Vapor-Liquid Interface of the Lennard-Jones Truncated and Shifted Fluid: Comparison of Molecular Simulation, Density Gradient Theory, and Density Functional Theory

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Abstract

The vapor-liquid interface of the Lennard-Jones truncated and shifted (LJTS) fluid with a cut-off radius of 2.5σ is investigated for temperatures covering the range between the triple point and the critical point. Three different approaches to model the vapor-liquid interface are used: molecular dynamics (MD) simulations, density gradient theory (DGT) and density functional theory (DFT). The surface tension, pressure and density profiles, including the oscillatory layering structure of the fluid at the interface, are investigated. The PeTS (Perturbed truncated and shifted) equation of state and PeTS-i functional, based on perturbation theory, are used to calculate the Helmholtz free energy in the DGT and DFT approach. They are consistent with the LJTS force field model. Overall, both DGT and DFT describe the results from computer experiments well. An oscillatory layering structure is found in MD and DFT.

Introduction

Interfacial properties, such as surface tension and adsorption, play an important role in many processes. It is practically impossible to study nanoscale properties of fluid interfaces experimentally, as the interface fluctuates and a spatial focussing cannot be realized with the required resolution. Therefore such nanoscale properties of fluid interfaces, have to be examined with theoretical methods. Different methods are available for this:^{1,2} molecular dynamics simulation (MD), density gradient theory (DGT), and density functional theory (DFT). The MD simulations can be considered as a reference case against which the results from DGT and DFT should be compared. We apply these three methods to study the planar vapor-liquid interface of the Lennard-Jones truncated and shifted fluid (LJTS) with a cut-off radius of 2.5σ .

There are many studies in the literature in which nanoscale properties of fluid interfaces have been investigated with the aforementioned methods. In some of these studies, also two of the methods were applied and compared.³⁻²¹ The results show that the methods agree qualitatively. For a rigorous comparison, the different approaches must be applied for studying the same fluid. This is not trivial, as MD simulations are based on force fields while DGT is based on an equation

of state (EoS) and DFT on a corresponding functional. Mostly, the force field and the EoS or functional are individually fitted to experimental data^{3,4,8–10,12,13,16–18} which is only a loose link because the methods will in general not agree even for the state points to which they were fitted. Furthermore, MD simulations yield a picture of the interfacial region that is three-dimensional and shows fluctuations, whereas DGT and DFT usually consider only a one-dimensional gradient and do not take into account the fluctuations.

The LJTS potential, is probably the simplest and computationally least expensive that describes properties of simple fluids well.^{22–29} The vapor-liquid interfacial properties of the Lennard-Jones (LJ) and the LJTS fluid have been investigated many times in the literature.^{19,28,30–36} But to the best of our knowledge no systematic comparison between the three different methods MD, DGT, and DFT has yet been conducted for this fluid or any other fluid on a consistent basis (force field, EoS and functional). The truncation of the Lennard-Jones potential in the LJTS potential affects both the thermodynamic bulk^{27,34,37,38} and interfacial properties.^{32,33,35,39–41} Only the LJTS potential is considered in the present work.

Recent work from our groups provides a foundation to perform the comparison that is carried out in the present work in a rigorous way: the Perturbed Truncated and Shifted (PeTS) EoS in case of DGT and the PeTS-interfacial (PeTS-i) functional in case of DFT⁴² provide an excellent description of the LJTS fluid not only for stable but also for metastable states and interfacial properties like the surface tension. In the present work we investigate the vapor-liquid interface in detail. The pressure and density profiles obtained with the three methods are reported for temperatures covering the range between the triple point and the critical point. Also, an empirical correlation for the density profiles is used – mainly for the curve deconvolution (see below) – that was adopted from Vrabec et al.²⁸

A second focus of this work lies in the investigation of the oscillatory layering structure^{43,44} on the liquid side of the vapor-liquid density profiles, which has been investigated in the literature by integral equation theory,^{40,43,45–51} density functional theory,^{20,40,41,52} and molecular simulations^{46–49} for some model fluids. The vapor phase of a vapor-liquid interface can be regarded as an external field⁴⁰ that causes a structuring of the molecules in the liquid phase – similar to what is observed at

wall-liquid interfaces. Evans and co-workers⁴⁰ have shown, that the density of an inhomogeneous fluid $\rho^*(z^*)$ of a short ranged potential decays from the liquid surface into the bulk in the same way as the radial distribution function $g(r^*)$ does for $r^* \rightarrow \infty$, i.e. either with exponentially damped oscillations or with a monotonic decay. The occurrence and magnitude of an oscillating decay at different state points is directly related to the Fisher-Widom (FW) line,⁵³ that describes the crossover between the oscillatory and monotonic decay of the radial distribution function for short ranged potentials in the bulk fluid.^{40,44–46} The oscillatory decay occurs when the repulsive forces dominate whereas the monotonic decay occurs when attractive forces dominate. The Fisher-Widom line of the LJTS fluid with a cut-off radius of 2.5σ has been investigated in the literature^{45,49,50} and its intersection point with the vapor-liquid coexistence curve was found to be at about $T^*/T_c^* = 0.9$ and $\rho^*/\rho_c^* = 1.9$.^{40,45,49,50} Density oscillations at vapor-liquid interfaces should therefore be expected up to that temperature.

A method for analyzing the oscillatory layering structure on the liquid side of vapor-liquid interfaces that is based on a Fourier transformation and curve deconvolution is proposed in the present work. It is thereby shown that the density oscillations are found in molecular simulation data of the LJTS fluid. To the best of our knowledge such oscillations have been observed only for force fields that were trained for that feature.^{46–48} The temperature dependency of the amplitude of the layering structure is investigated. It decreases with increasing temperature until it vanishes at about $T^*/T_c^* = 0.88$ which confirms predictions from the literature.^{49,50}

Throughout the present work, all physical properties are reduced using the potential parameters ε and σ as well as the mass of the particle M , cf. Table 1.

Modelling and simulation of interfacial properties

The methods used for calculating the surface tension, density and pressure profiles of the planar interface are briefly described in the following. The vapor-liquid interfacial properties are investigated in the temperature range: from $T^* = 0.65$ to 1.05 with an increment of $\Delta T^* = 0.05$. The upper and lower bounds of that range are close to the critical point temperature and the triple

temperature, respectively, of the LJTS fluid with a cut-off at 2.5σ . Table 2 reports literature data^{27,28,34,38,54–59} for these temperatures. In the present work values of Vrabec et al.²⁸ for the critical point and van Meel et al.⁵⁷ for the triple point are used.

Molecular simulations

The molecular dynamics (MD) simulations are performed with the MD code *ls1 mardyn*⁶⁰ in the NVT ensemble with 16,000 particles in a rectangular box. Periodic boundary conditions are applied in all directions. In the studied scenario the vapor phase coexists with a liquid phase. The liquid slab is in the middle of the box, resulting in two vapor-liquid interfaces which are oriented perpendicular to the z^* -axis.³⁹ For the calculation of the interfacial thickness and the oscillatory layering structure only one side of the liquid slab is taken into account. Also only one side of the pressure and density profiles is considered for the comparison with the other methods. The elongation of the simulation box in the z^* -direction, i.e. normal to the interface, is $l_z^* = 80$ and in the tangential direction at least $l_x^* = l_y^* = 24$. The pressure and density profiles were calculated at $N = 1,200$ bins, each with a width of $\Delta z^* = 0.0667$.

The equation of motion is solved by a leapfrog integrator.⁶¹ The temperature is kept constant by a slab-wise velocity scaling thermostat.⁴ A time step of $\Delta t^* = 0.001$ is used. The equilibration is conducted for 2 million time steps, while the production runs for further 3 million time steps. The statistical errors given in the present study are equal to three times the standard deviation of all sampled block averages, each over 1 million time steps. Also the density and pressure profiles from each state point are averaged over that block interval. Since the interaction potential is truncated at 2.5σ , no long range correction for the forces and the pressure is necessary.

The Lennard-Jones truncated and shifted potential u_{LJTS} used for the molecular simulations

is⁶¹

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

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

with u_{LJ} being the full Lennard-Jones potential, ε and σ being the energy and size parameter. The distance between two particles is denoted by r . The cut-off radius r_c of the potential is set to 2.5σ throughout the present work.

The surface tension is computed from the difference between the normal and the tangential diagonal components of the overall pressure tensor,⁶² i.e. the mechanical route

$$\gamma_{\text{MD}}^* = \frac{1}{2} \int_{-\infty}^{\infty} (p_{\text{N}}^* - p_{\text{T}}^*) dz^*. \quad (3)$$

Thereby, the normal pressure p_{N}^* is given by the z^* component of the diagonal of the pressure tensor, and the tangential pressure p_{T}^* is determined by averaging over x^* and y^* components of the diagonal of the pressure tensor. The pressure calculation is based on the method proposed by Irving and Kirkwood.⁶³

Perturbed truncated and shifted equation of state and functional

The perturbed truncated and shifted (PeTS) EoS was developed to describe the thermodynamic behavior of the LJTS fluid.⁴² It is based on the perturbation theory of Barker and Henderson.⁶⁴ The dispersion contribution in the PeTS EoS is modeled as a series expansion in the density as proposed by Gross and Sadowski.⁶⁵ The PeTS-i functional reduces to the PeTS EoS in the bulk and is also described in detail by Heier et al.⁴² The equations are summarized in the supplementary information.

The PeTS EoS was fitted to vapor-liquid equilibrium simulation data and describes the vapor pressure and the saturated densities of the LJTS fluid well for the entire range in which vapor and

liquid coexist. The PeTS EoS has an average absolute deviation (AAD) to such data²⁸ in the vapor pressure $\overline{\delta p_{\text{PeTS}}^{s*}} = 0.00026$ and $\overline{\delta \rho_{\text{PeTS}}'^*} = 0.00091$ and $\overline{\delta \rho_{\text{PeTS}}''^*} = 0.00049$ in the saturated liquid and vapor density respectively.⁴² The AAD of a given property X from method m to a reference is calculated by

$$\overline{\delta X_m} = \frac{1}{N} \sum_{i=1}^N |X_{\text{ref}} - X_m| . \quad (4)$$

Also the representation of homogeneous metastable states by the PeTS EoS is good, for details see.⁴²

Density gradient theory

Density gradient theory^{66–68} is a widely used framework for calculating surface tensions for pure substances^{69–71} and mixtures^{72–78} based on an EoS, especially for real substances. For a comprehensive introduction we refer to.⁶⁹ In density gradient theory the free energy of the heterogeneous system is developed around the free energy of the homogeneous system $a_0^*(\rho^*)$. For a planar interface of a pure substance the free energy can thereby be written as:

$$a^*(\rho^*, \nabla \rho^*) = a_0^*(\rho^*) + 1/2 \kappa^* \left(\frac{d\rho^*}{dz^*} \right)^2 . \quad (5)$$

To model fluid interfaces, density gradient theory only requires the free energy of the bulk fluid and the so-called influence parameter κ^* , which describes the resistance to the density gradient. In general, κ^* is a function of the substance, the temperature and the density¹ and can be related to the direct correlation function of the uniform fluid via linear response theory.^{2,21,70,79} Nevertheless, in many applications the influence parameter is treated as a state independent parameter,^{3,4,76} which is also done in the present study.

Density profiles and the surface tension at the interface are calculated from the Euler-Lagrange

equation as

$$z^* - z_0^* = \int_{\rho_0^*}^{\rho^*} \sqrt{\frac{\kappa^*}{2\Delta\Omega^*(\rho^*)}} d\rho^* , \quad (6)$$

$$\gamma_{\text{DGT}}^* = \int 2\Delta\Omega^* dz^* . \quad (7)$$

where $\Delta\Omega^*$ is the grand thermodynamic potential defined as $\Delta\Omega^*(\rho^*) = \rho^* a_0^*(\rho^*) - \rho^* \mu^{\text{s}*} + p^{\text{s}*}$ and $a_0^*(\rho^*)$ the homogeneous free energy at the local density ρ^* , $\mu^{\text{s}*}$ the saturated bulk phase chemical potential, and $p^{\text{s}*}$ the saturated bulk pressure. The pressure profiles $p_{\text{N}}^* - p_{\text{T}}^*(z^*)$ are calculated from comparing the integrand of Eq. (3) and Eq. (7) and identifying $2\Delta\Omega^*(z^*) = p_{\text{N}}^* - p_{\text{T}}^*(z^*)$. This expression can also be derived in a rigorous way for DGT.^{80–84}

The PeTS EoS is employed here for calculating the free energy in Eq. (6) and Eq. (7). The influence parameter for the PeTS EoS was fitted in a previous work⁴² to surface tension data of the LJTS fluid between the triple and critical point from molecular simulation. It was found to be constant within the error bars of the molecular simulations results. The resulting numeric value $\kappa_{\text{PeTS}}^* = 2.7334$ was used throughout the present work. The DGT density profiles are calculated in a 20σ domain with finite $\Delta z^* = 0.01$, resulting in $N = 2,000$ bins.

Density functional theory

The free energy in density functional theory is written as a sum of contributions

$$A^*[\rho^*(\mathbf{r}^*)] = A_{\text{id}}^*[\rho^*(\mathbf{r}^*)] + A_{\text{hs}}^*[\rho^*(\mathbf{r}^*)] + A_{\text{disp}}^*[\rho^*(\mathbf{r}^*)], \quad (8)$$

where the squared brackets indicate a functional dependency on the local density $\rho^*(\mathbf{r}^*)$ and $\mathbf{r}^*$ is the location.

The PeTS-i functional from a previous work of our group is used in the density functional theory.⁴² To be consistent with the PeTS EoS, the PeTS-i functional uses the white-bear version of fundamental measure theory (FMT) from Roth et al.,⁸⁵ which reduces in the bulk fluid to the Carnhan-Starling hard sphere EoS. The dispersion contribution according to Sauer and Gross¹⁸

is applied. Heier et al.⁴² have fitted the parameter of the dispersion contribution to the surface tension value from computer experiment at $T^* = 0.8$. The equations are summarized in the supplementary information.

DFT density profiles are calculated⁵ by solving the Euler-Lagrange equation obtained from functional minimization of the free energy.

The surface tension of a planar interface is calculated from

$$\gamma_{\text{DFT}}^* = \int (a^*[\rho^*(z^*)] + p^{\text{s}*} - \rho^*(z^*)\mu^{\text{s}*}) dz^*, \quad (9)$$

where $a^*[\rho^*(z^*)]$ is defined from Eq. (8) and

$$A^*[\rho^*(z^*)] = S^* \int a^*[\rho^*(z^*)] dz^*, \quad (10)$$

with S^* being the area of the surface perpendicular to z^* . Calculations are performed on a 20σ domain with finite $\Delta z^* = 0.01$, i.e. $N = 2,000$ bins.

The DFT pressure profiles $p_{\text{N}}^* - p_{\text{T}}^*(z^*)$ are calculated from comparing the integrand of Eq. (3) and Eq. (9) and identifying $p_{\text{N}}^* - p_{\text{T}}^*(z^*) = a^*[\rho^*(z^*)] + p^{\text{s}*} - \rho^*(z^*)\mu^{\text{s}*}$. Since any functional can be derived in a gradient expansion, the arguments from^{80–84} also hold for this formula.

Empirical Correlation

A simple analytical function for the density profiles is required for the curve deconvolution described below for the investigation of the oscillatory layering structure. Many empirical functions have been proposed in the past.^{28,86–89} Vrabec et al.²⁸ came to the conclusion, that the hyperbolic tangent profile

$$\rho^*(z^*) = \frac{1}{2}(\rho_{\text{l}}^* + \rho_{\text{v}}^*) - \frac{1}{2}(\rho_{\text{l}}^* - \rho_{\text{v}}^*)\tanh\left(\frac{2z^*}{K}\right), \quad (11)$$

originally proposed by van der Waals,⁹⁰ matches the LJTS density profiles from computer experiments best. K can be understood as a measure for the interfacial thickness. Vrabec et al.²⁸ used

a temperature dependent K -parameter, defined by¹

$$K = -1.720 \left(\frac{T_c^* - T^*}{T_c^*} \right)^{1.89} + 1.103 \left(\frac{T_c^* - T^*}{T_c^*} \right)^{-0.62}. \quad (12)$$

It is known^{36,91} that density profiles obey a different decay into both bulk phases, which can be related to the bulk isothermal compressibility.⁹² The decay towards the gas bulk phase is therefore more rapid than to the liquid bulk phase. This feature is not captured by the purely empirical correlation. Also the density profiles from the empirical correlation were calculated on a 20σ domain with finite $\Delta z^* = 0.01$, i.e. $N = 2,000$ bins. Vrabec et al.²⁸ also give a correlation for the surface tension of the LJTS fluid:

$$\gamma^* = 2.08(1 - T^*/T_c^*)^{1.21}, \quad (13)$$

which is used for comparison. This power law is strictly only valid in the vicinity of the critical point. However, it has been shown to be within the error bars of simulation data in the whole temperature range.^{28,93,94}

Characterization and comparison of density profiles

Density profiles

Four types of density profiles are compared in this study:

1. Molecular dynamics simulations (MD)
2. Density gradient theory + PeTS EoS (DGT)
3. Density functional theory + PeTS-i functional (DFT)
4. Empirical correlation of the MD data (Corr)

¹In the publication of Vrabec et al.²⁸ is a misprint in Eq. (13) in the first term, which is corrected here. [correspondence with the author]

where 4. is only used as a simple reference. The brackets indicate the corresponding abbreviation used in the following. The origin on the z^* -axis of each density profile is arbitrarily chosen such that $z^*(\rho_0^*) = 0$ with $\rho_0^* = \rho_v^* + 0.5(\rho_l^* - \rho_v^*)$.

Average difference to computer experiment

The average absolute deviation between the density profiles from molecular simulations and those obtained via the theoretical route (DGT and DFT) or the empirical correlation are calculated by:

$$\overline{\delta\rho_j^*} = \frac{1}{N} \sum_i^N \left| \rho_{\text{MD}}^*(z_i^*) - \rho_j^*(z_i^*) \right| \quad \text{with } j = \text{DGT, DFT, Corr} , \quad (14)$$

where N is the number of bins on the z^* -axis. A piecewise cubic interpolation scheme is used to calculate the density at corresponding z^* positions.

Also the differences between the empirical correlation²⁸ and molecular simulations are reported for the sake of completeness.

Interfacial thickness

We use the 90-10% definition for the effective interfacial thickness L_{10}^{90} according to Lekner and Henderson.⁸⁸ It is defined as the distance between the points where the local density reaches 10% and 90% of the corresponding bulk densities:

$$L_{10}^{90} = y^*(\rho_{90}^*) - y^*(\rho_{10}^*) \quad (15)$$

$$\rho_{10}^* = \rho_v^* + 0.1(\rho_l^* - \rho_v^*)$$

$$\rho_{90}^* = \rho_v^* + 0.9(\rho_l^* - \rho_v^*).$$

Oscillatory layering structure on the liquid side of density profiles

For the analysis of the oscillatory layering structure on the liquid side of the vapor-liquid interface, a Fourier transform⁹⁵ is applied. Thereby, the wavelength and average amplitude of the oscillatory layering structure can be analyzed.

To extract the sinusoidal part of the density profile, a Laplace filter⁹⁵ is applied to the density profiles by double numerical differentiation. The Laplace filter suppresses the average value of the signal and increases the sinusoidal part of the signal. To suppress the high frequency noise in the MD density profiles a Gaussian filter with a variance of $\sigma_\lambda = 0.04$ is applied to those profiles. The Fourier transform of $\nabla^2 \rho^*$ then reads

$$\mathcal{R}_j(\omega^*) = \int_0^\infty \nabla^2 \rho_j^*(z^*) e^{iz^* \omega^*} dz^* , \quad (16)$$

with ω^* being the angular frequency and $j = \text{MD, DGT, DFT, Corr.}$ Only the density profile for $z^* > z_0^*$ is evaluated since an oscillatory layering structure is only expected on the liquid side.⁴¹ Since the Fourier transform spectra $\mathcal{R}(\omega^*)$ contains information on the shape of the density profile itself as well as on the oscillations that are of interest here, a curve deconvolution scheme is applied.⁹⁶ The spectra $\mathcal{R}_j(\omega^*)$ are approximated by a linear combination of bell-shaped curves. The part of the Fourier transform that results from oscillations in the density profile $\mathcal{R}^{\text{oscill}}(\omega^*)$ can thereby be distinguished from the part that results from the shape of the density profile $\mathcal{R}^{\text{shape}}(\omega^*)$.

$$\mathcal{R}_j(\omega^*) = a_j(T^*) \mathcal{R}^{\text{oscill}}(\omega^*) + k_j(T^*) \mathcal{R}^{\text{shape}}(\omega^*) \quad (17)$$

In this linear combination, a_j and k_j are adjustable parameters for each spectrum. The Fourier transform that describes the shape of the density profile $\mathcal{R}^{\text{shape}}$ is approximated by eight Gaussian curves and the Fourier transform that describes the oscillatory layering structure $\mathcal{R}^{\text{oscill}}$ by a single Gaussian curve. The deconvolution model parameters, i.e. the frequency of each Gaussian curve, its mean value, and its variance are kept constant throughout this work. The deconvolution model is parametrized in two steps: First, by fitting $\mathcal{R}^{\text{shape}}(\omega^*)$ to the Fourier transform of the empirical correlation $\mathcal{R}_{\text{Corr}}^{\text{shape}}$ at $T^* = 0.65$ with $k = 1$, since the empirical correlation density profile Eq. (11)-(12) has no oscillating content ($\mathcal{R}_{\text{Corr}}(\omega^*) = 0$). Second, by fitting the frequency and the variance of the Gaussian curve $\mathcal{R}^{\text{oscill}}$ to the Fourier transform $j = \text{DFT}$ at $T^* = 0.65$ and $a = 1$. For other temperatures and density profile types $j = \text{DFT, DGT, MD}$ only a_j and k_j are adjusted

by a least square fit. The peak $\mathcal{R}^{\text{oscill}}(\omega^*)$ in the spectrum can thereby be identified as a result of the oscillatory layering structure in the interface.

The peak area A^* of the peak $\mathcal{R}^{\text{oscill}}$ is calculated for all types of density profiles and temperatures, since it is proportional to the average amplitude of the sinusoidal content resulting from the oscillatory layering structure.

Results and discussion

Surface tension

Figure 1 [Figure 1 near here] shows the results for the surface tension γ^* of the LJTS fluid as a function of the temperature obtained with the different methods. The molecular simulations results stem from the present study as well as from.²⁸ Furthermore, results from DGT and DFT are shown. The surface tension values from DGT and DFT lie within the error bars of the computer experiment data for most temperatures. All methods agree within 5% up to $T^* = 1.0$. The surface tension values by molecular simulations from Vrabec et al.²⁸ and this work are in good agreement. The numerical results for the surface tension from MD, DGT and DFT are reported in Table 3.

Pressure profiles

Figure 2 [Figure 2 near here] shows the pressure profiles obtained with MD, DGT and DFT for $T^* = 0.65, 0.85$ and 1.05 . The results from the different methods agree qualitatively, but clear differences can be identified. The maximum pressure position is shifted between the methods and also the maximum pressure differs. Furthermore a minimum pressure occurs in DFT and MD but not in DGT.

The effect of the oscillatory layering structure on the pressure profiles is clearly noticeable at low temperatures for DFT in the form of two shoulders on the right side of the pressure difference peak. Also in the molecular simulation pressure profile this can be seen, but to a smaller extent than in DFT.

Density profiles

The obtained density profiles from DGT and DFT are individually compared with those from computer experiment in Figure 3 [Figure 3 near here].

The agreement between the computer experiment and both DFT and DGT is better for lower temperatures while discrepancies increase towards the critical point. The deviations are highest in the 'knee' of the liquid and the vapor side of the density profile where the curvature is highest. None of the theoretical methods stand out in their capability of describing the computer experiment density profiles. The oscillatory layering structure of the fluid on the liquid side, especially in the DFT density profile at $T^* = 0.65$ and 0.7 will be discussed in detail below.

The density profiles from all methods and temperatures coincide at approximately $z^* = -0.2$ through $\rho^* = 0.31 \pm 0.01$ which is in very good agreement with the critical density $\rho_c^* = 0.318$. This interesting finding was already reported by Bongiorno and Davis.⁹⁷ A further investigation of this phenomenon is out of the scope of this work.

Figure 4 shows the deviation of the density profiles at $T^* = 0.65$ (a); 0.85 (b) and 1.05 (c) respectively [Figure 4 near here]. Molecular simulations, which we consider as a reference, shows stochastic fluctuations in the density throughout the profile. Therefore the differences to the empirical correlation ($\delta\rho_m^*(z) = \rho_{\text{Corr}}^*(z) - \rho_m^*(z)$ with $m = \text{MD, DGT, DFT}$) are plotted, i.e. the baseline $\Delta\rho^* = 0$ corresponds to the empirical correlation. The DGT and DFT density profiles essentially coincide close to the critical point. The deviations between the theoretical methods and the computer experiment are of the same order of magnitude as the deviations between the empirical correlation and the computer experiment. This is remarkable, since DGT and DFT are predictions. At $T^* = 0.65$ the DFT density profile shows a strong oscillatory behavior compared to the empirical correlation at $z^* > 0$ in Figure 4 (a), which is a result of the oscillatory layering structure at the interface. Such oscillations are expected in DFT density profiles at $T < T_{\text{FW}}$.⁴⁹ The oscillations are also present in the computer experiment (same figure), but to a much smaller extent.

The average absolute deviation in the density profile with respect to the MD results (cf. Eq.

(14)) is shown in Figure 5 [Figure 5 near here]. The difference between the empirical correlation and molecular simulations remains rather constant in a broad temperature range ($0.65 < T^* < 1$) and increases close to the critical point, while the differences between the theoretical methods (DGT, DFT) and molecular simulations increase monotonically with the temperature. DGT is theoretically only valid in the limit of slowly changing densities, i.e. close to the critical point.^{2,91} The increasing deviation with the temperature can therefore be attributed to the increasing differences between the EoS and the LJTS force field approaching the critical point. Approaching the critical point, DGT and DFT density profiles show a very similar deviation from molecular simulations. This might be due to the classical scaling of the underlying EoS compared to the expected Ising scaling of molecular simulations. The density profiles average absolute deviation between the theory and the computer experiments $\overline{\delta\rho_j^*}$ lies about one order of magnitude higher than the AAD of the bulk saturated densities between the PeTS EoS and the corresponding computer experiments.⁴²

The temperature dependence of the 90%-10% interfacial thickness, as defined by Eq. (15) is shown in Figure 6 [Figure 6 near here]. The interfacial thickness increases monotonically with the temperature approaching a pole at the critical temperature. The theoretical methods agree with each other well at high temperatures, while they differ at lower temperatures. The 90%-10% interfacial thickness by the theoretical methods is in the entire temperature range smaller than that from molecular simulations.

This is probably due to the fact that molecular dynamics is a 3-dimensional and dynamical method, in which the resulting density profiles are gained by averaging over the two dimensions parallel to the interface and the time. The breathing and moving of the liquid slab normal to the interface and so-called capillary waves, i.e. fluctuations of the liquid surface^{1,98–101} lead to a broadening of the density profiles.^{14,46,102–104} These are shown in Figure 7 as snapshots from molecular simulations of one σ thick slices perpendicular to the interface at two temperatures [Figure 7 near here]. The liquid surface has an undulation (parallel to the surface – here in x^* and y^* -direction) that increases with the temperature. DGT and DFT are static and one-dimensional methods and therefore describe the density change at a perfectly planar interface or through one

point on the so-called intrinsic surface.

Oscillatory layering structure

Figure 8 [Figure 8 near here] shows the 2nd derivative of the density profile $\nabla^2\rho^*(z^*)$ at $T^* = 0.65$ (top) and $T^* = 0.7$ (bottom). While the gas side of the density profiles has a smooth trend for all investigated methods (MD, DGT, DFT, and Corr), the liquid side of the density profiles shows strong oscillations for DFT and damped oscillations for MD. These oscillations are due to a layering structure of the dense liquid phase at a narrow interface. The density profiles from DGT and the empirical correlation do not show this feature at all.

The z^* -positions of the maxima and minima of DFT and MD agree well. We refer to this phenomenon as 'oscillatory layering structure'. The DFT density profiles show a higher amplitude of the oscillatory layering structure than those from molecular simulations.

The Fourier transform of $\nabla^2\rho^*(z^*)$ for $z^* > 0$ is shown in Figure 9 as a function of the wavelength λ^* for the two lowest investigated temperatures $T^* = 0.65$ (top) and $T^* = 0.7$ (bottom) [Figure 9 near here]. The density profiles from the square gradient model in DGT, cf. Eq. (5), can not contain any oscillation for a pure substance due to the simplified description of the repulsion between molecules. The density profiles from the empirical correlation can not contain any oscillation for mathematical reasons, cf. Eq. (11) and Eq. (12). Accordingly, the spectra $\mathcal{R}^{\text{DGT}}$ and $\mathcal{R}^{\text{corr}}$ can be used to identify $\mathcal{R}^{\text{shape}}$ as the long bow in Figure 9, which increases monotonically with λ^* . Following the curve deconvolution ansatz in Eq. (17) the peak at $\lambda_{\text{struc}} \approx \sigma$ in the Fourier transform of DFT and MD (Figure 9) can be attributed to the oscillatory layering structure on the liquid side of the interface. The wavelength of the oscillations in the DFT density profiles can also be examined visually in Figure 8 to be approximately one σ . The wavelength of the layering structure for both MD and DFT is almost constant over all temperatures even though the amplitude decreases with increasing temperature.

Even though a Gaussian filter is applied to the MD density profiles, as described in section , to suppress stochastic fluctuations, the Fourier transform from MD density profiles show noise at about $\lambda^* < 0.7$. Due to the applied narrow filter width, an interference of the filter with the band

at λ_{struc}^* can be excluded.

The Fourier transforms are deconvoluted as described above and the obtained peak due to the oscillatory layering structure at λ_{struc}^* is integrated. This results in the peak area A^* , which is proportional to the average amplitude of the density oscillations in each density profile. The peak area A^* is plotted in Figure 10 for MD and DFT in the entire temperature range between the triple and critical temperature of the LJTS fluid. The relative peak area with respect to that in the spectrum of MD at $T^* = 0.65$ is plotted. DFT and molecular simulations density profiles have their maximum peak area at low temperatures close to the triple point as expected.^{41,45,46,49} This is due to an increased structuring of particles at the rapidly changing density with respect to z^* at the interface at lower temperatures. The peak area of $\mathcal{R}^{\text{oscil}}$ decreases monotonically with the temperature for these types of density profiles. While the temperature dependency of A^* agrees well between DFT and MD, the magnitude differs significantly. The maximum relative peak area at $T^* = 0.65$ is about 6.69 for DFT. The relatively high amplitude in the DFT density profiles compared to the MD results is mainly due to the fact that MD density profiles are averaged over two spatial coordinates (x^* and y^*), cf. Figure 7.

Surface fluctuations are present in molecular simulations^{100,101} and smear the oscillatory layering structure in the density profiles due to the spatial and time averaging. This results in a much lower amplitude of the layering in the MD density profiles. The layering at the intrinsic surface (black solid line) is visible in Figure 7 but decreases with an increasing temperature. It is therefore likely, that the layering at the intrinsic surface is more pronounced than the layering in the time and space averaged MD density profiles. The influence of surface fluctuations, i.e. capillary waves, have been discussed in the literature numerous times.^{40,41,43,46,48,104–108} Hence, capillary waves that are present in 3D molecular simulations but are not captured by DGT and DFT lead to a Gaussian broadening of the interface, which also smears the oscillatory layering structure. It is expected, that capillary wave fluctuations reduce the amplitude of the oscillatory layering structure, but their wavelength and temperature decay remains unchanged – the decay is expected to be exponential with the surface roughness.^{41,46,107} This is in line with our finding that the oscillatory layering structure in computer experiment is much less prominent than that in DFT while the wavelength

is the same, i.e. neither capillary waves nor the temperature affect the wavelength.

The error bars shown for molecular simulations in Figure 10 are estimated from the signal-to-noise ratio, i.e. the average noise peak height at $0 < \lambda^* < 0.7$ and the peak height at $\lambda^* = 1$. Only data points for which the numerical value exceeds the corresponding error bar are plotted in 10, which is only the case for the three temperatures $T^* = 0.65, 0.7$ and 0.75 . Hence, the oscillatory layering structure in the molecular simulations can only be detected with the applied method up to a temperature of $T^* \simeq 0.75$. The shown dashed line is an extrapolation for the MD results with a simple $1/T^*$ function that also nicely reproduces the temperature dependency of A^* for DFT.

The dotted vertical line in 10 indicates the temperature $T^*/T_c^* = 0.88$ where the Fisher-Widom (FW) line for the LJTS fluid intersects the dew line according to.^{45,49,50} This is in very good agreement with the temperature decay and vanishing of the oscillatory layering structure for DFT and MD found in this work.

Conclusion

The vapor-liquid interface of the Lennard-Jones truncated and shifted (LJTS) fluid is investigated in the present work by molecular simulations, density gradient theory, and density functional theory. The PeTS (perturbed truncated and shifted) EoS and PeTS-i functional, developed in a previous work of our group,⁴² are applied.

DGT and DFT describe the interfacial properties, i.e. the density and pressure profiles and the surface tension, of the LJTS fluid from molecular simulations similarly well. The results for the surface tension from DGT and DFT lie mostly within the error bars of the molecular simulations results. It is thereby shown that the use of a very accurate EoS in density gradient theory or functional in density functional theory leads to good agreement between those theoretical methods and molecular simulations regarding the interfacial structure.

However, the comparison of molecular simulations, density gradient theory and density functional theory reveals some significant differences, i.e. DGT does not generate the drop in the pressure profile on the vapor side of the interface¹⁴ and the oscillatory layering structure on the

liquid side of the density profile.

The post-processing method that is applied here for the investigation of the oscillatory layering structure reveals that density oscillations, as predicted by DFT, are also present in molecular simulations density profiles for the LJTS fluid, however, with a lower amplitude. The decay of the amplitude of the oscillatory layering structure with an increasing temperature is found to be in very good agreement with predictions for the Fisher-Widom line by Dijkstra and Evans.⁴⁹ The amplitude decreases with an increasing temperature while the wavelength stays constant. Since the MD density profiles are smeared by surface fluctuations which are not present in DFT, the density oscillations are significantly smaller in their amplitude, as also discussed in.^{40,46,104} Investigating the influence of a Gaussian convolution on the DFT density profiles, which considers the temperature dependent surface fluctuation amplitudes and the statistical distribution of interface positions, could be helpful for future work.

The fact that density profiles from different temperatures seem to coincide at the critical density, if the origin of the spatial axis is set to the density of the rectilinear diameter at each temperature might be an interesting topic for future systematic investigations.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at "DOI-LINK". It comprises the full equations and derivation for the PeTS equation of state and the PeTS-i functional.

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Table 1: Definitions of physical properties in reduced units.

Length	$z^* = z/\sigma$
Area	$S^* = S/\sigma^2$
Temperature	$T^* = k_{\text{B}}T/\varepsilon$
Density	$\rho^* = \rho\sigma^3$
Pressure	$p^* = p\sigma^3/\varepsilon$
Surface tension	$\gamma^* = \gamma\sigma^2/\varepsilon$
Time	$t^* = t(\varepsilon/m)^{1/2}/\sigma$
Free energy per particle	$a^* = a/\varepsilon$
Free energy	$A^* = A/\varepsilon$
Potential energy	$u^* = u/\varepsilon$
Influence parameter	$\kappa^* = \kappa/(\sigma^5/\varepsilon)$

Table 2: Critical parameters (top) and triple parameters (bottom) of the LJTS fluid. The bold values indicate the values that were used in the present work.

	T_c^*	ρ_c^*	p_c^*
Dunikov et al. ³⁸	1.06	0.3173	0.097
Haye and Bruin ⁵⁸	1.08	–	–
PeTS EoS this work	1.089	0.3092	0.102
Shi and Johnson ⁵⁹	1.08	0.3211	–
Smit ²⁷	1.09	0.317	–
Thol et al. ⁵⁴	1.086	0.319	0.101
Trokymchuk and Alejandre ³⁴	1.073	0.323	0.0908
	1.186	0.319	0.1098
Vrabec et al. ²⁸	1.0779	0.319	–

	T_{trip}^*	p_{trip}^*
Bolhius and Chandler ⁵⁵	0.55	—
Toxvaerd ⁵⁶	0.62	—
van Meel et al. ⁵⁷	0.62	0.00271

Table 3: Surface tension data from MD, DGT, and DFT.

T^*	γ_{MD}^*	γ_{DGT}^*	γ_{DFT}^*
0.65	0.670(7)	0.683	0.669
0.7	0.584(7)	0.586	0.579
0.75	0.486(11)	0.493	0.489
0.8	0.400(4)	0.403	0.402
0.85	0.312(15)	0.317	0.317
0.9	0.229(7)	0.235	0.235
0.95	0.152(7)	0.158	0.157
1	0.075(2)	0.088	0.085
1.05	0.025(4)	0.029	0.022

Figure 1: Top: Surface tension of the LJTS fluid as a function of the temperature. Data obtained from molecular simulations (filled squares; ²⁸ empty squares: this work), DGT (circles) and DFT (triangles). The solid line is an empirical correlation for the surface tension proposed in, ²⁸ cf. Eq. (13). Bottom: Relative deviation for the surface tension from the empirical correlation: values by DGT (circles), DFT (triangles), MD from this work (empty squares), and Vrabec et al. ²⁸ (full squares) as a function of temperature.

Figure 2: Difference between normal and tangential pressure at the interface of the LJTS fluid at $T^* = 0.65$ (top); $T^* = 0.85$ (center) and $T^* = 1.05$ (bottom): molecular simulations (symbols), DGT (solid line) and DFT (dashed line).

Figure 3: Density profiles of the planar interface: results from molecular simulations (symbols) are compared to (a) DGT and (b) DFT, which are indicated as solid lines. The density profiles are compared at $T^* = 0.65$ ($\triangleright$); 0.7 ($\diamond$); 0.75 ($\triangleleft$); 0.8 ($\square$); 0.85 (∇); 0.9 ($\triangle$); 0.95 ($\circ$); 1.0 ($\triangleleft$); 1.05 ($\square$).

Figure 4: Deviation plots of density profiles at $T^* = 0.65$ (top), $T^* = 0.85$ (center), and $T^* = 1.05$ (bottom). The baselines represent the empirical correlation (Eq. (11) to Eq. (12)). The solid line indicates DGT, the dashed line DFT, and symbols molecular simulations.

Figure 5: Average absolute deviation of density profiles to molecular simulations results, cf. Eq. (14): circles indicate DGT, triangles DFT, and diamonds the empirical correlation. Dotted lines indicate triple temperature and critical temperature. Solid lines are a guide for the eye.

Figure 6: Temperature dependency of 90%–10% interfacial thickness (cf. Eq. (15)) from molecular simulations (symbols), and DGT (solid line), DFT (dashed line), and the empirical correlation (dashed-dotted line). Dotted vertical lines indicate triple temperature and critical temperature. The ordinate has a reciprocal scaling.

Figure 7: Snapshots of vapor-liquid interface from molecular simulations of the LJTS fluid at (a) $T^* = 0.65$ and (b) $T^* = 0.85$. The slice that is shown has a width of $\Delta y^* = 1$. The solid black line schematically indicates the intrinsic surface from the current molecular configuration. The black dotted line indicates the equidistant surface for the layering structure at the distance λ_{struc}^* from the intrinsic surface.

Figure 8: 2nd derivative of density profiles at $T^* = 0.65$ and $T^* = 0.7$: results from molecular simulations (symbols), DGT (solid line), DFT (dashed line), and the empirical correlation (dot-dash line).

Figure 9: Fourier transform $\mathcal{R}$ of second derivative of density profiles as a function of the wavelength λ^* at $T^* = 0.65$ and $T^* = 0.7$: molecular simulations (blue), DGT (orange), DFT (red), and the empirical correlation (pink). λ^*_{struc} indicates the wavelength from the oscillatory layering structure.

Figure 10: Temperature dependency of the relative peak area of $\mathcal{R}^{\text{oscill}}$ at λ_{struc}^* calculated by the curve deconvolution: molecular simulations (squares) and DFT (triangles). The dashed line is a $\propto 1/T^*$ extrapolation for the MD results to higher temperatures. The normalization is done with respect to A_{MD}^* at $T^* = 0.65$. The error bars from molecular simulations are estimated from the signal-to-noise ratio in the Fourier transform, cf. Figure 9. The dotted lines indicate the triple temperature, the temperature $T^*/T_c^* = 0.88$ at which the Fisher-Widom (FW) line crosses the dew line,⁴⁹ and the critical temperature respectively. Solid lines are a guide for the eye.

Graphical TOC Entry