Interfacial Properties of Binary Lennard-Jones Mixtures by Molecular Simulation and Density Gradient Theory

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A systematic study of interfacial properties of binary mixtures of simple fluids was carried out by molecular dynamics (MD) simulation and density gradient theory (DGT). The fluids are described by the Lennard-Jones truncated and shifted potential with truncation radius of 2.5 diameters (LJTS fluid). The following interfacial properties were studied: surface tension, relative adsorption, enrichment, and interfacial thickness. A recently developed equation of state for the LJTS fluid (PeTS EOS) was used as basis for the DGT. Six binary mixtures (components 1 + 2) were studied at a constant temperature, which was chosen such that the high-boiling component 1 is subcritical while the low-boiling component 2 is either subcritical or supercritical. Furthermore, a parameter ξ in the combination rule for the unlike dispersive interaction was varied such that the resulting mixtures showed three types of behavior: high-boiling azeotrope, ideal, and low-boiling azeotrope. The parameters of the LJTS potential, including ξ , were also used in the PeTS EOS without any adjustment. Despite this simple approach, excellent agreement between the results of the PeTS EOS and the MD results for the phase equilibrium and the interfacial properties is observed. Enrichment at the interface is only found for the low-boiling component 2. The enrichment increases with decreasing concentration of component 2 and is favored by high boiling point differences of the pure components 1 and 2 and positive deviations from Raoult's law for the mixture 1 + 2.

Keywords: interfacial properties, Lennard-Jones truncated shifted fluid, Molecular Dynamics, Density Gradient Theory

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I. INTRODUCTION

Properties of fluid interfaces play an important role in many processes, such as distillation and absorption. Experimental data on interfacial properties are in most cases limited to surface tension. For pure substances, numerous experimental data on the surface tension is available, while the data for mixtures is still limited¹⁻³.

Macroscopically, interfaces are treated as two-dimensional objects, while atomistically, it is found that the density changes continuously at the interface. There are presently no experimental methods that yield information on the density profiles in that interfacial region. However, such data can be obtained with molecular simulations based on classical force fields on the one side and equations of state (EOS) combined with density gradient theory (DGT) or density functional theory (DFT) on the other side^{4,5}. In the present work both molecular dynamics (MD) simulation and DGT are used to conduct a systematic study of different types of binary Lennard-Jones mixtures, regarding their vapor-liquid equilibrium (VLE) and interfacial properties.

The monotonous transition of the density from the vapor to the liquid phase at planar interfaces of pure fluids can be described well by a hyperbolic tangent function⁶⁻⁸. Interesting phenomena occur in the interfacial region of mixtures: While the total number density increases monotonously from the bulk vapor to the bulk liquid phase, this does not necessarily hold for all individual component densities. Maxima in the density profiles in the interfacial region have been observed for the low boiling component and can reach values that are several times larger than the larger of the two bulk densities. We refer to this phenomenon as *enrichment*. The enrichment of components at the interface of mixtures is of particular interest as it may affect the mass transfer through the interface. Mixtures that exhibit an interfacial enrichment have been investigated many times in the literature^{3,9-43} by molecular simulations, DGT and DFT, but no systematic evaluation of the phenomenon seems to have been conducted so far regarding the influence of the molecular interaction parameters. As these parameters also determine the type of phase behavior of the mixture⁴⁴ such a study yields also information on the relation between the type of phase behavior and the enrichment.

Significant enrichment has been reported for water-CO₂ mixtures, where the component density of CO₂ were reported to be up to 7 times higher at the interface than

in the bulk phases^{28,33-35}. In water-alcohols mixtures⁴⁵, as well as dimethylformamide-alkanes mixtures⁴⁶, component densities were found which were up to 10 times higher than the highest corresponding component density in the bulk phase. Only minor enrichments are reported for mixtures of alkanes^{26,47}, mixtures of poly(dimethylsiloxane)-acid gases⁴⁸, mixtures of carbon dioxide-sulfur dioxide, mixtures of carbon dioxide-hydrogen sulfide^{49,50}, mixtures of acetone-nitrogen and of acetone-oxygen¹⁶, mixtures of R32 and R290⁴¹. A strong enrichment is reported in many cases where the VLE exhibits a wide-boiling behavior^{3,14,15,28,31,32,36,37,40,51}.

In the present work, a systematic study of interfacial properties of mixtures of Lennard-Jones truncated and shifted (LJTS) fluids was carried out. The PeTS EOS (Perturbed Lennard-Jones truncated and shifted) was used to describe the LJTS fluid within DGT. The PeTS EOS was developed recently in our group and describes the properties of the LJTS fluid well both for stable and metastable fluid states⁵². Also the results for the density profiles in the interfacial region obtained by the PeTS EOS in combination with DGT agree well with those from MD simulations of the LJTS fluid⁷. For this purpose, the influence parameter κ of the DGT was adjusted to results from the surface tension from MD simulations of the LJTS fluid. Remaining differences between the results from MD and those from DGT mainly stem from the fact that fluctuations occur in MD but not in DGT⁷.

In the present work, the PeTS EOS is applied for the first time to mixtures. The extension is based on van der Waals one-fluid theory. The molecular interaction parameters of the LJTS model were simply adopted in the PeTS EOS, including those in the combination rule. The results from both approaches are compared for VLE and interfacial properties of the studied mixtures. The focus of the present study lies on the interfacial adsorption and enrichment and its dependency on the mixture type and composition. Conditions that favor the enrichment are thereby identified.

II. MODELING AND SIMULATION

A. Binary Lennard-Jones truncated shifted mixtures

The Lennard-Jones truncated and shifted (LJTS) potential with a truncation radius of 2.5σ is a simple and computationally efficient intermolecular potential that still gives

a reasonable picture of the behavior of simple fluids. Therefore, it is often used as a model fluid for studies of physical phenomena and the development of methods in molecular simulations^{3,7,53–58}.

The LJTS potential u_{LJTS} used for the molecular simulations in this work is⁵⁹

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

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

with u_{LJ} being the full Lennard-Jones potential, 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 set to 2.5σ throughout the present work. The truncation of the potential has an influence on the fluid's thermodynamic bulk^{60–63} and interfacial properties^{64–69}. Since the interaction potential is truncated at 2.5σ , no long range correction for the forces and the pressure is necessary.

Slightly different critical points are reported in the literature for the LJTS fluid with a cut-off at 2.5σ ^{6,57,61–63,70–74}. We adopt the values of Vrabec et al.⁶ for the critical point of the LJTS fluid: $T_c = 1.0779 \varepsilon k_B^{-1}$; $\rho_c = 0.319 \sigma^{-3}$. The temperature is chosen to be $T = 0.77 \varepsilon k_B^{-1}$ throughout this study, which corresponds approximately $0.7 T_c$. For a discussion of the influence of the temperature on vapor-liquid interfacial properties of the pure LJTS fluid, see Ref.⁷.

In the present study binary LJTS mixtures were investigated. The high boiling component (i.e. the component with the higher boiling point) is labeled with "1" and the low boiling component (the component with the lower boiling point) with "2". The size parameter of both components is the same in all mixtures, i.e. $\sigma_1 = \sigma_2 = \sigma$. Also the mass of both components is the same. For component 1 $\varepsilon_1 = 1$ and $\sigma_1 = 1$ in all mixtures. The low boiling character of the component 2 is obtained by decreasing the dispersion energy with respect to component 1. Two different low boiling components are investigated: $\varepsilon_2/\varepsilon_1 = 0.9$ and $\varepsilon_2/\varepsilon_1 = 0.5$. The resulting vapor pressure curves are shown in Fig. 1 [Fig. 1 close here]. They were calculated with the PeTS EOS, which has been shown to reproduce the LJTS vapor-liquid equilibrium very well⁵². The temperature for which the simulations of the present work were carried out is constant and indicated in Fig. 1 by a vertical dashed

line. For that temperature, the component 2 with $\varepsilon_2/\varepsilon_1 = 0.9$ is subcritical (dashed line) while the component 2 with $\varepsilon_2/\varepsilon_1 = 0.5$ is supercritical (dotted line).

For modeling LJTS mixtures, the modified Lorentz-Berthelot combination rules are employed^{75,76}:

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

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

where the indices 1 and 2 indicate the interaction of two particles of the same component and the double index 12 the cross interaction between different components. The binary interaction parameter ξ_{12} is often adjusted to VLE data of the binary mixture and found to be state-independent in many cases⁷⁷. The goal of the present work is to carry out a systematic study of the influence of the molecular interactions on the interfacial properties. Therefore, the binary interaction parameter was varied: $\xi_{12} = 1, 1.2$ and 0.85 .

These choices result in six binary LJTS mixtures that were investigated in the present work. They are summarized in Fig. 2 [Fig. 2 close here] using sketches of the phase diagrams at the studied temperature. In three of the mixtures, component 2 is subcritical, in the three others, it is supercritical, resulting in a critical point of the mixture. This depends on the choice of $\varepsilon_2/\varepsilon_1$. The parameter ξ_{12} is used to control the deviations from Raoult's law. For $\xi_{12} = 1$ the mixture is almost ideal, the value of $\xi_{12} = 1.2$ causes negative deviation from Raoult's law and $\xi_{12} = 0.85$ causes positive deviation from Raoult's law. The six systems are labeled A to F. For the subcritical systems, this leads to a low-boiling azeotrope and a high-boiling azeotrope, respectively.

Throughout the present work, all physical properties are reported referring to the Lennard-Jones potential parameters of the high boiling component ε_1, σ_1 and the molecular mass M , as well as the Boltzmann constant k_B .

B. Molecular simulations

In the MD simulations carried out in the present work, systems in the canonical ensemble were studied with $N = 16,000$ particles where the vapor and liquid phase coexist with each other in direct contact. By employing the standard periodic boundary conditions, two vapor-liquid interfaces which are oriented perpendicular to the z -axis exist in the simulation box.

The elongation of the simulation box normal to the interface was 80σ and the thickness of the liquid film in the center of the simulation box was 40σ to avoid finite size effects⁶⁴. The elongation in the directions parallel to the interface was at least 20σ . The equilibration was executed for 2,500,000 time steps. For the initialization, the bulk phase compositions were estimated with the PeTS EOS. The production was conducted for 7,500,000 time steps to reduce statistical uncertainties. Density and pressure profiles were calculated in block averages of 500,000 time steps during the production phase, resulting in 15 sampling points for each state point. The statistical error was estimated to be twice the standard deviation of all block averages.

The saturated densities ρ' and ρ'' , the vapor pressure p , and the saturated vapor and liquid phase composition x'_i and x''_i were calculated as an average over the respective phases excluding the area close to the interface, i.e. the area 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). 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. The equation of motion was solved by a leapfrog integrator⁷⁸ with a time step of $\Delta t = 0.001\sigma\sqrt{M/\varepsilon}$. The molecular simulations were performed with the MD code *ls1 mardyn*⁷⁹.

The interfacial tension was computed from the deviation between the normal and the tangential diagonal components of the overall pressure tensor^{80,81}, i.e. by the mechanical route

$$\gamma = \frac{1}{2} \int_{-\infty}^{\infty} (p_{\text{N}} - p_{\text{T}}) \, dz. \quad (5)$$

The normal pressure p_{N} is given by the z -component of the diagonal of the pressure tensor, and the tangential pressure p_{T} was 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 area of the cross section of the simulation volume normal to the z -axis.

C. Extending the PeTS EOS to mixtures

The perturbed truncated and shifted (PeTS) EOS was developed to model the thermodynamic properties of the LJTS fluid⁵². It is based on the perturbation theory of Barker and Henderson⁸², 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 a perturbation a_{pert} contribution due to dispersion, i.e.

$$a = a_{\text{id}} + a_{\text{hs}} + a_{\text{pert}}. \quad (6)$$

The perturbation contribution is modeled as a sum of first- and second-order contributions, i.e. $a_{\text{pert}} = a_1 + a_2$. In analogy to the approach of Gross and Sadowski^{52,83} these are developed in a Taylor series as functions of the packing fraction η . The PeTS EOS was fitted to vapor-liquid equilibrium simulation data of the LJTS fluid and describes the vapor pressure and the saturated densities well⁵².

The PeTS EOS was extended in the present work to binary mixtures based on the van der Waals one-fluid theory⁸⁴, which is known to perform well as long as the size parameters σ_1 and σ_2 of both components are similar^{85–87}.

The free energy of the hard sphere fluid mixtures is^{83,88,89}

$$a_{\text{hs}}/T = \zeta_0^{-1} \left(\frac{3\zeta_1\zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right) \ln(1-\zeta_3) \right) \quad (7)$$

where ζ_n is defined as

$$\zeta_n = \frac{\pi}{6} \rho \sum_{i=1}^2 x_i d_i^n \quad \text{with } n = 0, 1, 2, 3 \quad (8)$$

In Eq. (8) ρ is the total density of the mixture, x_i is the mole fraction of the component i and d_i the temperature dependent effective hard-sphere diameter of component i . Considering that the packing fraction is $\eta = \zeta_3$, the total density of the mixture can be calculated from

$$\rho = \frac{6}{\pi} \eta \left(\sum_{i=1}^2 x_i d_i^3 \right)^{-1}. \quad (9)$$

The temperature dependent diameter d_i is calculated according^{82,90} to:

$$d_i = \sigma_i (1 - \tilde{c}_1 \exp(-\tilde{c}_2 \varepsilon_i)), \quad (10)$$

where $\tilde{c}_1$ and $\tilde{c}_2$ are universal constants of the pure component PeTS EOS⁵². The first and second order dispersion term are given by⁸³

$$a_1/T = -2\pi\rho \sum_{k=0}^6 \tilde{a}_k \eta^k \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j (\varepsilon_{ij}/T) \sigma_{ij}^3 \quad (11)$$

$$a_2/T = -\pi\rho \left(1 + \frac{8\eta - 2\eta^2}{(1-\eta)^2}\right)^{-1} \sum_{k=0}^6 \tilde{b}_k \eta^k \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j (\varepsilon_{ij}/T)^2 \sigma_{ij}^3. \quad (12)$$

In the series expansion in η (first sum in both terms) $\tilde{a}_k$ and $\tilde{b}_k$ are also universal constants of the pure component PeTS EOS⁵². The numeric values of the constants $\tilde{c}_1$, $\tilde{c}_2$, $\tilde{a}_k$ and $\tilde{b}_k$ were adjusted to VLE data of the pure LJTS fluid; for details and the numeric values of all constants $\tilde{c}_1$, $\tilde{c}_2$, $\tilde{a}_k$ and $\tilde{b}_k$ we refer the reader to Heier et al.⁵². The equations are presented here for binary mixtures, but in a way that the extension to multicomponent mixtures is straightforward. For a comprehensive description of the implementation of the equations and derivatives see Gross and Sadowski⁸³.

For the calculation of the cross interaction parameters σ_{ij} and ε_{ij} in Eq. (11)-(12) the modified combination rules of Lorentz and Berthelot were used – exactly in the same way as they were used in the molecular simulations. I.e. Eq. (3) and (4) also apply for the PeTS EOS.

D. Density gradient theory

Density gradient theory^{91,92} (DGT) is a widely used framework for calculating surface tensions for pure substances^{93–95} and mixtures^{45,49,96–101}. To model fluid interfaces, density gradient theory only requires a model of the free energy of the bulk fluid and information on the so-called influence parameter κ that describes the influence of the density gradient on the free energy. For a comprehensive introduction into DGT we refer the reader to^{4,93,102}.

In density gradient theory the free energy of the heterogeneous system is expanded in a Taylor series in the derivatives of the component 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. For a planar interface of a binary mixture the free energy density can thereby be written as:

$$a[\rho] = a_0(\rho) + \sum_{i=1}^2 \sum_{j=1}^2 \frac{1}{2} \kappa_{ij} \nabla \rho_i \cdot \nabla \rho_j \quad (13)$$

where a_0 is the free energy density of the homogeneous system at the local composition and $\boldsymbol{\rho}$ the vector of number neglectable densities of the components and $\nabla \boldsymbol{\rho}$ the vector of the corresponding gradients. κ_{ij} are the influence parameters, for the pure substances (if $i = j$) and the cross interaction (if $i \neq j$).

The influence parameter is in general density and temperature dependent^{4,94,103}. However, it is often assumed that $\partial \kappa_{ij} / \partial \rho = 0$, see for example^{3,7,14,27,45}. It was shown by Heier et al.⁵² that the temperature dependence of the influence parameter is negligible for the LJTS fluid⁵². The influence parameter for the PeTS EOS was fitted to surface tension data between the triple and critical point from molecular simulation in a previous work⁵². It was found to be constant at

$$\frac{\kappa_{\text{PeTS}}}{\sigma^5 \varepsilon} = 2.7334 \quad (14)$$

within the error bars of the molecular simulations results⁵². Most authors use a geometric combination rule for the cross interaction influence parameters^{95,97}:

$$\kappa_{12} = \sqrt{\kappa_1 \kappa_2}. \quad (15)$$

For mixtures that have a complex phase behavior, sometimes an additional adjustable binary parameter is introduced^{28,104}. This was not done in the present work, i.e. κ_{12} was taken from Eq. (15). As only pure component interfacial data was used for the adjustment of the influence parameter of the PeTS EOS, the results for the interfacial properties of mixtures from DGT are predictions.

To obtain the equilibrium density profiles $\rho_i(z)$ for the components $i = 1, 2$ in the interfacial region, Eq. (13) has to be applied to that region and minimized. For solving the DGT equation for both components in the interfacial domain, the stabilized DGT algorithm proposed by Mu et al.⁹⁶ was applied, as it is known to be numerically robust. Other algorithms require selecting a reference component, which is known to have numerical pitfalls¹⁰⁵. The domain length is in all cases set to 20σ with a spatial discretization of 0.02σ .

The surface tension γ is calculated from

$$\gamma = \int \sum_{i=1}^2 \sum_{j=1}^2 \kappa_{ij} \nabla \rho_i \nabla \rho_j \, dz. \quad (16)$$

The PeTS EOS for the description of LJTS mixtures, is employed for calculating the free energy in Eq. (13). The results obtained by DGT in combination with the PeTS EOS are referred to in the following as "results from DGT" for brevity.

E. Density profiles, interfacial adsorption, -enrichment and -thickness

The MD simulation as well as calculations with the DGT yield the component density profiles $\rho_i(z)$ of both components $i = 1, 2$ respectively. On the basis of these density profiles, the relative adsorption defined by Gibbs¹⁰⁶ can be computed by the symmetric interface segregation according to refs.^{42,107}

$$\Gamma_i^{(j)} = -(\rho'_i - \rho''_i) \int_{-\infty}^{\infty} \left[\frac{\rho_j(y) - \rho'_j}{\rho'_j - \rho''_j} - \frac{\rho_i(y) - \rho'_i}{\rho'_i - \rho''_i} \right] dz \quad \text{with } i, j = 1, 2 \text{ and } i \neq j, \quad (17)$$

where ρ'_i , ρ''_i and ρ'_j , ρ''_j are the component densities at saturation in the bulk liquid and bulk vapor phase, respectively. $\Gamma_i^{(j)}$ is the relative surface adsorption of component i at component j .

Another way to characterize the interfacial excess is the interfacial enrichment E_i , which was introduced in ref.^{3,14} as the ratio between the maximum local density of component i in the interfacial region and the larger of the component densities of i in the two bulk phases:

$$E_i = \frac{\max(\rho_i(z))}{\max(\rho'_i, \rho''_i)} \quad \text{with } i = 1, 2 \quad (18)$$

By definition, the enrichment assumes values equal to or larger than unity. The adsorption and the enrichment are linked, but do not contain the same information^{3,14}. Adsorption may occur although no enrichment ($E_i = 1$) is present, e.g. if the two component density profiles are shifted relative to each other. But an enrichment $E_i > 1$ will only be observed if there is also a positive adsorption $\Gamma_i^{(j)} > 0$.

The interfacial thickness is defined here according to Lekner and Henderson¹⁰⁸ using the 90-10% definition L_{10}^{90} that measures 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 densities respectively:

$$\begin{aligned} L_{10}^{90} &= z(\rho_{90}^{\text{tot}}) - z(\rho_{10}^{\text{tot}}) \\ \rho_{10}^{\text{tot}} &= \rho''_{\text{tot}} + 0.1(\rho'_{\text{tot}} - \rho''_{\text{tot}}) \\ \rho_{90}^{\text{tot}} &= \rho''_{\text{tot}} + 0.9(\rho'_{\text{tot}} - \rho''_{\text{tot}}). \end{aligned} \quad (19)$$

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

III. RESULTS AND DISCUSSION

A. Vapor-liquid equilibria

Fig. 3, panels A - F show the binary phase diagrams of the six investigated mixtures, for the studied temperature $T = 0.77 \varepsilon k_B^{-1}$ [Fig. 3 near here]. The numerical results for the phase equilibria of the six studied systems obtained by MD and the PeTS EOS are given in the Supplementary Information. The solid lines are the PeTS EOS and the symbols are the computer experiments. The error bars are only shown where they exceed the symbol size. The left row shows the subcritical (A - C) and the right row the supercritical mixtures (D - F).

The molecular simulation results and those from the PeTS EOS agree generally very well, even though the parameters were simply transferred from the force field to the EOS and no adjustment was made. For mixture C some deviations in the pressure are observed, especially in the vicinity of the low-boiling azeotrope. For in the supercritical mixtures D - F the equation of state overestimates the pressure close the critical point compared to the computer experiment which is, however, a general feature of classical EOS.

The mixtures D and F show particularly wide two phase regions. Table I shows the partition coefficients at infinite dilution

$$K_2^\infty = \lim_{x'_2 \rightarrow 0} \frac{x''_2}{x'_2} \quad (20)$$

that were found from an extrapolation of the results of the PeTS EOS. The numbers of K_2^∞ are high for wide boiling mixtures. For Mixtures D and F high numbers of K_2^∞ are found. For the azeotropic mixture B the number for K_2^∞ is below 1, meaning that the component 2 is enriched in the liquid and not in the vapor phase contrary to all other mixtures that were studied here.

B. Interfacial properties

The vapor-liquid interface was investigated for all VLE state points shown in Fig. 3 by MD and DGT. The state points of the LJTS mixtures are specified in the following by the liquid phase composition x'_2 . The numerical values for the surface tension γ , the surface excess $\Gamma_2^{(1)}$, the enrichment E_2 , and the interfacial thickness L_{10}^{90} for all studied mixtures and

state points are presented in the supplementary material.

1. *Density profiles*

In Fig. 4 and 5 results for density profiles from MD and DGT are compared. Fig. 4 shows results for two state points of the mixture C, Fig. 5 is similar, but for the mixture D. The shown state points are at low concentrations x'_2 .

The density of the high boiling component $\rho_1(z)$ changes monotonously from the vapor to the liquid phase, while the density of the low boiling component $\rho_2(z)$ exhibits a maximum at the interface in all four cases shown in Figure 4 and 5. Overall, the results from MD and DGT are in good agreement. The density maximum is predicted by both MD and DGT, but its height is slightly larger for DGT than for MD. As already discussed by Becker et al.³ and Werth et al.¹⁴ this is due to fluctuations at the interface that are present in MD but not in DGT. Such fluctuations might also be the reason for the slightly shifted position of the density maximum in both interfacial profiles of the mixture C shown in Fig. 4. Also some differences in the interfacial thickness are observed: the MD density profiles are broader than those from DGT in all cases shown in Fig. 4 and 5. This can also be attributed to these fluctuations⁷. Considering the fact that the parameters $\varepsilon_2/\varepsilon_1$ and ξ_{12} of the LJTS force field model were simply adopted in the EOS and no mixture data was used for the adjustment of both methods, the results agree remarkably well. Good agreement was also observed for the other state points of the mixtures C and D as well as for all other studied mixtures (not shown).

Fig. 6 and 7 show the density profiles for the mixtures A - F for all studied state points. Since MD and DGT results agree very well in all cases, only the DGT results are shown here (the corresponding plots for the MD results are presented in the supplementary material).

An enrichment of the low boiling component, i.e. a maximum in the corresponding density profile, is observed not only in the mixtures C and D but also in the mixtures E and F (cf. Fig. 7). No enrichment of the low boiling component is found in the quasi ideal mixture A and in mixture B that exhibits a high boiling azeotrope (cf. Fig 6). No enrichment of the high boiling component 1 is found in any of the six investigated mixtures.

2. Surface tension, interfacial adsorption and enrichment

Fig. 8 shows the surface tension (top), interfacial adsorption (middle) and enrichment of the low boiling component 2 (bottom) as a function of the liquid phase composition x'_2 for the three investigated subcritical mixtures A, B and C. The surface tension of the pure components 1 and 2 calculated by MD and DGT agree very well, since the influence parameter for the pure LJTS fluid was fitted to such data^{7,52}. The pure low boiling component has a lower surface tension than the high boiling component due to the reduced dispersion energy.

The surface tension of the ideal mixture A decreases linearly with increasing mole fraction x'_2 . The surface tension of mixture B, which exhibits a high boiling azeotrope, has a maximum, which is found close to the azeotropic composition, cf. Fig. 3, middle. The surface tension of Mixture C shows a minimum of the surface tension, again close to the azeotropic composition, cf. Fig. 3, bottom. The results for the surface tension from DGT agree almost always within the error bars with the MD results. This is remarkable as in the model development no data on interfacial properties of mixtures was used.

The relative adsorption $\Gamma_2^{(1)}$ of the low boiling component 2 (cf. Fig. 8, middle) is zero for infinite dilution of component 2. In the ideal mixture A, starting at $x'_2 = 0$, the relative adsorption of component 2 increases linearly with the mole fraction x'_2 , which is in good agreement with the expectations from the Gibbs adsorption equation since the surface tension decreases monotonously. The relative adsorption $\Gamma_2^{(1)}$ of component 2 in mixture B, which has a high-boiling azeotrope, exhibits a minimum. On the contrary, the relative adsorption of component 2 in mixture C, which has a low-boiling azeotrope, exhibits a maximum. The composition at which the relative adsorption $\Gamma_2^{(1)}$ is zero – which also corresponds to the extrema in the surface tension according to the Gibbs adsorption equation – has been called *aneotropic concentration*¹⁰⁹. The component adsorbing at the interface therefore changes from 2 to 1 upon passing through the aneotropic point with increasing x'_2 . No proof has been found yet, that the aneotropic and azeotropic point must coincide⁴¹, nevertheless the aneotropic concentration agrees well with the azeotropic concentration for both mixtures B and C (cf. Fig. 3 and Fig. 8). This has already been reported in the literature for mixtures with a low boiling azeotrope, e.g. ref.^{41–43,110,111}. A further interesting finding is that the curves for the relative adsorption $\Gamma_2^{(1)}(x'_2)$ of the three investigated mixtures have

a common intersection point at approximately $x'_2 = 0.6 \text{ mol mol}^{-1}$. The relative adsorption results from DGT and MD agree within the MD error bars for all three mixture A, B, and C until this intersection point. Beyond this intersection point, the results from MD show an increasing scattering and increasing error bars, which is likely due to the fact that only few particles of component 1 are present.

The enrichment E_2 , cf. Eq. (18), for the three subcritical mixtures A, B, and C is shown as a function of the mole fraction x'_2 in Fig. 8, bottom. A significant enrichment of the low boiling component is only found in the mixture C, i.e. the mixture with the low boiling azeotrope. At the vapor-liquid interface of that mixture, the component density ρ_2 is up to 1.5 times higher than the highest of the bulk component density (the liquid phase in this case). The enrichment E_2 is highest at infinite dilution of the low boiling component and decreases with an increasing mole fraction x'_2 . The DGT results for the enrichment E_2 of the mixture C are higher than those from MD. DGT predicts no enrichment, i.e. $E_2 = 1$ for both mixtures A and B, while the molecular simulations show a slight enrichment in those two mixtures at low mole fractions of component 2 in the liquid phase. This is due to the fact that the fluctuations of the density ρ_2 in the MD results become more important at low concentrations x'_2 . Since the maximum of a fluctuating curve divided by its average value must be larger than one Eq. (18) always predicts an enrichment $E_2 \geq 1$ and this artifact from the fluctuations becomes more important at low concentrations x'_2 . In principle, other definitions of the enrichment could be applied to avoid such problems. But we prefer to keep the simple definition by Eq. 18 as the artifacts mentioned above are generally not important. The enrichment of the low boiling component E_2 converges to one at higher mole fractions x'_2 for all subcritical mixtures A, B, and C.

Fig. 8 shows the predicted surface tension γ (top), interfacial adsorption $\Gamma_2^{(1)}$ (middle) and enrichment of the low boiling component E_2 (bottom) for the mixtures D, E, and F as a function of the mole fraction of the low boiling component 2 in the liquid phase x'_2 . The surface tension of all three mixtures for which the low boiling component is supercritical decreases almost linearly with x'_2 , except in the vicinity of the critical point, where the surface tension goes to zero. The decay of the surface tension becomes steeper with a decreasing binary interaction parameter ξ_{12} . The results for the surface tension of the mixtures D, E, and F (Fig. 9, top) from DGT agree almost always within the error bars with the MD results, as for the mixtures A, B, and C (cf. Fig. 8, top).

The relative adsorption of the low boiling component $\Gamma_2^{(1)}$ as a function of the mole fraction x'_2 is shown in Fig. 9, middle. Starting at infinite dilution of the low boiling component 2, the relative adsorption $\Gamma_2^{(1)}$ of the low boiling component 2 increases with the mole fraction x'_2 . For mixture F, close to the critical point, i.e. approximately at the composition x'_2 where the surface tension decay changes from a linear decay to a non-linear decay, the relative adsorption exhibits a maximum for all three mixtures and then decreases to zero at the critical point. The steepness of $\Gamma_2^{(1)}$ increases with a decreasing binary interaction parameter ξ_{12} , which goes in line with the decay of the surface tension. This is again consistent with the expectations from the Gibbs adsorption equation. The agreement between the MD and DGT results for the relative adsorption is better in the linear-decay regime of the surface tension than close to the critical point. Close to the critical point only the trends are consistently predicted by both methods.

The enrichment of the low boiling component E_2 , cf. Eq. (18), is shown in Fig. 9, bottom as a function of the mole fraction x'_2 . In the mixture D, the component density ρ_2 is up to 2.1 times higher in the interface than in the bulk liquid phase, cf. Fig. 7. Such values have also been reported in the literature for supercritical systems, e.g. ethanol-CO₂³ and toluene-CO₂¹⁴. The mixture F shows a maximum enrichment of the low boiling component of up to 2.8. The mixture E on the other side has only a slight enrichment of up to 1.3. All three mixtures D, E, and F, for which the low boiling component is supercritical, have a monotonously decreasing enrichment E_2 with increasing mole fraction x'_2 , which goes to one at the critical point. This has already been reported by Becker et al.³ and Werth et al.¹⁴. An interesting fact is that the relative steepness of the surface tension observed for the mixtures D, E, and F seems to correlate with the relative steepness of the interfacial enrichment. Furthermore, the numeric values of the enrichment differs significantly among the investigated mixtures D, E and F, whereas the numeric values of the relative adsorption $\Gamma_2^{(1)}$ lie in the same range for these mixtures (cf. Fig. 9). The agreement between MD and DGT results for the interfacial enrichment is very good for the mixture E, while for the mixtures D and F only the trend of the composition dependency of the enrichment is predicted consistently by both methods.

All studied LJTS mixtures show the highest enrichment E_2 at low concentrations of component 2. The enrichment at infinite dilution E_2^∞ was computed by DGT, as the corresponding numbers are difficult to obtain from molecular simulations due to large statistical

uncertainties if only few particles of component 2 are present. The resulting numeric values of E_2^∞ for the mixtures and conditions studied in the present work are listed in Table I. For the ideal mixture A, E_2^∞ is basically one, i.e. there is almost no enrichment. However, this does not hold in a mathematical sense. A closer inspection of the DGT results for this system shows a slight positive number of 1.001. The high boiling azeotropic mixture B has no enrichment, i.e. $E_2^\infty = 1$ to the last digit. The enrichment of the low boiling component at infinite dilution E_2^∞ from the six investigated LJTS mixtures is plotted as a function of the partition coefficient at infinite dilution K_2^∞ in Fig. 10. For $K_2^\infty > 1$ the enrichment is found to increase fairly linearly with $\ln(K_2^\infty)$.

For the sake of completeness the relative adsorption and enrichment of the high boiling component 1 at the interface are shown in the Appendix B for the three investigated subcritical mixtures. The high boiling component 1 shows no enrichment in the DGT results. The MD results show a slightest enrichment, which is due to the numerical artifact as discussed above.

3. *Interfacial thickness*

Fig. 11 shows the interfacial thickness L_{10}^{90} as a function of the mole fraction of the low boiling component in the liquid phase x'_2 as obtained from the MD and DGT data using Eq. (19). Fig. 11, top shows the results of the interfacial thickness of the mixtures A, B, and C and Fig. 11, bottom of the mixtures D, E, and F.

The interfacial thickness for the ideal mixture A follows a linear trend with increasing x'_2 . The mixture B exhibits a minimum in the interfacial thickness. Mixture C has a maximum in the interfacial thickness. Comparing these findings to the results for the surface tension, shows that wider interfaces of a Lennard-Jones mixture have a lower surface tension, while narrower interfaces have higher surface tension.

The interfacial thickness L_{10}^{90} of the mixtures D, E, and F, where the low boiling component is supercritical, exhibits a pole at the critical point, because the interface becomes infinitely broad.

The density profiles in MD are broader than those from DGT which is attributed to fluctuations at the interface that are present in MD as a dynamical method but not in DGT⁷. Such deviations of results for the interfacial thickness obtained by DGT and MD

have been reported before in the literature^{3,14}. The results obtained in the present work show that the trend of the composition dependency of the interfacial thickness is predicted consistently by both methods. Increasing the interfacial thickness predicted by DGT by about 15% would lead to a good agreement between MD and DGT for all six investigated mixtures.

A more detailed discussion of the density profiles and the relation to the interfacial properties is given in the Appendix C.

IV. CONCLUSIONS

In the present work, interfacial and bulk properties of binary Lennard-Jones truncated and shifted mixtures were examined with molecular simulations and density gradient theory in combination with the PeTS EOS. The cross-interaction influence parameter in DGT is calculated by a geometric mixing rule. Six types of mixtures were investigated – all at the same temperature. Their phase behavior was set by the ratio of the two component’s dispersion energies and the binary cross interaction parameter in the modified Lorentz-Berthelot combination rules.

The agreement of the results from MD and DGT+PeTS for both bulk and interfacial properties is found to be excellent. The DGT results for the surface tension and relative adsorption agree within the MD error bars. Slight deviations between the MD and DGT results for the enrichment are observed, but the trends are consistently predicted from both methods. Significant deviations between MD and DGT are only found for the interfacial thickness, but the trends still agree well between both predictions. These deviations are attributed to surface fluctuations that broaden the interface present in MD but not in DGT⁷.

A significant enrichment of the low boiling component at the interface is found for mixtures where the low boiling component is supercritical or that exhibit a low-boiling azeotrope. The local density of the low boiling component at the interface is found to be up to three times the value in the bulk phase. Enrichment is in all cases only found for the low boiling component. Furthermore, the enrichment is found to decrease monotonously with the mole fraction of the low boiling component in the liquid phase in all investigated mixtures. I.e., the highest enrichment is found at infinite dilution of the low boiling component. The

magnitude of the enrichment is found to be related to the width of the phase boundary. Strong enrichment is therefore favored in mixtures that exhibit a wide boiling phase boundary, which reinforces observations in previous studies^{3,14}. The numeric values of the relative adsorption of the low boiling component are similar in the investigated mixtures, although the enrichment of the low boiling component differs significantly among the mixtures.

Future work will focus on the temperature dependency of the enrichment and the influence of the enrichment on the mass transfer through the interface.

The present work focuses on the influence of dispersive interactions on interfacial properties. Future work could benefit from an extension to H-bonding molecules and polar interactions^{112–115}.

Appendix A: Supplementary material

Supplementary data can be found at [online DOI-link]. All density profiles from molecular simulations and the numerical values for the bulk properties from MD and the PeTS EOS are listed there.

Appendix B: Relative adsorption and enrichment of the high boiling component

Fig. 12 shows the relative adsorption (top) of the high boiling component $\Gamma_1^{(2)}$ and the interfacial enrichment (bottom) of the high boiling component E_1 for the subcritical mixtures A, B, and C.

Appendix C: Detailed discussion of the density profiles

While the density profiles of the mixtures A and B are similar (cf. Fig. 6), the mixtures C, D, E, and F (cf. Fig. 6 and 7) have unique attributes which are discussed in the following. To illustrate these attributes, we use the 'knee on the liquid side of the density profiles' of the high boiling component 1, which is defined as the z -coordinate $z_{1,97}$ where the density $\rho_1(z)$ reaches 97% of the liquid bulk density ρ'_1 :

$$\rho_{1,97}(z_{1,97}) = \rho''_1 + 0.97(\rho'_1 - \rho''_1). \quad (\text{C1})$$

For the subcritical mixtures A (Fig. 6, top) and B (Fig. 6, middle), the density profiles of the low boiling component 2 have a similar composition dependency, while differences in the density profiles of the high boiling component 1 are found. In the ideal mixture A (Fig. 6, top), the knee on the liquid side of the density profiles of the high boiling component $z_{1,97}$ moves slightly monotonously to the right with increasing x'_2 . This results in a slight positive adsorption of the low boiling component with respect to the high boiling component (cf. Fig. 8, middle) and an increasing interfacial thickness with an increasing mole fraction x'_2 (cf. Fig. 11, top).

The high boiling component 1 in mixture B (cf. Fig. 6, middle) behaves differently, i.e. its liquid phase knee $z_{1,97}$ moves first left with increasing mole fraction x'_2 and then back right. The turning point can be estimated to be the azeotropic composition. This results in a minimum in the composition dependency of the interfacial thickness (cf. Fig. 11, top) and a negative adsorption of the low boiling component until the azeotropic composition (cf. Fig. 8, middle).

The mixture C, that exhibits a low boiling azeotrope, shows a completely different interfacial behavior (cf. Fig. 6, bottom) than the mixtures A and B. The density profiles of the low boiling component exhibit a maximum at low mole fractions x'_2 . The z -position of the maximum shifts right with increasing x'_2 , which goes in hand with a significant broadening of the interface (cf. Fig. 11, top). The liquid phase knee $z_{1,97}$ of the high boiling component 1 in mixture C (Fig. 6, bottom) shows the opposite behavior as in the mixture B (Fig. 6, middle), i.e. it moves first right with increasing x'_2 and then left, which is the reason for a positive relative adsorption of the low boiling component 2 (cf. Fig. 8, middle) and a maximum of the composition dependency of the interfacial thickness (cf. Fig. 11, top).

The density profiles of mixture D (cf. Fig. 7) show a strong enrichment of the low boiling component 2, central in the interfacial region. Its maximum position stays at a constant z -position throughout the investigated composition range in contrast to the mixture C. The interfacial thickness in mixture D monotonously increases and the enrichment decreases with increasing mole fraction of the low boiling component in the liquid phase x'_2 , cf. Fig. 11 and 9, respectively.

For the mixture E, the z -position of the enrichment slightly shifts right with increasing x'_2 , similar to mixture C (both have an elevated cross interaction, i.e. $\xi_{12} = 1.2$). The interfacial thickness of mixture E monotonously increases with increasing mole fraction x'_2 , cf. Fig. 11,

bottom. The density profiles of mixture E in Fig. 7 furthermore reveal, that this broadening is dominated by the low boiling component on the vapor side of the interface ($z < 0$), while it is dominated by the high boiling component on the liquid side of the interface ($z > 0$).

While the low boiling component’s bulk liquid densities are higher than the bulk vapor densities in the mixtures D and E, i.e. $\rho'_2 > \rho''_2$ (cf. Fig. 7, top and middle), this inverts for the mixture F (Fig. 7, bottom). The mixture F, which exhibits a particularly wide boiling phase envelope ($K_2^\infty = 87.8$), shows a large enrichment of the low boiling component 2 at the interface. The z -position of that maximum is about one σ left of the center of the interface at low x'_2 and shifts further left with increasing x'_2 . Also in the mixture F the interfacial thickness increases monotonously with increasing x'_2 , cf. Fig. 11, bottom. This broadening is mainly located on the vapor side of the interface ($z < 0$).

The density profiles of the high boiling component show the interesting feature of a common intersection point in all three supercritical mixtures mixtures D, E, and F (cf. Fig. 7). This common intersection point is one of the most noticeable features in the density profiles of the mixtures where the low boiling component is supercritical. This phenomenon has already been reported for pure substance density profiles^{7,116}. In these studies the density at the intersection point was identified as the critical density, which can be attributed to the law of the rectilinear diameter. In the three subcritical mixtures A, B, and C (cf. Fig. 6) no common intersection points of the density profiles are observed. The density ρ_1 at the intersection point of the mixtures D and E are slightly below the corresponding critical density. A detailed investigation of this phenomenon is not in the scope of this work.

ACKNOWLEDGMENTS

The authors gratefully acknowledge funding of the present work by the ERC Advanced Grant ENRICO (grant agreement No. 694807). The simulations were carried out on the ELWE supercomputer at Regional University Computing Center Kaiserslautern (RHRK) under the grant TUKL-MSWS. The present research was conducted under the auspices of the Boltzmann-Zuse Society of Computational Molecular Engineering (BZS). The authors thank Daniel Hoebbel for supporting the simulation work and Walter G. Chapman for his hospitality during the SAFT workshop 2017 and for fruitful discussions.

TABLES & FIGURES

FIG. 1. Vapor pressure curves for the three pure LJTS fluids that were considered in the present study. The temperature for which all simulations of the present work were carried out ($T = 0.77 \varepsilon k_B^{-1}$) is indicated by vertical dotted line. The heavy boiling component 1 is the solid curve. The light boiling components differ in their dispersion energies: dashed line: $\varepsilon_2/\varepsilon_1 = 0.9$, dotted line: $\varepsilon_2/\varepsilon_1 = 0.5$. Critical points are indicated by stars.

FIG. 2. Sketches of the isothermal phase diagrams of the six studied binary mixtures 1 + 2. The different choices of the ratio of the LJTS dispersion energies $\varepsilon_2/\varepsilon_1$ and the binary interaction parameter ξ_{12} lead to different types of phase behavior (A - F).

FIG. 3. Vapor-liquid equilibria of the binary LJTS mixtures A, B, C, D, E, and F at $T = 0.77 \varepsilon k_B^{-1}$. Symbols are MD results and the lines are the PeTS EOS.

FIG. 4. Comparison of the component density profiles in the interface of the binary LJTS mixture C at $x'_2 = 0.28 \text{ mol mol}^{-1}$ (top) and $x'_2 = 0.1 \text{ mol mol}^{-1}$ (bottom). Symbols: MD simulation; lines: DGT + PeTS EOS. Red: component 1 (high boiling); blue component 2 (low boiling).

FIG. 5. Comparison of the component density profiles in the interface of the binary LJTS mixture D at $x'_2 = 0.27 \text{ mol mol}^{-1}$ (top) and $x'_2 = 0.1 \text{ mol mol}^{-1}$ (bottom). Symbols: MD simulation; lines: DGT + PeTS EOS. Red: component 1 (high boiling); blue component 2 (low boiling).

FIG. 6. Density profiles of the binary LJTS mixtures A, B, and C at $T = 0.77 \varepsilon k_B^{-1}$. Results from DGT. Dashed lines: heavy boiling component 1; solid lines: light boiling component 2. The color indicates the liquid phase composition. Triangles indicate the position of the density maximum. Grey points indicate the z -coordinate, where the density of the high boiling component 1 reaches 97% of the bulk value, cf. Eq. (C1).

FIG. 7. Density profiles of the binary LJTS mixtures D, E, and F at $T = 0.77 \varepsilon k_B^{-1}$. Results from DGT. Dashed lines: heavy boiling component 1; solid lines: light boiling component 2. The color indicates the liquid phase composition. Triangles indicate the position of the density maximum. Grey points indicate the z -coordinate, where the density of the high boiling component 1 reaches 97% of the bulk value, cf. Eq. (C1).

FIG. 8. Interfacial tension (top), relative adsorption (middle) and interfacial enrichment of the light boiling component (bottom) of the binary mixtures A, B, and C as a function of the liquid phase composition x'_2 . The temperature is $T = 0.77 \epsilon k_B^{-1}$. Symbols: MD; lines: DGT. Black corresponds to system A, blue to system B and red to system C.

FIG. 9. Interfacial tension (top), relative adsorption (middle) and interfacial enrichment of the light boiling component (bottom) of the binary mixtures D, E, and F as a function of the liquid phase composition x'_2 . The temperature is $T = 0.77 \epsilon k_B^{-1}$. Symbols: MD; lines: DGT. Black corresponds to system D, blue to system E and red to system F.

FIG. 10. Enrichment of the low boiling component 2 at infinite dilution E_2^∞ computed from DGT as a function of the the partition coefficient at infinite dilution K_2^∞ , cf. Eq. (20), for the six investigated mixtures. The temperature is $T = 0.77 \varepsilon k_B^{-1}$. Line: linear fit of the data for mixtures with positive partition coefficients.

FIG. 11. Interfacial thickness of the mixtures A, B, and C (top) and mixtures D, E, and F (bottom) at $T = 0.77 \varepsilon k_B^{-1}$. Symbols: MD; lines: DGT. Black corresponds to systems with $\xi_{12} = 1$; blue to systems with $\xi_{12} = 1.2$ and red to systems with $\xi_{12} = 0.85$.

FIG. 12. Relative adsorption (top) and interfacial enrichment (bottom) of the heavy boiling component of the mixtures A, B, and C as a function of the liquid phase composition x_2' . The temperature is in all cases $T = 0.77 \varepsilon k_B^{-1}$. Symbols: MD; lines: DGT. Black corresponds to system A, blue to system B and red to system C.

TABLE I. Partition coefficient K_2 and interfacial enrichment of light boiling component E_2 at infinite dilution of the light boiling component ($x'_2 \rightarrow 0$) in the six investigated binary mixtures from DGT+PeTS EOS.

system	K_2^∞	E_2^∞
A	1.8	1.00
B	0.2	1.00
C	8.8	1.53
D	22.8	2.39
E	4.8	1.32
F	87.8	2.90

REFERENCES

- ¹“Dortmund data bank,” 2019, www.ddbst.com.
- ²C. Wohlfarth and B. Wohlfarth, *Surface Tension of Pure Liquids and Binary Liquid Mixtures*, Landolt–Börnstein, Numerical Data and Functional Relationships in Science and Technology, Vol. 16 (Springer, 1997).
- ³S. Becker, S. Werth, M. Horsch, K. Langenbach, and H. Hasse, “Interfacial tension and adsorption in the binary system ethanol and carbon dioxide: Experiments, molecular simulation and density gradient theory,” *Fluid Phase Equilibria* **427**, 476 (2016).
- ⁴J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Dover Publications, New York, 1982).
- ⁵R. Evans, *Fundamentals of Inhomogeneous Fluids*, edited by D. Henderson (Marcel Dekker, New York, 1992).
- ⁶J. Vrabec, G. K. Kedia, G. Fuchs, and H. Hasse, “Comprehensive study of the vapour-liquid coexistence of the truncated and shifted Lennard-Jones fluid including planar and spherical interface properties,” *Molecular Physics* **104**, 1509 (2006).
- ⁷S. Stephan, J. Liu, K. Langenbach, W. G. Chapman, and H. Hasse, “Vapor-liquid interface of the Lennard-Jones truncated and shifted fluid: Comparison of molecular simulation, density gradient theory, and density functional theory,” *The Journal of Physical Chemistry C* **122**, 24705–24715 (2018), <https://doi.org/10.1021/acs.jpcc.8b06332>.

- ⁸G. A. Chapela, G. Saville, S. M. Thompson, and J. S. Rowlinson, "Computer simulation of a gas-liquid surface. part 1," *Journal of the Chemical Society, Faraday Transactions 2*: **73**, 1133–1144 (1977).
- ⁹F. J. Martinez-Ruiz and F. J. Blas, "Interfacial properties of binary mixtures of square-well molecules from Monte Carlo simulation," *The Journal of Chemical Physics* **144**, 154705 (2016), <https://doi.org/10.1063/1.4947017>.
- ¹⁰F. J. Blas and L. F. Vega, "Thermodynamic behaviour of homonuclear and heteronuclear Lennard-Jones chains with association sites from simulation and theory," *Molecular Physics* **92**, 135 (1997).
- ¹¹D. J. Lee, M. M. Telo da Gama, and K. E. Gubbins, "The vapour-liquid interface for a Lennard-Jones model of argon-krypton mixtures," *Molecular Physics* **53**, 1113–1130 (1984), <http://dx.doi.org/10.1080/00268978400102891>.
- ¹²D. J. Lee, M. M. Telo da Gama, and K. E. Gubbins, "Adsorption and surface tension reduction at the vapor-liquid interface," *The Journal of Physical Chemistry* **89**, 1514–1519 (1985), <http://dx.doi.org/10.1021/j100254a041>.
- ¹³A. Mejía, J. C. Pmies, D. Duque, H. Segura, and L. F. Vega, "Phase and interface behaviors in type-I and type-V Lennard-Jones mixtures: Theory and simulations," *The Journal of Chemical Physics* **123**, 034505 (2005), <http://dx.doi.org/10.1063/1.1955529>.
- ¹⁴S. Werth, M. Kohns, K. Langenbach, M. Heilig, M. Horsch, and H. Hasse, "Interfacial and bulk properties of vapor-liquid equilibria in the system toluene+hydrogen chloride+carbon dioxide by molecular simulation and density gradient theory+PC-SAFT," *Fluid Phase Equilibria* **427**, 219 (2016).
- ¹⁵J. C. Neyt, A. Wender, V. Lachet, A. Ghoufi, and P. Malfreyt, "Molecular modeling of the liquid-vapor interfaces of a multi-component mixture: Prediction of the coexisting densities and surface tensions at different pressures and gas compositions," *The Journal of Chemical Physics* **139**, 024701 (2013), <https://doi.org/10.1063/1.4811679>.
- ¹⁶S. Eckelsbach and J. Vrabec, "Fluid phase interface properties of acetone, oxygen, nitrogen and their binary mixtures by molecular simulation," *Physical Chemistry Chemical Physics* **17**, 27195–27203 (2015).
- ¹⁷M. M. Telo da Gama and R. Evans, "Theory of the liquid-vapour interface of a binary mixture of Lennard-Jones fluids," *Molecular Physics* **41**, 1091–1112 (1980), <http://dx.doi.org/10.1080/00268978000103811>.

- ¹⁸M. M. Telo da Gama and R. Evans, "Surface segregation and surface tension at the liquid-vapour interface of a binary mixture of Lennard-Jones fluids," *Faraday Symposia of the Chemical Society* **16**, 45–58 (1981).
- ¹⁹S. P. Protsenko, V. G. Baidakov, and V. M. Bryukhanov, "Binary Lennard-Jones mixtures with highly asymmetric interactions of the components. 2. effect of the particle size on phase equilibria and properties of liquid-gas interfaces," *Fluid Phase Equilibria* **430**, 67–74 (2016).
- ²⁰S. P. Protsenko and V. G. Baidakov, "Binary Lennard-Jones mixtures with highly asymmetric interactions of the components. 1. effect of the energy parameters on phase equilibria and properties of liquid-gas interfaces," *Fluid Phase Equilibria* **429**, 242–253 (2016).
- ²¹C. Klink and J. Gross, "A density functional theory for vapor-liquid interfaces of mixtures using the perturbed-chain polar statistical associating fluid theory equation of state," *Industrial & Engineering Chemistry Research* **53**, 6169 (2014).
- ²²V. G. Baidakov and S. P. Protsenko, "Molecular-dynamics investigation of phase equilibrium and surface tension in argon-neon system," *The Journal of Physical Chemistry C* **112**, 17231–17234 (2008), <http://dx.doi.org/10.1021/jp805566g>.
- ²³V. G. Baidakov, A. M. Kaverin, and M. N. Khotienkova, "Surface tension of ethane-methane solutions: 1. experiment and thermodynamic analysis of the results," *Fluid Phase Equilibria* **356**, 90–95 (2013).
- ²⁴V. Baidakov and M. Khotienkova, "Surface tension of methane-nitrogen solutions: 2. description in the framework of the van der Waals gradient theory," *Fluid Phase Equilibria* **425**, 402–410 (2016).
- ²⁵F. Llorell, A. Galindo, F. J. Blas, and G. Jackson, "Classical density functional theory for the prediction of the surface tension and interfacial properties of fluids mixtures of chain molecules based on the statistical associating fluid theory for potentials of variable range," *The Journal of Chemical Physics* **133**, 024704 (2010).
- ²⁶C. I. Poser and I. C. Sanchez, "Interfacial tension theory of low and high molecular weight liquid mixtures," *Macromolecules* **14**, 361–370 (1981), <https://doi.org/10.1021/ma50003a026>.
- ²⁷O. G. Niño Amézquita, S. Enders, P. T. Jaeger, and R. Eggers, "Interfacial properties of mixtures containing supercritical gases," *The Journal of Supercritical Fluids* **55**, 724 (2010).

- ²⁸O. G. Niño-Amézquita, D. van Putten, and S. Enders, “Phase equilibrium and interfacial properties of water+CO₂ mixtures,” *Fluid Phase Equilibria* **332**, 40 (2012).
- ²⁹O. G. Niño-Amézquita, S. Enders, P. T. Jaeger, and R. Eggers, “Measurement and prediction of interfacial tension of binary mixtures,” *Industrial & Engineering Chemistry Research* **49**, 592–601 (2010), <https://doi.org/10.1021/ie901209z>.
- ³⁰O. G. Niño-Amézquita and S. Enders, “Phase equilibrium and interfacial properties of water+methane mixtures,” *Fluid Phase Equilibria* **407**, 143–151 (2016).
- ³¹F. Biscay, A. Ghoufi, V. Lachet, and P. Malfreyt, “Monte Carlo simulations of the pressure dependence of the water-acid gas interfacial tensions,” *The Journal of Physical Chemistry B* **113**, 14277–14290 (2009), <https://doi.org/10.1021/jp906953a>.
- ³²M. Sahimi and B. N. Taylor, “Surface tension of binary liquid-vapor mixtures: A comparison of mean-field and scaling theories,” *The Journal of Chemical Physics* **95**, 6749–6761 (1991).
- ³³X.-S. Li, J.-M. Liu, and D. Fu, “Investigation of interfacial tensions for carbon dioxide aqueous solutions by perturbed-chain statistical associating fluid theory combined with density-gradient theory,” *Industrial & Engineering Chemistry Research* **47**, 8911–8917 (2008), <https://doi.org/10.1021/ie800959h>.
- ³⁴T. Lafitte, B. Mendiboure, M. M. Pieiro, D. Bessires, and C. Miqueu, “Interfacial properties of water/CO₂: A comprehensive description through a gradient theory SAFT-VR Mie approach,” *The Journal of Physical Chemistry B* **114**, 11110–11116 (2010), <http://dx.doi.org/10.1021/jp103292e>.
- ³⁵O. Lobanova, A. Mejía, G. Jackson, and E. A. Müller, “SAFT-i force field for the simulation of molecular fluids 6: Binary and ternary mixtures comprising water, carbon dioxide, and n-alkanes,” *The Journal of Chemical Thermodynamics* **93**, 320–336 (2016).
- ³⁶H. Lin, Y.-Y. Duan, and Q. Min, “Gradient theory modeling of surface tension for pure fluids and binary mixtures,” *Fluid Phase Equilibria* **254**, 75 (2007).
- ³⁷E. A. Müller and A. Mejía, “Interfacial properties of selected binary mixtures containing n-alkanes,” *Fluid Phase Equilibria* **282**, 68–81 (2009).
- ³⁸C. Cumicheo, M. Cartes, H. Segura, E. A. Müller, and A. Mejía, “High-pressure densities and interfacial tensions of binary systems containing carbon dioxide + n-alkanes: (n-dodecane, n-tridecane, n-tetradecane),” *Fluid Phase Equilibria* **380**, 82 (2014).
- ³⁹L. M. Pereira, A. Chapoy, R. Burgass, and B. Tohidi, “Measurement and modelling of

- high pressure density and interfacial tension of (gas + n-alkane) binary mixtures,” *The Journal of Chemical Thermodynamics* **97**, 55–69 (2016).
- ⁴⁰S. Stephan, K. Langenbach, and H. Hasse, “Enrichment of components at vapour-liquid interfaces: A study by molecular simulation and density gradient theory,” *Chemical Engineering Transactions* **69**, 295–300 (2018).
- ⁴¹W. A. Fouad and L. F. Vega, “The phase and interfacial properties of azeotropic refrigerants: the prediction of azeotropes from molecular theory,” *Physical Chemistry Chemical Physics* **19**, 8977–8988 (2017).
- ⁴²M. M. Telo da Gama and R. Evans, “The structure and surface tension of the liquid-vapour interface near the upper critical end point of a binary mixture of Lennard-Jones fluids,” *Molecular Physics* **48**, 229–250 (1983), <https://doi.org/10.1080/00268978300100181>.
- ⁴³M. Telo da Gama and R. Evans, “The structure and surface tension of the liquid-vapour interface near the upper critical end point of a binary mixture of Lennard-Jones fluids,” *Molecular Physics* **48**, 251–266 (1983), <https://doi.org/10.1080/00268978300100191>.
- ⁴⁴V. Mazur, L. Boshkov, and V. Murakhovsky, “Global phase behaviour of binary mixtures of Lennard-Jones molecules,” *Physics Letters A* **104**, 415–418 (1984).
- ⁴⁵H. Kahl and S. Enders, “Interfacial properties of binary mixtures,” *Physical Chemistry Chemical Physics* **4**, 931–936 (2002).
- ⁴⁶E. Schäfer, G. Sadowski, and S. Enders, “Interfacial tension of binary mixtures exhibiting azeotropic behavior: Measurement and modeling with PCP-SAFT combined with density gradient theory,” *Fluid Phase Equilibria Special Issue on PPEPPD 2013*, **362**, 151 (2014).
- ⁴⁷H. Cardenas and A. Mejía, “Phase behaviour and interfacial properties of ternary system CO₂ + n-butane + n-decane: Coarse-grained theoretical modelling and molecular simulations,” *Molecular Physics* **114**, 2627–2640 (2016), <https://doi.org/10.1080/00268976.2016.1170221>.
- ⁴⁸W. Shi, N. S. Siefert, and B. D. Morreale, “Molecular simulations of CO₂, H₂, H₂O, and H₂S gas absorption into hydrophobic poly(dimethylsiloxane) (pdms) solvent: Solubility and surface tension,” *The Journal of Physical Chemistry C* **119**, 19253–19265 (2015), <https://doi.org/10.1021/acs.jpcc.5b05806>.
- ⁴⁹C. Bühl and S. Enders, “Prediction of interfacial properties of ternary, sulfur-containing mixtures,” *Journal of Chemical & Engineering Data* **61**, 4261–4269 (2016), <http://dx.doi.org/10.1021/acs.jced.6b00637>.

- ⁵⁰C. Bühl, A. Danzer, and S. Enders, “Prediction of surface properties of binary, sulfur containing mixtures,” *Fluid Phase Equilibria* **416**, 94–103 (2016).
- ⁵¹C. Miqueu, J. M. Miguez, M. M. Pineiro, T. Lafitte, and B. Mendiboure, “Simultaneous application of the gradient theory and Monte Carlo molecular simulation for the investigation of methane/water interfacial properties,” *The Journal of Physical Chemistry B* **115**, 9618–9625 (2011), <http://dx.doi.org/10.1021/jp202276k>.
- ⁵²M. Heier, S. Stephan, J. Liu, W. G. Chapman, H. Hasse, and K. Langenbach, “Equation of state for the Lennard-Jones truncated and shifted fluid with a cut-off radius of 2.5σ based on perturbation theory and its applications to interfacial thermodynamics,” *Molecular Physics* **116**, 2083–2094 (2018).
- ⁵³M. Horsch, H. Hasse, A. K. Shchekin, A. Agarwal, S. Eckelsbach, J. Vrabec, E. A. Müller, and G. Jackson, “Excess equimolar radius of liquid drops,” *Physical Review E* **85**, 031605 (2012).
- ⁵⁴W. Eckhardt, A. Heinecke, R. Bader, M. Brehm, N. Hammer, H. Huber, H.-G. Kleinhenz, J. Vrabec, H. Hasse, M. Horsch, M. Bernreuther, C. W. Glass, C. Niethammer, A. Bode, and H.-J. Bungartz, “591 tflops multi-trillion particles simulation on SuperMUC,” in *Supercomputing* (Springer, Berlin, Heidelberg, 2013) pp. 1–12.
- ⁵⁵M. Horsch, S. Miroshnichenko, and J. Vrabec, “Steady-state molecular dynamics simulation of vapour to liquid nucleation with McDonald’s daemon,” *Journal of Physical Studies* **13**, 4004 (2009).
- ⁵⁶M. Horsch and H. Hasse, “Molecular simulation of nano-dispersed fluid phases,” *Chemical Engineering Science* **107**, 235 (2014).
- ⁵⁷M. Thol, G. Rutkai, R. Span, J. Vrabec, and R. Lustig, “Equation of state for the Lennard-Jones truncated and shifted model fluid,” *International Journal of Thermophysics* **36**, 25 (2015).
- ⁵⁸S. Stephan, M. P. Lautenschlaeger, I. A. Alhafez, M. T. Horsch, H. M. Urbassek, and H. Hasse, “Molecular dynamics simulation study of mechanical effects of lubrication on a nanoscale contact process,” *Tribology Letters* **66**, 126 (2018).
- ⁵⁹M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1989).
- ⁶⁰A. Lotfi, J. Vrabec, and J. Fischer, “Vapour liquid equilibria of the Lennard-Jones fluid from the NpT plus test particle method,” *Molecular Physics* **76**, 1319–1333 (1992),

<http://dx.doi.org/10.1080/00268979200102111>.

- ⁶¹A. Trokhymchuk and J. Alejandre, “Computer simulations of liquid/vapor interface in Lennard-Jones fluids: Some questions and answers,” *The Journal of Chemical Physics* **111**, 8510–8523 (1999).
- ⁶²B. Smit, “Phase diagrams of Lennard-Jones fluids,” *The Journal of Chemical Physics* **96**, 8639–8640 (1992), <https://doi.org/10.1063/1.462271>.
- ⁶³D. O. Dunikov, S. P. Malysenko, and V. V. Zhakhovskii, “Corresponding states law and molecular dynamics simulations of the Lennard-Jones fluid,” *The Journal of Chemical Physics* **115**, 6623–6631 (2001), <https://doi.org/10.1063/1.1396674>.
- ⁶⁴S. Werth, S. V. Lishchuk, M. Horsch, and H. Hasse, “The influence of the liquid slab thickness on the planar vapor-liquid interfacial tension,” *Physica A* **392**, 2359 (2013).
- ⁶⁵M. Guo, D.-Y. Peng, and B. C.-Y. Lu, “On the long-range corrections to computer simulation results for the Lennard-Jones vapor-liquid interface,” *Fluid Phase Equilibria* **130**, 19–30 (1997).
- ⁶⁶M. J. P. Nijmeijer, A. F. Bakker, C. Bruin, and J. H. Sikkenk, “A molecular dynamics simulation of the Lennard-Jones liquid-vapor interface,” *The Journal of Chemical Physics* **89**, 3789–3792 (1988).
- ⁶⁷V. Baidakov, G. Chernykh, and S. Protsenko, “Effect of the cut-off radius of the intermolecular potential on phase equilibrium and surface tension in Lennard-Jones systems,” *Chemical Physics Letters* **321**, 315–320 (2000).
- ⁶⁸R. Evans, J. R. Henderson, D. C. Hoyle, A. O. Parry, and Z. A. Sabeur, “Asymptotic decay of liquid structure: Oscillatory liquid-vapour density profiles and the Fisher-Widom line,” *Molecular Physics* **80**, 755–775 (1993), <http://dx.doi.org/10.1080/00268979300102621>.
- ⁶⁹R. Evans, “Oscillatory behaviour of density profiles: Relevance for fluid interfacial phenomena,” *Berichte der Bunsengesellschaft für physikalische Chemie* **98**, 345–352 (1994).
- ⁷⁰P. G. Bolhuis and D. Chandler, “Transition path sampling of cavitation between molecular scale solvophobic surfaces,” *The Journal of Chemical Physics* **113**, 8154–8160 (2000), <https://doi.org/10.1063/1.1315997>.
- ⁷¹S. Toxvaerd, “Molecular dynamics simulation of prewetting,” *The Journal of Physical Chemistry C* **111**, 15620–15624 (2007), <http://dx.doi.org/10.1021/jp073665x>.
- ⁷²J. A. van Meel, A. J. Page, R. P. Sear, and D. Frenkel, “Two-step vapor-crystal nucleation

- close below triple point,” *The Journal of Chemical Physics* **129**, 204505 (2008).
- ⁷³M. J. Haye and C. Bruin, “Molecular dynamics study of the curvature correction to the surface tension,” *The Journal of Chemical Physics* **100**, 556–559 (1994).
- ⁷⁴W. Shi and J. Johnson, “Histogram reweighting and finite-size scaling study of the Lennard-Jones fluids,” *Fluid Phase Equilibria* **187**, 171–191 (2001).
- ⁷⁵H. A. Lorentz, “Ueber die Anwendung des Satzes vom Virial in der kinetischen Theorie der Gase,” *Annalen der Physik* **248**, 127–136 (1881).
- ⁷⁶D. Berthelot, “Sur le mélange des gaz,” *Comptes rendus hebdomadaires des séances de l’Académie des Sciences* **126**, 1703–1706 (1898).
- ⁷⁷T. Schnabel, J. Vrabec, and H. Hasse, “Unlike Lennard-Jones parameters for vapor-liquid equilibria,” *Journal of Molecular Liquids* **135**, 170–178 (2007).
- ⁷⁸D. Fincham, “Leapfrog rotational algorithms,” *Molecular Simulation* **8**, 165–178 (1992).
- ⁷⁹C. Niethammer, S. Becker, M. Bernreuther, M. Buchholz, W. Eckhardt, A. Heinecke, S. Werth, H.-J. Bungartz, C. W. Glass, H. Hasse, J. Vrabec, and M. Horsch, “ls1 mardyn: The massively parallel molecular dynamics code for large systems,” *Journal of Chemical Theory Computation* **10**, 4455 (2014).
- ⁸⁰J. Walton, D. J. Tildesley, J. S. Rowlinson, and J. R. Henderson, “The pressure tensor at the planar surface of a liquid,” *Molecular Physics* **48**, 1357–1368 (1983), <http://dx.doi.org/10.1080/00268978300100971>.
- ⁸¹J. G. Kirkwood and F. P. Buff, “The statistical mechanical theory of surface tension,” *The Journal of Chemical Physics* **17**, 338–343 (1949), <http://dx.doi.org/10.1063/1.1747248>.
- ⁸²J. A. Barker and D. Henderson, “Perturbation theory and equation of state for fluids. II. a successful theory of liquids,” *The Journal of Chemical Physics* **47**, 4714 (1967).
- ⁸³J. Gross and G. Sadowski, “Perturbed-Chain SAFT: An equation of state based on a perturbation theory for chain molecules,” *Industrial & Engineering Chemistry Research* **40**, 1244 (2001).
- ⁸⁴T. W. Leland, J. S. Rowlinson, G. A. Sather, and I. D. Watson, “Statistical thermodynamics of two-fluid models of mixtures,” *Transactions of the Faraday Society* **65**, 2034–2043 (1969).
- ⁸⁵J.-P. Hansen and I. McDonald, *Theory of Simple Liquids*, 4th ed. (Academic Press, 2013).
- ⁸⁶J. Gross and G. Sadowski, “Application of perturbation theory to a hard-chain reference fluid: an equation of state for square-well chains,” *Fluid Phase Equilibria* **168**, 183 (2000).

- ⁸⁷S. K. Shibata and S. I. Sandler, “Critical evaluation of equation of state mixing rules for the prediction of high-pressure phase equilibria,” *Industrial & Engineering Chemistry Research* **28**, 1893–1898 (1989), <https://doi.org/10.1021/ie00096a024>.
- ⁸⁸T. Boublík, “Hard sphere equation of state,” *The Journal of Chemical Physics* **53**, 471 (1970).
- ⁸⁹G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, “Equilibrium thermodynamic properties of the mixture of hard spheres,” *The Journal of Chemical Physics* **54**, 1523 (1971).
- ⁹⁰S. S. Chen and A. Kreglewski, “Applications of the augmented van der Waals theory of fluids.: I. pure fluids,” *Berichte der Bunsengesellschaft für physikalische Chemie* **81**, 1048 (1977).
- ⁹¹J. W. Cahn and J. E. Hilliard, “Free energy of a nonuniform system. I. interfacial free energy,” *The Journal of Chemical Physics* **28**, 258 (1958).
- ⁹²J. W. Cahn, “Free energy of a nonuniform system. II. thermodynamic basis,” *The Journal of Chemical Physics* **30**, 1121 (1959).
- ⁹³C. Miqueu, B. Mendiboure, A. Graciaa, and J. Lachaise, “Modelling of the surface tension of pure components with the gradient theory of fluid interfaces: a simple and accurate expression for the influence parameters,” *Fluid Phase Equilibria* **207**, 225 (2003).
- ⁹⁴P. M. Cornelisse, *The Square Gradient Theory Applied Simultaneous Modelling of Interfacial Tension and Phase Behaviour*, Ph.D. thesis, Technische Universiteit Delft (1997).
- ⁹⁵B. S. Carey, L. E. Scriven, and H. T. Davis, “Semiempirical theory of surface tension of binary systems,” *AIChE Journal* **26**, 705–711 (1980).
- ⁹⁶X. Mu, F. Frank, F. O. Alpak, and W. G. Chapman, “Stabilized density gradient theory algorithm for modeling interfacial properties of pure and mixed systems,” *Fluid Phase Equilibria* **435**, 118–130 (2017).
- ⁹⁷C. Miqueu, B. Mendiboure, C. Graciaa, and J. Lachaise, “Modelling of the surface tension of binary and ternary mixtures with the gradient theory of fluid interfaces,” *Fluid Phase Equilibria* **218**, 189–203 (2004).
- ⁹⁸C. Miqueu, B. Mendiboure, A. Graciaa, and J. Lachaise, “Modeling of the surface tension of multicomponent mixtures with the gradient theory of fluid interfaces,” *Industrial & Engineering Chemistry Research* **44**, 3321–3329 (2005), <http://dx.doi.org/10.1021/ie049086l>.

- ⁹⁹B. S. Carey, L. E. Scriven, and H. T. Davis, "On gradient theories of fluid interfacial stress and structure," *The Journal of Chemical Physics* **69**, 5040–5049 (1978).
- ¹⁰⁰J. Mairhofer and J. Gross, "Modeling of interfacial properties of multicomponent systems using density gradient theory and PCP-SAFT," *Fluid Phase Equilibria* **439**, 31 (2017).
- ¹⁰¹S. Enders and H. Kahl, "Interfacial properties of water + alcohol mixtures," *Fluid Phase Equilibria* **263**, 160–167 (2008).
- ¹⁰²P. M. Cornelisse, C. J. Peters, and J. de Swaan Arons, "On the fundamentals of the gradient theory of van der Waals," *The Journal of Chemical Physics* **106**, 9820–9834 (1997).
- ¹⁰³V. G. Baidakov, S. P. Protsenko, G. G. Chernykh, and G. S. Boltachev, "Statistical substantiation of the van der Waals theory of inhomogeneous fluids," *Physical Review E* **65**, 041601 (2002).
- ¹⁰⁴X. Liang, M. L. Michelsen, and G. M. Kontogeorgis, "A density gradient theory based method for surface tension calculations," *Fluid Phase Equilibria* **428**, 153–163 (2016).
- ¹⁰⁵X. Liang, M. L. Michelsen, and G. M. Kontogeorgis, "Pitfalls of using the geometric-mean combining rule in the density gradient theory," *Fluid Phase Equilibria* **415**, 75–83 (2016).
- ¹⁰⁶J. W. Gibbs, *The Scientific Papers of J. W. Gibbs* (Dover Publications, 1961).
- ¹⁰⁷T. Wadewitz and J. Winkelmann, "Density functional theory: Structure and interfacial properties of binary mixtures," *Berichte der Bunsengesellschaft für physikalische Chemie* **100**, 1825–1832 (1996).
- ¹⁰⁸J. Lekner and J. R. Henderson, "Surface tension and energy of a classical liquid-vapour interface," *Molecular Physics* **34**, 333–359 (1977), <http://dx.doi.org/10.1080/00268977700101771>.
- ¹⁰⁹I. A. McLure, B. Edmonds, and M. Lal, "Extremes in surface tension of fluorocarbon + hydrocarbon mixtures," *Nature Physical Science* **241**, 71–71 (1973).
- ¹¹⁰I. A. McLure, V. A. M. Soares, and A. M. Williamson, "Total surface segregation. a fresh look at the Gibbs adsorption isotherm for binary liquid mixtures." *Langmuir* **9**, 2190–2201 (1993), <https://doi.org/10.1021/la00032a048>.
- ¹¹¹R. Defay, I. Prigogine, A. Bellmans, and D. H. Everett, *Surface Tension and Adsorption* (Longmans, London, 1966).
- ¹¹²J. Gross and J. Vrabec, "An equation-of-state contribution for polar components: Dipolar

- molecules,” *AIChE Journal* **52**, 1194–1204 (2006).
- ¹¹³W. G. Chapman, G. Jackson, K. E. Gubbins, and M. Radosz, “New reference equation of state for associating liquids,” *Industrial & Engineering Chemistry Research* **29**, 1709 (1990).
- ¹¹⁴W. G. Chapman, G. Jackson, and K. E. Gubbins, “Phase equilibria of associating fluids. Chain molecules with multiple bonding sites,” *Molecular Physics* **65**, 1057 (1988).
- ¹¹⁵K. Langenbach, “Co-oriented fluid functional equation for electrostatic interactions (coffee),” *Chemical Engineering Science* **174**, 40 – 55 (2017).
- ¹¹⁶V. Bongiorno and H. T. Davis, “Modified van der Waals theory of fluid interfaces,” *Physical Review A* **12**, 2213–2224 (1975).

SUPPLEMENTARY MATERIAL

Interfacial properties of binary Lennard-Jones mixtures by molecular simulation and density gradient theory

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8 May 2019

The supplementary material for the publication *Interfacial Properties of Binary Lennard-Jones Mixtures by Molecular Simulation and Density Gradient Theory* contains the MD density profiles plots from all six investigated mixtures, cf. Fig. 1 – 6 and the numeric values for the computed phase equilibria (Table I – VI) and interfacial properties (Table VII – XII) for both MD and DGT .

1. Density profiles from molecular simulations

FIG. 1. Density profiles of the binary LJTS mixture A as a function of the coordinate z normal to the interface at $T = 0.77 \varepsilon k_B^{-1}$. Results from MD. Dashed lines: heavy boiling component 1, solid lines: light boiling component 2. The color indicates the liquid phase composition.

FIG. 2. Density profiles of the binary LJTS mixture B as a function of the coordinate z normal to the interface at $T = 0.77 \varepsilon k_B^{-1}$. Results from MD. Dashed lines: heavy boiling component 1, solid lines: light boiling component 2. The color indicates the liquid phase composition.

FIG. 3. Density profiles of the binary LJTS mixture C as a function of the coordinate z normal to the interface at $T = 0.77 \varepsilon k_B^{-1}$. Results from MD. Dashed lines: heavy boiling component 1, solid lines: light boiling component 2. The color indicates the liquid phase composition.

FIG. 4. Density profiles of the binary LJTS mixture D as a function of the coordinate z normal to the interface at $T = 0.77 \varepsilon k_B^{-1}$. Results from MD. Dashed lines: heavy boiling component 1, solid lines: light boiling component 2. The color indicates the liquid phase composition.

FIG. 5. Density profiles of the binary LJTS mixture E as a function of the coordinate z normal to the interface at $T = 0.77 \varepsilon k_B^{-1}$. Results from MD. Dashed lines: heavy boiling component 1, solid lines: light boiling component 2. The color indicates the liquid phase composition.

FIG. 6. Density profiles of the binary LJTS mixture F as a function of the coordinate z normal to the interface at $T = 0.77 \varepsilon k_B^{-1}$. Results from MD. Dashed lines: heavy boiling component 1, solid lines: light boiling component 2. The color indicates the liquid phase composition.

2. Tables of numeric values from the MD and DGT+PeTS results

The numerical results from MD and the PETS EOS for the vapor-liquid equilibrium of the studied mixtures are summarized in Table I - VI. The numerical results for the interfacial properties are summarized in Table VII – XII.

TABLE I. MD and PeTS EOS results for the vapor-liquid equilibrium of the binary LJTS mixture A ($\varepsilon_2/\varepsilon_1 = 0.9$ and $\xi_{12} = 1$). The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$p / \varepsilon \sigma^{-3}$		$x''_2 / \text{mol mol}^{-1}$		ρ' / σ^{-3}		ρ'' / σ^{-3}	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.000	0.0105(2)	0.0104	0.000	0.000	0.7486(4)	0.7480	0.015(2)	0.0150
0.064(2)	0.0110(3)	0.0110	0.110(12)	0.1102	0.7456(7)	0.7451	0.016(7)	0.0160
0.110(1)	0.0116(2)	0.0114	0.191(15)	0.1812	0.7435(8)	0.7430	0.017(9)	0.0167
0.154(2)	0.0119(3)	0.0118	0.257(13)	0.2450	0.7412(10)	0.7410	0.018(9)	0.0174
0.202(2)	0.0124(2)	0.0123	0.313(12)	0.3111	0.7391(9)	0.7387	0.018(9)	0.0181
0.246(2)	0.0129(4)	0.0127	0.366(18)	0.3662	0.7370(9)	0.7366	0.019(11)	0.0188
0.296(2)	0.0134(4)	0.0132	0.424(15)	0.4263	0.7346(9)	0.7342	0.020(11)	0.0196
0.334(1)	0.0137(3)	0.0136	0.466(18)	0.4691	0.7327(10)	0.7323	0.020(11)	0.0202
0.392(2)	0.0143(4)	0.0141	0.532(11)	0.5303	0.7297(10)	0.7294	0.021(10)	0.0211
0.436(1)	0.0146(3)	0.0145	0.573(11)	0.5742	0.7275(10)	0.7271	0.022(10)	0.0218
0.484(2)	0.0150(4)	0.0150	0.618(11)	0.6199	0.7249(11)	0.7247	0.023(11)	0.0226
0.527(2)	0.0156(4)	0.0154	0.653(12)	0.6584	0.7228(11)	0.7224	0.024(13)	0.0233
0.574(2)	0.0158(3)	0.0159	0.694(9)	0.6985	0.7202(11)	0.7199	0.024(12)	0.0241
0.617(2)	0.0163(4)	0.0163	0.726(14)	0.7345	0.7178(10)	0.7176	0.025(12)	0.0248
0.662(1)	0.0168(2)	0.0167	0.769(10)	0.7700	0.7154(10)	0.7151	0.026(10)	0.0256
0.714(2)	0.0173(3)	0.0172	0.813(6)	0.8097	0.7125(11)	0.7122	0.027(10)	0.0265
0.764(1)	0.0179(3)	0.0177	0.846(7)	0.8457	0.7096(11)	0.7093	0.028(9)	0.0273
0.808(2)	0.0183(4)	0.0181	0.881(8)	0.8761	0.7072(10)	0.7068	0.028(8)	0.0281
0.863(1)	0.0188(3)	0.0187	0.910(6)	0.9133	0.7039(12)	0.7035	0.029(9)	0.0291
0.904(1)	0.0192(2)	0.0191	0.939(5)	0.9404	0.7012(15)	0.7010	0.030(7)	0.0298
0.952(1)	0.0197(3)	0.0196	0.973(4)	0.9706	0.6985(10)	0.6981	0.031(6)	0.0307
1.000	0.0203(3)	0.0201	1.000	1.000	0.6955(9)	0.6951	0.032(3)	0.0316

TABLE II. MD and PeTS EOS results for the vapor-liquid equilibrium of the binary LJTS mixture B ($\varepsilon_2/\varepsilon_1 = 0.9$ and $\xi_{12} = 1.2$). The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$p / \varepsilon \sigma^{-3}$		$x''_2 / \text{mol mol}^{-1}$		ρ' / σ^{-3}		ρ'' / σ^{-3}	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.000	0.0105(2)	0.0104	0.0000	0.0000	0.7486(4)	0.7480	0.015(2)	0.0150
0.069(1)	0.0097(2)	0.0097	0.019(4)	0.0184	0.756(6)	0.7564	0.0139(6)	0.0139
0.119(1)	0.0092(2)	0.0091	0.041(6)	0.0409	0.761(8)	0.7613	0.0132(6)	0.0130
0.163(1)	0.0087(2)	0.0086	0.066(7)	0.0696	0.764(7)	0.7647	0.0124(6)	0.0123
0.212(1)	0.0082(2)	0.0081	0.112(11)	0.1151	0.767(8)	0.7678	0.0116(6)	0.0115
0.256(1)	0.0079(2)	0.0077	0.171(13)	0.1682	0.769(8)	0.7698	0.0112(6)	0.0110
0.305(1)	0.0075(2)	0.0074	0.251(11)	0.2448	0.770(9)	0.7713	0.0106(7)	0.0105
0.343(1)	0.0073(2)	0.0073	0.304(11)	0.3139	0.771(8)	0.7720	0.0103(6)	0.0103
0.399(1)	0.0073(2)	0.0073	0.435(14)	0.4284	0.771(10)	0.7722	0.0103(7)	0.0103
0.442(1)	0.0075(2)	0.0075	0.525(23)	0.5223	0.770(9)	0.7716	0.0105(7)	0.0106
0.486(1)	0.0079(2)	0.0078	0.611(18)	0.6141	0.769(9)	0.7705	0.0111(7)	0.0111
0.528(1)	0.0085(2)	0.0083	0.697(19)	0.6944	0.767(8)	0.7688	0.0120(7)	0.0118
0.572(1)	0.0091(2)	0.0090	0.768(13)	0.7678	0.765(8)	0.7664	0.0129(7)	0.0128
0.614(1)	0.0099(3)	0.0098	0.828(9)	0.8247	0.762(8)	0.7636	0.0142(7)	0.0140
0.659(1)	0.0108(2)	0.0108	0.879(9)	0.8740	0.758(8)	0.7597	0.0156(8)	0.0155
0.712(2)	0.0122(3)	0.0121	0.914(8)	0.9170	0.753(8)	0.7541	0.0178(8)	0.0176
0.759(1)	0.0133(2)	0.0134	0.942(7)	0.9446	0.747(8)	0.7481	0.0196(8)	0.0197
0.804(1)	0.0148(3)	0.0147	0.961(6)	0.9635	0.740(7)	0.7414	0.0221(9)	0.0219
0.858(1)	0.0164(2)	0.0163	0.980(2)	0.9795	0.730(7)	0.7316	0.0247(8)	0.0246
0.900(1)	0.0177(1)	0.0174	0.988(3)	0.9879	0.722(6)	0.7228	0.0272(9)	0.0267
0.949(1)	0.0189(3)	0.0188	0.994(1)	0.9950	0.710(5)	0.7104	0.0294(9)	0.0292
1.000	0.0203(3)	0.0201	1.000	1.0000	0.695(3)	0.6951	0.0320(9)	0.0316

TABLE III. MD and PeTS EOS results for the vapor-liquid equilibrium of the binary LJTS mixture C ($\varepsilon_2/\varepsilon_1 = 0.9$ and $\xi_{12} = 0.85$). The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$p / \varepsilon \sigma^{-3}$		$x''_2 / \text{mol mol}^{-1}$		ρ' / σ^{-3}		ρ'' / σ^{-3}	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.000	0.0105(2)	0.0104	0.000	0.000	0.7486(4)	0.7480	0.015(2)	0.0150
0.096(1)	0.0174(3)	0.0178	0.414(12)	0.4216	0.733(8)	0.7315	0.0259(1)	0.0272
0.136(2)	0.0189(3)	0.0197	0.465(11)	0.4832	0.727(13)	0.7247	0.029(1)	0.0306
0.183(3)	0.0204(4)	0.0212	0.512(9)	0.5276	0.720(13)	0.7170	0.032(1)	0.0335
0.226(2)	0.0213(3)	0.0222	0.541(10)	0.5551	0.714(17)	0.7102	0.034(1)	0.0355
0.276(3)	0.0221(3)	0.0230	0.573(12)	0.5771	0.707(18)	0.7026	0.035(1)	0.0371
0.316(4)	0.0224(3)	0.0235	0.577(10)	0.5901	0.701(18)	0.6968	0.036(2)	0.0381
0.377(5)	0.0231(5)	0.0239	0.599(11)	0.6051	0.694(25)	0.6889	0.038(3)	0.0390
0.425(5)	0.0234(2)	0.0242	0.612(11)	0.6150	0.690(23)	0.6834	0.038(1)	0.0396
0.473(4)	0.0238(3)	0.0244	0.629(12)	0.6238	0.684(22)	0.6789	0.041(9)	0.0400
0.520(5)	0.0241(2)	0.0245	0.643(9)	0.6327	0.682(19)	0.6752	0.039(2)	0.0403
0.572(5)	0.0241(4)	0.0247	0.651(15)	0.6435	0.680(25)	0.6724	0.039(1)	0.0406
0.614(3)	0.0241(6)	0.0248	0.664(11)	0.6535	0.674(24)	0.6710	0.045(20)	0.0408
0.668(2)	0.0243(3)	0.0248	0.676(9)	0.6689	0.670(17)	0.6704	0.040(2)	0.0409
0.722(4)	0.0242(12)	0.0247	0.708(9)	0.6888	0.672(25)	0.6713	0.047(25)	0.0408
0.772(2)	0.0238(4)	0.0246	0.730(9)	0.7124	0.678(12)	0.6733	0.039(1)	0.0404
0.816(2)	0.0238(17)	0.0243	0.762(9)	0.7392	0.667(45)	0.6759	0.053(22)	0.0398
0.873(2)	0.0236(4)	0.0236	0.803(6)	0.7870	0.684(11)	0.6806	0.038(1)	0.0384
0.912(1)	0.0228(3)	0.0229	0.844(6)	0.8311	0.686(8)	0.6845	0.037(2)	0.0370
0.956(1)	0.0217(3)	0.0217	0.915(10)	0.9009	0.691(6)	0.6896	0.035(1)	0.0347
1.000	0.0203(3)	0.0201	1.000	1.000	0.696(3)	0.6951	0.032(1)	0.0316

TABLE IV. MD and PeTS EOS results for the vapor-liquid equilibrium of the binary LJTS mixture D ($\varepsilon_2/\varepsilon_1 = 0.5$ and $\xi_{12} = 1$). The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$p / \varepsilon \sigma^{-3}$		$x''_2 / \text{mol mol}^{-1}$		ρ' / σ^{-3}		ρ'' / σ^{-3}	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.000	0.0105(2)	0.0104	0.0000	0.0000	0.7486(4)	0.7480	0.015(2)	0.0150
0.038(1)	0.0225(3)	0.0215	0.490(12)	0.4750	0.740(6)	0.7403	0.034(1)	0.03209
0.050(1)	0.0256(3)	0.0247	0.537(10)	0.5320	0.737(6)	0.7380	0.039(1)	0.03726
0.071(1)	0.0303(3)	0.0308	0.593(9)	0.6062	0.731(8)	0.7333	0.046(1)	0.04729
0.099(2)	0.0380(4)	0.0382	0.654(6)	0.6642	0.724(10)	0.7272	0.060(2)	0.06039
0.131(3)	0.0464(6)	0.0466	0.702(7)	0.7055	0.715(10)	0.7196	0.076(2)	0.07628
0.162(3)	0.0537(6)	0.0545	0.724(8)	0.7310	0.706(10)	0.7118	0.090(2)	0.09261
0.196(5)	0.0619(6)	0.0627	0.747(10)	0.7483	0.696(13)	0.7029	0.108(3)	0.11104
0.224(3)	0.0681(5)	0.0692	0.751(5)	0.7574	0.686(13)	0.6950	0.124(3)	0.12718
0.271(5)	0.0769(6)	0.0799	0.758(7)	0.7651	0.669(13)	0.6806	0.147(3)	0.15682

TABLE V. MD and PeTS EOS results for the vapor-liquid equilibrium of the binary LJTS mixture E ($\varepsilon_2/\varepsilon_1 = 0.5$ and $\xi_{12} = 1.2$). The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$p / \varepsilon \sigma^{-3}$		$x''_2 / \text{mol mol}^{-1}$		ρ' / σ^{-3}		ρ'' / σ^{-3}	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.000	0.0105(2)	0.0104	0.0000	0.0000	0.7486(4)	0.7480	0.015(2)	0.0150
0.056(1)	0.0142(4)	0.0133	0.276(13)	0.2409	0.741(6)	0.7427	0.021(1)	0.0196
0.098(2)	0.0171(2)	0.0161	0.402(15)	0.3809	0.735(8)	0.7380	0.026(1)	0.0240
0.136(2)	0.0205(3)	0.0191	0.499(10)	0.4832	0.728(9)	0.7333	0.031(1)	0.0287
0.179(1)	0.0248(3)	0.0230	0.583(10)	0.5739	0.721(7)	0.7274	0.038(1)	0.0350
0.217(3)	0.0286(6)	0.0270	0.649(14)	0.6378	0.713(9)	0.7214	0.045(2)	0.0417
0.262(2)	0.0339(4)	0.0324	0.695(9)	0.6975	0.704(9)	0.7135	0.054(2)	0.0511
0.295(2)	0.0378(6)	0.0369	0.726(11)	0.7328	0.695(8)	0.7068	0.061(2)	0.0593
0.345(2)	0.0458(4)	0.0443	0.767(7)	0.7728	0.682(10)	0.6959	0.077(2)	0.0734
0.383(3)	0.0520(7)	0.0508	0.792(8)	0.7966	0.671(8)	0.6860	0.089(2)	0.0865
0.425(3)	0.0586(8)	0.0585	0.802(6)	0.8160	0.657(9)	0.6739	0.104(3)	0.1032
0.464(4)	0.0656(8)	0.0662	0.819(8)	0.8292	0.642(8)	0.6610	0.121(3)	0.1218
0.505(3)	0.0736(7)	0.0748	0.828(5)	0.8382	0.624(8)	0.6456	0.142(3)	0.1448
0.551(10)	0.0806(15)	0.0851	0.827(6)	0.8426	0.596(11)	0.6250	0.165(4)	0.1768
0.598(6)	0.0894(10)	0.0961	0.830(8)	0.8404	0.564(10)	0.5996	0.196(5)	0.2180

TABLE VI. MD and PeTS EOS results for the vapor-liquid equilibrium of the binary LJTS mixture F ($\varepsilon_2/\varepsilon_1 = 0.5$ and $\xi_{12} = 0.85$). The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$p / \varepsilon \sigma^{-3}$		$x''_2 / \text{mol mol}^{-1}$		ρ' / σ^{-3}		ρ'' / σ^{-3}	
	MD	EOS	MD	EOS	MD	EOS	MD	EOS
0.000	0.0105(2)	0.0104	0.0000	0.0000	0.7486(4)	0.7480	0.015(2)	0.0150
0.006(1)	0.0169(3)	0.0171	0.341(11)	0.3543	0.747(4)	0.7468	0.024(1)	0.0248
0.016(1)	0.0264(4)	0.0278	0.547(5)	0.5684	0.745(5)	0.7449	0.039(2)	0.0411
0.027(1)	0.0362(2)	0.0389	0.642(10)	0.6657	0.742(6)	0.7429	0.055(2)	0.0595
0.037(1)	0.0458(5)	0.0506	0.699(6)	0.7188	0.740(8)	0.7409	0.071(2)	0.0802
0.049(2)	0.0573(5)	0.0637	0.737(9)	0.7521	0.737(8)	0.7387	0.092(2)	0.1056
0.061(2)	0.0681(5)	0.0776	0.760(8)	0.7714	0.734(8)	0.7365	0.114(3)	0.1359
0.077(2)	0.0772(4)	0.0972	0.768(7)	0.7821	0.729(9)	0.7338	0.134(3)	0.1836
0.093(2)	0.0901(3)	0.1179	0.782(6)	0.7812	0.725(11)	0.7316	0.164(3)	0.2388
0.110(6)	0.1025(10)	0.1452	0.773(8)	0.7710	0.720(15)	0.7298	0.198(4)	0.3095
0.123(4)	0.1168(7)	0.1684	0.778(6)	0.7597	0.718(14)	0.7290	0.236(5)	0.3613
0.140(5)	0.1316(10)	0.2048	0.754(13)	0.7421	0.713(19)	0.7289	0.287(7)	0.4252

TABLE VII. Interfacial properties of the binary LJTS mixture A ($\varepsilon_2/\varepsilon_1 = 0.9$ and $\xi_{12} = 1$). Results from MD and DGT+PETS EOS. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$\gamma / \varepsilon \sigma^{-2}$		$\Gamma_2^{(1)} / \sigma^{-2}$		E_2		L_{10}^{90} / σ	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.000	0.446(18)	0.4566	-	-	-	-	2.68(6)	2.33
0.064(2)	0.439(14)	0.4432	0.027(26)	0.0173	1.09(5)	1.00	2.72(4)	2.36
0.110(1)	0.423(16)	0.4339	0.056(20)	0.0290	1.06(2)	1.00	2.75(6)	2.38
0.154(2)	0.417(18)	0.4251	0.022(32)	0.0401	1.03(2)	1.00	2.76(4)	2.40
0.202(2)	0.410(13)	0.4154	0.065(47)	0.0519	1.03(2)	1.00	2.81(6)	2.42
0.246(2)	0.405(16)	0.4070	0.102(56)	0.0621	1.04(2)	1.00	2.88(8)	2.44
0.296(2)	0.393(15)	0.3973	0.007(57)	0.0737	1.01(2)	1.00	2.86(5)	2.46
0.334(1)	0.385(15)	0.3902	0.118(61)	0.0821	1.02(1)	1.00	2.90(7)	2.48
0.392(2)	0.376(11)	0.3794	0.100(62)	0.0945	1.02(1)	1.00	2.91(5)	2.52
0.436(1)	0.369(14)	0.3714	0.129(88)	0.1036	1.02(1)	1.00	2.96(8)	2.54
0.484(2)	0.361(16)	0.3627	0.096(85)	0.1133	1.02(1)	1.00	2.99(6)	2.56
0.527(2)	0.350(17)	0.3552	-0.018(18)	0.1216	1.01(2)	1.00	3.00(7)	2.58
0.574(2)	0.343(20)	0.3470	0.203(15)	0.1304	1.02(1)	1.00	3.08(7)	2.60
0.617(2)	0.327(15)	0.3395	0.211(12)	0.1384	1.02(1)	1.00	3.11(7)	2.62
0.662(1)	0.323(17)	0.3319	0.123(87)	0.1464	1.01(1)	1.00	3.12(7)	2.66
0.714(2)	0.317(18)	0.3230	0.177(13)	0.1553	1.01(1)	1.00	3.17(7)	2.66
0.764(1)	0.319(14)	0.3148	0.198(18)	0.1635	1.012(4)	1.00	3.22(11)	2.70
0.808(2)	0.302(14)	0.3077	0.316(15)	0.1704	1.011(4)	1.00	3.23(7)	2.72
0.863(1)	0.292(12)	0.2988	-0.099(14)	0.1789	1.007(4)	1.00	3.28(7)	2.74
0.904(1)	0.288(14)	0.2921	0.038(22)	0.1850	1.009(4)	1.00	3.28(7)	2.78
0.952(1)	0.283(15)	0.2846	0.452(37)	0.1918	1.008(1)	1.00	3.36(10)	2.80
1.000	0.273(18)	0.2920	-	-	-	-	3.38(6)	2.88

TABLE VIII. Interfacial properties of the binary LJTS mixture B ($\varepsilon_2/\varepsilon_1 = 0.9$ and $\xi_{12} = 1.2$). Results from MD and DGT+PETS EOS. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$\gamma / \varepsilon \sigma^{-2}$		$\Gamma_2^{(1)} / \sigma^{-2}$		E_2		L_{10}^{90} / σ	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.0000	0.446(18)	0.4566	-	-	-	-	2.68(6)	2.33
0.069(1)	0.474(16)	0.4792	-0.018(30)	-0.0224	1.08(5)	1.00	2.62(4)	2.26
0.119(1)	0.498(17)	0.4947	-0.044(42)	-0.0309	1.03(2)	1.00	2.56(5)	2.22
0.163(1)	0.523(21)	0.5069	-0.043(25)	-0.0336	1.04(1)	1.00	2.52(7)	2.18
0.212(1)	0.529(20)	0.5185	-0.044(44)	-0.0317	1.03(1)	1.00	2.49(8)	2.14
0.256(1)	0.527(18)	0.5262	-0.044(45)	-0.0260	1.02(1)	1.00	2.47(6)	2.10
0.305(1)	0.548(17)	0.5318	-0.046(46)	-0.0154	1.02(1)	1.00	2.42(5)	2.08
0.343(1)	0.545(17)	0.5337	-0.030(45)	-0.0044	1.02(1)	1.00	2.45(4)	2.08
0.399(1)	0.542(18)	0.5323	-0.03(7)	0.0164	1.01(1)	1.00	2.44(5)	2.08
0.442(1)	0.550(22)	0.5278	0.11(8)	0.0364	1.02(1)	1.00	2.43(5)	2.08
0.486(1)	0.547(20)	0.5202	0.07(7)	0.0599	1.01(1)	1.00	2.43(4)	2.10
0.528(1)	0.525(15)	0.5101	0.09(9)	0.0856	1.01(1)	1.00	2.50(6)	2.12
0.572(1)	0.515(21)	0.4965	0.14(8)	0.1163	1.02(1)	1.00	2.53(5)	2.14
0.614(1)	0.493(17)	0.4813	0.12(7)	0.1486	1.011(4)	1.00	2.60(5)	2.16
0.659(1)	0.476(16)	0.4622	0.18(8)	0.1879	1.012(4)	1.00	2.62(5)	2.22
0.712(2)	0.443(17)	0.4369	0.22(13)	0.2397	1.009(4)	1.00	2.77(7)	2.28
0.759(1)	0.419(19)	0.4123	0.34(5)	0.2918	1.011(3)	1.00	2.81(7)	2.34
0.804(1)	0.395(14)	0.3874	0.35(19)	0.3469	1.009(3)	1.00	2.90(7)	2.44
0.858(1)	0.357(15)	0.3564	0.46(11)	0.4213	1.009(3)	1.00	3.02(7)	2.52
0.900(1)	0.326(16)	0.3326	0.44(23)	0.4838	1.008(2)	1.00	3.14(6)	2.62
0.949(1)	0.300(16)	0.3045	0.51(43)	0.5648	1.008(3)	1.00	3.28(8)	2.72
1.0000	0.273(18)	0.2920	-	-	-	-	3.38(6)	2.88

TABLE IX. Interfacial properties of the binary LJTS mixture C ($\varepsilon_2/\varepsilon_1 = 0.9$ and $\xi_{12} = 0.85$). Results from MD and DGT+PETS EOS. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$\gamma / \varepsilon \sigma^{-2}$		$\Gamma_2^{(1)} / \sigma^{-2}$		E_2		L_{10}^{90} / σ	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.000	0.446(18)	0.4566	-	-	-	-	2.68(6)	2.33
0.096(1)	0.363(14)	0.3625	0.144(46)	0.1476	1.28(8)	1.47	3.04(10)	2.68
0.136(2)	0.336(17)	0.3332	0.156(55)	0.2069	1.21(6)	1.43	3.18(9)	2.82
0.183(3)	0.308(16)	0.3064	0.25(8)	0.2673	1.19(7)	1.37	3.29(9)	2.94
0.226(2)	0.292(15)	0.2872	0.29(10)	0.3137	1.17(6)	1.32	3.40(9)	3.06
0.276(3)	0.275(18)	0.2703	0.39(11)	0.3515	1.13(6)	1.25	3.52(9)	3.14
0.316(4)	0.265(13)	0.2601	0.34(13)	0.3676	1.06(3)	1.19	3.51(9)	3.18
0.377(5)	0.252(16)	0.2489	0.37(6)	0.3651	1.05(2)	1.12	3.63(11)	3.22
0.425(5)	0.236(12)	0.2423	0.38(13)	0.3404	1.05(3)	1.07	3.65(11)	3.22
0.473(4)	0.234(15)	0.2374	0.19(12)	0.2996	1.03(2)	1.03	3.56(7)	3.22
0.520(5)	0.224(15)	0.2335	0.32(14)	0.2460	1.03(1)	1.01	3.75(16)	3.24
0.572(5)	0.223(14)	0.2303	-0.17(15)	0.1761	1.01(1)	1.00	3.68(9)	3.22
0.614(3)	0.230(12)	0.2284	0.16(13)	0.1131	1.02(1)	1.00	3.62(14)	3.22
0.668(2)	0.223(17)	0.2271	0.02(20)	0.0265	1.01(1)	1.00	3.67(11)	3.22
0.722(4)	0.224(14)	0.2275	-0.006(100)	-0.0665	1.02(2)	1.00	3.55(19)	3.20
0.772(2)	0.229(14)	0.2298	-0.10(19)	-0.1540	1.01(1)	1.00	3.70(7)	3.16
0.816(2)	0.231(10)	0.2336	0.09(14)	-0.2321	1.02(3)	1.00	3.59(22)	3.14
0.873(2)	0.241(13)	0.2418	-1.00(36)	-0.3343	1.01(1)	1.00	3.64(10)	3.08
0.912(1)	0.250(15)	0.2498	-0.26(33)	-0.4018	1.009(2)	1.00	3.57(5)	3.02
0.956(1)	0.253(12)	0.2619	-0.26(66)	-0.4774	1.009(3)	1.00	3.48(8)	2.94
1.000	0.273(18)	0.2920	-	-	-	-	3.38(6)	2.88

TABLE X. Interfacial properties of the binary LJTS mixture D ($\varepsilon_2/\varepsilon_1 = 0.5$ and $\xi_{12} = 1$). Results from MD and DGT+PETS EOS. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$\gamma / \varepsilon \sigma^{-2}$		$\Gamma_2^{(1)} / \sigma^{-2}$		E_2		L_{10}^{90} / σ	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.000	0.446(18)	0.4566	-	-	-	-	2.68(6)	2.33
0.038(1)	0.370(12)	0.3812	0.106(28)	0.0947	2.02(9)	2.11	3.05(6)	2.58
0.050(1)	0.347(17)	0.3611	0.143(27)	0.1190	1.88(6)	2.04	3.18(7)	2.66
0.071(1)	0.317(14)	0.3255	0.146(34)	0.1610	1.66(4)	1.92	3.27(9)	2.82
0.099(2)	0.276(10)	0.2844	0.202(33)	0.2083	1.57(5)	1.78	3.58(10)	3.02
0.131(3)	0.233(11)	0.2415	0.257(51)	0.2557	1.47(5)	1.65	3.90(12)	3.28
0.162(3)	0.191(16)	0.2043	0.27(6)	0.2952	1.37(4)	1.54	4.28(13)	3.54
0.196(5)	0.155(15)	0.1691	0.33(7)	0.3304	1.31(4)	1.45	4.74(18)	3.88
0.224(3)	0.131(9)	0.1431	0.34(6)	0.3542	1.25(3)	1.38	5.12(17)	4.20
0.271(5)	0.098(11)	0.1050	0.38(8)	0.3830	1.17(3)	1.28	5.9(5)	4.80

TABLE XI. Interfacial properties of the binary LJTS mixture E ($\varepsilon_2/\varepsilon_1 = 0.5$ and $\xi_{12} = 1.2$). Results from MD and DGT+PETS EOS. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$\gamma / \varepsilon \sigma^{-2}$		$\Gamma_2^{(1)} / \sigma^{-2}$		E_2		L_{10}^{90} / σ	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.0000	0.446(18)	0.4566	-	-	-	-	2.68(6)	2.33
0.056(1)	0.406(22)	0.4157	0.056(23)	0.0480	1.17(6)	1.22	2.84(4)	2.45
0.098(2)	0.372(14)	0.3845	0.121(22)	0.0798	1.11(4)	1.17	3.00(7)	2.50
0.136(2)	0.337(14)	0.3557	0.091(31)	0.1069	1.07(3)	1.13	3.11(7)	2.55
0.179(1)	0.306(11)	0.3230	0.177(29)	0.1357	1.07(2)	1.10	3.30(7)	2.65
0.217(3)	0.277(18)	0.2937	0.18(4)	0.1602	1.06(2)	1.08	3.47(11)	2.75
0.262(2)	0.243(14)	0.2585	0.22(7)	0.1882	1.03(1)	1.05	3.76(9)	2.95
0.295(2)	0.213(15)	0.2323	0.222(31)	0.2082	1.02(1)	1.04	3.85(13)	3.05
0.345(2)	0.174(11)	0.1947	0.291(35)	0.2356	1.02(1)	1.02	4.33(12)	3.30
0.383(3)	0.150(11)	0.1657	0.25(7)	0.2554	1.02(1)	1.01	4.51(13)	3.50
0.425(3)	0.122(10)	0.1354	0.27(7)	0.2744	1.02(1)	1.01	4.94(17)	3.80
0.464(4)	0.098(11)	0.1084	0.28(4)	0.2889	1.01(1)	1.00	5.61(18)	4.20
0.505(3)	0.068(9)	0.0821	0.30(8)	0.2989	1.01(1)	1.00	6.60(63)	4.70
0.551(10)	0.044(11)	0.0552	0.26(12)	0.3005	1.015(4)	1.00	8.9(41)	5.50
0.598(6)	0.032(9)	0.0321	0.24(11)	0.2837	1.012(3)	1.00	9.2(16)	6.75

TABLE XII. Interfacial properties of the binary LJTS mixture F ($\varepsilon_2/\varepsilon_1 = 0.5$ and $\xi_{12} = 0.85$). Results from MD and DGT+PETS EOS. The number in the parentheses indicates the statistical uncertainty in the last decimal digit. The temperature is $T = 0.77 \varepsilon k_B^{-1}$.

$x'_2 / \text{mol mol}^{-1}$	$\gamma / \varepsilon \sigma^{-2}$		$\Gamma_2^{(1)} / \sigma^{-2}$		E_2		L_{10}^{90} / σ	
	MD	DGT	MD	DGT	MD	DGT	MD	DGT
0.0000	0.446(18)	0.4566	-	-	-	-	2.68(6)	2.33
0.006(1)	0.420(16)	0.4296	0.035(10)	0.0352	2.42(16)	2.80	2.78(7)	2.45
0.016(1)	0.382(16)	0.3884	0.087(9)	0.0891	2.25(7)	2.64	2.99(5)	2.60
0.027(1)	0.349(20)	0.3474	0.14(3)	0.1426	2.12(7)	2.47	3.19(10)	2.80
0.037(1)	0.314(13)	0.3075	0.19(3)	0.1937	1.94(5)	2.28	3.43(9)	3.00
0.049(2)	0.267(15)	0.2662	0.24(3)	0.2440	1.84(3)	2.07	3.75(12)	3.20
0.061(2)	0.240(14)	0.2265	0.27(2)	0.2868	1.70(3)	1.86	4.05(12)	3.55
0.077(2)	0.203(19)	0.1793	0.28(3)	0.3213	1.61(2)	1.59	4.32(14)	3.90
0.093(2)	0.165(17)	0.1401	0.36(3)	0.3206	1.46(2)	1.38	4.83(23)	4.30
0.110(6)	0.144(20)	0.1037	0.33(4)	0.2783	1.36(2)	1.19	5.16(21)	4.55
0.123(4)	0.103(20)	0.0824	0.39(4)	0.2324	1.25(1)	1.10	6.11(47)	4.70
0.140(5)	0.077(23)	0.0604	0.38(8)	0.1702	1.15(2)	1.04	6.75(56)	4.85