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Modeling of interfacial phenomena in disperse liquid-liquid systems

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ABSTRACT

Interfaces are critical in chemical engineering, as they govern mass transfer between phases and play a key role in the formation and behavior of droplets and bubbles. This is particularly true in liquid-liquid extraction columns, where droplet interactions such as coalescence and breakage are pivotal. In decades of research, droplet coalescence remains a complex phenomenon that is not yet fully understood, partly due to the challenges in experimentally analyzing the small-scale and fluid nature of interfaces. To address this gap, we propose a thermodynamically consistent simulation approach to accurately resolve interfaces and study droplet interactions. The developed model builds on the incompressible Density Gradient Theory (DGT) by Cahn and Hilliard, coupling it with the Navier-Stokes equations to form a novel Navier-Stokes/DGT framework. Within this framework, the Non-Random Two-Liquid model is employed as the thermodynamic foundation, enabling the accurate modeling of interfacial properties and prediction of coalescence behavior in liquid-liquid systems. The Navier-Stokes/DGT model, comprising a system of highly nonlinear partial differential equations is solved using the finite volume method in OpenFOAM. This approach enables the simulation of the single stages of droplet coalescence. Furthermore, complex interfacial effects like Marangoni convection and de-mixing behavior are investigated in more detail.

1. Introduction

Extraction is of crucial importance in the chemical industry as it is a key technology for separating, purifying and isolating valuable substances from complex raw materials. It enables the recovery of starting materials necessary for the manufacture of a wide range of products, from medicines and foods to plastics and chemical compounds. Without extraction techniques, it would be almost impossible to obtain these valuable materials in the required purity and concentration. Examples of technical implementations of liquid-liquid extraction apparatuses include mixer-settler cascades and extraction columns [1]. In these apparatuses, various dynamic processes impact their efficiency, such as droplet rising velocity, axial dispersion, and rates of breakage or coalescence [2]. The limited availability of detailed physical insight into the underlying mechanisms necessitates extensive experimental investigation during the design of separation processes. A critical parameter in this context is the droplet size distribution, as it governs the interfacial area available for mass transfer. Given its central role in determining the overall mass transfer rate, considerable research effort has been devoted to developing predictive models for droplet size distributions. One commonly employed modeling framework is the droplet population balance approach, which relies on rate expressions for droplet formation, breakup, collision, and coalescence, typically derived from empirical or semi-empirical correlations [2–4]. Numerical investigations of single droplets can contribute to the refinement of these correlations through the application of transfer coefficient models and can also serve as a valuable complement to experimental methodologies [5,6].

To more accurately capture the hydrodynamic behavior within extraction equipment, population balance models are integrated with Computational Fluid Dynamics (CFD), enabling detailed simulation of the flow field throughout the apparatus. This combined approach reduces the need for extensive experimental trials, thereby conserving both material and time during process development and design [7]. However, these correlations often rely on equilibrium properties - such as interfacial tension - as essential input parameters. More detailed insights into the prevailing flow regimes can be achieved through advanced interface-capturing techniques, including the Volume of Fluid (VOF) method [8] and the Level-Set method [9]. Sharp-interface methods necessitate the formulation of a transport equation to track

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the interface, along with additional boundary conditions to describe system behavior across the interfacial discontinuity. These include the appropriate treatment of the stress tensor and mass transport when dealing with systems beyond immiscible liquids or pure components. Within such frameworks, interfacial tension is typically introduced as a model parameter rather than being computed explicitly. For systems involving partially miscible components, interfacial tension becomes concentration-dependent, thereby requiring detailed thermodynamic modeling. Consequently, accurately capturing droplet interactions demands a modeling approach capable of describing interfacial properties, which cannot be adequately achieved using sharp-interface representations alone.

Van der Waals proposed a gradient contribution [10] to the interfacial free energy, later reformulated by Cahn and Hilliard [11,12]. Poser and Sanchez [13] rediscovered the work of Cahn and Hilliard and applied it to model the interfacial properties of polymer solutions. Based on this work Enders et al. developed the density gradient theory (DGT) to describe the surface properties of compressible vapor-liquid equilibria using an equation of state [14–16] or to describe the interfacial tension of incompressible liquid-liquid systems using a g^E-model [17–19]. In the framework of the DGT, the Helmholtz energy functional is expressed by a Taylor series, with the homogeneous state as the starting point, which is minimized to evaluate the interfacial properties as interfacial tension and thickness. In the mathematical formulation of Density Gradient Theory (DGT), the series expansion is truncated, and an empirical parameter - referred to as influence parameter - is introduced. This parameter is typically fitted to single experimental measurement of the interfacial tension. Comparative studies between Monte Carlo and molecular dynamics simulations demonstrate that, when an appropriate scaling law is applied, both theoretical predictions and simulation results exhibit good agreement in terms of concentration profiles and interfacial tension [20]. In practice, DGT has been applied across a wide range of fields, including the analysis of surface tension in refrigeration fluids to support the optimization of industrial processes such as heat pumps [21], as well as the investigation of geological oil-brine systems aimed at enhancing oil recovery in the context of carbon capture and storage technologies [22].

Building upon the equilibrium framework of DGT, Cahn and Hilliard formulated a dynamic diffusion equation that incorporates phase equilibrium [23] and including the diffusive mobility coefficient, this formulation enables the calculation of interfacial mass transfer driven by diffusion. Nauman et al. [24] employed the Flory-Huggins theory [25] as a thermodynamic model for polymer solutions, initially focusing solely on diffusion. Subsequently, they extended the model by incorporating the Stokes equation to represent the flow field [26], using a discontinuous stress tensor formulation that explicitly depends on interfacial tension. Furthermore, they derived an expression for volumetric body forces resulting from concentration gradients and applied the framework to simulate spinodal decomposition in polymer blends subjected to shear flow. The application of Fickian diffusion in combination with linearized chemical potentials near equilibrium leads to the homogenization of concentration fields, thereby inhibiting phase separation. However, using a phase field approach with a thermodynamic model allows phase separation to be calculated. Unlike traditional models that track sharp interfaces, phase-field models use a diffuse interface approach [27]. The interface is represented by a smooth transition between phases, which simplifies the mathematical treatment. Phase field models use an order parameter that varies continuously across the interface, taking distinct values in each phase. This diffuse interface approach eliminates the need for explicit tracking of the interface. But the application of these phase field models often leads to thermodynamic inconsistencies as they often apply double well potential not able to represent the thermodynamic properties of any mixture.

Joseph and Renardy [28] and Falk [29] incorporated density gradient terms into the stress tensor formulation, following the approach originally proposed by Korteweg [30]. Their work builds upon continuum mixture theory frameworks developed by Atkin and Craine [31] and Bedford and Drumheller [32], while assuming linear constitutive relations for diffusive mass transport. The Cahn-Hilliard/Navier-Stokes framework has been widely employed to investigate the dynamics of immiscible viscous liquid flows, accounting for capillary forces and coarsening phenomena. This approach utilizes an order parameter to represent the phase field and typically assumes constant density within each phase. Truskinovsky and Lowengrub [33] extended this framework by incorporating the square gradient term from the Cahn-Hilliard formulation into the surface free energy expression. By using the concentration of a single component as the phase field, they obtained a quasi-incompressible density field. Alternative modeling strategies have employed level-set functions to represent the phase field, with the interface evolution governed by a transport equation analogous to the Cahn-Hilliard formulation [34]. A variety of numerical techniques have been developed to solve the coupled Cahn-Hilliard/Navier-Stokes equations, including spectral methods [35], finite difference multigrid methods, and finite element methods [36]. However, when the phase variable is not directly related to molar concentration or molar fraction, and the velocity field is averaged using such a phase indicator, additional correction terms must be introduced into the momentum balance to ensure momentum conservation. Moreover, these modeling frameworks typically lack incorporation of thermodynamic equilibrium principles. Despite the utility of such phase field models, a significant limitation remains: the Helmholtz energy functional lacks a rigorous physical foundation. The Helmholtz energy functions used are often simplified representations - such as double-well potentials - that restrict the analysis to a single tie line of the phase diagram for the given mixture. Exemplary approaches for the Helmholtz energy function f are given by the following equations:

$$f = \left(\varphi - \frac{1}{2}\right)^2 \cdot \left(\varphi + \frac{1}{2}\right)^2 \text{ [34]} \tag{1}$$

$$f = \frac{1}{\eta} \cdot \left(|\varphi|^2 - 1\right)^2 \text{ [35]} \tag{2}$$

Whereas φ represents the order parameter of the system and η is a positive parameter determining the shape of the potential. A graphical representation of the double-well potential, as defined by Eq. (2), is provided by Fig. 1.

When the order parameter φ is employed as a phase field variable in apparatus design, the model does not directly provide information about

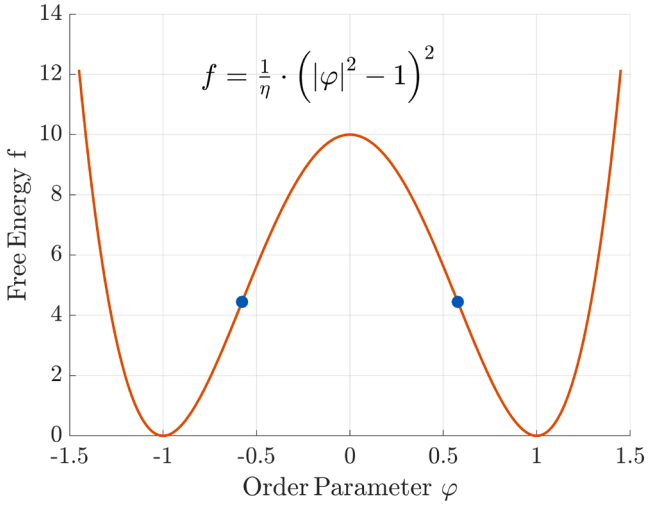

Fig. 1. Double-well potential for the Helmholtz energy of a binary system as function of the order parameter φ according to Liu et al. [35]. The parameter η was set to 0.1 for representational purposes.

the component concentrations, thereby limiting its applicability for processes requiring concentration-dependent analysis. In the context of chemical process design, however, accurate thermodynamic characterization is essential. To address these limitations, the present work proposes an approach that integrates a thermodynamically consistent free energy model into the Cahn-Hilliard framework, enabling the use of detailed equilibrium data in hydrodynamic simulations.

2. Theoretical Framework

2.1. Density Gradient Theory in Equilibrium Systems

In DGT for systems in equilibrium [17], the interfacial tension in inhomogeneous systems is proportional to the grand thermodynamic potential $\Delta\Omega$. To evaluate this potential, the Helmholtz energy is employed as the thermodynamic potential of the system [17]. Under the assumption of incompressibility, the Helmholtz energy becomes equivalent to the Gibbs energy. In this context, the relevant quantity is not the density gradient but rather the concentration gradient of each component across the interface between two bulk phases. These concentration gradients serve as the basis for calculating the interfacial tension. The grand thermodynamic potential $\Delta\Omega$ of a multicomponent liquid equilibrium (LLE) can be expressed as follows:

$$\boldsymbol{\Delta\Omega} = \boldsymbol{\Delta g}(\boldsymbol{x_i}) - \sum_{i=1}^{n} \boldsymbol{\mu_i x_i} \tag{3}$$

where $\Delta g(x_i)$ denotes Gibbs energy at the corresponding composition, evaluated using an appropriate g^E-model and μ_i represents the chemical potential of component *i*. At equilibrium, the grand potential is minimized, resulting in a Euler-Lagrange equation. Solving this equation and applying a coordinate transformation from the spatial domain to the concentration domain yields the expression for the minimal grand potential and the interfacial tension can be calculated as follows:

$$\boldsymbol{\sigma} = \int_{x_1^I}^{x_1^{II}} \sqrt{2\boldsymbol{\kappa}\boldsymbol{\Delta\Omega}(\boldsymbol{x}_1)}\, \boldsymbol{dx}_1 \tag{4}$$

where x_1^I and x_1^{II} are the compositions of the corresponding phases and κ is the so-called influence parameter. This parameter represents the partial derivative of the free energy with respect to the curvature of the concentration and is typically assumed to be constant or temperature dependent. Previous studies have shown that adjusting the influence parameter to match a single experimentally obtained interfacial tension is sufficient [17–19]. This allows for the prediction of interfacial tensions at other temperatures and/or compositions with qualitative accuracy.

2.2. Navier-Stokes & Density Gradient Theory

To characterize interfacial interactions in multicomponent mixtures of liquids with similar densities on a macroscopic scale, it is essential to consider hydrodynamics. The evolution over time of the molar fraction fields and velocities can be conveniently described using the Navier-Stokes equations for incompressible fluids, coupled with the transport equation for the phase-forming component. The Cahn-Hilliard equation uses the density gradient to calculate the Helmholtz energy of the system [12,13]. Applying the incompressible version of the Cahn-Hilliard equations allows for consideration of concentration gradients in the system. In combination with the Navier-Stokes equation the Navier-Stokes/DGT model is proposed. In this context, it is taken into account that the order variable is not the density as in the classical DGT but the concentration, since this is an incompressible system [37].

$$\nabla\cdot\boldsymbol{u} = 0 \tag{5}$$

$$\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{t}} + (\boldsymbol{u}\cdot\nabla)\boldsymbol{u} = -\frac{1}{\boldsymbol{\rho}}\nabla\boldsymbol{p} + \boldsymbol{\nu}\boldsymbol{\Delta u} - \frac{1}{\boldsymbol{M}}\sum_{i=1}^{n} \boldsymbol{x_i}\nabla\boldsymbol{\mu_i} \tag{6}$$

$$\frac{\partial \boldsymbol{x_i}}{\partial \boldsymbol{t}} + \boldsymbol{u}\cdot\nabla\boldsymbol{x_i} = \nabla\cdot\left[\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\boldsymbol{L_{ij}}}{\boldsymbol{RT}}\boldsymbol{x_i x_j}\nabla\left(\boldsymbol{\mu_i} - \boldsymbol{\mu_j}\right)\right] \tag{7}$$

The first equation Eq. (5) is the conservation equation for an incompressible system with the velocity vector $\boldsymbol{u}$ and the second equation Eq. (6) is the momentum balance with the density ρ, the pressure p, the viscosity ν and the chemical potential μ_i of component *i*. The last term of Eq. (6) is the Korteweg tensor which accounts for capillary effects in a fluid [30]. The third equation Eq. (7) represents the species transport, whereas x_i is the mole fraction of component *i* and L_{ij} is the binary mobility coefficient. Here we consider the Onsager relations [38]. In equilibrium and bulk phase thermodynamics, the chemical potential μ_i of incompressible liquids is derived from the Gibbs energy using the DGT approach as follows:

$$\boldsymbol{g} = \boldsymbol{g}(\boldsymbol{x_i}) + \frac{\boldsymbol{\kappa}}{2}(\nabla\boldsymbol{x_i})^2 \tag{8}$$

The total Gibbs energy comprises the bulk phase contribution and a gradient term, weighted by the influence parameter κ. The bulk Gibbs energy itself includes contributions from an ideal mixture and an excess part:

$$\boldsymbol{g}(\boldsymbol{x_i}) = \boldsymbol{g^{id}}(\boldsymbol{x_i}) + \boldsymbol{g^E}(\boldsymbol{x_i}) = \boldsymbol{RT}\left(\sum_{i=1}^{n} \boldsymbol{x_i}\ln\boldsymbol{x_i}\right) + \boldsymbol{g^E}(\boldsymbol{x_i}) \tag{9}$$

In this work, the Non-Random Two-Liquid (NRTL) model developed by Prausnitz and Renon [39] is employed to calculate the excess Gibbs energy, as described by the following equation:

$$\frac{\boldsymbol{g^E}(\boldsymbol{x_i})}{\boldsymbol{RT}} = \sum_{i=1}^{n} \boldsymbol{x_i}\left[\frac{\sum_{j=1}^{n}\boldsymbol{\tau_{ji}}\boldsymbol{g_{ji}}\boldsymbol{x_j}}{\sum_{k=1}^{n}\boldsymbol{g_{ki}}\boldsymbol{x_k}}\right] \tag{10}$$

Where $\tau_{ij} = A_{ij} + \frac{B_{ij}}{T}$ is a temperature dependent parameter and $g_{ij} = \exp(-\alpha_{ij}\tau_{ij})$ contains the symmetric parameter α_{ij} which accounts for the non-randomness of local concentrations.

The Gibbs energy formulation is employed in this context as it facilitates the treatment of incompressible systems, avoiding internal numerical solutions for the pressure, but necessitates the calculation of a pressure-like field to maintain mass balance. Without additional assumptions, the current formulation cannot account for systems involving fluids with differing densities, and thus gravitationally induced sedimentation is excluded. To visualize DGT as an incompressible version, the Gibbs energy of a two-phase liquid-liquid system can be considered (Fig. 2), determine the phase equilibrium as well the decomposition of the phases.

This process occurs when the system is quenched into the unstable/metastable region of its phase diagram [40]. The free energy of a de-mixing system shows a concave region. When the systems concentration is within this concave region, any small fluctuation in composition will lower the free energy, leading to spontaneous phase separation. The spinodal region is defined by the points where the second derivative of the free energy with respect to composition is zero. In the spinodal region, the mixture is unstable and undergoes rapid spontaneous decomposition into two distinct phases. For systems where interfacial effects are significant, it is necessary to account for the metastable and unstable regions in phase diagrams, where g^E-models are not defined. Therefore, a functional expression is necessary as provided by DGT. This is a key feature of the Navier-Stokes/DGT framework, as it enables the incorporation of a thermodynamically consistent fluid dynamic model applicable to real systems.

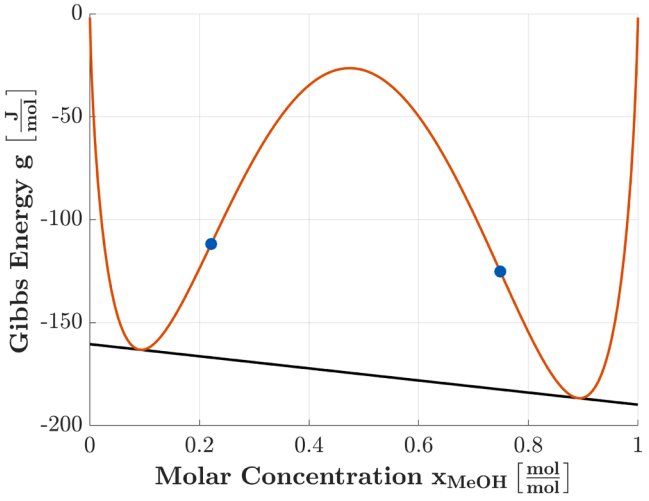

Fig. 2. Gibbs energy of the binary system Methanol (MeOH) - n-hexane at 5 °C. The blue dots represent the spinodal points (inflection points) of the Gibbs energy.

The Navier-Stokes/DGT model consists of highly non-linear balance equations for mass, momentum and species transport. To solve accurately the balance model equations, they are solved numerically in every cell at each timestep to obtain the concentration and velocity field. It turns out, these iterations are the bottleneck of the calculations. Additionally, to the solution of the non-linear equations in every cell, three waves of spatial derivatives are applied. To describe the evolution of the system's composition, nonlinear diffusion is modeled as a function of the gradient of the chemical potentials, which, within the framework of the Cahn-Hilliard model, depend on the second spatial derivative of the density distribution in the system. The change of the systems composition itself then is the divergence of the diffusion fluxes.

The Navier-Stokes/DGT model is implemented into OpenFOAM based on the PISO-Solver for transient simulations [41]. OpenFOAM is an open-source finite volume method library based on C++. The Navier-Stokes/DGT framework is incorporated into the source code of OpenFOAM while the convection term is solved implicitly, and the diffusion term is treated explicitly. The convection term is discretized using a linear central differencing interpolation scheme, while the Laplacian operators in the diffusion term are evaluated using a surface-normal gradient scheme with explicit non-orthogonal correction. Time discretization is performed using a backward differencing scheme, which is a second-order implicit method offering improved stability for transient simulations. The conservation equations are solved on a 2D mesh starting with 1024 × 1024 hexaeder mesh. The mesh is continuously adapted in the region of large concentration gradients using adaptive mesh refinement. The time resolution of the system with is set to $\Delta t = 10^{-8}$ s since the occurring gradients in chemical potential reach high values. The mesh and time resolution are chosen carefully since they depend on the influence parameter κ which determines the thickness of the interface in the system. As Zimmermann et al. [42] already demonstrated does the numerical stability as well as the formation of the interfaces depend strongly on this influence parameter.

3. Results and Discussion

This work utilizes thermodynamic data for the binary systems methanol (MeOH) - n-hexane and toluene-water, as well as the ternary system MeOH - n-hexane - isopropanol, obtained from previously conducted diffusion experiments [43]. The NRTL parameters are retrieved from literature [44] linearly interpolated regarding temperature dependency.

For the binary system toluene-water the combination of the NRTL model with DGT enables the calculation of interfacial tension in equilibrium. To perform this calculation, a single experimental measurement [45] of interfacial tension with $34.7{\cdot}10^{-3}\frac{mN}{m}$ at 295 K was fit to obtain an influence parameter $\kappa = 7.64{\cdot}10^{-7}\frac{Jmol}{m^4}$. Fig. 3 shows the interfacial tension (IFT, Eq. 4) of the binary system toluene - water with respect to temperature.

The predicted interfacial tension for the toluene-water system shows good agreement with available experimental data [45,46]. The close correspondence between calculated and experimental values suggests that the influence parameter, derived from a single data point, provides a reliable basis for modeling interfacial properties. This further validates the applicability to systems exhibiting sharp phase boundaries and significant differences in polarity and molecular interactions, as is characteristic of the toluene-water system.

All binary interaction parameters employed in this work are summarized in the following Table 1. It should be noted that the influence parameter is zero, if the considered subsystem shows no LLE.

3.1. Phase Separation

Phase separation in liquid-liquid systems occurs when a homogeneous mixture of two or more liquids separates into distinct phases. This phenomenon is driven by differences in the physical or chemical properties of the components, such as density, solubility, or molecular interactions. Phase separation is governed by the principles of thermodynamics. When the Gibbs energy of the system is minimized, the mixture separates into phases with different compositions.

A binary mixture of MeOH and n-hexane is investigated within a simulation domain of approximately 10 × 10 mm. The initial composition is set to an equal ratio, with a molar fraction MeOH of 0.5 $\frac{mol}{mol}$. To introduce variability and simulate realistic conditions, perturbations of the local composition are applied. These perturbations are generated using normally distributed random numbers, which create slight variations in the range of 10^{-4} $\frac{mol}{mol}$ in the concentration of MeOH and n-hexane throughout the domain. This approach helps to mimic the natural fluctuations that might occur in a real-world scenario, providing a more accurate representation of the system's behavior over time. Furthermore, the process is visualized in an LLE phase diagram. In the following Fig. 4 the decomposition of the binary system MeOH - n-Hexane can be seen.

The interfacial tension between the separated phases influences the

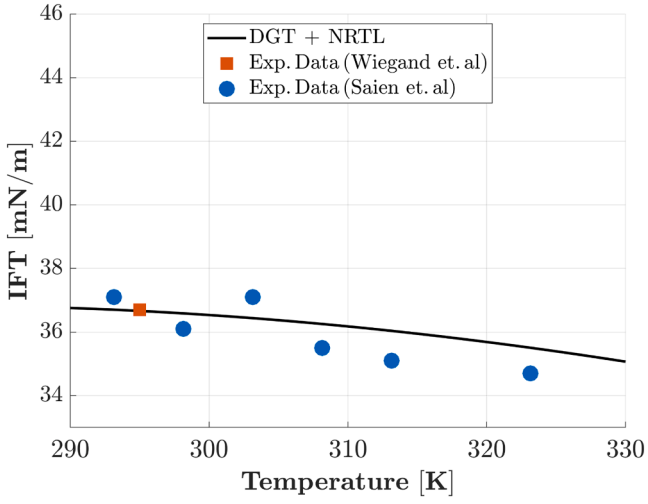

Fig. 3. Experimental and calculated IFT (Eq. 4) for the system toluene-water in dependence of the temperature. Exp. data obtained from the literature [45,46] are indicated by dots and squares. The line represents interfacial tension predicted by DGT with NRTL.

Table 1
Binary parameters used in this work.

Model	Parameter	Units	Component pair $i-j$			
			MeOH – n-Hexane	MeOH – Isopropanol	n-Hexane – Isopropanol	Toluene – Water
NRTL [44]	A_{ij}	$[-]$	−0.26	0	0	−7.2357
	A_{ji}	$[-]$	−4.347	0	0	3.9884
	B_{ij}	$[T]$	496.44	234.41	−340.72	3433.95
	B_{ji}	$[T]$	1664.56	−1351.52	−889.36	647.86
	α_{ij}	$[-]$	0.20	0.20	0.20	0.20
DGT	κ_{ij}	$10^{-7}\left[\frac{Jmol}{m^4}\right]$	1.13 [47]	0	0	7.64
Diffusion	L_{ij}	$10^{-16}\left[\frac{mol^3}{Jsm^4}\right]$	28.0 [47]	2.64 [43]	19.1 [43]	1.64 [38]

shape and stability of the phases. As observed in the early stages of the simulation, the decomposition into distinct phases is primarily driven by diffusion. The interfaces between the phases are forming while the MeOH bulk concentrations in the respective phases are increasing and decreasing. Further, it can be observed, that faster mass transfer behavior can be observed in the regions where the concentration is in the metastable region. As soon as the concentration reaches the metastable region the process slows down. The occurrence of interfaces in the system leads also to convective flow which mixes the phases while the concentrations in the phases further change. The simulation captures both coalescence and breakup of individual droplets and larger structures, ultimately resulting in the formation of two macroscopically distinct phases. Additionally, droplet repulsion phenomena are observed within the domain. These two phases continue to grow, while the bulk, minimal and maximal compositions evolve toward the equilibrium compositions predicted by the underlying thermodynamic model. These points determine the physical limits for the system while the conservation equations for mass, momentum and species transport control the dynamics. The phase separation of a system cannot be modeled by a classical CFD approach based on Euler-Euler framework as in the two-phase flow was inherently implemented and is not a result of the thermodynamic driving force because of the difference in the chemical potential.

3.2. Droplet Coalescence

Droplet coalescence describes the merging of two or more individual droplets upon contact to a single, larger droplet, driven by interfacial forces and governed by thermodynamic and hydrodynamic conditions. The single stages of droplet coalescence are displayed in the following Fig. 5 for the binary system toluene - water with respect to the temporal evolution. For the system two droplets with a size of about 2 *mm* in diameter are collided. The simulation domain is 10×10 *mm*.

In Fig. 5 all stages of drop coalescence are visible as described in the review of Kamp et al. [3]. The two droplets move towards each other due to external forces like gravity fields or surface tension gradients (Fig. 5A). As the droplets come close, they displace the surrounding liquid and touch, forming a thin liquid bridge (or neck) between them (Fig. 5B). This bridge is driven by surface tension, which acts to minimize the surface area. The liquid bridge rapidly expands as surface tension pulls the droplets together. The rate of expansion is influenced by the viscosity and surface tension of the liquid. The growth of the liquid bridge can occur in different regimes depending on the balance between viscous and inertial forces. In the viscous regime, the growth is slower and dominated by the liquid's viscosity. In the inertial regime, the growth is faster and dominated by the liquid's inertia (Fig. 5C) Eventually, the liquid bridge grows large enough that the two droplets fully merge into a single, larger droplet (Fig. 5D). This process is driven by the minimization of surface energy. Following coalescence, the newly formed droplet undergoes a relaxation process driven by surface tension forces, ultimately adopting a stable, typically spherical shape. In contrast to classical Euler-Euler CFD models, where droplet coalescence must be incorporated through explicit modeling approaches, this phenomenon is inherently captured in interface resolving simulations using the Navier-Stokes/DGT model. The necessity for direct implementation of coalescence in Euler-Euler models has been demonstrated by Wecker and Kenig [48].

3.3. Marangoni Convection

Marangoni convection [49,50] is driven by gradients in surface tension along an interface between two fluids. This phenomenon can be caused by variations in temperature or concentration. The primary driver of Marangoni convection is the gradient in surface tension. Surface tension decreases with increasing temperature or changes in concentration. This gradient causes the fluid to flow from regions of low surface tension to regions of high surface tension. In technical applications the Marangoni convection leads to an enhancement in the mass transfer. This phenomenon is investigated in the ternary system MeOH - n-hexane - isopropanol, whereas MeOH - n-hexane are forming the immiscible system and isopropanol the transferring component. Hereby, the mass transfer of isopropanol leads to a change in the interfacial tension causing Marangoni convection. The simulation domain is 10×10 *mm*. At the start of the simulation isopropanol is enriched in the middle of the drop and starts to diffuse to the interface. The following Fig. 6 shows a single droplet and the surrounding concentration field.

In the vicinity of a droplet with a diameter of approximately 5 mm, Marangoni convection induces characteristic flow patterns resulting from gradients in surface tension, typically caused by compositional or thermal variations. These gradients drive fluid motion along the droplet interface, with liquid ascending along the outer surface and descending along the droplet's interior toward the contact point at the substrate. This circulation forms a toroidal convection cell, often referred to as a Marangoni vortex. The resulting flow significantly enhances internal mixing and mass transport within the droplet. In systems involving isopropanol, the induced interfacial tension gradients give rise to visible Marangoni streaks around the droplet, which have also been characterized through experimental observation [51]. Such flow phenomena play a crucial role in understanding droplet dynamics, interfacial transport, and the evolution of concentration fields in multicomponent systems. Unlike traditional CFD approaches [52], variations in interfacial tension emerge naturally from the thermodynamic formulation and do not require empirical correlations.

4. Conclusion and Outlook

This work introduces an alternative modeling approach based on the coupled Cahn-Hilliard and Navier-Stokes equations in a Navier-Stokes/DGT framework to simulate droplet interactions in liquid-liquid systems, incorporating key physical properties such as interfacial tension, viscosity, diffusion coefficients, and phase equilibrium. The proposed methodology enables the direct integration of experimentally deter-

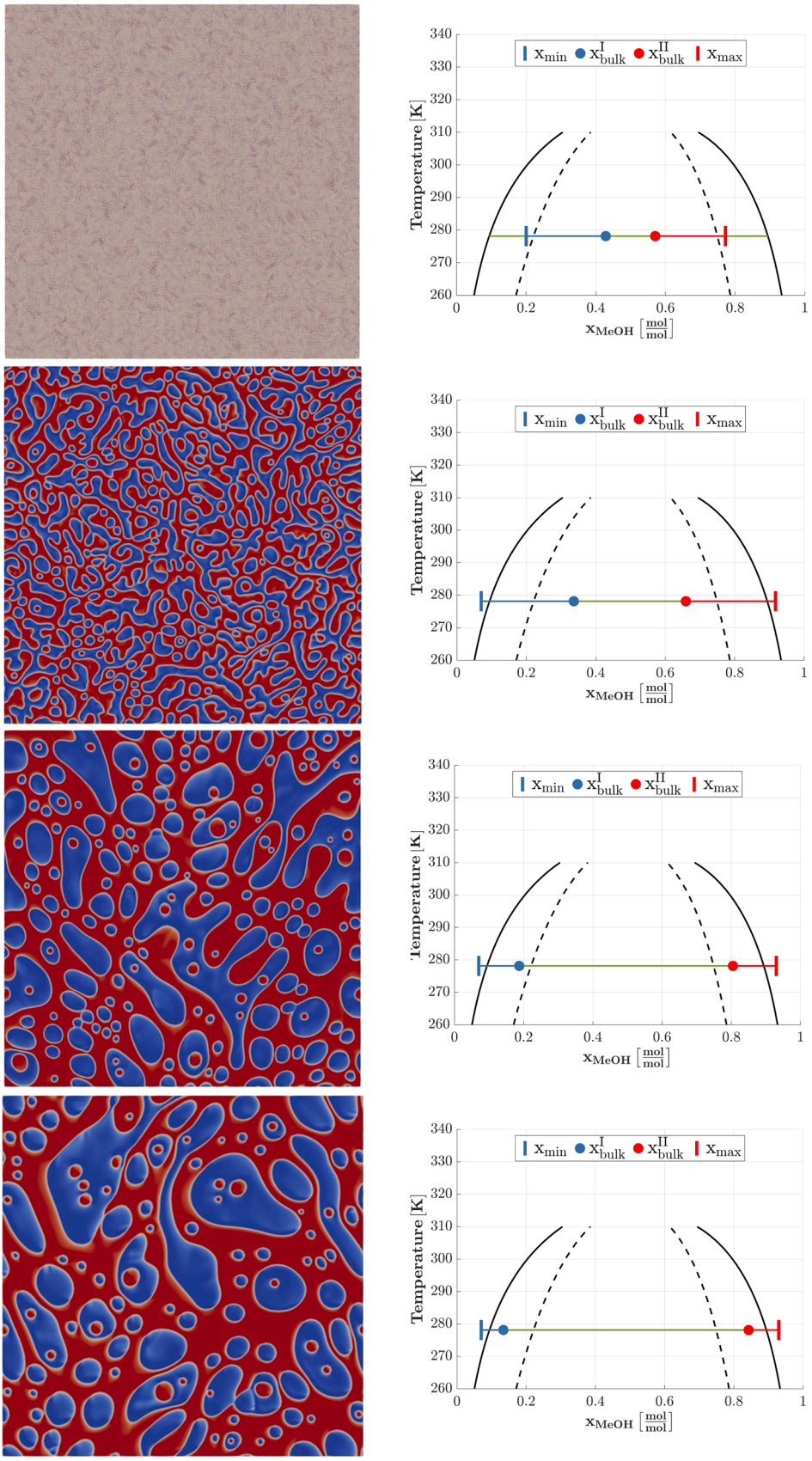

Fig. 4. De-mixing of the binary system MeOH - n-hexane using the parameters shown in Table 1. Left: the decomposition of the mixture in the simulation domain. Right the visualization of the process in the phase diagram (line: binodal curve, dotted line: spinodal curve).

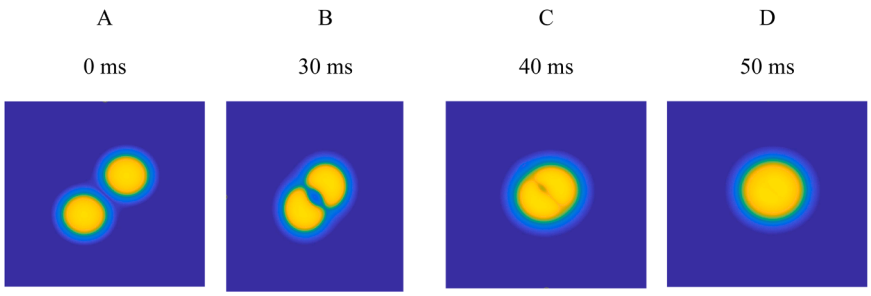

Fig. 5. Single stages of the droplet coalescence in the binary system toluene-water with the parameter shown in Table 1.

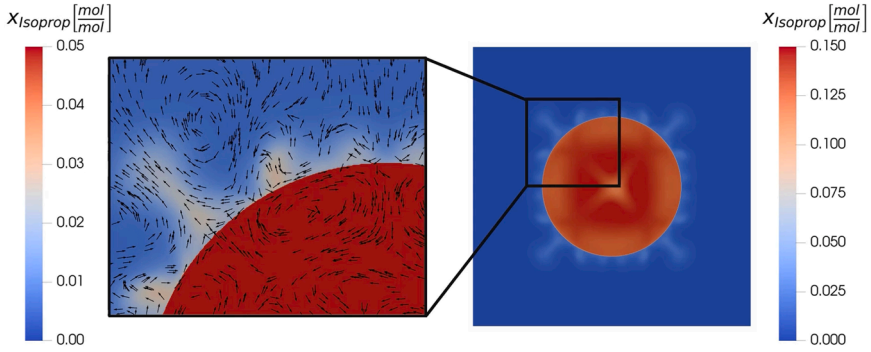

Fig. 6. Marangoni streaks formation around a droplet in the ternary system MeOH - n-hexane - isopropanol. Simulation parameters can be found in Table 1.

mined phenomena - such as phase equilibrium data, interfacial tension measurements, and droplet coalescence behavior - into numerical fluid dynamics simulations, without relying on predefined assumptions regarding the distributions of the dispersed and continuous phases. In contrast to classical phase field models, the present approach employs a thermodynamically consistent model to define the driving forces governing phase field evolution. This is achieved by applying the molar fraction as the concentration field and using the NRTL model that has been successfully applied in equilibrium thermodynamics to dictate flow directions. The Navier-Stokes/DGT framework allows for the consideration of interfacial effects and the investigation of droplet interactions. However, accounting for these effects necessitates a high cell resolution, limiting the model to small system sizes of about $10 \times 10\ mm$. Nonetheless, numerical investigations of small systems can help parameterize large-scale models like population balances.

As an example, the qualitative and quantitative de-mixing in a binary mixture of MeOH and n-hexane was investigated. Within this de-mixing process complex interfacial behavior was investigated as mass transfer between the immiscible phases as well as the occurring of phase separation, coalescence behavior and break-up of droplets. Furthermore, the Navier-Stokes/DGT model proves suitable for calculating the coalescence processes with respect to their single stages. This theoretical framework can be used to perform multiple numerical tests to determine coalescence or break-up probabilities based on droplet size, shape, distance, and shear influences, aiding in the parameterization of large-scale simulations for technical applications. Furthermore, complex interfacial phenomena as Marangoni convection around a single droplet in a ternary system could be predicted. The transfer component produced a distinct flow pattern, forming a toroidal convection pattern leading to observable Marangoni streaks.

A major advantage of the proposed approach compared to classical CFD methods is that phase formation emerges naturally from chemical potential gradients, without the need to predefine the presence or distribution of individual phases at the beginning of the simulation. Consequently, the interfacial phenomena observed in this work cannot be replicated in this form using traditional CFD models. Furthermore, the developed Navier-Stokes/DGT framework offers a significant benefit over conventional phase-field methods by enabling direct parameterization with experimental data, thereby enhancing the physical fidelity and predictive capability of the simulations.

Further consideration of different densities and additional components could lead to a fully thermodynamically consistent and spatially resolved description of extraction systems. Numerical experiments using this framework can then be compared to experiments such as droplet collision and droplet behavior in shear flow found in the literature. Further experiments could lead to the development of a formalism to extract droplet size distributions based on initial conditions, mass transfer, or interfacial enrichment.

CRediT authorship contribution statement

Matthias Singer: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Patrick Zimmermann:** Writing – original draft, Supervision. **Tim Zeiner:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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