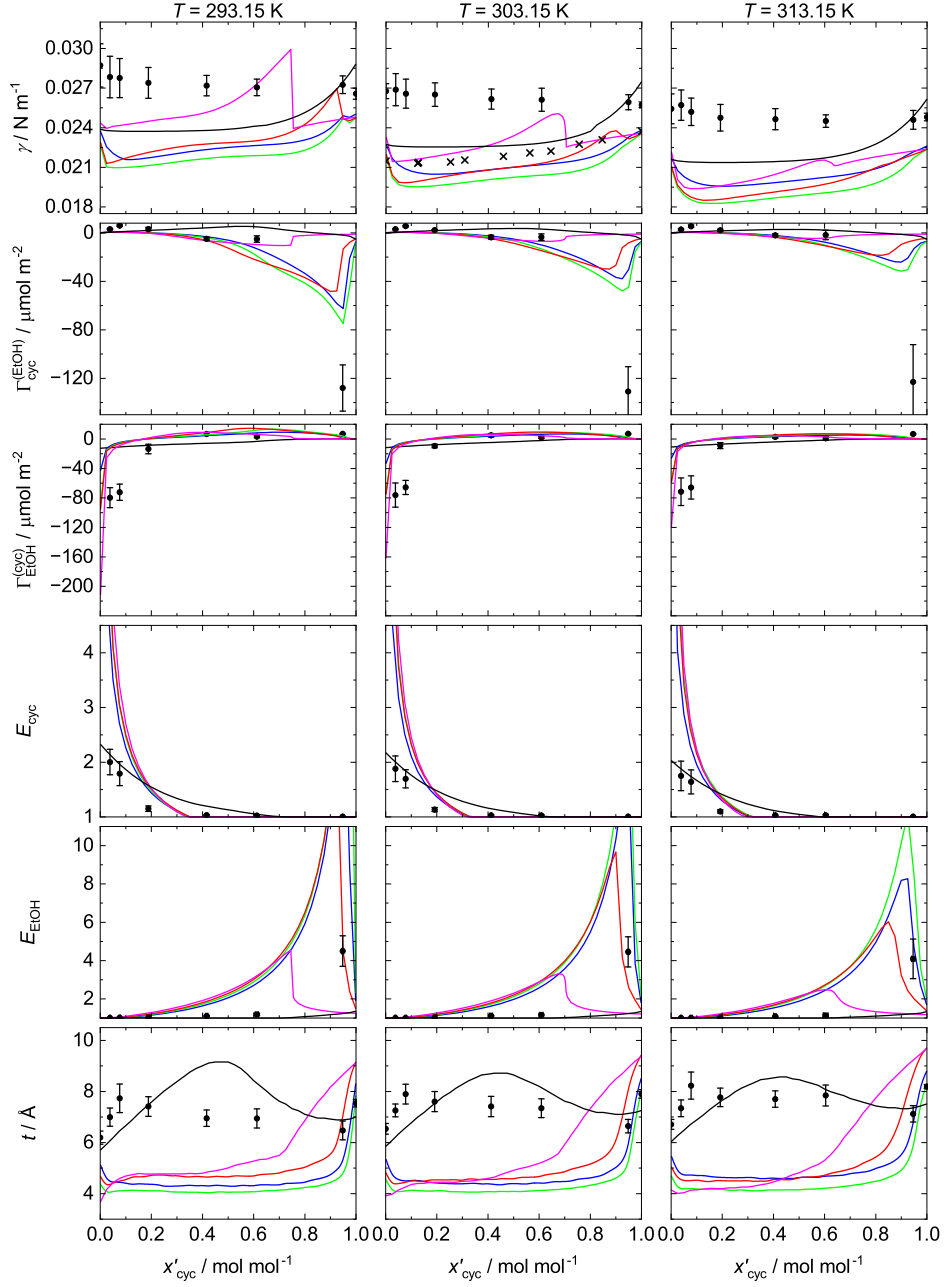


Figure 4: Surface tension (top), relative adsorption (second and third from the top), enrichment (second and third from the bottom) and interfacial thickness (bottom) of the system cyclohexane + ethanol as a function of the liquid phase mole fraction of cyclohexane x'_{cyc} at $T = 293.15$ K, 303.15 K, and 313.15 K, respectively. Black dots are MD results, solid lines are results from PCP-SAFT (blue), SAFT-VR Mie (green), sCPA (red), Peng-Robinson (magenta) EOS + DGT, PCP-SAFT EOS + DFT (black) and the crosses (top middle) are experimental data from *Myers and Clever*.¹⁴²

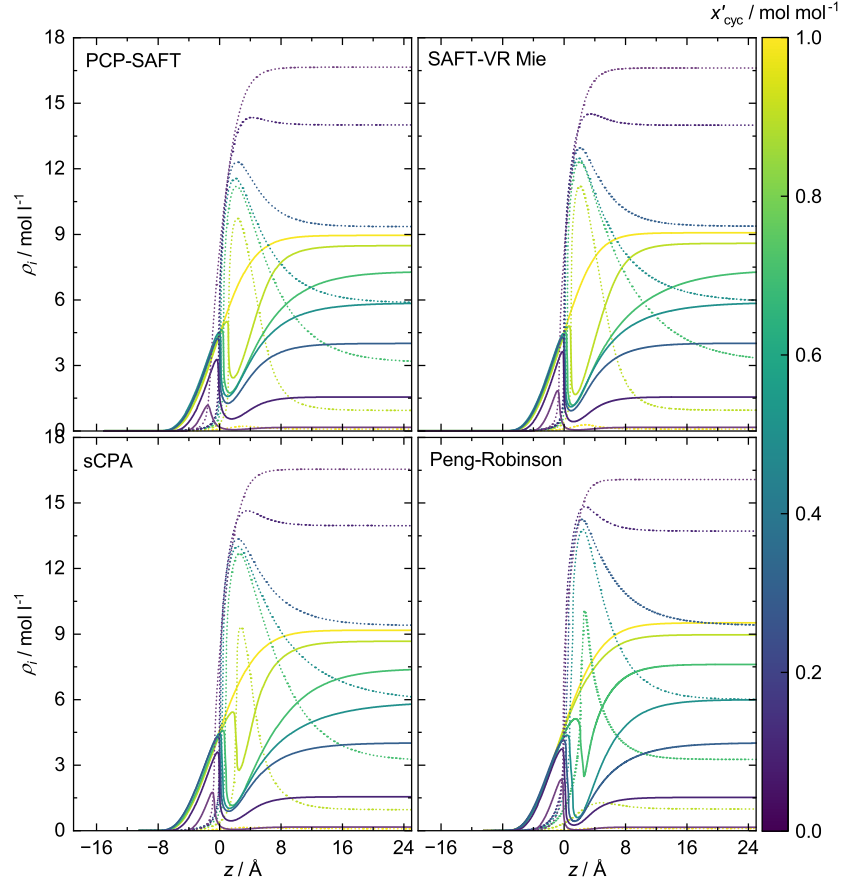


Figure 5: Density profiles of PCP-SAFT EOS (top left), SAFT-VR Mie EOS (top right), sCPA EOS (bottom left), Peng-Robinson EOS (bottom right) + DGT, of the binary mixture of cyclohexane + ethanol at $T = 303.15$ K. The liquid phase mole fraction of cyclohexane is color coded. The dotted lines indicate ethanol; the solid lines cyclohexane. The depicted concentrations are $x'_{\text{cyc}} = 0.01, 0.1, 0.3, 0.5, 0.7, 0.9, 0.99$ mol mol⁻¹.

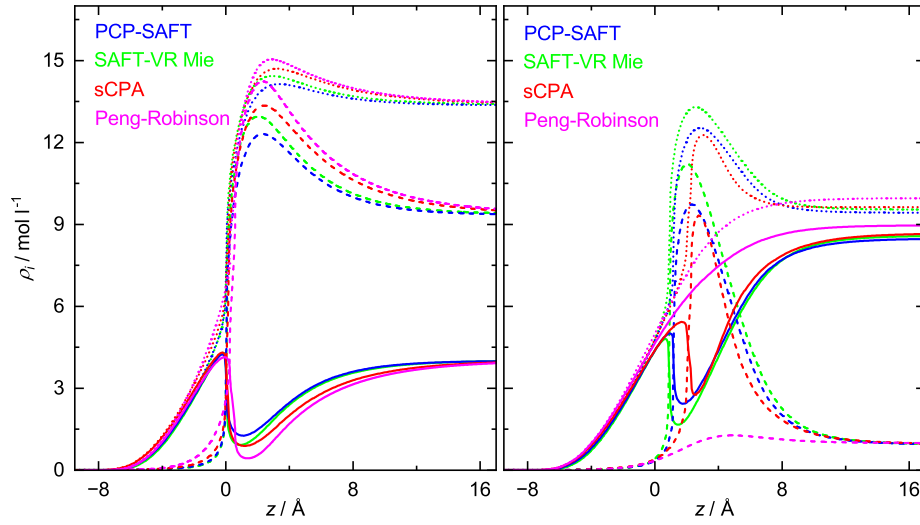


Figure 6: Density profiles of the binary mixture of cyclohexane + ethanol at $T = 303.15$ K with different compositions. Results from PCP-SAFT (blue), SAFT-VR Mie (green), sCPA (red), Peng-Robinson (magenta) EOS + DGT. The dashed line indicates ethanol, the solid line cyclohexane, and the dotted line the total density. The depicted concentrations are $x'_{\text{cyc}} = 0.3$ (left), and 0.9 (right) mol mol⁻¹.

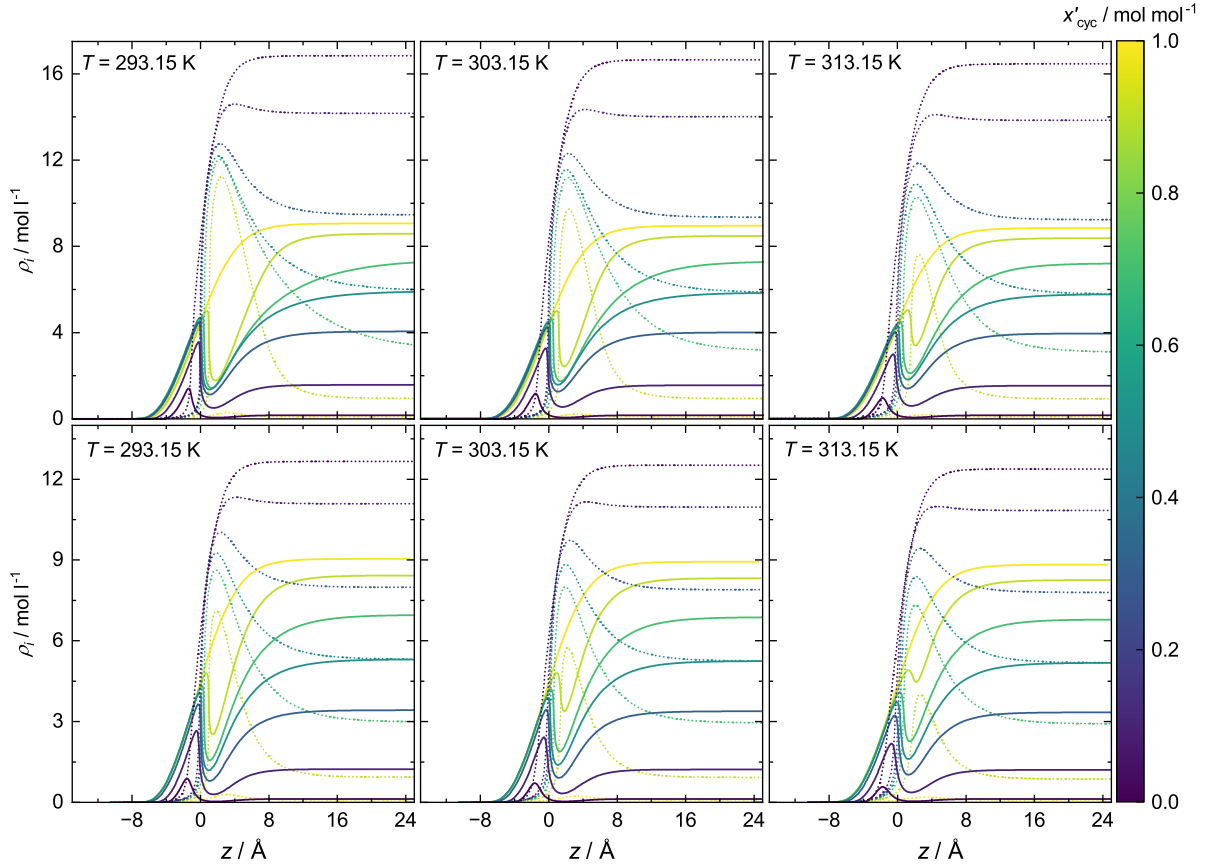


Figure 7: Density profiles of PCP-SAFT EOS + DGT, of the binary mixture of cyclohexane + ethanol (top) and cyclohexane + 2-propanol (bottom) at $T = 293.15$ K, 303.15 K, and 313.15 K, respectively. The liquid phase mole fraction of cyclohexane is color coded. The dotted lines indicate 2-propanol (top figures) and ethanol (bottom figures); the solid lines cyclohexane. The depicted concentrations correspond to a liquid phase mole fraction of cyclohexane of $x'_{\text{cyc}} = 0.01, 0.1, 0.3, 0.5, 0.7, 0.9, 0.99$ mol mol⁻¹.

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