

Molecular interactions at vapor-liquid interfaces: Binary mixtures of simple fluids

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Properties of vapor-liquid equilibria and planar interfaces of binary Lennard-Jones truncated and shifted mixtures were investigated with molecular dynamics simulations, density gradient theory, and conformal solution theory at constant liquid phase composition and temperature. The results elucidate the influence of the liquid phase interactions on the interfacial properties (surface tension, surface excess, interfacial thickness, and enrichment). The studied mixtures differ in the ratios of the dispersion energies of the two components $\varepsilon_2/\varepsilon_1$ and the binary interaction parameter ξ . By varying ξ and $\varepsilon_2/\varepsilon_1$, a variety of types of phase behavior is covered by this paper. The dependence of the interfacial properties on the variables ξ and $\varepsilon_2/\varepsilon_1$ reveals regularities that can be explained by conformal solution theory of the liquid phase. It is thereby shown that the interfacial properties of the mixtures are dominated by the mean liquid phase interactions whereas the vapor phase has only a minor influence.

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I. INTRODUCTION

Properties of vapor-liquid interfaces play a crucial role in many chemical engineering applications, such as distillation and absorption. Experimental data on interfacial properties are in most cases limited to surface tension, from which sometimes data on the adsorption at the fluid interface are derived [1,2]. Hence, reliable and predictive models for such properties are an essential need.

On a molecular level, fluid interfaces are three-dimensional objects. In the interfacial region, which is generally only a few nanometers wide, the density changes smoothly from the value in one bulk phase to that in the other. This holds for the total density as well as for the component densities. Experimental methods for the investigation of such density profiles on a molecular level are presently not available. However, density profiles can be obtained by theoretical methods [3,4], namely, by molecular simulation based on classical force fields on the one side and density gradient theory (DGT) or density functional theory (DFT) combined with an equation of state (EOS) of the fluid on the other side. In the present paper both molecular dynamics (MD) simulation and DGT are used to conduct a comprehensive study of binary Lennard-Jones truncated and shifted (LJTS) mixtures, regarding their vapor-liquid equilibrium (VLE) and interfacial properties. Based on that data set, it is shown by applying a conformal solution theory (CST) that the mean molecular interactions in the liquid phase dominate the interfacial properties of the studied systems.

While the profile of the total density in the interfacial region increases monotonously from the bulk vapor to the bulk liquid phase, this does not necessarily hold for the profiles of all individual component densities. A maximum of the component density in the interfacial region is observed in many

cases for the low-boiling component and can reach values several times larger than the largest value of the two bulk densities of that component [1,5]. We refer to this phenomenon as *enrichment*. The enrichment of components at the interface of mixtures is of particular interest as it is suspected to affect the mass transfer through the interface [6–8]. Interfacial enrichment has been found in many mixtures in studies [1,5,6,8–41] that were carried out with molecular simulations, DGT, and DFT, but no systematic evaluation of the phenomenon of interfacial enrichment has been conducted so far to elucidate its dependency on the type of the mixture. However, it is known that a strong enrichment is favored by a wide-boiling behavior of the mixture [1,5,8,14,26,29,31,35,36,42]. The relation between the relative adsorption and the enrichment and their relation to the molecular interactions are not yet fully understood [1,5].

While the global phase behavior of Lennard-Jones mixtures or mixtures of other simple spherical molecules has been investigated numerous times in the literature [43–47], no systematic study of the global behavior of interfacial properties is available.

We have therefore carried out such a study using both molecular dynamics simulation and DGT. The focus lies on the interfacial adsorption and enrichment and its dependency on the molecular interactions. The studied fluid is described by the LJTS potential. The perturbed Lennard-Jones truncated and shifted (PeTS) EOS [5,48] is used to describe the LJTS fluid within DGT. The planar vapor-liquid interface of 90 binary LJTS mixtures was investigated at constant temperature ($T = 0.77 \varepsilon k_B^{-1}$) and constant liquid phase composition ($x'_2 = 0.05 \text{ mol mol}^{-1}$). The temperature is 0.7 of the critical temperature of the high-boiling component.

The 90 investigated mixtures were obtained by varying the dispersion energies of the two components $\varepsilon_2/\varepsilon_1$ and the binary interaction parameter ξ in the modified Berthelot combination rule [49]. The size parameter of both components was the same and was not varied in this paper. For the planar

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interfaces of these mixtures the surface tension, interfacial thickness, relative adsorption, and enrichment of the low-boiling component were determined, such that a large body of data for elucidating the influence of the different interactions on the interfacial properties became available.

All interfacial properties of different studied mixtures were found to have common regularities regarding their ξ , $\varepsilon_2/\varepsilon_1$ dependency. Using a CST, it is shown that these regularities can be explained in terms of the mean liquid phase interactions, i.e., the internal energy. This methodology is used to correlate the interfacial properties as functions of the internal energy of the liquid phase. CST has been applied to bulk properties (static [50–55] and transport [56]) but to the best of our knowledge not to interfacial properties.

By computing the Henry's law constants of the investigated LJTS mixtures, the results and the physical insight from the interfacial properties behavior are furthermore put into relation with the gas solubility of the low-boiling component in the high-boiling component.

II. MODELING AND SIMULATION

A. Binary Lennard-Jones truncated shifted mixtures

One of the cheapest intermolecular potentials in terms of the required computational effort which still gives a correct description of the behavior of simple fluids is the LJTS potential [57,58] with a truncation radius of 2.5σ . It is therefore often used as model fluid in studies of physical phenomena [59–63] and for the development of simulation methods.

The LJTS potential v_{LJTS} is

$$v_{\text{LJ}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad \text{and} \quad (1)$$

$$v_{\text{LJTS}}(r) = \begin{cases} v_{\text{LJ}}(r) - v_{\text{LJ}}(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}, \quad (2)$$

with v_{LJ} being the full Lennard-Jones potential [64,65] and ε and σ being the energy and size parameter, respectively. The distance between two particles is denoted by r . The truncation radius r_c of the potential is 2.5σ throughout the present paper. The abbreviation “LJTS” refers to the fluid with this specific truncation radius here. Note that the truncation of the potential influences the fluid's thermodynamic bulk [66–69] and interfacial properties [70–75].

We investigated 90 binary LJTS mixtures in the present paper. The high-boiling component is denoted as component 1 and the low-boiling component is denoted as 2. The size parameter of both components is the same for all investigated mixtures, i.e., $\sigma_1 = \sigma_2 = \sigma$. Also the mass of both components is the same. Component 1 is considered as reference component here and is the same for all mixtures with $\varepsilon_1 = 1$ and $\sigma_1 = 1$. The low-boiling character of component 2 is obtained by varying the dispersion energy with respect to component 1 between $\varepsilon_2/\varepsilon_1 = 0.5$ and 0.95 with a decrement of 0.05 . The critical points of the high-boiling component 1 and the ten different low-boiling components 2 are shown in Fig. 1 together with the vapor pressure curves of component 1 and two of the pure components 2 with the highest and lowest dispersion energy ratio $\varepsilon_2/\varepsilon_1$. The results shown in Fig. 1 were calculated with the PeTS EOS, which is known

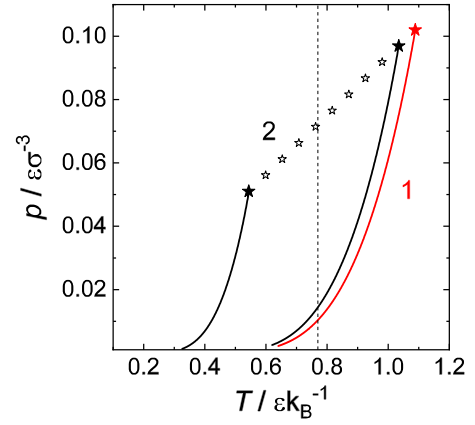


FIG. 1. Vapor pressure curves for the pure LJTS fluids that were considered in the present paper. The temperature for which all simulations of the present work were carried out is $T = 0.77 \varepsilon k_B^{-1}$ and is indicated as a vertical dotted line. The high-boiling component 1 is indicated in red; the different low-boiling components 2 are indicated in black. The low-boiling components 2 with lowest ($\varepsilon_2/\varepsilon_1 = 0.5$) and highest ($\varepsilon_2/\varepsilon_1 = 0.95$) dispersion energy used in this study are indicated as black lines. For clarity only two out of the ten low-boiling components' vapor pressure curves are shown. Stars indicate the critical points of all 11 investigated pure substances. The empty stars indicate the critical points of the low-boiling fluids with $\varepsilon_2/\varepsilon_1 = 0.55, 0.6, \dots, 0.85, 0.9$.

to reproduce the LJTS vapor-liquid equilibrium very well [5,48]. Throughout the present paper, the temperature is $T = 0.77 \varepsilon k_B^{-1}$, which corresponds to approximately 0.7 of the critical temperature of the pure component 1 (see dashed line in Fig. 1).

The modified Lorentz-Berthelot combination rules were employed [49,76] for describing the interactions between unlike LJTS particles:

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}, \quad (3)$$

$$\varepsilon_{12} = \xi \sqrt{\varepsilon_1 \varepsilon_2}, \quad (4)$$

where the indices 1 and 2 indicate the interaction of two particles of the same component and the double index 12 indicates the cross interaction between different components. The value of ε_{12} describes the cross affinity between the two components which is systematically varied by varying ξ . The binary interaction parameter ξ is used as adjustable parameter, which is considered to be state independent. For the modeling of real fluid mixtures, its number is often obtained from a fit to experimental data [77]. The present paper does not aim at reproducing the phase behavior of selected real mixtures. We are interested in studying the influence of the molecular interactions on the interfacial behavior of LJTS mixtures. Therefore, the binary interaction parameter is varied in the range $\xi = 0.85$ and 1.25 with a decrement of 0.05 . This results in 90 binary LJTS mixtures as shown in Fig. 2.

The liquid phase composition is prescribed by setting $x'_2 = 0.05 \text{ mol mol}^{-1}$ throughout this study. This composition was chosen based on the experience from our previous studies, which showed that the enrichment is strongest at low

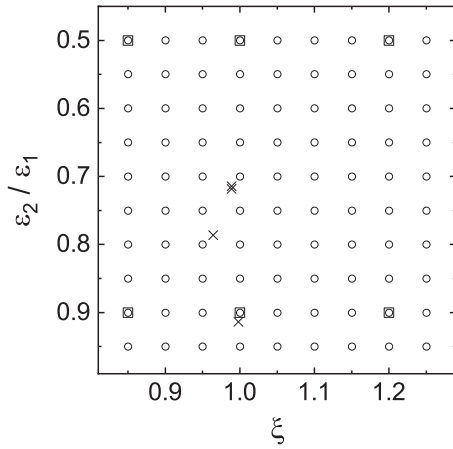


FIG. 2. Overview of the investigated binary LJTS mixtures in the plane of the binary interaction parameter ξ and the ratio of the dispersion energies of the low- and high-boiling component $\varepsilon_2/\varepsilon_1$. Circles indicate the 90 mixtures that were investigated in the present work. Squares mark the mixtures investigated by Stephan *et al.* [5]. The stars indicate Lennard-Jones parameters of models of real binary mixtures proposed by Vrabec *et al.* [78] for argon-krypton, argon-methane, krypton-xenon, and methane-krypton.

concentrations of the low-boiling component in the saturated liquid phase [1,5,8,30].

The binary interaction parameter ξ and the ratio of the dispersion energies $\varepsilon_2/\varepsilon_1$ is not only used in the MD simulations, but the same number is also used in the PeTS EOS, and therefore also in the DGT calculations. It has been shown before that no adjustments are necessary: the phase behavior and interfacial properties that are obtained from both methods match well, when the same numbers for ξ and $\varepsilon_2/\varepsilon_1$ are used in MD and DGT [5,30].

Throughout the present paper, all physical properties are reduced using the Lennard-Jones parameters of the high-boiling component ε_1 and σ_1 , the molecular mass M , as well as the Boltzmann constant k_B [64].

B. Molecular simulations

1. Direct vapor-liquid equilibrium simulations

In the MD simulations of vapor-liquid interfaces, systems were studied in which a liquid phase that is arranged as a slab in the middle of the simulation volume is equilibrated with two vapor phases 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 80σ and the thickness of the liquid slab in the middle of the simulation box was 40σ to avoid finite size effects [5,70]. The elongation in the directions parallel to the interfaces was at least 20σ . The simulations were performed with the MD code *ls1 MARDYN* [79] in the *NVT* ensemble with $N = 16\,000$ particles. The equation of motion was solved by a leapfrog integrator [80] with a time step of $\Delta t = 0.001\sigma\sqrt{M/\varepsilon}$. The equilibration was executed for 2.5×10^6 time steps. The production was conducted for 7.5×10^6 time steps. Density and pressure profiles were computed in block averages of 500 000 time steps during

the production phase. The statistical error was estimated to be three times the standard deviation of all block averages.

The vapor pressure p^s , the saturated densities ρ' and ρ'' , and the saturated vapor and liquid phase mole fractions x'_i and x''_i were computed as an average over the respective phases excluding the area close to the interface, where the first derivative of the density with respect to the z coordinate significantly deviates from zero.

Also the density profiles were obtained as averages over all sampling points (blocks) in the production phase. To avoid smearing of the averaged density profiles from fluctuations of the liquid slab position in the box, the individual density profiles from one block average were shifted by setting the z -axis origin at $\rho_{\text{tot}} = \rho''_{\text{tot}} + 0.5(\rho'_{\text{tot}} - \rho''_{\text{tot}})$, where ρ_{tot} is the total local density $\rho_{\text{tot}} = \rho_1 + \rho_2$ before averaging, as it was done in our previous works [5,8,30].

The initial bulk phase compositions and number densities were estimated with the PeTS EOS [5,48] to ensure that the desired value of $x'_2 = 0.05 \text{ mol mol}^{-1}$ was found in the simulations after equilibration. Further details on this procedure are given in the Supplemental Material [112].

The interfacial tension was obtained from the deviation between the normal and the tangential diagonal components of the overall pressure tensor [81,82], i.e., the mechanical route:

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} (p_N - p_T) dz. \quad (5)$$

The normal pressure p_N is given by the z component of the diagonal of the pressure tensor, and the tangential pressure p_T is determined by averaging over x and y components of the diagonal of the pressure tensor. The interfacial area S of each vapor-liquid interface is given by the cross section of the simulation volume normal to the z axis.

2. Henry's law constant simulations

Henry's law constants $H_{2,1}$ of the low-boiling component 2 in the solvent 1 were determined in the *NpT* ensemble with 1372 solvent particles using Widom's test particle method [83]. The simulations were performed with the program *ms2* [84]. In the simulations, the residual chemical potential μ_2^∞ of the solute is sampled, which is directly related to the Henry's law constant by [85]

$$H_{2,1} = \rho' T \exp(\mu_2^\infty/T), \quad (6)$$

where ρ' is the saturated liquid density of the solvent and T is the temperature. Each simulation run consisted of 300 000 time steps of equilibration and 1×10^6 time steps of production. The time step was set to $\Delta t = 0.001\sigma\sqrt{M/\varepsilon}$. We carried out 5200 trial insertions per time step. The statistical uncertainty of the Henry's law constant is estimated to be three times the standard deviation of the ten block averages (the block size was 100 000 time steps).

C. PeTS EOS and density gradient theory

1. PeTS EOS

The PeTS EOS [5,48] was developed to model the thermodynamic properties of the LJTS fluid. It is based on the perturbation theory of Barker and Henderson [86], which splits

the free energy per particle a into the ideal gas contribution a_{ID} , the free energy of a hard sphere potential a_{HS} , and the perturbation contribution a_{pert} due to dispersion:

$$a = a_{\text{ID}} + a_{\text{HS}} + a_{\text{pert}}. \quad (7)$$

The perturbation contribution is modeled as a sum of first- and second-order contributions, i.e., $a_{\text{pert}} = a_1 + a_2$, which are developed in Taylor series as functions of the packing fraction η .

The PeTS EOS was extended to binary mixtures [5] using van der Waals one-fluid theory [53], which is known to perform well as long as the size parameters σ_1 and σ_2 of both components are similar [87–89]. The modified combination rules of Lorentz and Berthelot are used for the computation of the cross interaction parameters σ_{12} and ε_{12} [see Eqs. (3) and (4)]. The full equations of the PeTS EOS are given in [5,48].

The PeTS EOS was fitted to vapor-liquid equilibrium simulation data of the LJTS fluid [48]. It was shown in previous work that the PeTS EOS accurately describes thermodynamic properties of the LJTS fluid both for stable and metastable states [48] as well as interfacial properties [63]. The PeTS EOS describes not only the pure LJTS fluid well but also LJTS mixtures [5]. No adjustment of parameters is required for the accurate description of both bulk and interfacial properties of LJTS mixtures.

2. Density gradient theory

The free energy of the heterogeneous system is expanded in DGT in a Taylor series in the derivatives of the density with respect to the spatial coordinate normal to the interface $\nabla^m \rho$, $m = 1, 2, \dots$ and truncated after the square gradient term. To model fluid interfaces, DGT only requires a model of the free energy of the bulk fluid and the so-called influence parameter κ_{ij} . The influence parameter describes the influence of the density gradients on the free energy. For a comprehensive introduction we refer to [3,90–92]. For a planar interface of a binary mixture with the components i and j , the free energy can be written as

$$a(\underline{\rho}) = a_0(\underline{\rho}) + \sum_{i=1}^2 \sum_{j=1}^2 1/2 \kappa_{ij} \nabla \rho_i \cdot \nabla \rho_j, \quad (8)$$

where $a_0(\underline{\rho})$ is the free energy of the homogeneous system at the local composition, $\underline{\rho}$ indicates the vector of the number densities ρ_i , and $\nabla \rho$ are the corresponding gradients. κ_{ij} are the influence parameters for the pure substances (if $i = j$) and the cross interaction (if $i \neq j$). In the case of $i = j$, indices are labeled only with one subscript for simplicity in the following, e.g., $\kappa_{11} = \kappa_1$. The PeTS EOS is employed for calculating the free energy in Eq. (8).

The cross-interaction influence parameter was assumed here to be the geometric mean of the pure substance influence parameters [93,94]

$$\kappa_{ij} = \sqrt{\kappa_i \kappa_j}. \quad (9)$$

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 [5] for LJTS mixtures in the entire composition range. The influence parameter of the high-boiling component was adopted from [48], i.e.,

$\kappa_1 = 2.7334 \sigma^5 \varepsilon$. The influence parameters of the low-boiling component 2 were calculated by $\kappa_2 = \kappa_1 \frac{\varepsilon_2}{\varepsilon_1}$. The results for the interfacial properties of mixtures are thereby predictions.

To obtain the equilibrium density profiles $\rho_i(z)$ of both components connecting the bulk phases, Eq. (8) has to be minimized. For solving the DGT equation for both components in the interfacial domain, we used the stabilized DGT algorithm proposed by Mu *et al.* [95], which is numerically robust and avoids choosing a reference component, which has numerical pitfalls [96]. The domain length is set to 20σ with a spatial discretization of 0.02σ .

The surface tension γ was calculated by

$$\gamma = \int \sum_{i=1}^2 \sum_{j=1}^2 \kappa_{ij} \nabla \rho_i \nabla \rho_j dz. \quad (10)$$

D. Interfacial properties

The MD simulations as well as the DGT yield the component density profiles $\rho_i(z)$ of both components $i = 1, 2$ in the interfacial region. On the basis of the density profiles $\rho_1(z)$ and $\rho_2(z)$, the relative adsorption of the low-boiling component as defined by Gibbs [97] can be computed by the symmetric interface segregation according to Telo da Gama and Evans (see [98,99]):

$$\Gamma_2^{(1)} = -(\rho_2' - \rho_2'') \int_{-\infty}^{\infty} \left[\frac{\rho_1(z) - \rho_1'}{\rho_1' - \rho_1''} - \frac{\rho_2(z) - \rho_2'}{\rho_2' - \rho_2''} \right] dz, \quad (11)$$

where ρ_1' , ρ_1'' and ρ_2' , ρ_2'' are the component densities at saturation in the bulk liquid and bulk vapor phase, respectively. $\Gamma_2^{(1)}$ is the relative surface adsorption of component 2 at component 1.

The interfacial excess can also be characterized by the so-called enrichment E_i [1] which is defined as the ratio of the maximum local density of component i in the interfacial region and the larger of the corresponding densities in the two bulk phases. Hence, the enrichment of the low-boiling component 2 is

$$E_2 = \frac{\max[\rho_2(z)]}{\max(\rho_2', \rho_2'')}. \quad (12)$$

The relative adsorption and the enrichment are linked, but do not contain the same information [1,5]. Adsorption may occur although no enrichment ($E_2 = 1$) is present, for example, if the two component density profiles are shifted relative to each other [5]. But an enrichment will generally result in an adsorption.

To describe the thickness of the planar interface, we use the 90-10% definition for the effective interfacial thickness L_{10}^{90} according to Lekner and Henderson [100], which is the distance between the points where the total local density $\rho_{\text{tot}}(z) = \rho_1(z) + \rho_2(z)$ reaches 10 and 90% of the total bulk number densities, respectively:

$$\begin{aligned} L_{10}^{90} &= z(\rho_{90}^{\text{tot}}) - z(\rho_{10}^{\text{tot}}), \\ \rho_{10}^{\text{tot}} &= \rho_{\text{tot}}'' + 0.1(\rho_{\text{tot}}' - \rho_{\text{tot}}''), \\ \rho_{90}^{\text{tot}} &= \rho_{\text{tot}}'' + 0.9(\rho_{\text{tot}}' - \rho_{\text{tot}}''). \end{aligned} \quad (13)$$

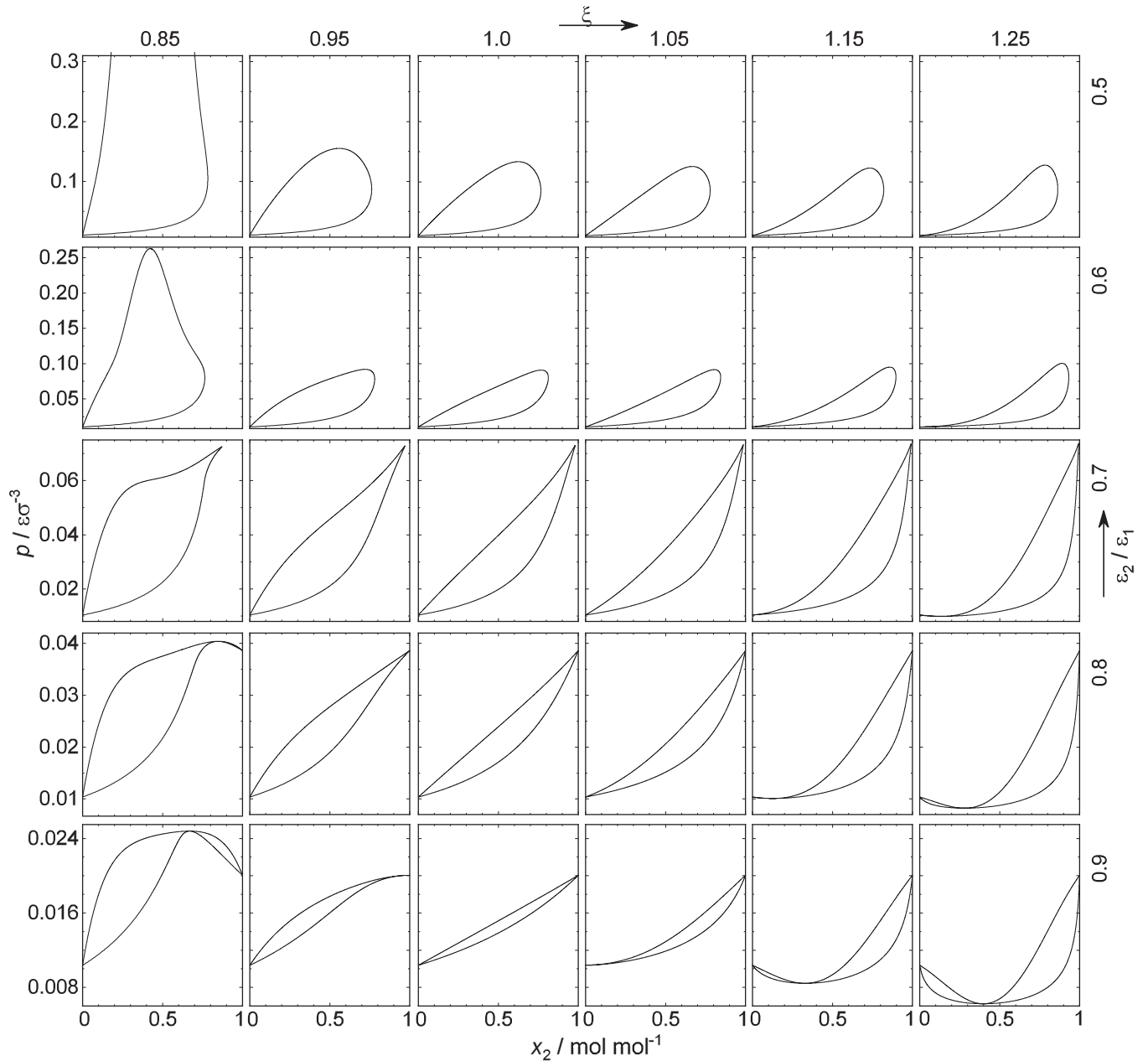


FIG. 3. Selection of isothermal p - x phase diagrams of binary LJTS mixtures at $T = 0.77 \epsilon k_B^{-1}$ for different binary interaction parameters ξ and ratios of the dispersion energies of both components ϵ_2/ϵ_1 . The phase diagrams were calculated by the PeTS EOS [5,48]. Columns have constant binary interaction parameter as indicated at the top; rows have constant ratio of the dispersion energies as indicated on the right. Corner A is top left, and corner B is bottom right (see text).

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

III. RESULTS AND DISCUSSION

A. Vapor-liquid equilibria

The vapor-liquid equilibrium of LJTS mixtures (see Fig. 2) was investigated at $T = 0.77 \epsilon k_B^{-1}$ with both MD simulations and the PeTS EOS. The MD simulations were carried out for a liquid phase mole fraction of the low-boiling component 2 of $x'_2 = 0.05 \text{ mol mol}^{-1}$. The numerical values of the VLE data

at $x'_2 = 0.05 \text{ mol mol}^{-1}$ and $T = 0.77 \epsilon k_B^{-1}$ obtained from MD and the PeTS EOS are reported for all 90 mixtures in the Supplemental Material [112] (vapor pressure, gas phase composition, and saturated densities). The PeTS EOS was used to calculate the isothermal phase diagrams of all 90 mixtures. Representative results for 30 systems are shown in Fig. 3. For all mixtures the high-boiling component 1 is the same. Its vapor pressure is $p^s = 0.0104 \epsilon \sigma^{-3}$ at $T = 0.77 \epsilon k_B^{-1}$. The low-boiling component 2 in the mixtures varies. Results for different values of ϵ_2/ϵ_1 are shown in the different rows of the matrix depicted in Fig. 3. For high values of ϵ_2/ϵ_1 , the component 2 is subcritical, for small values of ϵ_2/ϵ_1 , it is

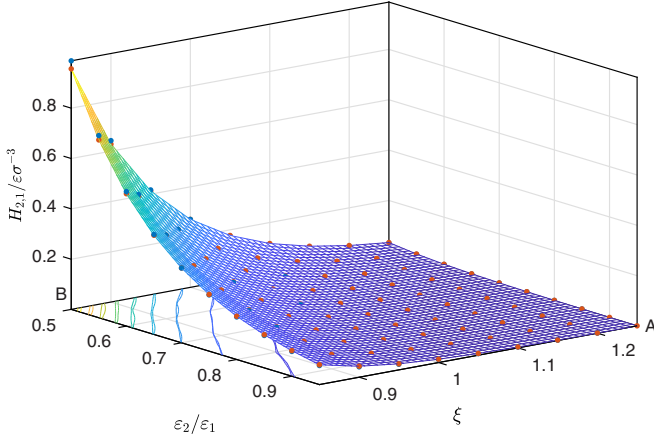


FIG. 4. Henry's law constant of binary LJTS mixtures 1 + 2 at $T = 0.77 \epsilon k_B^{-1}$ as a function of the binary interaction parameter ξ and the ratio of the dispersion energies ϵ_2/ϵ_1 . Results from MD: blue points; results from PeTS EOS [5,48]: orange points. The surface is a linear interpolation of the EOS results. The color of the surface is coded by its height.

supercritical. The critical temperature of the pure component 2 is $T_c = 0.77 \epsilon k_B^{-1}$ for $\epsilon_2/\epsilon_1 = 0.71$. In the columns of the matrix shown in Fig. 3, results for different choices of ξ are presented. For $\xi = 1$ the mixtures are almost ideal in the sense of Raoult's law. For $\xi > 1$ attractive interactions prevail and the mixtures tend to form high-boiling azeotropes, while for $\xi < 1$ repulsive interactions prevail and the mixtures tend to form low-boiling azeotropes. Decreasing ξ below the lowest value that was studied in the present work ($\xi = 0.85$) leads to a liquid-liquid phase split at $T = 0.77 \epsilon k_B^{-1}$. As studying liquid-liquid equilibria was out of the scope of the present paper, only mixtures with $\xi > 0.85$ were studied. The critical pressures of the mixtures with small values of ϵ_2/ϵ_1 show an interesting behavior: they remain almost constant upon lowering ξ and increase only sharply for the lowest value of ξ shown in Fig. 3.

Qualitatively, the bubble lines of the mixtures in the ξ , ϵ_2/ϵ_1 plane differ more than the dew lines. This can be interpreted as a consequence of the fact that the interactions in the liquid phase are dominating the VLE behavior compared to a minor influence of the vapor phase. This is evident, since the self interactions and cross interactions have a stronger impact in the dense liquid phase.

The results for the Henry's law constants of all 90 investigated mixtures at $T = 0.77 \epsilon k_B^{-1}$ that were obtained from the MD simulations as well as from the PeTS EOS are shown in Fig. 4 as a function of the binary interaction parameter ξ and the ratio of the dispersion energies ϵ_2/ϵ_1 . The numeric values are reported in the Supplemental Material [112]. The results from the computer experiment and the theory are found to be in good agreement for all mixtures. As expected, the Henry's law constant $H_{2,1}$ increases steadily with decreasing ratio of dispersion energies ϵ_2/ϵ_1 as well as with decreasing values of ξ .

The plot of $H_{2,1}$ over ϵ_2/ϵ_1 and ξ shown in Fig. 4 has some interesting features. First, moving along the diagonal connecting the corner points ($\epsilon_2/\epsilon_1 = 0.5$, $\xi = 0.85$, labeled

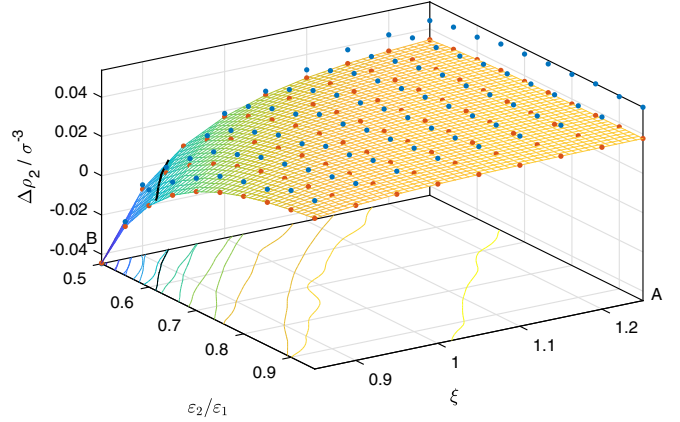


FIG. 5. Difference in the bulk number density of the low-boiling component $\Delta \rho_2 = \rho'_2 - \rho''_2$ at $T = 0.77 \epsilon k_B^{-1}$ and $x'_2 = 0.05 \text{ mol mol}^{-1}$ as a function of the binary interaction parameter ξ and the ratio of the dispersion energies ϵ_2/ϵ_1 . Results from MD: blue points; results from PeTS EOS [5,48]: orange points. The surface is a linear interpolation of the EOS results. The color of the surface is coded by its height position. The black line indicates the trace of the zero crossing line $\Delta \rho_2 = 0$ from the EOS results.

here as *corner A*, and $\epsilon_2/\epsilon_1 = 0.95$, $\xi = 1.25$, labeled here as *corner B*), the Henry's law constant first increases only weakly but then steeply. This is due to the fact that towards corner B the mean dispersive interactions in the liquid phase become less attractive, which decreases the solubility of the low-boiling component 2 in the high-boiling component 1.

Furthermore, the surface $H_{2,1} = H_{2,1}(\epsilon_2/\epsilon_1, \xi)$ has a remarkably simple shape. The traces of the level curves in the ϵ_2/ϵ_1 , ξ plane can be approximated by segments of root functions (see Fig. 4), which results in an approximately radial symmetry of the function $H_{2,1} = H_{2,1}(\epsilon_2/\epsilon_1, \xi)$ in the investigated range of ϵ_2/ϵ_1 and ξ . As only a segment of the function is plotted in Fig. 4, the curvature can only be seen by inspecting the traces of the isolines. Going from corner A to corner B in a straight line follows the gradient of that function.

Figure 5 shows the difference of the number density of the low-boiling component between the bulk vapor and bulk liquid phase $\Delta \rho_2 = \rho'_2 - \rho''_2$ at $x'_2 = 0.05 \text{ mol mol}^{-1}$ and $T = 0.77 \epsilon k_B^{-1}$ as a function of the binary interaction parameter ξ and the ratio of the dispersion energies ϵ_2/ϵ_1 . The difference of the number density of the low-boiling component $\Delta \rho_2$ was calculated for all 90 LJTS mixtures using both MD simulation and the PeTS EOS. The computer experiments and the EOS have a distinct offset which vanishes in corner B, but the qualitative behavior of the results from both methods agrees well.

The deviations show that the VLE behavior of LJTS mixtures is not described perfectly by the PeTS EOS, but in assessing the deviations it has to be considered that $\Delta \rho_2$ is a very sensitive property. The same symmetry as for the Henry's law constant (see Fig. 4) is also found for $\Delta \rho_2(\epsilon_2/\epsilon_1, \xi)$ (Fig. 5) but the trends are inverse: $\Delta \rho_2$ is low where $H_{2,1}$ is high. This is not unexpected since both properties express the tendency of the low-boiling component to portion on both phases.

An interesting feature of $\Delta \rho_2(\epsilon_2/\epsilon_1, \xi)$ is the zero crossing line of $\Delta \rho_2$ close to corner B. In a wide range of investigated mixtures $\Delta \rho_2 > 0$, i.e., the low-boiling component

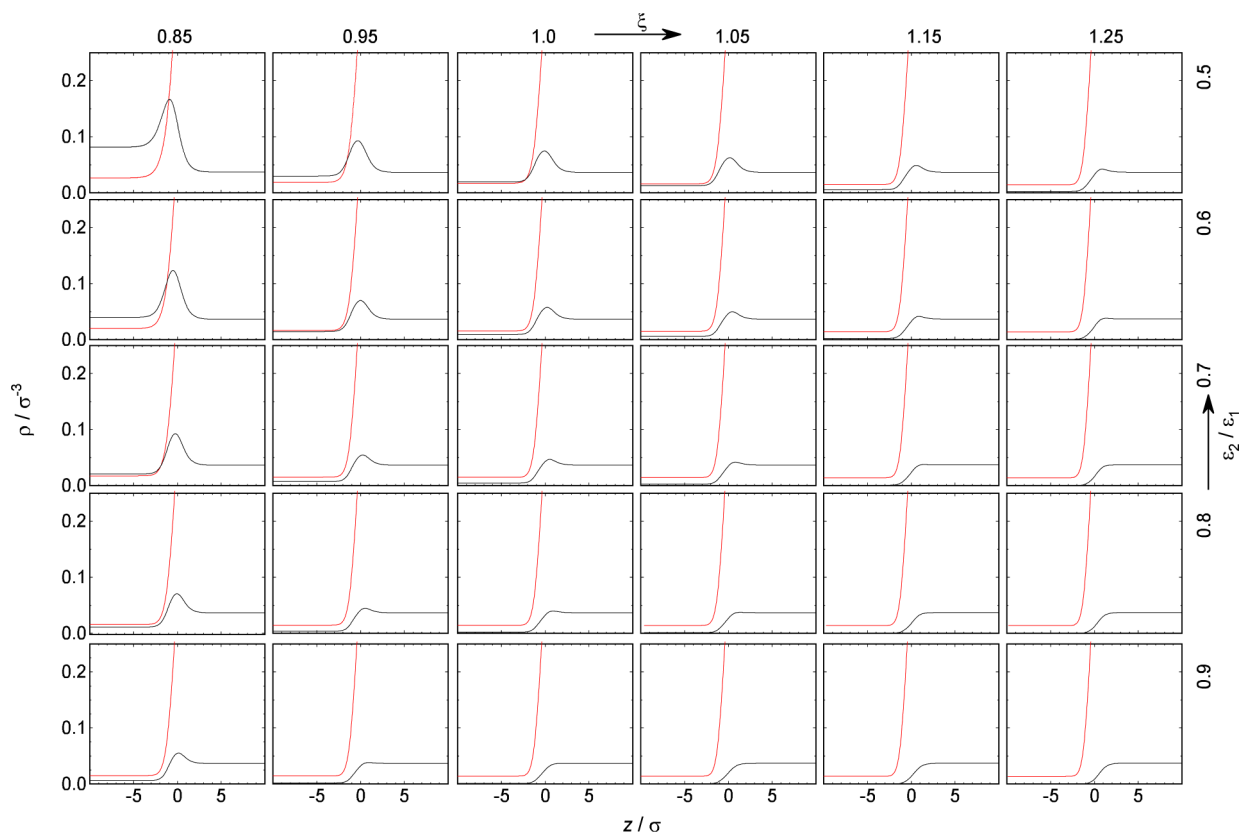


FIG. 6. Selection of density profiles at planar vapor-liquid interfaces calculated by DGT: local density of the low-boiling component 2 (black line) and high-boiling component 1 (red line) as a function of the spatial coordinate z normal to the interface in the plane of the binary interaction parameter ξ and the ratio of the dispersion energies $\varepsilon_2/\varepsilon_1$. Columns have constant binary interaction parameter as indicated on the top; rows have constant ratio of the dispersion energies as indicated on the right. The temperature is always $T = 0.77 \varepsilon k_B^{-1}$ and the liquid phase concentration is $x'_2 = 0.05 \text{ mol mol}^{-1}$. Corner A is top left, and corner B is bottom right (see text).

accumulates in the liquid phase. In contrast, for $\Delta\rho_2 < 0$ the low-boiling component has a preferential residency in the vapor phase.

B. Vapor-liquid interfaces

Planar vapor-liquid interfaces were investigated by both MD and DGT at $T = 0.77 \varepsilon k_B^{-1}$ and $x'_2 = 0.05 \text{ mol mol}^{-1}$. Besides the density profiles, the interfacial enrichment [see Eq. (12)], relative adsorption [see Eq. (11)], interfacial tension [see Eqs. (10) and (5)], and interfacial thickness [see Eq. (13)] were investigated for all 90 binary LJTS mixtures (see Fig. 2). Density profiles are shown in Fig. 6, the enrichment is shown in Fig. 7, the relative adsorption is shown in Fig. 8, the surface tension is shown in Fig. 9, and the interfacial thickness is shown in Fig. 10.

The prescribed liquid phase composition is exactly matched in DGT, but not by MD due to fluctuations. The mole fraction of the low-boiling component in the liquid phase obtained from the MD simulations is in the range $x'_2 = 0.05\text{--}0.07 \text{ mol mol}^{-1}$. The numeric values of the interfacial properties from both MD and DGT as well as the actual liquid phase composition in MD are reported in Table I. The error bars of the MD simulation results are not shown in the plots

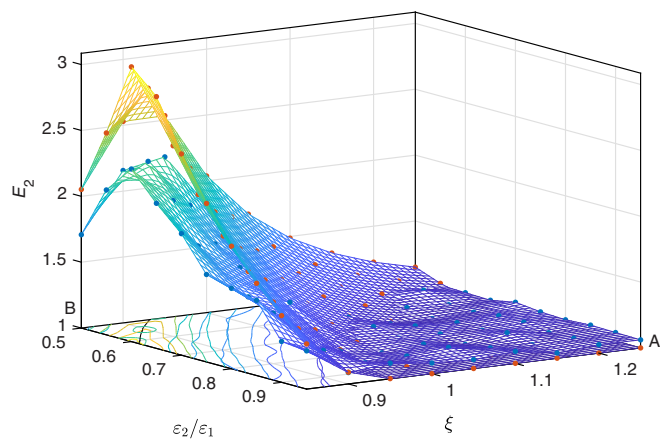


FIG. 7. Enrichment E_2 of the low-boiling component 2, as defined by Eq. (12), at the interface as a function of the binary interaction parameter ξ and the ratio of the dispersion energies $\varepsilon_2/\varepsilon_1$ at $T = 0.77 \varepsilon k_B^{-1}$ and $x'_2 = 0.05 \text{ mol mol}^{-1}$. Results from MD: blue points; results from DGT: orange points. The surfaces are linear interpolations of the respective results. The color of the surfaces is coded by its height position. The black line indicates the trace of zero crossing line $\Delta\rho_2 = 0$ from the DGT results (see Fig. 5). Corners A and B to which the text refers are indicated.

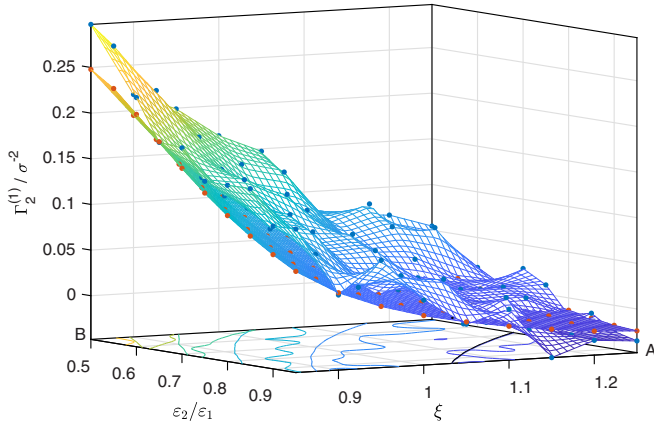


FIG. 8. Relative adsorption $\Gamma_2^{(1)}$ of the low-boiling component 2, as defined by Eq. (11), at the interface as a function of the binary interaction parameter ξ and the ratio of the dispersion energies $\varepsilon_2/\varepsilon_1$ at $T = 0.77 \varepsilon k_B^{-1}$ and $x'_2 = 0.05 \text{ mol mol}^{-1}$. Results from MD: blue points; results from DGT: orange points. The surfaces are linear interpolations of the respective results. The color of the surfaces is coded by its height position. The black line indicates the trace of the zero crossing line $\Gamma_2^{(1)} = 0$ from the DGT results.

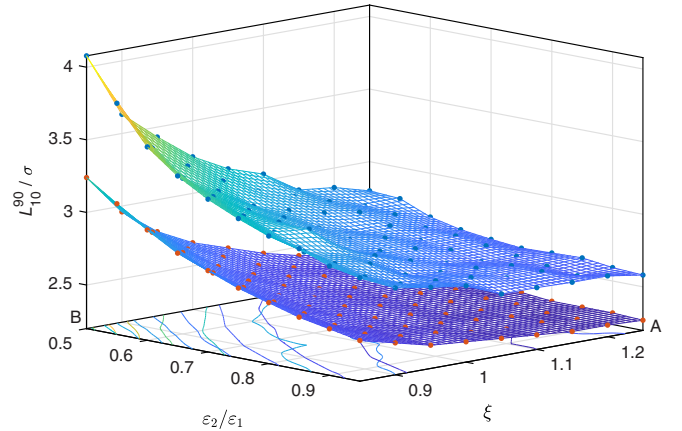


FIG. 10. Interfacial thickness L_{10}^{90} , as defined by Eq. (13), as a function of the binary interaction parameter ξ and the ratio of the dispersion energies $\varepsilon_2/\varepsilon_1$ at $T = 0.77 \varepsilon k_B^{-1}$ and $x'_2 = 0.05 \text{ mol mol}^{-1}$. Results from MD: blue points; results from DGT: orange points. The surfaces are linear interpolations of the respective results. The color of the surfaces is coded by its height position.

in Figs. 7–10 for clarity, but the statistical uncertainties are reported in Table I.

1. Density profiles and enrichment

Selected results for the density profiles are shown in Fig. 6. The plot is organized in the same way as Fig. 3, i.e., the selected systems are the same. The density profiles are plotted as a function of the spatial coordinate z normal to the planar interface. For clarity, only the DGT density profiles

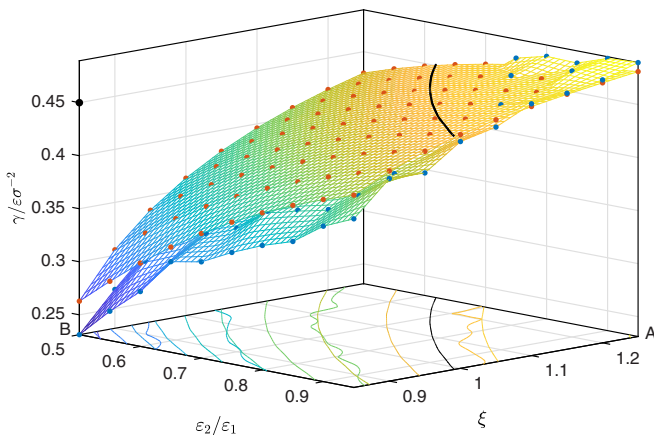


FIG. 9. Interfacial tension γ , as defined by Eqs. (10) and (5), as a function of the binary interaction parameter ξ and the ratio of the dispersion energies $\varepsilon_2/\varepsilon_1$ at $T = 0.77 \varepsilon k_B^{-1}$ and $x'_2 = 0.05 \text{ mol mol}^{-1}$. Results from MD: blue points; results from DGT: orange points. The surfaces are linear interpolations of the respective results. The color of the surfaces is coded by its height position. The black dot indicates the surface tension γ_1 of the pure component 1 at $T = 0.77 \varepsilon k_B^{-1}$ according to Stephan *et al.* [63]. The black line indicates the crossing line of $\gamma = \gamma_1$ from the DGT results.

are shown here. It was already shown by Stephan *et al.* [5] that the density profiles of LJTS mixtures predicted by MD and DGT + PeTS agree very well. This is confirmed in the present paper. It can be seen from Fig. 6 that the enrichment of the low-boiling component E_2 , i.e., the relative height of the peak in $\rho_2(z)$, generally increases with decreasing $\varepsilon_2/\varepsilon_1$ and decreasing ξ . Details become clearer in Fig. 7, where E_2 is plotted as a function of $\varepsilon_2/\varepsilon_1$ and ξ . The layout of the plot is similar to that in Figs. 4 and 5.

In contrast to the density profile of the low-boiling component 2, which dramatically changes in the $\xi, \varepsilon_2/\varepsilon_1$ plane, the density profile of the high-boiling component 1 remains fairly similar among the different mixtures, as already discussed in our previous work [5]. No enrichment of the high-boiling component 1 is observed in any mixture.

Starting in corner A, no enrichment of the low-boiling component 2 is found. The enrichment increases with a decreasing $\Delta\rho_2$ towards corner B (see Fig. 5). The density profiles in the region of the $\xi, \varepsilon_2/\varepsilon_1$ plane where $\Delta\rho_2$ is close to zero show a particularly high enrichment. A significant enrichment of the low-boiling component is found for mixtures that exhibit a low solubility of the low-boiling component in component 1, i.e., large Henry's law constants (see Fig. 4).

The predictions for the enrichment E_2 from the computer experiments and the theory are found to be in good qualitative agreement for all investigated mixtures. DGT overestimates the enrichment predicted by MD for mixtures close to corner B. Such an overestimation of the enrichment E_2 by DGT compared to MD results was also reported previously by Becker *et al.* [1] and Stephan *et al.* [5] for mixtures where the low-boiling component is supercritical. The enrichment predicted by MD in corner A is slightly above unity, while DGT predicts no enrichment, i.e., $E_2 = 1$, in that region. As already discussed in [5], the deviation of the MD results from $E_2 = 1$ is attributed to the fluctuations in connection with the definition of the enrichment [see Eq. (12)].

TABLE I. Interfacial properties of the investigated binary LJTS mixtures. Results from MD and DGT+PeTS EOS. The temperature is $T = 0.77 \varepsilon k_B^{-1}$. The DGT results are calculated at the liquid phase composition $x'_2 = 0.05 \text{ mol mol}^{-1}$. The exact MD liquid phase composition is given in the second column. The other columns are, from left to right, the surface tension, the relative adsorption, the enrichment of the low-boiling component 2, and the interfacial thickness. The number in the parentheses indicates the statistical uncertainty in the last decimal digit.

$\varepsilon_2/\varepsilon_1$	$x'_2/\text{mol mol}^{-1}$	$\gamma/\varepsilon\sigma^{-2}$		$\Gamma_2^{(1)}/\sigma^{-2}$		E_2		L_{10}^{90}/σ	
		MD	EOS	MD	EOS	MD	EOS	MD	EOS
$\xi = 0.85$									
0.5	0.058(2)	0.23(3)	0.263	0.30(3)	0.248	1.71(3)	2.05	4.08(9)	3.24
0.55	0.058(1)	0.26(3)	0.287	0.28(2)	0.231	2.10(3)	2.53	3.8(1)	3.10
0.6	0.063(3)	0.28(2)	0.310	0.23(4)	0.207	2.3(2)	3.09	3.53(9)	2.96
0.65	0.062(2)	0.32(2)	0.330	0.18(4)	0.181	2.1(1)	2.91	3.37(8)	2.84
0.7	0.061(1)	0.32(2)	0.349	0.18(2)	0.156	1.92(8)	2.53	3.3(1)	2.76
0.75	0.063(2)	0.34(2)	0.365	0.15(3)	0.133	1.66(8)	2.20	3.16(7)	2.68
0.8	0.062(2)	0.35(2)	0.379	0.15(3)	0.112	1.6(1)	1.93	3.08(8)	2.62
0.85	0.061(1)	0.36(1)	0.392	0.15(2)	0.094	1.57(7)	1.70	3.03(8)	2.56
0.9	0.065(2)	0.38(2)	0.403	0.11(4)	0.077	1.3(1)	1.51	2.95(4)	2.52
0.95	0.064(1)	0.39(2)	0.413	0.11(4)	0.063	1.29(9)	1.34	2.91(5)	2.48
$\xi = 0.9$									
0.5	0.059(4)	0.27(2)	0.305	0.22(3)	0.195	2.16(5)	2.53	3.63(9)	2.96
0.55	0.059(3)	0.30(1)	0.326	0.23(2)	0.172	2.3(1)	2.83	3.44(7)	2.86
0.6	0.059(1)	0.31(2)	0.346	0.18(2)	0.149	2.0(1)	2.45	3.27(9)	2.76
0.65	0.062(1)	0.34(2)	0.363	0.14(3)	0.128	1.74(7)	2.13	3.19(7)	2.66
0.7	0.061(2)	0.35(2)	0.378	0.12(2)	0.108	1.6(1)	1.87	3.09(6)	2.60
0.75	0.062(2)	0.37(2)	0.391	0.11(3)	0.090	1.46(8)	1.65	3.02(6)	2.54
0.8	0.062(1)	0.38(2)	0.402	0.09(2)	0.074	1.38(6)	1.47	2.93(6)	2.50
0.85	0.063(2)	0.38(3)	0.413	0.10(1)	0.060	1.3(1)	1.32	2.89(4)	2.46
0.9	0.065(2)	0.40(2)	0.422	0.07(3)	0.048	1.20(7)	1.19	2.83(5)	2.44
0.95	0.066(1)	0.42(2)	0.429	0.03(3)	0.037	1.09(6)	1.09	2.80(4)	2.42
$\xi = 0.95$									
0.5	0.057(1)	0.30(2)	0.337	0.20(3)	0.152	2.22(5)	2.53	3.43(7)	2.78
0.55	0.059(1)	0.33(2)	0.355	0.17(2)	0.131	1.90(7)	2.19	3.27(8)	2.70
0.6	0.061(3)	0.34(2)	0.372	0.14(2)	0.111	1.7(1)	1.91	3.14(9)	2.62
0.65	0.061(1)	0.36(3)	0.386	0.13(1)	0.092	1.53(8)	1.68	3.05(8)	2.56
0.7	0.062(2)	0.37(3)	0.399	0.11(3)	0.076	1.4(1)	1.49	3.01(8)	2.50
0.75	0.061(1)	0.37(2)	0.410	0.10(2)	0.062	1.38(3)	1.34	3.00(5)	2.46
0.8	0.064(2)	0.40(2)	0.419	0.09(2)	0.049	1.21(8)	1.22	2.87(8)	2.44
0.85	0.065(1)	0.41(2)	0.428	0.05(3)	0.038	1.11(8)	1.12	2.84(7)	2.40
0.9	0.067(2)	0.42(2)	0.435	0.04(3)	0.028	1.07(6)	1.04	2.74(6)	2.38
0.95	0.067(1)	0.42(2)	0.442	0.07(2)	0.019	1.12(4)	1.00	2.76(7)	2.36
$\xi = 1$									
0.5	0.059(2)	0.32(2)	0.361	0.17(3)	0.119	1.82(8)	2.04	3.25(9)	2.66
0.55	0.062(1)	0.34(2)	0.377	0.14(3)	0.100	1.55(8)	1.78	3.13(7)	2.60
0.6	0.062(1)	0.36(1)	0.392	0.10(2)	0.082	1.43(7)	1.57	2.99(7)	2.52
0.65	0.062(2)	0.37(2)	0.404	0.11(2)	0.067	1.35(1)	1.40	2.95(6)	2.48
0.7	0.065(1)	0.39(3)	0.415	0.07(4)	0.053	1.12(7)	1.27	2.87(6)	2.44
0.75	0.065(2)	0.41(2)	0.424	0.06(2)	0.041	1.13(5)	1.16	2.81(5)	2.42
0.8	0.066(2)	0.41(2)	0.433	0.04(3)	0.031	1.09(6)	1.08	2.81(6)	2.38
0.85	0.067(2)	0.43(3)	0.440	0.02(5)	0.022	1.05(7)	1.02	2.72(7)	2.36
0.9	0.068(2)	0.43(2)	0.446	0.05(3)	0.013	1.08(6)	1.00	2.72(8)	2.36
0.95	0.068(2)	0.45(2)	0.452	0.02(3)	0.006	1.08(7)	1.00	2.73(4)	2.34
$\xi = 1.05$									
0.5	0.059(2)	0.36(2)	0.380	0.15(3)	0.094	1.6(1)	1.71	3.13(6)	2.58
0.55	0.061(1)	0.36(2)	0.395	0.13(3)	0.076	1.44(7)	1.51	3.01(8)	2.50
0.6	0.063(1)	0.38(2)	0.407	0.09(2)	0.061	1.25(6)	1.36	2.92(7)	2.46
0.65	0.064(1)	0.40(2)	0.418	0.07(2)	0.048	1.17(6)	1.23	2.84(6)	2.42
0.7	0.065(2)	0.41(2)	0.428	0.07(3)	0.036	1.13(6)	1.14	2.80(4)	2.40
0.75	0.067(2)	0.42(3)	0.436	0.06(2)	0.026	1.11(7)	1.07	2.76(9)	2.38

TABLE I. (Continued.)

$\varepsilon_2/\varepsilon_1$	$x'_2/\text{mol mol}^{-1}$	$\gamma/\varepsilon\sigma^{-2}$		$\Gamma_2^{(1)}/\sigma^{-2}$		E_2		L_{10}^{90}/σ	
		MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.8	0.067(1)	0.43(2)	0.443	0.02(2)	0.017	1.08(5)	1.02	2.73(6)	2.36
0.85	0.067(1)	0.44(2)	0.449	0.03(1)	0.010	1.08(3)	1.00	2.69(4)	2.34
0.9	0.068(2)	0.45(2)	0.455	0.04(4)	0.003	1.11(9)	1.00	2.70(9)	2.32
0.95	0.069(1)	0.45(2)	0.460	-0.01(2)	-0.003	1.07(4)	1.00	2.63(5)	2.32
$\xi = 1.1$									
0.5	0.061(1)	0.37(2)	0.396	0.08(3)	0.073	1.38(7)	1.49	3.05(5)	2.50
0.55	0.063(2)	0.39(2)	0.409	0.07(2)	0.058	1.24(9)	1.34	2.93(7)	2.44
0.6	0.065(2)	0.41(2)	0.420	0.06(3)	0.044	1.12(7)	1.22	2.86(6)	2.42
0.65	0.065(2)	0.41(2)	0.430	0.04(3)	0.033	1.08(5)	1.13	2.77(8)	2.38
0.7	0.066(1)	0.42(3)	0.438	0.01(3)	0.023	1.04(5)	1.06	2.77(4)	2.36
0.75	0.067(2)	0.43(2)	0.445	0.03(3)	0.014	1.08(4)	1.02	2.73(6)	2.34
0.8	0.068(1)	0.44(2)	0.452	0.01(2)	0.007	1.07(4)	1.00	2.67(5)	2.32
0.85	0.069(1)	0.46(2)	0.457	-0.02(4)	0.000	1.04(6)	1.00	2.68(6)	2.32
0.9	0.070(1)	0.46(2)	0.462	-0.01(3)	-0.006	1.07(3)	1.00	2.65(5)	2.30
0.95	0.070(2)	0.47(2)	0.466	0.01(3)	-0.011	1.09(4)	1.00	2.63(7)	2.30
$\xi = 1.15$									
0.5	0.063(2)	0.38(3)	0.409	0.07(2)	0.057	1.2(1)	1.33	2.89(3)	2.44
0.55	0.063(1)	0.40(2)	0.421	0.09(3)	0.043	1.17(6)	1.22	2.85(7)	2.40
0.6	0.065(1)	0.40(2)	0.431	0.07(2)	0.031	1.11(4)	1.13	2.82(7)	2.38
0.65	0.066(1)	0.43(2)	0.439	0.04(2)	0.021	1.08(5)	1.06	2.77(4)	2.36
0.7	0.068(2)	0.43(2)	0.447	0.00(5)	0.013	1.04(5)	1.02	2.71(7)	2.34
0.75	0.068(1)	0.45(3)	0.453	0.01(3)	0.005	1.06(5)	1.00	2.68(5)	2.32
0.8	0.069(1)	0.45(2)	0.459	0.00(3)	-0.001	1.06(3)	1.00	2.64(7)	2.30
0.85	0.070(2)	0.46(1)	0.464	0.01(3)	-0.007	1.09(6)	1.00	2.65(8)	2.30
0.9	0.070(1)	0.46(2)	0.468	-0.02(2)	-0.012	1.05(5)	1.00	2.65(7)	2.30
0.95	0.071(1)	0.47(2)	0.472	-0.05(2)	-0.017	1.04(4)	1.00	2.62(5)	2.28
$\xi = 1.2$									
0.5	0.064(2)	0.39(2)	0.420	0.07(3)	0.043	1.13(8)	1.23	2.87(9)	2.40
0.55	0.067(2)	0.42(2)	0.431	0.02(3)	0.031	1.07(6)	1.13	2.78(5)	2.38
0.6	0.066(2)	0.43(2)	0.440	0.06(2)	0.021	1.12(5)	1.07	2.76(6)	2.34
0.65	0.067(1)	0.43(2)	0.447	0.01(2)	0.012	1.06(3)	1.02	2.71(4)	2.34
0.7	0.069(1)	0.45(2)	0.454	0.00(2)	0.004	1.05(3)	1.00	2.69(5)	2.32
0.75	0.069(1)	0.45(2)	0.460	0.01(2)	-0.002	1.08(3)	1.00	2.67(4)	2.30
0.8	0.070(1)	0.47(3)	0.465	0.00(3)	-0.008	1.08(4)	1.00	2.63(5)	2.30
0.85	0.070(2)	0.46(3)	0.469	-0.03(2)	-0.013	1.05(4)	1.00	2.61(5)	2.28
0.9	0.070(1)	0.48(3)	0.473	-0.03(1)	-0.018	1.06(3)	1.00	2.58(7)	2.28
0.95	0.070(1)	0.48(2)	0.476	-0.03(3)	-0.022	1.06(3)	1.00	2.62(7)	2.28
$\xi = 1.25$									
0.5	0.065(1)	0.41(2)	0.430	0.05(3)	0.032	1.09(4)	1.15	2.80(5)	2.36
0.55	0.067(1)	0.42(2)	0.439	0.02(2)	0.021	1.06(3)	1.08	2.79(8)	2.32
0.6	0.067(1)	0.43(2)	0.447	0.02(1)	0.012	1.06(2)	1.03	2.70(4)	2.30
0.65	0.069(1)	0.45(2)	0.454	0.00(3)	0.004	1.05(3)	1.00	2.65(7)	2.30
0.7	0.069(1)	0.45(2)	0.460	0.02(2)	-0.003	1.09(4)	1.00	2.63(4)	2.28
0.75	0.070(1)	0.47(2)	0.465	0.01(3)	-0.008	1.07(3)	1.00	2.61(8)	2.30
0.8	0.070(1)	0.48(2)	0.470	-0.02(1)	-0.014	1.06(2)	1.00	2.61(6)	2.28
0.85	0.071(1)	0.48(2)	0.474	-0.01(2)	-0.018	1.07(4)	1.00	2.62(7)	2.28
0.9	0.070(1)	0.49(2)	0.477	-0.03(2)	-0.022	1.07(3)	1.00	2.59(6)	2.28
0.95	0.071(1)	0.49(2)	0.481	-0.04(1)	-0.024	1.06(4)	1.00	2.58(8)	2.28

Again, the same symmetry as in the plots shown in Figs. 4 and 5 (Henry's law constant $H_{2,1}$ and density difference $\Delta\rho_2$) is also found for $E_2(\varepsilon_2/\varepsilon_1, \xi)$.

In corner A (high mean dispersive interactions), practically no enrichment E_2 is found, while strong enrichment is found in corner B. Starting in corner A and going to corner B on a straight line, the enrichment E_2 remains around unity for a

while, and then increases sharply. Interestingly, there is a drop in E_2 , before corner B is reached.

The position of the line of the maximal enrichment E_2 in the $\xi, \varepsilon_2/\varepsilon_1$ plane, as indicated in Fig. 7, is in very good agreement with the zero crossing line of the difference of the number density of component 2 $\Delta\rho_2 = 0$ (see Fig. 5), i.e., it corresponds to mixtures for which the density of the

component 2 is equal in both phases. For mixtures on that line, any adsorption of the low-boiling component at the interface must result in an enrichment for geometric reasons. In contrast, for mixtures with $\Delta\rho_2 \neq 0$ a relative adsorption can also arise from a relative shift of $\rho_2(z)$ with respect to $\rho_1(z)$. Even though the predicted magnitude of the enrichment by MD and DGT differs slightly, the position of the maximum line in the $\xi, \varepsilon_2/\varepsilon_1$ plane agrees perfectly.

2. Relative adsorption

Figure 8 shows the relative adsorption $\Gamma_2^{(1)}$ of the low-boiling component at the vapor-liquid interface, as defined by Eq. (11), as a function of the binary interaction parameter ξ and the ratio of the dispersion energies $\varepsilon_2/\varepsilon_1$. Again results from both MD and DGT are shown. The predictions from the computer experiment and the theory are found to be in good agreement for all investigated mixtures. The MD results show some scattering due to fluctuations in the simulations, while results from the theory are smooth. The symmetry that was observed in the previous plots of this type is also observed here. In contrast to the enrichment E_2 , the relative adsorption increases steadily when going from corner A to corner B. The relative adsorption of the low-boiling component 2 is negative close to the corner A, i.e., high mean attractive interactions, and positive elsewhere. The zero crossing line of the relative adsorption (black line in Fig. 8) is roughly identical with the line that separates mixtures with high-boiling azeotropes from zeotropic mixtures (see Fig. 3). Hence, the relative adsorption $\Gamma_2^{(1)}$ is negative for mixtures with high-boiling azeotropes, while it is positive for other mixtures, which reinforces findings for the surface excess in [5,39,101–103].

Furthermore, the relative adsorption dependency on ξ and $\varepsilon_2/\varepsilon_1$ can be split into two characteristic regions: one region exhibiting a nonlinear regime and one region exhibiting a linear regime. Going from corner A to corner B, the relative adsorption exhibits first a convex increase, whereas approaching corner B $\Gamma_2^{(1)}$ increases linearly. This can only be seen in the results obtained from DGT, since the MD results are superimposed by significant scattering. The breakup between the linear and nonlinear regime of $\Gamma_2^{(1)}$ corresponds well with the region where the enrichment of the low-boiling component is close to unity and the region of significant enrichment. This indicates again [1,5] that the enrichment and the relative adsorption contain different information and it is emphasized that both should be discussed. Relative adsorption may occur even if there is no enrichment, but an enrichment will in general result in an adsorption.

3. Surface tension

Figure 9 shows the surface tension as a function of the binary interaction parameter ξ and the ratio of dispersion energies $\varepsilon_2/\varepsilon_1$. The results from both MD and DGT are shown. The predictions from the computer experiments and the theory agree remarkably well for all investigated mixtures, i.e., the DGT results mostly lie within the MD error bars (see Table I). Only slight systematic deviations are found in corner B, where the DGT results overestimate those from computer experiments. The same type of symmetry as for the properties

discussed above (see Figs. 4, 5, 7, and 8) is also observed for $\gamma(\varepsilon_2/\varepsilon_1, \xi)$.

Going from corner A to corner B, the surface tension decreases steadily. It is found that the line, for which the surface tension of the mixture equals the surface tension of the pure component 1 (see Fig. 9), is in good agreement with the line for which the relative adsorption is zero (see Fig. 8). This is related to the Gibbs adsorption equation which relates the surface excess to the concentration dependence of the surface tension. Adding component 2 to the pure component 1 in corner A, i.e., the region of mixtures with the highest mean dispersive interactions, leads to an increase of the surface tension. This is a typical finding for mixtures with a high-boiling azeotrope [5,39,104]. For mixtures with a low-boiling azeotrope, on the other hand, adding component 2 usually results in a decreased surface tension [5,39,104], which is also found in our data.

4. Interfacial thickness

Figure 10 shows the interfacial thickness L_{10}^{90} as defined by Eq. (13) as a function of the binary interaction parameter ξ and the ratio of dispersion energies $\varepsilon_2/\varepsilon_1$ for both MD and DGT. The predictions from the computer experiments and the theory agree qualitatively very well, but are shifted significantly. The interfacial thickness from DGT is systematically lower than that from the computer experiments. This could be caused by fluctuations that are present in MD but not in DGT [1,5,63], but it could also be caused by differences between the PeTS EOS and the LJTS force field. The latter hypothesis is supported by the fact that in a recent study no such differences were observed for the LJ fluid [30].

On the average the DGT underestimates the MD interfacial thickness by approximately -15% , which is in line with results reported earlier for the corresponding pure substances [63] as well as for selected LJTS mixtures in the entire composition range [5].

Again, a symmetric behavior is found for $L_{10}^{90}(\varepsilon_2/\varepsilon_1, \xi)$. Going from corner A to corner B, the interfacial thickness increases steadily. This is in line with the decay of the surface tension, since broader and smoother density profiles result in a lower surface tension. The interfacial thickness is almost twice as high in corner B as in corner A.

The comparison of Figs. 4, 6–10 shows that all investigated bulk and interfacial properties exhibit a regular behavior when plotted as a function of $\varepsilon_2/\varepsilon_1$ and ξ . For all properties, a symmetry is found. It is shown in the Supplemental Material [112] that this symmetry is likewise observed for the vapor pressure and vapor phase composition at constant temperature and liquid phase composition. The symmetry is also found in the matrix diagram of the density profiles in Fig. 6. This interesting regularity can be explained by a conformal solution theory, as shown in the following section.

IV. CONFORMAL SOLUTION THEORY AT FLUID INTERFACES

A. Modeling the regularity of VLE and interfacial properties

The regularity of the properties of the studied binary LJTS mixtures (see previous section) can be explained with a CST of the liquid phase. The regularity is thereby put into

direct relation with the underlying molecular interactions. The employed CST is adopted from the literature and therefore only outlined here. For brevity, a mixture n is defined by its coordinates in the ξ , $\varepsilon_2/\varepsilon_1$ plane as

$$\underline{a}_n = (\xi_n, (\varepsilon_2/\varepsilon_1)_n). \quad (14)$$

Our starting hypothesis is that the observed regularity is due to the mean dispersive interactions in the liquid phase. To validate this assumption, the configurational contribution of the internal energy u'_{config} of the saturated liquid phase is studied, where the total internal energy u' is the sum of the kinetic energy contribution u'_{kin} and the configurational contribution u'_{config} . For a pairwise additive intermolecular potential v , the configurational internal energy for a given point in the configurational space $\underline{r}$ is $u'_{\text{config}}(\underline{r}) = \sum_{k=1}^N \sum_{l>k}^N v(r_{kl})$, where N is the number of particles and r_{kl} is the distance between two particles k and l . The configurational internal energy u'_{config} of a binary mixture can be calculated from rigorous statistical mechanics from the pair potential v and the radial distribution function (RDF) $g(r)$ [50,87,105]:

$$\begin{aligned} u'_{\text{config}} &= \frac{U'_{\text{config}}}{N} \\ &= \frac{1}{2} \rho' \sum_{i=1}^2 \sum_{j=1}^2 x'_i x'_j \int_0^\infty g_{ij}(r) v_{ij}(r) r^2 4\pi dr, \end{aligned} \quad (15)$$

where ρ' is the total number density and x'_i is the mole fraction of component i , N is the total number of particles, g_{ij} is the radial distribution function between two components i and j , and v_{ij} is the pair potential energy. To compute and evaluate u'_{config} for a given mixture $\underline{a}_n$ at given $T = 0.77 \varepsilon k_B^{-1}$ and $x'_2 = 0.05 \text{ mol mol}^{-1}$, the CST of Leland and coworkers [52,53,106] is applied here, which goes back to the original work of van der Waals (see [50,107]) and Longuet-Higgins [51]. The CST of Leland and coworkers was developed to provide a statistical-mechanical framework to compute excess thermodynamic functions of mixing from the intermolecular potentials and the radial distribution functions of the pure components (see [51,52,108]). The properties of the studied mixture are thereby approximated by those of a hypothetical pure fluid, indicated with the index $_{00}$.

Using the assumptions of the conformal solution theory [52,87] as summarized in Appendix A, Eq. (15) simplifies to

$$\begin{aligned} u'_{\text{config}} &= u'_{\text{config},00} = \frac{1}{2} \rho' \sum_{i=1}^2 \sum_{j=1}^2 x'_i x'_j \varepsilon_{ij} \sigma_{ij}^3 \\ &\quad \times \int_0^\infty g_{00}(\tilde{r}) v_{00}(\tilde{r}) \tilde{r}^2 4\pi d\tilde{r}. \end{aligned} \quad (16)$$

By identifying

$$\sum_{i=1}^2 \sum_{j=1}^2 x'_i x'_j \varepsilon_{ij} \sigma_{ij}^3 = \varepsilon_{00} \sigma_{00}^3, \quad (17)$$

Eq. (16) can then be written as

$$u'_{\text{config},00} = \varepsilon_{00} \sigma_{00}^3 \cdot \frac{1}{2} \rho' \int_0^\infty g_{00}(\tilde{r}) v_{00}(\tilde{r}) \tilde{r}^2 4\pi d\tilde{r}. \quad (18)$$

Equation (17) is the well-known first mixing rule of the van der Waals one-fluid theory, which is also used for modeling LJTS mixtures with the PeTS EOS [5]. Since $\sigma_{ij} = \sigma_1 = 1$ holds for the entire present paper, a second mixing rule is obsolete here. The LJTS potential of the reference component 1 is used in Eq. (18), i.e., $v_{00} = v_{\text{LJTS}}$.

As the dependency of ρ' on ξ or $\varepsilon_2/\varepsilon_1$ can be neglected here in a good approximation, only the first term $\varepsilon_{00} \sigma_{00}^3$ in Eq. (18) depends on the mixture $\underline{a}_n$. The resulting configurational internal energy u'_{config} depends evidently directly on the chosen combination rule. In accordance with the MD, EOS, and DGT calculations, the modified Lorentz-Berthelot combination rule [see Eq. (3)] was also employed for the CST.

A correlation for the radial distribution function of the Lennard-Jones fluid $g_{00} = g_{\text{LJ}}$ was adopted from Morsali *et al.* [109]. They propose an empirical correlation of the Lennard-Jones RDF as a function of the temperature and the density $g_{\text{LJ}} = g_{\text{LJ}}(\tilde{r}, T, \rho)$. Morsali *et al.* developed an RDF correlation for the full Lennard-Jones fluid [109], whereas the present paper investigates the Lennard-Jones truncated and shifted fluid. This is incorporated by employing a corresponding state principle, i.e., the Lennard-Jones RDF from Morsali *et al.* [109] was calculated at the same reduced temperature and density with respect to its critical quantity, i.e., $T_{\text{red}} = T^{\text{LJ}}/T_c^{\text{LJ}} = T^{\text{LJTS}}/T_c^{\text{LJTS}}$ and $\rho_{\text{red}} = \rho^{\text{LJ}}/\rho_c^{\text{LJ}} = \rho^{\text{LJTS}}/\rho_c^{\text{LJTS}}$. The critical parameters were adopted from Vrabec *et al.* [110] and Lotfi *et al.* [66] for the LJTS and LJ fluid, respectively. The influence of the potential truncation on the RDF is therefore neglected. Morsali *et al.* [109] compared results from their RDF with a large number of computer experiment data and found excellent agreement. A comparison of u'_{config} obtained from the PeTS EOS and the outlined CST is given in the Supplemental Material [112]. They agree well; the absolute average deviation is 2%.

In summary, Eq. (18) enables the computation of the configurational internal energy of binary LJTS mixtures $u'_{\text{config}}(\underline{a})$ from CST, using only the RDF of the pure LJTS fluid $g_{\text{LJTS}}(\tilde{r}, T, \rho)$ and the potential function $v_{\text{LJTS}}(\tilde{r})$. $u'_{\text{config}}(\underline{a})$ is used here to characterize the mean interactions in the saturated liquid phase and subsequently put these in relation to the regularity of interfacial properties.

B. Evaluation of the CST model

The configurational internal energy u'_{config} at $T = 0.77 \varepsilon k_B^{-1}$ and $x'_2 = 0.05 \text{ mol mol}^{-1}$, computed by Eq. (18), is shown in Fig. 11 as a function of ξ and $\varepsilon_2/\varepsilon_1$ for all 90 investigated LJTS mixtures. Starting in corner A, the absolute value of the configurational internal energy $|u'_{\text{config}}|$, and thereby also the magnitude of the mean dispersive interactions, steadily decreases with decreasing ξ and decreasing $\varepsilon_2/\varepsilon_1$ towards corner B, which is a direct result of the molecular interactions. The internal energy of the liquid phase $u'_{\text{config}}(\varepsilon_2/\varepsilon_1, \xi)$ obeys the same regular behavior as the bulk and interfacial properties (see Figs. 4, 5, and 7–10), i.e., radially shaped traces for $u'_{\text{config}} = \text{const.}$ are found in the $\varepsilon_2/\varepsilon_1$, ξ plane.

According to the discussion of Eq. (18), the configurational internal energy of a binary mixture u'_{config} at a given temperature and composition depends on the mixture type only via the term $\varepsilon_{00} \sigma_{00}^3$, that is defined by Eq. (17). Both the integral

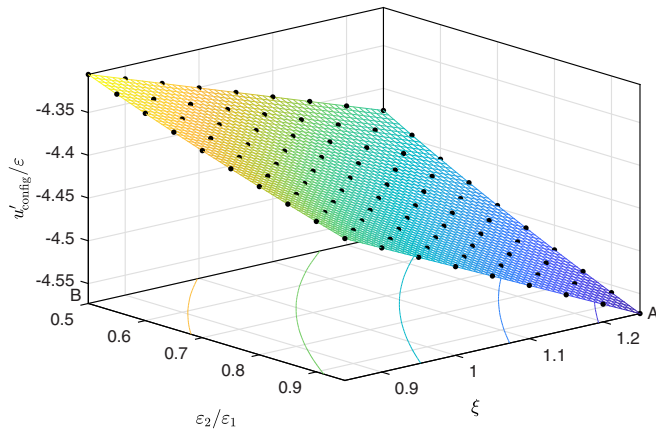


FIG. 11. Configurational internal energy of the saturated liquid phase u'_{config} calculated from the conformal solution theory Eq. (18) as a function of the binary interaction parameter ξ and the ratio of the dispersion energies $\varepsilon_2/\varepsilon_1$ at $x'_2 = 0.05 \text{ mol mol}^{-1}$ and $T = 0.77 \varepsilon k_B^{-1}$. The surface is a linear interpolation of the data points. The color of the surface is coded by its height position.

and the factor $\frac{1}{2}\rho'$ in Eq. (18) can be merged to a constant I at a given temperature and composition. Introducing $\zeta = \varepsilon_2/\varepsilon_1$, and employing the modified Berthelot combination rule, Eq. (18) can be written as

$$\begin{aligned} \frac{u'_{\text{config}}}{I} &= \sum_{i=1}^2 \sum_{j=1}^2 x'_i x'_j \varepsilon_{ij} \sigma_{ij}^3 \\ &= x_1'^2 \varepsilon_1 + 2x'_1 x'_2 \varepsilon_1 \xi \sqrt{\zeta} + x_2'^2 \varepsilon_1 \zeta. \end{aligned} \quad (19)$$

The functional form of $u'_{\text{config}}(\xi, \zeta)$ described by Eq. (19) yields the regularity with the approximatively radial traces of $u'_{\text{config}} = \text{const.}$ in the $\varepsilon_2/\varepsilon_1, \xi$ plane, as depicted in Fig. 11. Equation (19) indicates that the regular traces that were observed in Figs. 4, 5, and 7–10 are not strictly radial but obey a more complicated law.

In our case, x'_1, x'_2 , and ε_1 are constant and the last term in Eq. (19) is small, as x'_2 is small. Hence, the traces depicted in Fig. 11 as well as Figs. 4, 5, and 7–10 are basically curves in which $\xi\sqrt{\zeta}$ are constant. They only appear to be approximatively radial in the plots used here, due to the investigated $\varepsilon_2/\varepsilon_1, \xi$ range.

The regular behavior found in $u'_{\text{config}}(\varepsilon_2/\varepsilon_1, \xi)$ is the same regular behavior as obtained for the bulk and interfacial properties (see Figs. 4–10). Hence, the observed regularity (for both bulk and interfacial properties) is a consequence of the employed mixing and combination rule in DGT + EOS and the combination rule in MD. However, the regularity and the shape of the traces evidently depend on the composition [see Eq. (19)]. The results from this paper indicate that the van der Waals one-fluid theory mixing rule used in the PeTS EOS [5,48] yields an excellent description of molecular simulation results for both bulk and interfacial mixture properties. The fact that the bulk and interfacial properties in the VLE are dominated by the liquid phase interactions and can be described by the CST can be exploited to find simple correlations of all studied properties. The hypothesis is here

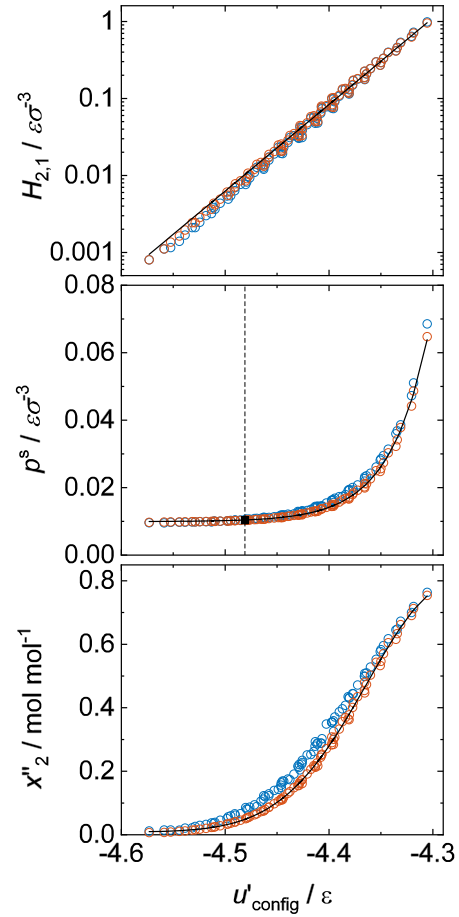


FIG. 12. Results for the conformal solution theory applied to the VLE properties (Henry's law constant $H_{2,1}$, vapor pressure p^s , and vapor phase composition x''_2): The respective VLE properties computed by MD (blue) and the EOS (orange) are shown as a function of the configurational internal energy of the saturated liquid phase u'_{config} as computed by Eq. (18). The black lines indicate the fitted functions (B1)–(B3) (fitted to the DGT results). All results are at $x'_2 = 0.05 \text{ mol mol}^{-1}$ and $T = 0.77 \varepsilon k_B^{-1}$. The dashed line indicates u'_{config} of the high-boiling pure component 1 computed by Eq. (18). The black symbol indicates the vapor pressure of the pure component 1 obtained from the EOS.

that they can be described as simple functions of the internal energy of the liquid phase.

Figures 12 and 13 show that this hypothesis is confirmed by the data from the present paper: bulk and interfacial properties of the 90 LJTS mixtures are plotted, as a function of the corresponding liquid phase configurational internal energy u'_{config} . All properties are at constant temperature and liquid phase composition. The results from both MD and DGT are shown. The investigated VLE bulk properties (Fig. 12) and interfacial properties (Fig. 13) from both MD and DGT are found to be a simple function of each mixture's liquid phase configurational internal energy, which strongly indicates that there is a direct link between them. For all studied properties, a simple relation is found, for both the results obtained from MD and those from EOS + DGT.

Instead of the internal energy from CST also the internal energy from the EOS or the force field could have been

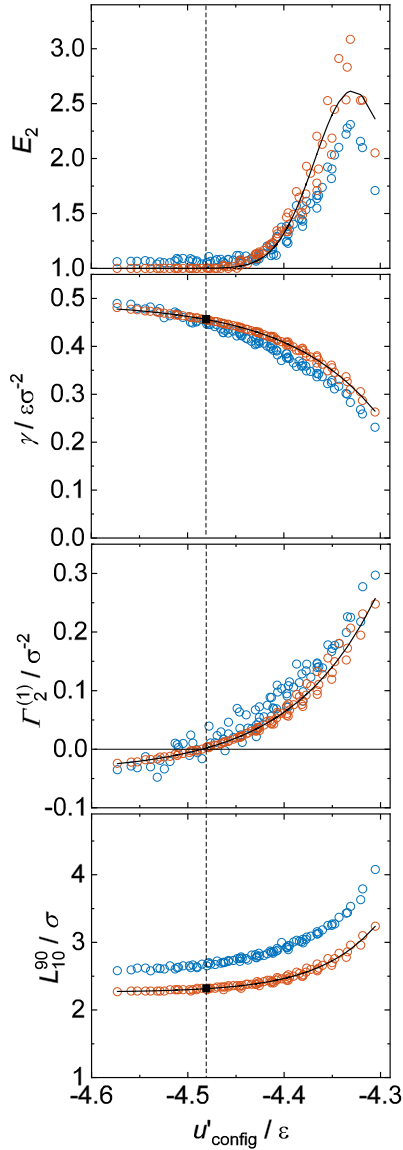


FIG. 13. Results for the conformal solution theory applied to the interfacial properties (enrichment E_2 , relative adsorption $\Gamma_2^{(1)}$, surface tension γ , and interfacial thickness L_{10}^{90}): The respective interfacial properties computed by MD (blue) and DGT (orange) are shown as a function of the configurational internal energy of the saturated liquid phase u'_{config} as computed by Eq. (18). The black lines indicate the fitted functions (B1) and (B2) (fitted to the DGT results). All results are at $x'_2 = 0.05 \text{ mol mol}^{-1}$ and $T = 0.77 \text{ } \epsilon k_B^{-1}$. The dashed line indicates u'_{config} of the high-boiling pure component 1 computed by Eq. (18). Black symbols indicate the values for the pure component 1 obtained from the EOS + DGT.

used for establishing plots like the ones shown in Figs. 12 and 13. The basic findings would have been the same, as the internal energies of the liquid phase determined by the three methods agree very well (see the Supplemental Material [112]). However, using the CST gives further insight on the underlying mechanism, i.e., the fact that the choice of the combination rule is responsible for the regularity behavior [see Eq. (19)].

TABLE II. Parameters for the correlations (B1)–(B3).

	$\hat{Y}$	a_1	a_2	a_3	AAD
^c $H_{2,1}$	$2.32E + 48$			25.87506	9.5%
^a p^s	0.00993	1.05E+49		−0.03718	1.8%
^b x'_2	0.00823	0.77992	−4.28011	0.08256	3.5%
^b E_2	1	1.61673	−4.32865	0.03954	3.9%
^a $\Gamma_2^{(1)}$	−0.03928	3.19E+20		−0.08891	12.8%
^a γ	0.49078	−2.03E+19		−0.09371	0.6%
^a L_{10}^{90}	2.26152	8.42E+30		−0.06044	0.7%

^auses Eq. (B1).

^buses Eq. (B2).

^cuses Eq. (B3).

A fit function $Y = Y(u'_{\text{config}})$ was parametrized to the DGT and EOS results for each bulk and interfacial property $Y = \langle H_{2,1}, p^s, x'_2, E_2, \Gamma_2^{(1)}, \gamma, L_{10}^{90} \rangle$. The mathematical forms and the parameters of the fitted functions are reported in Appendix B. The differences between the DGT and the MD results in Figs. 12 and 13 are due to differences in the data from these methods and not related to the CST (see Figs. 4, 5, and 7–10).

Figure 12 shows the results for the Henry's law constant $H_{2,1}$, the vapor pressure p^s , and the gas phase mole fraction x'_2 for the conditions studied in the present paper as a function of the corresponding liquid phase configurational internal energy. The three properties increase with decreasing mean dispersive interactions in the liquid phase, i.e., with decreasing absolute value of u'_{config} . Figure 13 shows that the same holds for the relative adsorption $\Gamma_2^{(1)}$ and interfacial thickness L_{10}^{90} . The enrichment of the low-boiling component E_2 also generally increases with decreasing mean dispersive interactions, with the exception of the region near corner B. This exception is due to the difference in the number density (see Fig. 5). Only the surface tension γ shows the inverse trend: it decreases with decreasing mean dispersive interactions. In all cases, simple functional relations between the studied properties and u'_{config} are found, which are, however, of different types. The fitted functions for all seven investigated properties agree excellently with the underlying DGT results. Similar fits were obtained for the MD results, but are not shown in Figs. 12 and 13 for clarity. The DGT and EOS results for all properties exhibit only low scattering around the respective fitted curves, i.e., the investigated bulk and interfacial properties are highly correlated with the liquid phase mean interactions. The scattering of the MD results is larger than that of the DGT and EOS results due to the fluctuations from the sampling during the simulation. The absolute average deviation (AAD) from the DGT and EOS results from the corresponding fitted curves were calculated for each property and are reported in Table II.

The scattering of the DGT and EOS results for the vapor pressure p^s and the vapor phase composition x'_2 around the respective fitted curve is fairly constant in the entire range of u'_{config} , i.e., the range of investigated mixtures. In contrast to this, the scattering of the results for the interfacial properties around the respective fitted curves varies with varying u'_{config} . The scattering is significantly lower for mixtures with large

mean dispersive interactions than for those with low mean dispersive interactions (see results for $\Gamma_2^{(1)}$, γ , and L_{10}^{90} in Fig. 13). Furthermore, the scattering is lower for the surface tension and the interfacial thickness than for the relative adsorption and the enrichment, which indicates that the latter are less dominated by the liquid phase interactions but also influenced by the vapor phase interactions and the anisotropic interactions at the interface. This is supported by the corresponding AADs given in Table II.

High absolute values of u'_{config} are found for mixtures with strong mean liquid phase interactions. Equation (19) shows that for the conditions that were studied in the present paper the variation of the mean liquid phase interaction stems mainly from the variation of the unlike dispersive interactions between component 1 and 2. The higher the absolute value of u'_{config} is (left side in the diagrams in Figs. 12 and 13), the stronger is the attraction between the components 1 and 2. This explains why high absolute values of u'_{config} lead to low Henry's law constants $H_{2,1}$ (high solubilities of component 2 in component 1), low vapor pressures, and low concentrations of the component 2 in the gas phase (see Fig. 12). On the other hand, low absolute values of u'_{config} (weak 1-2 attraction) lead to high Henry's law constants $H_{2,1}$ (low solubilities of 2 in 1), high vapor pressures, and high concentrations of the component 2 in the gas phase (see Fig. 12).

For mixtures with large mean dispersive interactions, a variation of u'_{config} (which goes in hand with a variation of $\varepsilon_2/\varepsilon_1$ and ξ) has only little influence on the bulk and interfacial properties. Note that $H_{2,1}$ is plotted on a ln scale. Furthermore, the magnitude of the interfacial properties is small for these mixtures, e.g., small adsorption and enrichment of the low-boiling component.

Equation (19) shows that the unlike dispersive interactions increase both with ξ (which controls the dispersion energy ε_{12}) and with $\zeta = \varepsilon_2/\varepsilon_1$ (which controls the relative volatility). The unlike dispersive interactions are therefore high in corner A and decrease going to corner B (see Figs. 4, 5, and 7–10). This also explains the observed phase behavior (see Fig. 3).

For high mean dispersive interactions (left side in the plot shown in Fig. 13), the interfacial thickness L_{10}^{90} is low. For weaker interactions L_{10}^{90} increases, as it might have been expected. Also the dependence of the surface tension γ on the mean dispersive interactions is expected: it decreases with decreasing mean dispersive interactions.

Furthermore, Figs. 12 and 13 show that the developed CST also works in the limit of the pure component. The vapor pressure, surface tension, and interfacial thickness of the pure component 1 computed from DGT + EOS at $T = 0.77 \varepsilon k_B^{-1}$ are shown as black symbols. Its liquid phase configurational internal energy u'_{config} was computed by Eq. (19). The pure component values agree excellently with mixture values at the same u'_{config} . Hence, the vapor pressure, surface tension, and interfacial thickness of the pure component have the same values as those of mixtures with the same liquid phase mean interactions. Using these observables, a pure component could not be distinguished from these mixtures at the investigated temperature. Also, those mixtures have zero relative adsorption $\Gamma_2^{(1)} = 0$ (see Fig. 13). This strongly supports the picture of the one-fluid theory and the CST applied in this paper.

Interestingly, the dependency of the interfacial properties on the liquid phase mean interactions is not symmetric; i.e., starting at the mixtures with $\Gamma_2^{(1)} = 0$, an increase and decrease of u'_{config} has qualitatively different effects.

The surface tension that is reported here is the number for $x'_2 = 0.05 \text{ mol mol}^{-1}$. As the surface tension of the pure component 1 is the same in all cases, a decrease in the reported surface tension goes along with an increase of the gradient of the surface tension with varying x'_2 . It therefore follows from the Gibbs adsorption equation that the relative adsorption $\Gamma_2^{(1)}$ must increase, which is in line with the results shown in Fig. 13. High numbers for the relative adsorption of component 2 also go along with an enrichment of that component at the interface E_2 [see Fig. 13].

The increase of $\Gamma_2^{(1)}$ and E_2 with decreasing u'_{config} can also be understood based on Eq. (19). A decrease in u'_{config} stems either from a decrease in ξ or from a decrease in $\varepsilon_2/\varepsilon_1$. The picture we invoke in the following is that of a dynamic equilibrium. Assume that a particle of component 2 is on the way of entering the liquid phase coming from the gas phase. The liquid phase contains basically only component 1. The chance that the particle 2 will successfully enter the liquid phase decreases with decreasing mixed unlike dispersive interactions 1-2 in the liquid phase, i.e., with decreasing ξ and $\varepsilon_2/\varepsilon_1$. Furthermore, low values of $\varepsilon_2/\varepsilon_1$ lead to high concentrations of component 2 in the gas phase (see Fig. 12), such that there are many particles of component 2 near the interface, which could in principle enter but face difficulties in doing so. This leads to the enrichment E_2 and the positive relative adsorption $\Gamma_2^{(1)}$. In a more colorful picture, the situation resembles that at the door of a disco: there are many people (particles 2) roaming outside and they are attracted by the disco's neon lights (the interface), but there are only few places available in the disco (in the liquid phase). Hence, there will be a crowd at the entrance (enrichment and adsorption).

V. CONCLUSIONS

The vapor-liquid equilibrium and interfacial properties of binary Lennard-Jones mixtures (Henry's law constant, vapor pressure, composition, surface tension, adsorption, interfacial thickness, and enrichment) were determined for a broad range of mixtures of different types (zeotropic, low-boiling azeotrope, high-boiling azeotrope; subcritical, supercritical) by MD and EOS + DGT. The study was carried out at constant temperature and liquid phase composition. The results from MD and EOS + DGT were found to be in good agreement. The relation of both the VLE bulk properties and the interfacial properties with the underlying molecular interactions was investigated.

All considered bulk and interfacial properties exhibit a regular behavior when they are considered as a function of the variables $\varepsilon_2/\varepsilon_1$ and ξ , which describe the molecular interactions. A theory was developed which explains this behavior based on a conformal solution theory of the molecular interactions. It is based on the assumption that the behavior of the studied systems is dominated by the liquid phase mean interactions and that the liquid phase can be described with a one-fluid theory. The gas phase has only a minor influence. The basic finding is a monovariate relationship between the

studied VLE properties and the mean liquid phase interactions, i.e., the configurational internal energy. This resembles the physical theory of the so-called entropy scaling, which uses a monovariate relationship between transport coefficients and the entropy [111]. For the interfacial and bulk VLE properties, different combinations of $\varepsilon_2/\varepsilon_1$ and ξ may lead to different types of phase behavior, but when the internal energy of the liquid phase is the same the value of the studied properties is the same. The theory also works in the limit of the pure component, such that mixtures with the same liquid phase mean interactions as a pure component have the same vapor pressure, surface tension, and interfacial thickness as that pure component—and zero relative adsorption. The theory also enables predictions outside the range of the parameters $\varepsilon_2/\varepsilon_1$ and ξ that was studied in the present paper.

The interfacial enrichment, which is assumed to have an important influence on the mass transfer through interfaces, is found to be particularly high for Lennard-Jones mixtures that have low numbers for $\varepsilon_2/\varepsilon_1$ and for ξ . Furthermore, the enrichment exhibits a maximum for mixtures with $\Delta\rho_2 = \rho'_2 - \rho''_2 = 0$, which forces all adsorption at the interface into an enrichment. Both large enrichment and large relative adsorption of the low-boiling component are found for mixtures with relatively low mean interactions in the liquid phase, which also goes in hand with low solubilities, i.e., wide-boiling mixtures that tend to form low-boiling azeotropes. Such mixtures also tend to show liquid-liquid phase splits. Systems with liquid-liquid equilibria were, however, not investigated here as this would have overloaded the study. It would be interesting to extend the study to such systems in future work.

As only data for constant temperature and liquid phase composition were taken in the present work, it would be interesting to extend the study to other temperatures and compositions and test if the monovariate relationship established in this work also holds for those dimensions.

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APPENDIX A: ASSUMPTIONS MADE IN THE CONFORMAL SOLUTION THEORY

The main assumptions of the employed conformal solution theory [see Eqs. (15)–(18)] are summarized in the following. In Eq. (15) $4\pi\rho'g(r)dr = n'(r)dr$ can be identified [105] as

the mean number of particles n' in a range between r and $r + dr$. The configurational internal energy u'_{config} is obtained by integrating $n'(r)v(r)$ over all r ranges and weighted by the respective mole fraction; the factor 1/2 ensures that each pair interaction is only counted once. In general the three radial distribution functions g_{11} , g_{12} , and g_{22} are functions of the type of both components (ε , σ), the composition, the temperature, the density, and the distance r between two particles [50,113–115], i.e., $g_{ij} = g_{ij}(\varepsilon_{ij}, \sigma_{ij}, x, T, \rho, r)$. It is known that the RDF is only weakly depending on the composition and the dispersion energies of the components [113,114].

For the one-fluid CST, the properties of a mixture are approximated by those of a hypothetical pure fluid. The molecular interactions of that hypothetical fluid are to be *conformal* to those of the pure components that constitute the mixture, i.e., their pair potentials v_{ij} must be described [87] by the same mathematical function $v_{ij} = \varepsilon_{ij} v(r/\sigma_{ij})$. The hypothetical pure fluid—in our case a spherical Lennard-Jones pair potential—is then characterized by the two interaction parameters σ_{00} and ε_{00} and a single radial distribution function $g_{00} = g_{00}(\tilde{r}, T, \rho)$ [50,52]. The central assumption in the “one-fluid” CST is that the radial distribution functions $g_{ij}(r)$ scale with the respective size parameter σ_{ij} , i.e.,

$$g_{ij}(r/\sigma_{ij}) = g_{00}(\tilde{r}/\sigma_{00}), \quad (\text{A1})$$

which includes a coordinate transformation [87] $r \rightarrow \tilde{r}$. Thereby, the internal energy of the liquid phase of a binary mixture can be written as Eq. (16).

APPENDIX B: FITTED FUNCTIONS FOR BULK AND INTERFACIAL PROPERTIES IN CST

For each of the seven considered properties $Y = \langle H_{2,1}, p^s, x_2'', E_2, \Gamma_2^{(1)}, \gamma, L_{10}^{90} \rangle$, a simple correlation function was parametrized to describe $Y = Y(u'_{\text{config}})$. The DGT results were used for this fit since they do not exhibit stochastic scattering as the MD results do. Three function types were used:

$$Y/[Y] = \hat{Y} + a_1 \exp\left(\frac{u'_{\text{config}}/\varepsilon - a_2}{a_3}\right), \quad (\text{B1})$$

$$Y/[Y] = \hat{Y} + a_1 \exp\left[-0.5\left(\frac{u'_{\text{config}}/\varepsilon - a_2}{a_3}\right)^2\right], \quad (\text{B2})$$

$$Y/[Y] = \hat{Y} \exp(a_3 u'_{\text{config}}/\varepsilon), \quad (\text{B3})$$

where $\hat{Y}$ and a_i are fitting parameters. $[Y]$ indicates the corresponding units of Y as $[Y] = \langle \varepsilon\sigma^{-3}, \varepsilon\sigma^{-3}, \text{mol mol}^{-1}, 1, \sigma^{-2}, \varepsilon\sigma^{-2}, \sigma \rangle$. The obtained numeric values for $\hat{Y}$ and a_i are summarized in Table II. Equation (B1) was used for correlating p^s , $\Gamma_2^{(1)}$, γ , L_{10}^{90} , Eq. (B2) for x_2'' , E_2 , and Eq. (B3) for correlating $H_{2,1}$. The AADs between the fitted curves and the DGT results are also given in Table II.

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