Three-Dimensional Phase Field Modeling of Inhomogeneous Gas-Liquid Systems Using the PeTS Equation of State

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Abstract

Recently, an equation of state (EoS) for the Lennard-Jones truncated and shifted (LJTS) fluid has become available. As it describes metastable and unstable states well, it is suited for predicting density profiles in vapor-liquid interfaces in combination with density gradient theory (DGT). DGT is usually applied to describe interfaces in Cartesian one-dimensional scenarios. In the present work, the PeTS EoS is implemented into a three-dimensional phase field (PF) model which can be used for studying inhomogeneous gas-liquid systems in a more general way. The results are compared with results from molecular dynamics (MD) simulations for the LJTS fluid that are carried out in the present work and good agreement is observed. The PF model can therefore be used to overcome the scale limit of molecular simulations. A finite element (FE) approach is applied for the implementation of the PF model. This requires the first and second derivatives of the PeTS EoS which are calculated using hyper-dual numbers. Several tests and examples of applications of the new PeTS PF model are discussed.

1. Introduction

In order to investigate vapor-liquid interfaces, molecular dynamics (MD) simulations as well as density gradient theory (DGT, also known as square gradient theory) based on equations of state (EoS) can be applied. One-dimensional vapor-liquid interfaces have often been the focus of DGT simulations, see e.g. [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. However, to the best of our knowledge, DGT is currently not applied for the three-dimensional case.

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Phase field (PF) models are used in a variety of research fields including solidification, solid-state phase transformation, and crack propagation. For a broader overview, the reader is referred to [11] and the references therein.

A key component of a PF model is the free energy density which is minimized to determine the evolution of the order parameter of the PF model. As mentioned in [12], the free energy density used within a PF model should reproduce interfacial properties that are determined on an atomistic scale. The fact that it can be difficult to determine the necessary parameters for the free energy of the PF model experimentally makes it favorable to link the free energy of the PF model to atomistic simulations [13].

The general concept of feeding a PF model with data from atomistic simulations has therefore been applied by various researchers. For PF models dealing with simulations of solidification, an approach in which the properties of the solid-liquid interface of the PF simulations are taken from MD simulations is presented in [14]. In [13] the authors extract input parameters for their PF simulations of solidification from MD simulations and sensitize the fact that when extracting parameters from MD simulations one has also to consider the difference of the methods regarding the underlying assumptions and approximations. A PF simulation with parameters that are determined by MD simulations can also be found in [12]. As shown in [15] MD simulations cannot only be used to determine the input parameters for a PF simulation but can also provide a meaningful initialization state of the PF order parameter. Along these lines we mention that the authors of [16] show a method of mapping the discrete data of atomistic grain boundary simulations to a continuous order parameter. Regarding the field of ferroelectric materials, a fitting of the free energy of the used PF model to atomistic simulations can be found in [17, 18]. A multiscale approach for the simulation of precipitation in an aluminum alloy can be found in [19, 20]. There, the energy contributions of the bulk, interface, and strain are provided from atomistic simulations and are included in the PF model.

A drawback of these models is that the information on the physics obtained from the molecular models is incorporated into the PF model by fits. It is more attractive to directly incorporate an EoS which adequately represents the behavior of the considered substance into the PF model. This is, to the best of the authors' knowledge, done here for the first time.

The Lennard-Jones truncated and shifted (LJTS) model is probably the most simple molecular model which describes the thermodynamic behavior of fluids realistically. It is therefore often used in systematic thermodynamic studies of fluids by atomistic simulations, including studies on interfaces [21, 22, 23, 24, 25, 26, 27, 28]. Throughout the present paper LJTS refers to a model with a cut-off radius of 2.5 the LJ size parameter σ .

Recently, an EoS (PeTS: perturbed LJ truncated and shifted [29]) was developed. The PeTS EoS was formed based on perturbation theory in such a way as to match results of MD simulations of the LJTS fluid and describes the properties of the LJTS fluid well not only for stable states but also for metastable and unstable sates. This distinguishes the PeTS EoS from the two other available EoS for the LJTS fluid [30, 31]. Hence, the PeTS EoS lends itself for coupling with DGT or PF models of fluid interfaces.

The present work reports on the incorporation of the PeTS EoS into a three-dimensional PF model. As a result of the direct coupling with the EoS, all properties determined in the PF simulation gain physical meaning, not only the bulk properties but also all properties in the transition zone, including the width of that zone and the density gradient. An investigation of the sharp interface limit beyond which the PF results do not depend on the width of the transition zone, see for instance [32, 33], is therefore not necessary. In other words, the scale level of the presented PF model is the same as the scale level of the MD simulations. The general aim of the authors' effort is to formulate a PF model that is in close accordance with the underlying physics of the MD simulations but can overcome their scale limitation.

It shall be mentioned that the presented model can be viewed from two different perspectives. On the one hand, the model can be viewed as a PF model that incorporates a much more evolved and physically correct energy density function than the commonly used generic double-well potential. On the other hand, the model can also be seen as a three-dimensional extension of DGT based on an EoS.

The PeTS EoS has a high level of complexity. The first and second derivatives of the EoS are needed for an implementation of the proposed PF model in the finite element (FE) context. Therefore, the concept of hyper-dual numbers [34, 35] is used here in order to automatically compute the exact values of the first and second derivatives of the EoS without an explicit differentiation of the EoS. This makes it possible to interchange the EoS used for the PF model in a fast and straightforward manner. To the best of our knowledge, this is the first time that hyper-dual numbers are used to calculate thermodynamic derivatives, which is astonishing as thermodynamics is known to be a field in which derivatives are highly important and often have to be obtained for functions with a high level of complexity.

In the following, first the PF model and its coupling with the PeTS EoS are described. Then, results from PF simulations of different scenarios are presented and compared to results from MD simulations with the LJTS model. This includes scenarios in which one-dimensional DGT cannot be applied.

2. Phase field model

2.1. Free energy

The basic framework for the free energy $F_{\rm PF}$ of a PF model for inhomogeneous gas-liquid systems in a computational domain \mathcal{B} consists of two parts. One depending on the local value of the order parameter $\varphi(\boldsymbol{x},t)$ and the other depending on the local gradient of the order parameter $\nabla \varphi(\boldsymbol{x},t)$ where \boldsymbol{x} and tdesignate the position in space and the time,

$$F_{\rm PF}[\varphi, \nabla \varphi] = \int_{\mathcal{B}} \left[f_1(\varphi) + f_2(\nabla \varphi) \right] \, \mathrm{d}V \,. \tag{1}$$

Since the PF simulation strives to minimize the free energy $F_{\rm PF}$ of the system, the slope of the first part $f_1(\varphi)$ defines the value of the order parameter φ in the bulk phases where the gradient of the order parameter is

zero. Moreover, it also defines the free energy of the bulk phases. In classical PF models, often a double-well potential or double-obstacle potential is used for $f_1(\varphi)$ [11]. They typically lead to bulk values of $\varphi = 0$ and $\varphi = 1$ and a vanishing free energy density $f_1(0) = f_1(1) = 0$ in the bulk phases. In this case, the bulk values $\varphi = 0$ and $\varphi = 1$ do only indicate which phase is present at a certain location and are not a physical quantity by themselves. Using only the first part $f_1(\varphi)$ might lead to infinitely often alternating bulk phases with sharp interfaces between them. The second part $f_2(\nabla \varphi)$ punishes too steep and too many transitions between the bulk phases. The combination of both parts allows to adjust the width of the transition zone between the bulk phases as well as the excess energy of the interface by two parameters that are included in $f_1(\varphi)$ and $f_2(\nabla \varphi)$. Here, the excess energy of the interface is the difference between the actual free energy of the interface and the interfacial free energy that results from linearly interpolating the free energy densities of the bulk phases.

The term free energy is commonly used for designating $F_{\rm PF}$, cf. (1), also when only empirical expressions are used for the construction of the functions $f_1(\varphi)$ and $f_2(\nabla \varphi)$. In the present work, rather than using an empirical expression for the free energy, results from a molecular EoS, the PeTS EoS, are used. Throughout the present paper the LJ dimensions are used for all physical quantities, e.g. the free energy. For the values of the size parameter of the LJ potential σ as well as its energy parameter ε the convention $\sigma = \varepsilon = 1$ is employed. Density always refers to particle density.

For a fluid with a homogeneous density ρ the free energy density is given by

$$f_1^{\text{EoS}}(\rho, T) = \rho \cdot a(\rho, T) , \qquad (2)$$

where ρ and the temperature T are used as variables and the free energy per particle $a(\rho, T)$ is determined from the PeTS EoS. As the temperature T is held constant in each simulation, it will be omitted in the notation. As the density determines the bulk phases and the transition zone between them, ρ can be identified as the order parameter of the present PF model. Following [36], the free energy density of an inhomogeneous fluid, for which the density $\rho(\mathbf{x}, t)$ depends on \mathbf{x} and t, depends not only on the local density but also on the density of the immediate environment of each point according to

$$f_2^{\text{EoS}}(\nabla\rho) = \frac{1}{2}\kappa|\nabla\rho|^2, \qquad (3)$$

with κ determining the weight of the (spatial) gradient term. The constant κ is determined in such a way that the excess energy of a liquid-vapor interface is consistent with its surface tension. Details are explained in the next section. The free energy F_{EoS} reads

$$F_{\rm EoS}[\rho, \nabla \rho] = \int_{\mathcal{B}} \left[\rho \cdot a(\rho) + \frac{1}{2} \kappa |\nabla \rho|^2 \right] \, \mathrm{d}V \,. \tag{4}$$

The term $\rho \cdot a(\rho)$ plays the same role as the double-well potential or obstacle potential in classical PF models. A plot of $\rho \cdot a(\rho)$ as obtained from the PeTS EoS can be seen in Fig. 1 (left), where the local

density of the liquid bulk phase is denoted by ρ' and the local density of the gas bulk phase by ρ'' . The order parameter of this PF model is not some variable φ without a physical background but the actual local particle density ρ . This is why this PF model can also be viewed as a three-dimensional extension of classical DGT, as mentioned in the introduction.

A PF model derived from (4) does not necessarily conserve the number of particles, i.e. the mass, inside the computational domain. In order to meet the constraints of an NVT ensemble, a Lagrange multiplier λ is added to (4) as described in [37]

$$F[\rho, \nabla \rho] = \int_{\mathcal{B}} \left[\rho \cdot a(\rho) + \frac{1}{2} \kappa |\nabla \rho|^2 \right] \, \mathrm{d}V + \lambda \left(\int_{\mathcal{B}} \rho \, \mathrm{d}V - N \right) \,. \tag{5}$$

Here, N is the number of particles inside the computational domain.

2.2. Computation of κ

In order to make the model physically meaningful it is not enough to determine $\rho \cdot a(\rho)$ from the PeTS EoS. Also κ has to be chosen in a consistent way. This can be done by considering the fact that the excess free energy of the interface between the liquid and the gas phase is related to the surface tension γ_{vl} between them. The excess free energy ΔF (or excess grand potential $\Delta \Omega$) is computed from

$$\Delta F[\rho, \nabla \rho] = \Delta \Omega[\rho, \nabla \rho] = \int_{\mathcal{B}} \left[\rho \cdot a(\rho) + \frac{1}{2} \kappa |\nabla \rho|^2 \right] dV - \int_{\mathcal{B}} \left[\mu^{s} \cdot \rho - p^{s} \right] dV$$
$$= \int_{\mathcal{B}} \left[\Delta \omega + \frac{1}{2} \kappa |\nabla \rho|^2 \right] dV,$$
(6)

with the homogeneous excess free energy density

$$\Delta \omega = \rho \cdot a(\rho) - \mu^{s} \cdot \rho + p^{s}, \qquad (7)$$

the saturated chemical potential

$$\mu^{s} = \left. \frac{\partial(\rho \cdot a(\rho))}{\partial \rho} \right|_{\rho = \rho'} = \left. \frac{\partial(\rho \cdot a(\rho))}{\partial \rho} \right|_{\rho = \rho''},\tag{8}$$

and the vapor pressure p^{s} [36]. An illustration of $\Delta \omega$ is shown in Fig. 1.

For a single planar vapor-liquid interface normal to the x-direction with an interface surface area $A, \Delta F$ reduces to

$$\Delta F[\rho, \nabla \rho] = \Delta \Omega[\rho, \nabla \rho] = A \int_{-\infty}^{+\infty} \left[\Delta \omega + \frac{1}{2} \kappa |\nabla \rho|^2 \right] \, \mathrm{d}x \,. \tag{9}$$

Since $\frac{\Delta F}{A} = \gamma_{\rm vl}$, the Euler equation as well as the fact that $\Delta \omega$ is nonzero at the interface only, leads to

$$\gamma_{\rm vl} = \sqrt{2\kappa} \int_{\rho''}^{\rho'} \sqrt{\Delta\omega} \,\mathrm{d}\rho \tag{10}$$

[36]. Therefore, κ can be computed from

$$\kappa = \frac{1}{2} \left[\frac{\gamma_{\rm vl}}{\int_{\rho''}^{\rho'} \sqrt{\Delta\omega} \,\mathrm{d}\rho} \right]^2 \,. \tag{11}$$



Figure 1: Free energy density $\rho \cdot a(\rho)$ and homogeneous excess free energy density $\Delta \omega$ over particle density ρ . The densities ρ' and ρ'' denote the bulk densities, μ^{s} the saturated chemical potential, and p^{s} the vapor pressure. Temperature T = 0.7.

In [29] MD simulation data of the surface tension $\gamma_{\rm vl}$ of the LJTS fluid [28] are used to determine κ for the PeTS EoS. It is found that a temperature independent value of $\kappa = 2.7334$ gives good results. This value is used here, too.

2.3. Numerical solution strategy

A necessary condition for a static solution configuration of the order parameter ρ is given by the first order optimality condition of F. As there is often a large distance between the initial configuration and the static solution, an evolution equation of Allen-Cahn [38] type is chosen in order to reduce the distance to the solution. This numerical relaxation solves

$$\dot{\rho} = -M \frac{\delta_{\rho} \left(\rho \cdot a(\rho) + \frac{1}{2} \kappa |\nabla \rho|^2 + \lambda \rho \right)}{\delta \rho} \quad \text{and} \quad \delta_{\lambda} F = 0 \tag{12}$$

for a number of computational time steps to approach the static solution. Here, (\cdot) is the derivative with respect to the computational time, M is the mobility and $\delta_b A$ is the first variation of A with respect to b. Since (5) does include an additional Lagrange multiplier constraint to conserve the number of particles, i.e. the mass, within the computational domain, the fact that the Allen-Cahn evolution equation does not conserve mass is meaningless. Once the configuration is close to the stationary solution

$$\int_{\mathcal{B}} 0.5 \left(\frac{\dot{\rho}}{M}\right)^2 \,\mathrm{d}V \le \mathrm{tol}\,,\tag{13}$$

the quasi static limit conditions

$$\delta_{\rho}F = 0 \quad \text{and} \quad \delta_{\lambda}F = 0,$$
(14)

are solved instead of (12). With n denoting the outer normal to the boundary of the computational domain, the natural boundary condition reads

$$\nabla \rho \cdot \boldsymbol{n} = 0. \tag{15}$$

Without further ado, this leads to a contact angle of 90° at the boundary of the computational domain. Other contact angles are possible by including the energy contributions of the surface tensions from the solid-liquid as well as the solid-vapor interfaces into (5), see e.g. [39, 40, 41, 37].

The finite element method (FEM) is applied to solve (12) and (14). For this, ρ and λ are discretized as

$$\rho^{e} = \overline{N} \,\overline{\rho} = \begin{bmatrix} N_{1} & N_{2} & \dots & N_{n} \end{bmatrix} \begin{bmatrix} \rho_{1} \\ \rho_{2} \\ \dots \\ \rho_{n} \end{bmatrix} \quad \text{and} \quad \lambda^{g} = \overline{N_{\lambda}} \,\overline{\lambda} = \lambda \,. \tag{16}$$

Here, $\rho_i (i = 1, 2, ..., n)$ are the values at the *n* FE nodes and N_i the FE shape functions. As λ is a global degree of freedom that is located on the entire domain, $\overline{N_{\lambda}} = 1$ and $\overline{\lambda} = \lambda$. The superscripts $(\cdot)^e$ and $(\cdot)^g$ will be omitted in the following. Solving (14) using Newton's method leads to the linearized system of equations for the increments $\overline{\Delta\rho}$ and $\overline{\Delta\lambda}$

$$\begin{bmatrix} \overline{\delta\rho} \\ \overline{\delta\lambda} \end{bmatrix}^T \left(\begin{bmatrix} \overline{K_{\rho\rho}} & \overline{K_{\rho\lambda}} \\ \overline{K_{\lambda\rho}} & 0 \end{bmatrix} \begin{bmatrix} \overline{\Delta\rho} \\ \overline{\Delta\lambda} \end{bmatrix} = \begin{bmatrix} \overline{R_{\rho}} \\ \overline{R_{\lambda}} \end{bmatrix} \right),$$
(17)

with

$$\overline{R_{\rho}} = \int_{\mathcal{B}} \left[\frac{\partial \left(\rho \cdot a(\rho) \right)}{\partial \rho} \, \overline{N}^{\mathrm{T}} + \kappa \nabla \rho \, \overline{B}^{\mathrm{T}} + \lambda \, \overline{N}^{\mathrm{T}} \right] \, \mathrm{d}V \,, \tag{18}$$

$$\overline{R_{\lambda}} = \left(\int_{\mathcal{B}} \rho \,\mathrm{d}V - N\right) \,\overline{N_{\lambda}}^{\mathrm{T}} \,, \tag{19}$$

as the residuals belonging to ρ and λ , and

$$\overline{K_{\rho\rho}} = \int_{\mathcal{B}} \left[\frac{\partial^2 \left(\rho \cdot a(\rho) \right)}{\partial \rho^2} \,\overline{N}^{\mathrm{T}} \,\overline{N} + \kappa \,\overline{B}^{\mathrm{T}} \,\overline{B} \right] \,\mathrm{d}V \,, \tag{20}$$

$$\overline{K_{\rho\,\lambda}} = \int_{\mathcal{B}} \overline{N}^{\mathrm{T}} \,\overline{N_{\lambda}} \,\mathrm{d}V\,,\tag{21}$$

$$\overline{K_{\lambda\rho}} = \overline{K_{\rho\lambda}}^{\mathrm{T}}$$
(22)

as their derivatives with respect to ρ and λ . Here, \overline{B} contains the spatial derivatives of the shape functions. With (18) it becomes apparent that the Lagrange multiplier λ can be identified as the chemical potential with a change of sign $-\mu$.

2.4. Hyper-dual numbers

The computation of (18) and (20) requires the first and second derivatives of $a(\rho)$ with respect to ρ . Since $a(\rho)$ is a very evolved formula, its explicit derivation is time consuming and prone to errors. This is why the concept of hyper-dual numbers [34, 35] is applied here to compute the first and second derivatives. Hyper-dual numbers extend the concept of a complex step first derivative approximation. They enable calculating exact and step-size independent first and second derivatives. A hyper-dual number $x_{\rm hd}$ consists of one real and three imaginary parts

$$x_{\rm hd} = a + \epsilon_1 b + \epsilon_2 c + \epsilon_1 \epsilon_2 d \,. \tag{23}$$

The imaginary units ϵ_i have the properties

$$\epsilon_1^2 = \epsilon_2^2 = (\epsilon_1 \epsilon_2)^2 = 0, \qquad (24)$$

and

$$\epsilon_1 \neq \epsilon_2 \neq \epsilon_1 \epsilon_2 \neq 0. \tag{25}$$

Developing the Taylor series of a function g at the position of the real variable x and evaluating it at the new position $y_{\rm hd} = x + \epsilon_1 h_1 + \epsilon_2 h_2 + \epsilon_1 \epsilon_2 \cdot 0$ with arbitrary constants h_1 and h_2 leads to

$$g(y_{\rm hd}) = g(x) + (\epsilon_1 h_1 + \epsilon_2 h_2)g'(x) + \epsilon_1 \epsilon_2 h_1 h_2 g''(x) \,. \tag{26}$$

All terms of higher order vanish in the Taylor series due to (24). Therefore, (26) is the complete Taylor series and the exact derivatives can be obtained as

$$g'(x) = \frac{\operatorname{Im}_{\epsilon_1} g(y_{\mathrm{hd}})}{h_1} = \frac{\operatorname{Im}_{\epsilon_2} g(y_{\mathrm{hd}})}{h_2} \quad \text{and} \quad (27)$$

$$g''(x) = \frac{\operatorname{Im}_{\epsilon_1 \epsilon_2} g(y_{\mathrm{hd}})}{h_1 h_2} \,. \tag{28}$$

Within the FE code of the present model, a subprogram is used in order to compute the values of

$$\frac{\partial \left(\rho \cdot a(\rho)\right)}{\partial \rho} \quad \text{and} \quad \frac{\partial^2 \left(\rho \cdot a(\rho)\right)}{\partial \rho^2} \tag{29}$$

at each integration point. The subprogram is written in Fortran and extends the mathematical operations to the new variable class of hyper-dual numbers using operator overloading. The subprogram contains the formula for the free energy per particle $a(\rho, T)$ but not for its derivatives. However, by feeding $\rho_{hd} =$ $\rho + \epsilon_1 h_1 + \epsilon_2 h_2 + \epsilon_1 \epsilon_2 \cdot 0$ and T the values for (29) which are needed in (18) and (20) are obtained, see Fig. 2. It is easy to interchange the EoS as one only needs to change the term for $a(\rho, T)$ but does not have to derive the analytic expressions for (29).



Figure 2: Subprogram computes (29) using hyper-dual numbers. Input: ρ_{hd} and T. Output: derivatives with respect to density.

3. Simulation

In this section, four three-dimensional scenarios for application of the PF model based on the PeTS EoS are discussed. In the first example a situation with a random initial density distribution is studied. The second and third examples regard the basic configurations of a planar interface and a liquid droplet surrounded by a gas phase. The last example shows different evolution paths of two droplets.

3.1. Modeling

The PF model is implemented into the FE program *FEAP* [42]. For all PF simulations the computational area is a cube with an edge length of $l_e = 20$ and $n_e = 80$ hexahedral elements across each edge. 8-node elements with tri-linear shape functions are used. The temperature T and the number of particles N (defining the average density of the computational domain) vary between the scenarios and are given below. The free energy is computed from (5).

The MD simulations, with which the PF results are compared, are carried out in the canonical (NVT) ensemble using the massively parallel code *ls1 mardyn* [43]. For all simulations the LJTS potential is used. The temperature is kept constant with the Andersen thermostat [44] with a collision frequency of $\nu = 0.05$. The starting configuration corresponds to a supersaturated vapor in all scenarios. The time step is $\Delta t = 0.0005$. Further details (e.g. the number of particles $N_{\rm MD}$) vary between the scenarios and are given below.

The level of parallel computing is different for the PF and MD simulations. They are also not carried out on the same machine and the PF simulations are not optimized for speed. Solely to give an idea on how the computational effort compares, the computation times are stated. Here, computation time refers to the sum of the times spend on the individual CPUs.

Phase separation

In order to test the robustness of the model to describe phase separation, the computational domain is initialized with a random density distribution. The random density distribution is obtained by setting the value for each of the 81³ nodes of the FE mesh to a random density value between ρ' and ρ'' . The random density values are generated using *MATLAB* ($\rho_{init} = (\rho' - \rho'') \cdot rand(81^3, 1) + \rho''$). Due to the steep density gradients, this initialization is very challenging for the PF model. The temperature is set to T = 0.7 and the number of particles is N = 3200. The value of the mobility constant is M = 10.

Planar interface

The PF simulations regarding a planar interface between a liquid and a gas phase are done for three different temperatures $T \in \{0.7 \ 0.8 \ 0.9\}$. The number of particles is N = 3200. Each PF simulation is initialized with the same density profile, cf. dashed line in Fig. 4 (right). The solution density profile is evaluated across a line that goes through the center of the computational area and is perpendicular to the interface (Fig. 4 (left)).

The MD simulations of the same scenario are carried out using $N_{\rm MD} = 25\,624$ particles, a cubic simulation box with an edge length of 40 and periodic boundary conditions in every direction. Due to the periodic boundary conditions the edges of the MD simulation box have to be twice the size as those of the PF simulation box, i.e. the volume and therefore also the number of particles are eight (2³) times as large as in the PF simulations. The simulations took at least 11 000 000 time steps until equilibrium was reached and a planar interface was developed.

The width of the interface is evaluated for the PF and MD simulations. There are different definitions for the width of the interface [45]. Often the "10-90 thickness" L_{10-90} is evaluated

$$L_{10-90} = x(\rho = \rho_2) - x(\rho = \rho_1)$$
(30)

with

$$\rho_1 = \rho'' + 0.9(\rho' - \rho'') \quad \text{and} \quad \rho_2 = \rho'' + 0.1(\rho' - \rho''),$$
(31)

cf. Fig. 5. Another option is based on constructing the tangent to the point where the density is in the arithmetic mean of the bulk phases with the slope

$$t_{\overline{\rho}} = \left. \frac{\mathrm{d}\rho(x)}{\mathrm{d}x} \right|_{\rho = \overline{\rho} = 0.5(\rho' + \rho'')}.$$
(32)

The width of the interface L_t is then given by the difference of the x-positions at which the tangent reaches the values of the bulk phases, cf. Fig. 5.

To check if κ is chosen correctly and is valid for all three temperatures, the excess free energy for all three PF solution states is computed using (6) in a post-processing step. This excess free energy divided by the surface area of the interface A is the surface tension calculated from the PF model and has to be equal to the surface tension values given in [28].

Liquid droplet in gas phase

In this scenario liquid droplets surrounded by a gas phase are studied. To study the stability of droplets, different numbers of particles inside the computational domain, i.e. different average densities of the domain,

are considered. If the number of particles is too low, only a homogeneous gas phase is observed. For higher number of particles drops of different sizes are observed. The temperature is set to T = 0.7.

For N = 800 particles inside the computational domain the PF results are compared to MD simulations. The MD simulations are carried out using a cubic simulation box with an edge length of 20 and $N_{\rm MD} = 841$ particles. The simulation ran for 12 000 000 time steps. The statistical error of the density of the liquid droplet and the vapor phase is estimated as three times the standard deviation of five block averages where the block length is 500 000 time steps.

For the other numbers of particles, the PF results are compared to results from analytic solutions for the case of a droplet surrounded by a gas phase with an approximated vapor-liquid interface as well as for the case of a homogeneous density distribution. The analytic free energy F_d of the droplet is obtained by approximating the density profile of the interface between the liquid droplet and the gas phase by a linear transition ($\rho \sim r$) from ρ' to ρ'' as shown in Fig. 9(a). Here, r is the distance to the center of the droplet. The width of this approximated interface is chosen in accordance with L_t^{PF} from the *planar interface* section (cf. Fig. 5) and set to L = 2.042. The radius r_{ini} is defined as the distance from the center of the droplet to the position where the density is in the arithmetic mean of ρ' and ρ'' . The value of r_{ini} therefore determines the number of particles. Following the approach of [46] and classical nucleation theory (CNT) based on the capillarity approximation [47, 48], i.e., assuming that the surface tension and the width of the interface are constant, the free energy (4) is computed analytically. The analytic free energy of the homogeneous density distribution is given by F_h . Details regarding the computation of the analytic free energies F_d and F_h are shown in Appendix A. The PF simulations are initialized according to (A.5) for different r_{ini} values

$$r_{\rm ini} \in \{2 \ 3 \ 3.25 \ 3.5 \ 3.75 \ 4 \ 4.25 \ 4.5 \ 5\}. \tag{33}$$

The number of particles N is set to match the initialization radius.

Additionally, for all values of N that lead to a solution configuration with a liquid droplet surrounded by a gas phase the equimolar radius

$$r_{\rm e} = \left(\frac{3\int_0^\infty (\rho(r) - \rho_\infty) r^2 \,\mathrm{d}r}{\rho_0 - \rho_\infty}\right)^{\frac{1}{3}}$$
(34)

[49] is computed. Here, ρ_0 and ρ_∞ are the PF solution densities of the droplet and the gas phase. Since $\rho(r) = \rho_\infty$ in the gas phase, the integral needs to be evaluated from 0 to 10, only. The pressure values p_0 and p_∞ that correspond to ρ_0 and ρ_∞ (and T = 0.7) are obtained from the PeTS EoS and the pressure difference

$$\Delta p = p_0 - p_\infty \tag{35}$$

is calculated. For comparison, the pressure difference resulting from the Young-Laplace equation

$$\Delta p_{\rm YL} = \frac{2\gamma_{\rm vl}}{r_{\rm e}} \tag{36}$$

[50] is calculated using the $\gamma_{\rm vl}$ value computed in the *planar interface* section.

Two droplets

This scenario contains two droplets within the computational domain. In the first case, two droplets of the same size are initialized such that their respective transition zones between the liquid and the gas phase are in contact with each other. The number of particles is N = 503. In the second case, one droplet is larger than the other and the two are not in contact. The number of particles is N = 367. For both cases the temperature is set to T = 0.7 and the value of the mobility constant is M = 10. This scenario demonstrates how the present PF model can be applied to scenarios in which a radially symmetric extension of one-dimensional DGT cannot be applied.

3.2. Results

Phase separation

Fig. 3 shows iso-surfaces of the local density for different computational times t. The first plot shows the initialization state and the total computational runtime is given by t_s . During the evolution of the PF one can at first see that the liquid and gas phase separate from each other creating numerous interfaces $(t = 0.010 t_s \text{ and } t = 0.015 t_s)$. In the next phase of the evolution the smaller interfaces start to vanish $(t = 0.049 t_s \text{ and } t = 0.148 t_s)$. The solution is given by a planar interface between liquid and gas, which is the expected result. The PF model can cope with the challenging initialization.

Planar interface

The PF density profiles are compared to those of the MD simulations in Fig. 4 (right). Due to the periodic boundary conditions the position of the interface is different for each of the MD simulations. Therefore, the MD profiles were moved arbitrarily in Fig. 4 (right) so that a comparison between the PF and MD simulations is possible. As one can see, the bulk values of the PF simulations match the ones of the MD simulations well. The resulting interface widths are given in Table 1. The widths of the interfaces determined by the MD simulations are larger than those from the PF simulations (cf. L_{10-90} and L_t values). This can be explained by the fact that a surface of equal density is not a plane in the MD simulations but rather a corrugated surface that changes its shape in time. The dots in Fig. 4 (right) show a time averaged profile (over 500 000 time steps) of the density averaged in the directions tangential to the interface. The fact that the difference in the width of the interface between the PF and the MD simulations is larger for high temperatures supports this explanation. Except for the MD simulations at T = 0.9, the L_{10-90} interface widths are wider than then the L_t interface widths. The computation times are approximately 30 h for each of the PF simulations and approximately 1 500 h for each of the MD simulations.

The surface tension calculated from the PF simulations is found to be in excellent agreement with the values given in [28], cf. Fig. 6. Therefore, κ is chosen correctly and is valid for all three temperatures.



Figure 3: Evolution of density iso-surfaces determined by PF simulations using the PeTS EoS for an initialization with a random density distribution and T = 0.7. The random density distribution is obtained by setting the value for each of the 81³ nodes of the FE mesh to a random density value between ρ' and ρ'' . t_s denotes the total computational runtime.



Figure 4: Density profile across a planar interface as determined by PF simulations using the PeTS EoS and MD simulations with the LJTS fluid for three different temperatures. The picture on the left shows a contour plot from the PF simulations. The diagram on the right does also show the density profile used for the PF initialization.



Figure 5: Representative comparison between interface width definitions L_{10-90} and $L_{\rm t}.$

Table 1: Widths of the planar interfaces of the LJTS fluid as determined by PF and MD simulations. Results for different temperatures and definitions of the interface width (cf. Fig. 5).

T	0.7	0.8	0.9
$L_{10-90}^{\rm PF}$	2.070	2.492	3.229
$L^{\rm MD}_{10-90}$	2.353	3.124	4.232
$L_{\rm t}^{\rm PF}$	2.042	2.471	3.122
$L_{\rm t}^{\rm MD}$	2.205	2.660	4.274



Figure 6: Surface tension calculated from the PF simulations using the PeTS EoS and surface tension given in [28] for different temperatures.

Liquid droplet in gas phase

For N = 800 a contour plot of the PF solution state is shown in Fig. 7 (left). The solution densities of the PF simulations are $\rho = 0.8060$ for the liquid droplet and $\rho = 0.0113$ for the gas. The solution densities of the MD simulations are $\rho = 0.806(15)$ for the liquid droplet and $\rho = 0.0112(26)$ for the gas (The number in parentheses indicates the statistical uncertainty in the last decimal digit.). These density values are higher than they would be for a planar interface at the same temperature (see section *planar interface*), cf. black lines in Fig. 7 (right). The curvature of the interface with the surface tension γ_{vl} causes the pressure (and thereby the density) inside the droplet to rise. Since the chemical potentials of the liquid and the gas phase have to be the same in an equilibrium, this causes a rise in the density of the gas phase. The PF results agree with the results from the MD simulations within the error bars of the MD simulations (Fig. 7 (right)). The computation time is approximately 3.3 h for the PF simulations and approximately 14 h for the MD simulations.

In the PF simulations for the other numbers of particles the droplet disappears for small values of $r_{\rm ini}$ and the corresponding solution is given by a homogeneous density distribution. Fig. 8 (left) shows the initialization (top) and solution (bottom) state for $r_{\rm ini} = 3$. The homogeneous density of the solution state is higher than the density of the initialized gas phase leaving the computational area in an oversaturated state. A PF solution configuration with a liquid droplet surrounded by a gas phase is obtained for higher values of r_{ini} . The first value of r_{ini} that leads to a solution configuration with a liquid droplet surrounded by a gas phase is $r_{\rm ini} = 3.75$. Fig. 8 (right) shows the initialization (top) and solution (bottom) state for $r_{\rm ini} = 5$. The densities of the liquid as well as the gas phase in the solution state are higher than their initialization values. This is in accordance with the influence of the curvature of the interface shown above. The symbols in Fig. 9 (b) show the free energies from the solution states of the PF simulations and the lines show plots of the analytically determined free energies $F_{\rm d}$ and $F_{\rm h}$ for different values of $r_{\rm ini}$. The fact that the free energy of the homogeneous density distribution $F_{\rm h}$ is smaller than the free energy of the droplet configuration F_d for small values of r_{ini} indicates that the homogeneous configuration is favored and a liquid droplet is not stable for the number of particles that is defined by those values of $r_{\rm ini}$. Analogously, the configuration of the liquid droplet becomes favorable (and thereby stable) for larger values of $r_{\rm ini}$. The PF results follow the low energy path of $F_{\rm d}$ and $F_{\rm h}$, cf. Fig. 9 (b). It is stated above that the first value of $r_{\rm ini}$ that leads to a PF solution configuration with a liquid droplet surrounded by a gas phase is $r_{\rm ini} = 3.75$. The value of $r_{\rm ini}$ for which $F_{\rm d}$ and $F_{\rm h}$ cross each other is $r_{\rm ini} = 3.99$. The PF result for the smallest stable droplet is in good agreement with the analytic result. The difference can be explained by the linear approximation of the interface in the analytic expressions.

Fig. 10 (a) shows the equimolar radius $r_{\rm e}$ over the number of particles for the values of $r_{\rm ini}$ that lead to a solution configuration with a liquid droplet surrounded by a gas phase. The equimolar radius of the smallest



Figure 7: Liquid droplet in gas phase for N = 800 and T = 0.7. Contour plot of PF with PeTS EoS solution (left) and comparison between PF and MD solution (right). Densities are higher than the liquid and gas densities of the *planar interface* (black lines).

stable droplet is $r_{\rm e}^{\rm min} = 3.17$. A plot of Δp over $r_{\rm e}$ is shown in Fig. 10 (b). Fig. 10 (b) also shows $\Delta p_{\rm YL}$ resulting from the Young-Laplace equation. The pressure differences Δp and $\Delta p_{\rm YL}$ show good agreement for larger $r_{\rm e}$ values. For smaller values of $r_{\rm e}$ the droplet is so small that its radius is of similar size as the finite width of the diffuse interface. Therefore, the assumptions on which the Young-Laplace equation is based do not hold and the disagreement of Δp and $\Delta p_{\rm YL}$ does not surprise. Investigating spherical droplets using DGT the authors of [51] show that the predictions of the Young-Laplace equation do not hold for droplet radii smaller than around 5σ . This agrees well with our results. The same breakdown has been shown by [52] for bubbles with radii below 5σ to 10σ depending on temperature.

$Two \ droplets$

Fig. 11 shows iso-surfaces of the local density of the first case (left) and the second case (right) for different computational times t. The iso-surfaces are cut through the center of the droplets. The top plots show the initialization and the bottom plots the solution state. During the evolution of the first case the two droplets unite and form a single droplet. During the evolution of the second case the smaller droplet shrinks and vanishes. As the number of particles is held constant, this causes the larger droplet to grow. Due to this growing the larger droplet gets in contact with the boundary of the computational domain. A 90° contact angle evolves according to (15) and the solution shows a hemisphere.

4. Summary and Outlook

The present work incorporates the PeTS EoS into a three-dimensional PF model. The PeTS EoS describes the properties of the LJTS fluid well not only in the stable range but also in the metastable and unstable range. Therefore, all properties (also those in the transition zone between the liquid and the gas



Figure 8: PF simulations using the PeTS EoS with an initialization according to (A.5). Initialization (top) and solution (bottom) contour plots for $r_{\rm ini} = 3$ (left) and $r_{\rm ini} = 5$ (right).



Figure 9: (a) Real (PF) density profile across vapor-liquid interface and approximated density profile. (b) Analytic free energy for homogeneous density distribution $F_{\rm h}$ and droplet configuration $F_{\rm d}$ for different numbers of particles (defined by the value of $r_{\rm ini}$). The symbols show the free energy from PF simulations using the PeTS EoS initialized according to (A.5). Temperature T = 0.7.



Figure 10: (a) Equimolar radius over the number of particles of PF simulations using the PeTS EoS that result in a solution configuration with a liquid droplet surrounded by a gas phase. (b) Difference between the pressure of the droplet and the pressure of the gas phase for the simulations shown in (a), for comparison, the plot also shows the pressure difference resulting from the Young-Laplace equation using the surface tension computed in the *planar interface* section. Temperature T = 0.7.



Figure 11: Evolution of density iso-surfaces determined by PF simulations using the PeTS EoS for an initialization with two droplets of same size in contact (left) and an initialization with two droplets of different size not in contact (right). The top plots show the initialization and the bottom plots the solution state. Temperature T = 0.7.

phase) determined by the PF simulations are physically meaningful. Hence, the PF model can also be seen as a three-dimensional extension of DGT based on EoS. The FE implementation of the presented model is assisted by the use of hyper-dual numbers. The approach is presented in a way that does not depend on the specific choice of the EoS and can easily be applied for other EoS. Several numerical examples demonstrate the pertinency of the presented approach. The PF model is able to properly separate phases when starting with an unfavorable initialization with a random density distribution. The PF results are in good agreement with MD simulations for the case of a planar interface as well as a droplet surrounded by a gas phase. The correct surface tension is obtained and the size of the smallest stable droplet is in agreement with theory. The model can be used for studying scenarios in which one-dimensional DGT cannot be applied.

Future work will strive towards the ability to study scenarios in which solid walls are relevant so that wetting phenomena can be investigated. Additionally, the model shall gain the ability to properly describe the dynamics of droplet motion. With this, scenarios like droplet coalescence and dynamic wetting on different scale levels will move into the scope of the present PF model.

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Appendix A. Analytic free energy approximation for liquid droplet surrounded by gas phase and homogeneous density distribution

The free energy of the droplet configuration $F_{\rm d}$ consists of three parts. The free energy of the liquid inside the droplet $F_{\rm dl}$, the free energy of the gas phase $F_{\rm dg}$, and the free energy of the interface between liquid and gas $F_{\rm di}$,

$$F_{\rm d} = F_{\rm dl} + F_{\rm dg} + F_{\rm di} \,. \tag{A.1}$$

The free energy of the liquid domain \mathcal{B}_1 inside the droplet is given by

$$F_{\rm dl} = \int_{\mathcal{B}_{\rm l}} \rho' \cdot a(\rho') \,\mathrm{d}V = \rho' \cdot a(\rho') \cdot V' \qquad \text{with} \qquad V' = \frac{4}{3}\pi \left(r_{\rm ini} - \frac{L}{2}\right)^3. \tag{A.2}$$

The free energy of the gas domain \mathcal{B}_g is given by

$$F_{\rm dg} = \int_{\mathcal{B}_{\rm g}} \rho'' \cdot a(\rho'') \,\mathrm{d}V = \rho'' \cdot a(\rho'') \cdot V'' \qquad \text{with} \qquad V'' = V_{\mathcal{B}} - \frac{4}{3}\pi \left(r_{\rm ini} + \frac{L}{2}\right)^3. \tag{A.3}$$

In this, $V_{\mathcal{B}}$ is the volume of the entire computational area. The free energy of the interface between the liquid and the gas phase (domain \mathcal{B}_i) can by computed from

$$F_{\rm di} = \int_{\mathcal{B}_{\rm i}} \left[\rho \cdot a(\rho) + \frac{1}{2} \kappa |\nabla \rho|^2 \right] dV$$

$$= \int_{\mathcal{B}_{\rm i}} \left[\Delta \omega + \frac{1}{2} \kappa |\nabla \rho|^2 + \mu^{\rm s} \cdot \rho - p^{\rm s} \right] dV$$

$$= \gamma_{\rm vl} \cdot 4\pi r_{\rm ini}^2 + \int_{\mathcal{B}_{\rm i}} \left[\mu^{\rm s} \cdot \rho - p^{\rm s} \right] dV.$$
(A.4)

This holds true since the excess free energy density $\Delta \omega + \frac{1}{2}\kappa |\nabla \rho|^2$ integrated across the interface is equivalent to the surface tension $\gamma_{\rm vl}$ multiplied by the surface area of the droplet. With the already mentioned approximation of the interface profile

$$\rho = \rho(r) = \frac{\rho'' - \rho'}{L} \left(r - r_{\rm ini} + \frac{L}{2} \right) + \rho', \qquad (A.5)$$

as well as a spherical coordinate system, the free energy of the interface between liquid and gas can be written as

$$F_{\rm di} = \gamma_{\rm vl} \cdot 4\pi r_{\rm ini}^2 + \int_{\mathcal{B}_{\rm i}} \left[\mu^{\rm s} \cdot \left[\frac{\rho'' - \rho'}{L} \left(r - r_{\rm ini} + \frac{L}{2} \right) + \rho' \right] - p^{\rm s} \right] \, \mathrm{d}V$$

$$= \gamma_{\rm vl} \cdot 4\pi r_{\rm ini}^2 + 4\pi \int_{r_{\rm ini} - 0.5L}^{r_{\rm ini} + 0.5L} \left[r^2 \mu^{\rm s} \cdot \left[\frac{\rho'' - \rho'}{L} \left(r - r_{\rm ini} + \frac{L}{2} \right) + \rho' \right] - r^2 p^{\rm s} \right] \, \mathrm{d}r \,.$$
(A.6)

Here, r is the distance to the center of the liquid droplet.

The free energy $F_{\rm h}$ of the homogeneous density distribution is given by

$$F_{\rm h} = \rho_{\rm h} \cdot a(\rho_{\rm h}) \cdot V_{\mathcal{B}} \,, \tag{A.7}$$

with $\rho_{\rm h}$ as the homogeneous density

$$\rho_{\rm h} = \left[\rho' V' + \rho'' V'' + \int_{\mathcal{B}_{\rm i}} \rho \,\mathrm{d}V\right] \frac{1}{V_{\mathcal{B}}}$$

$$= \left[\rho' V' + \rho'' V'' + 4\pi \int_{r_{\rm ini} - 0.5L}^{r_{\rm ini} + 0.5L} r^2 \left[\frac{\rho'' - \rho'}{L} \left(r - r_{\rm ini} + \frac{L}{2}\right) + \rho'\right] \,\mathrm{d}r\right] \frac{1}{V_{\mathcal{B}}}.$$
(A.8)

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