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Systematic Extensions and Applications of Density Gradient Theory

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ABSTRACT

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Due to the importance of interfacial tension (IFT) in many industrial processes and daily activities, different methods have been developed to obtain IFT information for better process design and quality control in a variety of chemical systems. Compared with experimental measurements, model calculation is faster and lower-cost, allowing interpolation and extrapolation of data. Among many other models, density gradient theory (DGT) has gained popularity for simple functional form and accurate IFT predictions. Through more than a century of history, DGT has been developed and successfully implemented in IFT calculations of many pure and mixed systems. The strengths of the conventional DGT model have been well studied, while several major limitations are identified in our implementations, which restrict the model from being applied to a broader range of systems. These limitations include:

• The established reference fluid algorithm for DGT equations needs the pre-selection of a component with a monotonic density profile, and there is no clear strategy for this selection. Furthermore, the algorithm does not allow any extensions to the current DGT functional form.

• The conventional DGT model built for open systems fails to describe the IFT on spherical interfaces, since no stable droplets form when the system is allowed
to have mass exchange with the ambient environment. A closed system with conserved mass would stabilize the droplet, but applications of DGT to closed systems are lacking in literature.

- The conventional DGT model assumes that each molecule occupies a single position in space regardless of its molecular structure. This assumption prevents accurate application of DGT for surfactant molecules with amphiphilic chain structures.

In addition to the model limitations, we also identify several potential applications of the DGT model that are highly needed in this field:

- A quick and accurate surface energy model for DGT that defines the wetting boundary conditions for a 2D or 3D fluid model.

- Software with different DGT models that can be easily used by engineers with relatively little background.

In this thesis, we present a multistage work that addresses these challenges and needs. Firstly, we develop a novel and robust algorithm, which handles DGT equations smoothly and serves as a powerful tool to support the next-step model developments. Secondly, we construct a mass-conserved DGT model for closed systems, which can be used to study the IFT of droplets during the nucleation process. Thirdly, a modified DGT model for surfactant molecules is developed by introducing a chain formation term in the free energy expression. Fourthly, a surface free energy model is derived to define solid-fluid interactions. Finally, we develop a MATLAB based software, which integrates different DGT models and numerical algorithms into an user-friendly interface.

With systematic extensions of the DGT model, we have shaped the model to meet IFT calculation requirements in different scenarios. These model development progresses also unveil the great potential of DGT as an interface model for broader academic and industrial applications in the future.
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# Contents

Abstract  
Acknowledgments  
List of Illustrations  
List of Tables  

1 Introduction  

1.1 Motivation  
1.2 Density gradient theory  
1.3 Surfactant  
1.4 Droplet nucleation  
1.5 Statistical ensembles  
1.6 Scope of this thesis  

2 Theory and model equations  

2.1 DGT equations  
2.2 Equation of state  
2.2.1 Cubic equation of state  
2.2.2 SAFT equation of state  
2.3 Influence parameter  

3 The stabilized density gradient theory algorithm  

3.1 The reference fluid algorithm  
3.1.1 DGT equation manipulations  
3.1.2 Mathematical model
3.1.3 Limitations of the RF algorithm .................................................. 37
3.2 The stabilized density gradient theory algorithm .............................. 38
  3.2.1 Modified DGT equations ......................................................... 38
  3.2.2 Mathematical model .............................................................. 39
  3.2.3 Boundary conditions and initial conditions ................................. 45
3.3 DGT model results with the SDGT algorithm .................................. 47
  3.3.1 Phase equilibrium calculations ............................................... 47
  3.3.2 One component VLE system .................................................. 49
  3.3.3 Multicomponent VLE system ................................................ 52
  3.3.4 Multicomponent LLE system ................................................ 56
  3.3.5 Free energy analysis ............................................................ 60

4 The mass-conserved density gradient theory model ............................ 63
  4.1 The mass-conserved DGT model .................................................. 64
    4.1.1 DGT equations in closed systems ......................................... 64
    4.1.2 Mass-conservation term $\lambda_i$ ........................................ 65
    4.1.3 Physical justification of $\lambda_i$ ........................................ 66
  4.2 Mathematical model ................................................................. 68
    4.2.1 Model equations .............................................................. 68
    4.2.2 Energy dissipation ............................................................ 69
    4.2.3 Planar interface case ......................................................... 70
    4.2.4 Spherical interface case .................................................... 71
  4.3 Discretization .............................................................................. 71
    4.3.1 Space discretization ............................................................ 71
    4.3.2 Time discretization ............................................................. 72
    4.3.3 Fully discretized equations .................................................. 72
  4.4 Applications of the mass-conserved DGT model ................................ 74
    4.4.1 Results for planar interface cases ....................................... 74
5 The modified density gradient theory model for surfactants

5.1 The modified DGT model for surfactant systems

5.2 Numerical methods for modified DGT equations

5.2.1 SDGT algorithm for modified DGT equations

5.2.2 Fast Fourier transform for convolution integrals

5.3 Applications of the modified DGT model

6 Surface free energy and wetting boundary conditions

6.1 Equilibrium wetting boundary conditions

6.2 Surface free energy

7 DGT software package

7.1 Overview of the PMFS Helper Tool

7.2 User interface of the PMFS Helper Tool

7.2.1 Start page

7.2.2 Input page

7.2.3 Results page

7.3 Applications of the PMFS Helper Tool

8 Concluding remarks

8.1 Summary

8.2 Future work

8.2.1 Nucleation of multicomponent systems
Illustrations

2.1 Influence parameters of butane at different temperatures. 27
2.2 Influence parameters of hydrocarbons with different carbon numbers. 28
2.3 Fitted influence parameters using the PC-SAFT EoS. 29

3.1 The reference fluid algorithm flowchart. 36
3.2 Space discretization of the domain. 41
3.3 Equilibrium density profiles of propane/hexane mixture at 300 K, 1 bar with different domain sizes. 46
3.4 Density profiles convergence history of methane/propane mixture at 303 K, 50 bar with different initial conditions. 47
3.5 Phase diagrams of pure and mixed systems. 48
3.6 Density profile convergence history of hexane at 313 K. 49
3.7 Equilibrium density profiles of seven pure hydrocarbons at 273 K. 50
3.8 IFT results of pure hydrocarbons and water at different temperatures. 51
3.9 Equilibrium density profiles of a mixture containing seven hydrocarbons from methane to heptane at 313.15 K, 5 bar. 53
3.10 IFT results of binary hydrocarbon mixtures at 313.15 K and different mole fractions. 54
3.11 IFT results of binary nitrogen/hydrocarbon and carbon dioxide/hydrocarbon mixtures at different temperatures. 55
3.12 Density profiles convergence history of water/hexane mixture at 300 K, 1 bar. 56
3.13 IFT results of binary water/hydrocarbon mixtures at 1 bar and different temperatures. ........................................ 58
3.14 Equilibrium density profiles of water/dodecane, water/toluene, and water/toluene/dodecane mixtures at 110 °C, 250 psig. .............. 58
3.15 IFT results of binary and ternary water/hydrocarbon mixtures. .... 59
3.16 Free energy analysis of the surface accumulation. .................. 61
3.17 Free energy analysis of low mutual solubilities between water and oil. 62

4.1 Diffusion process. .................................................. 67
4.2 Density profile convergence history of hexane at 293.15 K in (a) an open system and (b) a closed system. .............................. 74
4.3 Comparison of hexane’s equilibrium density profiles (293.15 K) of DGT models in open and closed systems. .......................... 75
4.4 Comparison of workflows of conventional DGT model and the mass-conserved DGT model. ......................................... 77
4.5 Phase envelope of hexane. ....................................... 77
4.6 Equilibrium density profiles of hexane at 293.15 K with different mass in the system. .................................................. 78
4.7 Density profile convergence history of hexane droplet at 293.15 K. ... 79
4.8 Equilibrium density profiles of hexane droplet at different temperatures. .................................................. 80
4.9 Liquid and vapor phase pressures at different radius calculated by the mass-conserved DGT model. ......................................... 82
4.10 IFT results of different radius hexane droplet at 293.15 K. .......... 82

5.1 Molecular structure of 2-methoxyethanol. .......................... 85
5.2 Equilibrium density profiles of a surfactant system by the conventional DGT model. ........................................ 85
5.3 The two-group surfactant molecule model. .................. 88
5.4 Surfactant molecules’ average orientation in the interface. .... 90
5.5 Coordinate transformation from rectangular to spherical coordinate. . 91
5.6 The region that the head group density is a constant. ............. 95
5.7 Density profiles convergence history of the water/hexane/$H_1T_1$
surfactant system at 293.15 K, 1.01 bar. .......................... 98
5.8 Equilibrium density profiles of the water/hexane/surfactant system at
293.15 K, 1.01 bar with different surfactant mole fraction in the water
phase. ........................................................................ 99
5.9 IFT results of the water/hexane/$H_1T_1$ surfactant system as a
function of the surfactant concentrations. ......................... 100
5.10 The tail length effect on surfactant performances. ................ 101
6.1 The contact angle $\theta$ of liquid droplet sitting on the solid surface. . . 107
7.1 Start page of the PMFS Helper Tool. ............................... 111
7.2 Input page of the PMFS Helper Tool: example 1. .................. 112
7.3 Input page of the PMFS Helper Tool: example 2. .................. 113
7.4 Result page of the PMFS Helper Tool. ............................. 114
7.5 Density profiles and computational progresses displayed during the
calculation. .................................................................. 116
7.6 IFT results of nitrogen/methane and methane/propane mixtures by
the PMFS Helper Tool. .................................................. 118
8.1 Molecular structure of nonylphenol. ................................. 123
Tables

2.1 PC-SAFT parameters of pure components. .......................... 21
2.2 List of fitted influence parameters using the PC-SAFT EoS. .... 30

3.1 Feed composition of the mixture with seven hydrocarbons. ... 52

7.1 Input requirements of the PMFS Helper Tool. .................... 115
Chapter 1

Introduction

1.1 Motivation

Interfacial tension (IFT) is a material property that resists the creation of a new surface [1]. It has the unit of force per unit length [N/m] or energy per unit area [J/m$^2$]. In many cases, the term “IFT” is defined on the interface between two immiscible liquids, and the term “surface tension” is defined on the interface between liquid and gas phases. In this work, we used IFT as a general term for liquid/gas, liquid/liquid, liquid/solid and gas/solid interfaces.

In our daily life, many phenomena are affected by the IFT on different interfaces. For example, a floating paper clip on water is supported by the IFT on the water/air interface. Plant’s capacity to transport water from roots to leaves is due to the capillaries inside the xylem vessels, which is caused by the IFT of water on the xylem walls. The reason that soap can wash oil away is because soap contains surface active agent that helps reduce the IFT between the oil/water interface, and thus makes oil soluble in water.

Besides, IFT also plays an important role in many industrial processes, such as the crude oil recovery, oil transport and distillation. For example in upstream operations, crude oil droplets are trapped in rock pores, and much oil is left in the reservoir after water flooding. For oil droplets to deform and pass through the pores, low IFT between oil and water is required [2]. In the enhanced oil recovery (EOR) process,
surfactant along with water are injected into the oil reservoir, a process called “surfactant flooding”. The injected surfactant molecules accumulate in the interfacial region, and significantly lower the IFT between oil and water phases. As a result, surfactant flooding mobilizes the trapped oil in the reservoir, and effectively increases the oil recovery efficiency.

Another example is in the food industry, in which the falling film evaporators are widely used to process heat sensitive liquids [3]. A minimum flow rate is required within the evaporator to maintain the continuous liquid film, which is important to keep heat transfer efficiency and prevent evaporator fouling. The solid/liquid and liquid/gas IFTs have strong influence on this operation, and the substance with proper IFT is required to ensure normal operations.

To obtain the IFT information of certain systems, experimental measurement is a straightforward way, and in most of time it is accurate and reliable. Methods developed for IFT measurement include the Wilhelmy plate/ring method [4], maximum bubble pressure method [5] and methods of analyzing the shape of a pendant, sessile liquid drop or gas bubble [6]. Despite the advantages, there exist several limitations of experimental methods, which include:

- Experimental measurements can be expensive and time-consuming. For example, one measurement of oil IFT would take more than $1000 and one week of time.

- Heavy tasks could be imposed on IFT measurement labs. For example, crude oil is a very complex mixture, and its compositions and conditions would vary from reservoir to reservoir, or time to time. Measuring the IFT of each system requires many repeated experiments over a range of conditions.
• The accuracy of the experimentally measured IFT might be affected by the equipment condition. For example if the fluid is contaminated, the measured IFT could deviate much from its actual value.

To makeup for the limitations of experimental measurements, computational models for IFT calculations were developed. In practice, the verified experimental data is the foundation for the model development and parameter fitting, while the models could be used to interpolate and extrapolate data efficiently and economically. In many cases, the validated model could also be used to check or improve the accuracy of newly measured IFT data. For example, by measuring the contaminant concentrations, a model can estimate IFT for a digitally cleaned sample.

Different IFT models can be broadly categorized into three major types: correlation methods, statistical thermodynamics based methods and molecular simulations. Correlation functions, such as the parachor method [7, 8, 9], have been popular in industry for its easy implementation and fast calculation, but its accuracy is not satisfying in many situations especially for complex mixtures. Molecular simulation, such as molecular dynamics (MD) [10, 11], tracks the force experienced by each molecule, and it is a powerful tool to describe surface physics at the expense of long computational time.

In our work, density gradient theory (DGT), which is a type of statistical thermodynamics based method, is employed for IFT calculations. With a history of over 100 years, DGT has been successfully applied in many pure and mixed systems, and it is still gaining attention from both academia and industry.
1.2 Density gradient theory

The idea of DGT model was first proposed by Van der Waals [12]. In his work, an interface area was described by a diffuse thin layer where a smooth density variation exists. According to DGT, the inhomogeneous free energy is a function of the local density and its gradient. The DGT model was later reformulated by Cahn and Hillard [13], and since then it has been widely adopted. Two inputs are required in the DGT model: the bulk equation of state (EoS) and the influence parameter, which is an interface characteristic parameter of each component.

In the later development of the DGT model, Carey [14] made a significant contribution to this theory by proposing a numerical algorithm for DGT equations. The approach is called the reference fluids (RF) algorithm, since a component with monotonic density profile needs to be chosen as a reference fluid, and the density profiles of other components are calculated based on the density of the reference fluid. Up to today, the RF algorithm is still the most widely accepted algorithm for DGT calculations. In later works, Carey and his coworkers introduced their implementation of the DGT model in IFT calculations of alkanes, alcohols and several of their mixtures [15, 16].

Miqueu et al. did systematic developments and applications of DGT in a series of papers. They proposed a simple correlation function for influence parameters of non-polar components [17], and then applied the DGT model in IFT calculations of binary and ternary mixtures [18]. Later, a general DGT workflow for any number of components was developed [19], with which they were able to calculate the IFT of a real petroleum mixture at reservoir conditions with more than five components in the system [20].

At the early stage, DGT was mainly used to treat systems forming vapor-liquid

To test the performance of the DGT model, Sahimi et al. [26, 27] compared it with the two scale-factor universality method in IFT calculation of CO$_2$ and hydrocarbon mixtures. It was reported that DGT not only produced IFT results of better agreement with experimental data, but also required less adjustable parameters. Cornelisse et al. [28, 29] compared the performance of DGT with the parachor method in several binary and ternary CO$_2$/alkanes mixtures, with the conclusion that DGT had a higher accuracy in IFT predictions.

As one of the inputs, the bulk EoS is a key factor that affects the accuracy of DGT predictions. Cubic EoS, including van der Waals (VDW) EoS [30], Peng–Robinson (PR) EoS [31], and Soave–Redlich–Kwong (SRK) EoS [32, 33], is so far the most commonly used EoS in the DGT model [14, 15, 16, 28, 29, 26, 27, 34, 35, 36]. Cubic EoS gives good bulk property predictions for non-polar molecules, such as alkanes, nitrogen. However, its performance is less satisfying for polar systems, especially those containing associating components. In later works, the Associated-Perturbed-Anisotropic-Chain Theory (APACT) EoS was employed in DGT calculations [37, 38], which improved the calculation accuracy for polar and associating species.

An important breakthrough in the DGT community was the use of the Statistical Association Fluid Theory (SAFT) EoS. Since its invention by Chapman et al. [39, 40, 41], SAFT EoS has demonstrated its excellent performance in phase behav-
ior descriptions of complex systems [42]. Kahl and Enders compared the performances of PR and SAFT EoS in DGT calculations for alcohol/alkane [43] and water/alcohol mixtures [44], and it was proved that DGT+SAFT produced better IFT predictions. Different versions of SAFT have been developed and implemented with DGT, including perturbed-chain (PC) SAFT [45, 46], perturbed-chain polar (PCP) SAFT [47], and SAFT of variable range employing a Mie potential (VR-Mie) [48, 49].

1.3 Surfactant

Surfactants as surface active agents are frequently used to alter IFT on different surfaces, such as detergents in dish washing or surfactant flooding in the EOR process. The surface active nature of the surfactant molecule is due to its amphiphilic structure, which consists of a hydrophilic group and a hydrophobic group. When added into water/oil mixtures, the surfactant head would form hydrogen bonds or electrostatic interactions with water molecules depending on the charge type of the surfactant head, and therefore makes the head prefer to stay in the water phase. The tail group, on the other hand, is normally formed by alkyl chains, which is repelled by water and prefers the oil phase. As a result, surfactant molecules would accumulate at the water/oil interface, and lower the system’s IFT.

Based on the chemical properties of the hydrophilic groups, surfactants can be classified into two major categories: nonionic surfactant and ionic surfactant. An ionic surfactant further breaks down into three buckets: anionic, cationic and zwitterionic surfactants [50]. In practice, different types of surfactants are often mixed to achieve specific goals by taking advantage of each surfactant’s strength [51, 52, 53, 54, 55]. Besides the charge types on the hydrophilic group, other characteristics such as the length of the head/tail group, and the system conditions (temperature, pressure,
salinity, etc.) also have significant impacts on the interfacial behaviors of surfactants.

Due to the sophistication and expense of experiments [56, 57], many theoretical and simulation methods have been developed to model surfactant behaviors in mixtures. MD simulation [58, 59, 60] and the classical Density Functional Theory (DFT) [61, 62, 63, 64, 65] are among the most successful methods for surfactant modeling due to their capabilities of describing the special amphiphilic structure of surfactant molecules. MD simulation has the advantage of providing potentially atomistic details, and classical DFT, which is derived from statistical mechanics, requires a less detailed molecular model that is consistent with bulk equations of state.

The conventional DGT model is a simpler model compared with MD and DFT, but it has not been successfully implemented in any surfactant systems due to the lack of molecular structure description in the model. Challenges as well as opportunities both exist on this topic.

1.4 Droplet nucleation

The nucleation process is a commonly observed phenomena that occurs in nature, science and industry, e.g., the crystallization of salt from sea water, the vapor condensation in the condenser of a distillation tower, or simply water freezing into ice. The homogeneous droplet formation is a type of nucleation process in which the liquid droplet forms from the supersaturated vapor phase away from a surface. Studying the homogeneous droplet nucleation process is of significant importance. For example, in the artificial precipitation operation, anthropogenic aerosol particles serve as seeds (nuclei) for cloud droplets to nucleate. One of the biggest challenges in simulations of climate and climate change is modeling the droplet nucleation process in clouds, which represent much of the complexity of the simulation [66, 67].
Over a long period of time, classical nucleation theory (CNT) [68, 69, 70, 71, 72] has served as a major tool in nucleation calculations because of its easily-accessed inputs and good prediction performances for critical supersaturations. In CNT, the droplet’s IFT plays an important factor in determining the nucleation rate [73]. MD simulation has been successfully implemented to compute droplet IFT [73, 74]. The classical DFT also serves as a powerful tool in describing interfacial properties of droplets [75, 76, 77, 78].

We found several attempts in the literature to apply the DGT model in nucleation calculations. Barrett [79] adopted DGT together with the PR EoS for n-nonane nucleation, and derived equations for a spherically symmetric surface. However, the pressures in the liquid and vapor phases were set to be equal in the calculation, which is not the case on a spherical interface. In other works, the authors either did not conduct any IFT calculations [80] or did the IFT calculation by combining DGT with Young–Laplace equation [81], which sacrifices DGT’s advantages at the nano-scale.

In fact, the current basis of the DGT model in a grand canonical ensemble system is incapable to generate a stable droplet with finite radius. A closed system with no mass exchange, on the other hand, can help stabilize the droplet, and one example of the closed system is the canonical ensemble. A working DGT model in canonical ensemble is therefore required to study a droplet’s IFT.

1.5 Statistical ensembles

As discussed in the last section, the development of DGT in different ensembles would significantly affect model equations as well as boundary conditions, and would generate quite different interfacial behaviors. In statistical mechanics, the concept of ensemble is first introduced by Josiah Willard Gibbs [82]. An ensemble is a collection
of very large number of systems, each constructed to be a replica on a thermodynamic level that represents a possible state the real system might be in [83]. The ensemble average of some mechanical properties can be set equal to the corresponding thermodynamic properties. In practice, three important thermodynamic ensembles that are defined by Gibbs are frequently used: grand canonical ensemble, canonical ensemble and microcanonical ensemble.

1. Grand canonical ensemble

A grand canonical ensemble is the statistical ensemble that is used to represent an open system, which is in thermodynamic equilibrium with a large reservoir. In the grand canonical ensemble, the chemical potential ($\mu$), system volume ($V$), and temperature ($T$) are fixed, while the system is allowed to have mass and energy exchange with the external reservoir. Therefore, the grand canonical ensemble is often referred to as the $\mu VT$ ensemble. The characteristic energy of the grand canonical ensemble is the grand potential $\Omega$. The system reaches a thermodynamic equilibrium state when $\Omega$ is minimized: $\delta \Omega / \delta \rho_i = 0$.

2. Canonical ensemble

A canonical ensemble is the statistical ensemble that is used to represent a closed system, which is in equilibrium with a heat bath at fixed temperature. In the canonical ensemble, the number of particles ($N$), system volume ($V$) and temperature ($T$) are fixed, while the system is allowed to have energy exchange with the environment. A canonical ensemble system is also referred to as the $NVT$ ensemble. The characteristic energy of the canonical ensemble is the Helmholtz free energy $A$. The system reaches a thermodynamic equilibrium state when $A$ is minimized: $\delta A / \delta \rho_i = 0$.

3. Microcanonical ensemble

A microcanonical ensemble is the statistical ensemble that is used to represent an
isolated system, which means the system is not allowed to have either mass or energy exchange with the environment. Therefore in a microcanonical ensemble, the number of particles \(N\), system volume \(V\) and total energy \(E\) are fixed. This ensemble is also referred to as the \(NVE\) ensemble. A microcanonical ensemble does not evolve over time since the ensemble is strictly defined as a function of the conserved energy. In fact, the microcanonical ensemble does not correspond to any experimental systems because it is not realistic to completely isolate a system.

1.6 Scope of this thesis

To meet the demand for a fast and accurate IFT prediction model, and to address the existing challenges in the established model, we have done systematic studies, extensions and applications of the DGT model to make it widely applicable to various simple and complex systems.

In Chapter 2, the concepts of the DGT model and DGT equations are introduced. Two major inputs in DGT, the EoS and the influence parameter, are discussed as well. The PR EoS, PC-SAFT EoS, and their corresponding correlation functions for influence parameter are presented in detail.

Chapter 3 introduces the numerical algorithms used to solve DGT equations. The popular reference fluid (RF) algorithm is reviewed first. By realizing the limitations of the established algorithm, a novel and more robust stabilized density gradient theory (SDGT) algorithm is introduced. The performance of the DGT model with the SDGT algorithm is tested in many pure and mixed systems.

In Chapter 4, we extend the DGT model from open systems to closed systems by adding a mass-conservation term and no-flux boundary conditions. The mass-conserved DGT models are built for both planar and spherical interfaces, and have
been successfully applied to calculate the IFT in droplet formation for the first time.

In Chapter 5, a modified DGT model for surfactant systems is developed, which removes the major limitation of the DGT model that no molecular structure is considered. The modified DGT model describes surfactant molecules by bonding a head group with a tail group, and it has been applied to study surfactant behaviors on water/oil interfaces.

In Chapter 6, we present the derivations of the surface free energy and the equilibrium wetting boundary condition for fluids in contact with a solid wall. These models can be applied to define the contact angle in 2D or 3D oil reservoir simulators.

Chapter 7 introduces the MATLAB–based PMFS Helper Tool which is developed for IFT calculations by bundling different DGT models with a user-friendly operating interface. The software can be readily used by engineers to conduct fast phase equilibrium and interfacial properties calculations.

Chapter 8 summarizes the thesis, and proposes future works. All symbols and abbreviations used in this thesis are defined in the Nomenclature.
Chapter 2

Theory and model equations

In this chapter, we review the conventional DGT model, including the model assumptions and equations (Section 2.1). Two major inputs into DGT, the bulk EoS (Section 2.2) and the influence parameter (Section 2.3), are also discussed.

2.1 DGT equations

The DGT model was derived from modified van der Waals (MVDW) model by applying the Taylor expansion to the local density \([14, 84]\). The expression of the inhomogeneous Helmholtz free energy \(A\) of DGT depends on both the local density and the density gradient:

\[
A = \int a[\rho(r)]d^3r = \int \left(a_0[\rho(r)] + \sum_{i,j=1}^{N} \frac{1}{2} v_{ij} \nabla \rho_i(r) \cdot \nabla \rho_j(r) + \ldots \right) d^3r, \tag{2.1}
\]

where \(a_0\) is the homogeneous Helmholtz free energy given by a bulk EoS, \(N\) is the total number of components in the system, \(\rho\) is the density vector of all component \(i\) in the system, \(r\) is the position vector, and \(v_{ij}\) is the matrix of influence parameters \(v_i\). Gradient terms of fourth and higher orders are neglected in calculations. Detailed derivations to the DGT free energy functions are documented in Appendix A.

According to the DGT free energy functional, the homogeneity of the system is described by a bulk EoS, while the inhomogeneity is accounted for by the density gradient term. In bulk phases where the density of each component \(\rho_i\) is homogeneous,
the gradient term vanishes, and the Helmholtz free energy density $a$ reduces to $a_0$. This feature guarantees that the phase behavior predictions of the DGT model are consistent with the bulk EoS, which becomes a major advantage of the DGT model.

In an open isothermal system, where the bulk chemical potential $\mu_{i,\text{bulk}}$, volume $V$ and temperature $T$ are fixed, the system’s grand potential energy $\Omega$ is given by:

$$\Omega = A - \int \sum_i \rho_i(\mathbf{r}) (\mu_{i,\text{bulk}} + V^{\text{ext}}) \, d^3 \mathbf{r}$$

$$= \int \left( a_0[\rho(\mathbf{r})] + \sum_{i,j=1}^N \frac{1}{2} v_{ij} \nabla \rho_i(\mathbf{r}) \cdot \nabla \rho_j(\mathbf{r}) - \sum_{i=1}^N \rho_i(\mathbf{r}) (\mu_{i,\text{bulk}} + V^{\text{ext}}) \right) \, d^3 \mathbf{r}, \tag{2.2}$$

where $V^{\text{ext}}$ is the external potential energy, such as the solid-fluid interaction potential when the fluid is close to a solid wall.

The grand potential energy $\Omega$ is minimized when the system reaches an equilibrium state. The minimization leads to the following Euler-Lagrange equation for each component $i$:

$$\frac{\delta \Omega}{\delta \rho_i} = 0$$

$$\mu_i[\rho(\mathbf{r})] - \mu_{i,\text{bulk}} - V^{\text{ext}} - \sum_{j=1}^N v_{ij} \nabla^2 \rho_j(\mathbf{r}) + \frac{1}{2} \sum_{j,k=1}^N \frac{\partial v_{jk}}{\partial \rho_i} \nabla \rho_j(\mathbf{r}) \cdot \nabla \rho_k(\mathbf{r}) = 0, \tag{2.3}$$

where $\mu_i := \partial a_0 / \partial \rho_i$ is the homogeneous chemical potential evaluated at the local density using the bulk EoS.

In the case of a planar interface system with no external field, the density $\rho_i$ only varies along the $z$ direction and $V^{\text{ext}} = 0$. By assuming that the influence parameter is not a function of density ($\partial v_i / \partial \rho_j = 0$), an assumption that is supported by McCoy and Davis [85], as well as Carey et al. [16], Eqn. 2.3 can be simplified to:

$$\mu_i[\rho(z)] - \mu_{i,\text{bulk}} - \sum_{j=1}^N v_{ij} \frac{d^2 \rho_j}{dz^2} = 0. \tag{2.4}$$
Eqn. 2.4 is a set of ordinary differential equations (ODE), which are subjected to the following boundary conditions:

\[ \rho_i(z_L) = \rho_{i,A}, \quad \rho_i(z_R) = \rho_{i,B}, \quad (2.5) \]

where \( z_L \) and \( z_R \) are boundary positions in space, \( \rho_{i,A} \) and \( \rho_{i,B} \) are bulk densities of component \( i \) in phase \( A \) and \( B \) respectively. The boundary conditions mean that at far from the interface region, for example \( z_L = -\infty \) and \( z_R = +\infty \), the component’s densities equal to its bulk densities. In practice, \( z_L \) is often set at the origin point \( z_L = 0 \), and \( z_R \) is set to be a value of \( D \), which should be large enough compared with the interface width \( L_w \) to make sure that the right boundary falls in the bulk phase. Solving Eqn. 2.4 subjected to the corresponding boundary conditions generates the system’s equilibrium density profile \( \rho_i(z) \) in space.

With the equilibrium density profiles, the system’s IFT can be calculated. IFT by definition is the surface excess grand potential energy:

\[ \gamma = \frac{\Omega - \Omega_0}{A_s}, \quad (2.6) \]

where \( A_s \) is the interface area, and \( \Omega_0 = -P_0V \) is the bulk grand potential energy, in which \( P_0 \) is the equilibrium bulk pressure and \( V \) is the system volume.

Plugging the expression of the grand potential energy (2.2) into Eqn. 2.6 yields the expression of IFT on a planar interface:

\[ \gamma = \int_{z_L}^{z_R} \left( a_0[\rho(z)] + \frac{1}{2} \sum_{i,j=1}^{N} v_{ij} \nabla \rho_i(z) \cdot \nabla \rho_j(z) - \sum_{i=1}^{N} \rho_i(z) \mu_{i,\text{bulk}} + P_0 \right) \, dz. \quad (2.7) \]

So far, we have reviewed the model equations of the DGT model, including the free energy expression, the objective function for equilibrium density profiles and the expression for IFT. In order to implement the DGT model in practical calculations, the following three things are required:
• A bulk EoS to provide the homogeneous chemical potential expression $\mu_i$,
• The influence parameter matrix $v_{ij}$ for pure or mixed systems,
• A robust numerical algorithm to solve the Euler-Lagrange equations (2.4).

In the rest of this chapter, the bulk EoS and the influence parameter will be introduced. And we will discuss the numerical algorithm for DGT equations in Chapter 3.

2.2 Equation of state

An EoS is a thermodynamic relation, which relates state variables such as temperature ($T$), pressure ($P$), volume ($V$), density ($\rho$), chemical potential ($\mu$) or free energy ($A$) [86]. One of the most important application of the EoS is to predict phase behaviors under different system conditions. The simplest EoS is the ideal gas law:

$$PV = nRT,$$

where $n$ is the number of moles, and $R = 8.3144598 \text{ J mol}^{-1}\text{K}^{-1}$ is the gas constant.

Since the ideal gas law assumes no molecular interactions, more advanced EoS have been developed to treat realistic systems. In our work, we have mainly employed two types of EoS, the cubic EoS and the SAFT EoS, for their respective advantages: the cubic EoS family has a simpler functional form and is widely accepted by industry [87, 88], and the SAFT EoS family describes complex systems more accurately [89].

2.2.1 Cubic equation of state

The cubic EoS is named so because it is written in a form of third order of the molar volume $V_m$. This is so far one of the most widely used and successful tool for phase behavior calculations in both industrial and academic applications [88]. The
The first practical cubic EoS is derived in 1873 by Johannes Diderik van der Waals, who received the Nobel Prize in 1910 for “his work on the equation of state for gases and liquids” [90]. The van der Waals (VDW) EoS is a modified version of the ideal gas law which takes inter-particle interactions into consideration. In 1949, Redlich and Kwong [32] proposed a modified VDW EoS for the prediction of gas phase behaviors, which is called Redlich-Kwong (RK) EoS. Later in 1976, Peng and Robinson [31] improved upon the RK EoS by recalculating the $\alpha$ function and modifying the volume dependency of the attractive term. These changes allowed them to obtain better results for liquid volumes and better representations of vapor-liquid equilibrium (VLE) for mixtures. Their work is named as Peng-Robinson (PR) EoS. In this section, we presented in details the PR EoS.

The pressure equation of the PR EoS is given as:

$$P = \frac{RT}{V_m} - b - \frac{a\alpha}{V_m^2 + 2bV_m - b^2},$$

where $V_m$ is the molar volume, $a$, $\alpha$ and $b$ are PR parameters, which are defined as:

$$a = 0.4574 \frac{R^2 T^2}{P_c},$$

$$b = 0.0778 \frac{RT_c}{P_c},$$

$$\alpha = [1 + (0.37464 + 1.54226\tilde{\omega} - 0.26992\tilde{\omega}^2)(1 - \sqrt{T_r})]^2,$$

in which, $T_c$ is the critical temperature, $P_c$ is the critical pressure, $\tilde{\omega}$ is the acentric factor, and $T_r$ is the reduced temperature $T_r = T/T_c$.

For mixtures, the mixed parameters $a_m$ and $b_m$ are required, and they can be obtained with the following mixing rules:

$$a_m = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j (1 - k_{ij}) \sqrt{(aa)_i(aa)_j},$$

$$b_m = \sum_{i=1}^{N} x_i b_i,$$
where $x_i$ is the mole fraction, and $k_{ij}$ is the binary interaction parameter.

The Helmholtz free energy density of a homogeneous system consists of the ideal gas contribution and the residual free energy contribution:

$$a_0 = a_0^\text{id} + a_0^\text{res}.$$  

(2.12)

The ideal gas Helmholtz free energy is known from thermodynamics:

$$a_0^\text{id} = RT \sum_{i=1}^{N} \rho_i (\ln \rho_i - 1),$$  

(2.13)

in which, the de Broglie wavelength and other temperature independent terms that do not affect the fluid structure are neglected.

The residual Helmholtz free energy by definition is:

$$a_0^\text{res} = -\frac{1}{V_0} \int_{V_0}^{V} \left( P - \frac{nRT}{V} \right) dV.$$  

(2.14)

Plugging the pressure equation (2.9) in, and integrating over volume gives:

$$a_0^\text{res} = -\rho_t RT \ln(1 - \rho b_m) - \frac{\rho_t a_m}{2\sqrt{2} b_m} \ln \frac{E_m}{S_m},$$  

(2.15)

where $\rho_t = \sum_i \rho_i$ is the total density in the bulk phase, $E_m = 1 + e \rho_t b_m$, $S_m = 1 + s \rho_t b_m$, and $e = 1 + \sqrt{2}$, $s = 1 - \sqrt{2}$ are constants.

In the residual Helmholtz free energy expression, the first term accounts for the repulsion interaction and the second term describes the attraction interaction between molecules. The chemical potential $\mu_i$ is obtained by taking the first derivative of the Helmholtz free energy density $a_0$ with respect to molar density $\rho_i$ at constant temperature, volume and number of other particles. For PR EoS, the chemical potential
expression of component \(i\) is given as:

\[
\mu_i = \left( \frac{\partial a_0}{\partial \rho_i} \right)_{T,V,N_j \neq i} = RT \left( \ln \frac{\rho_i}{1 - \rho_t b_m} + \frac{\rho_t b_i}{1 - \rho_t b_m} \right) - \frac{\rho_t a_m b_i}{b_m E_m S_m} \left( \frac{\sum_j (a_{ij} \rho_j)}{\sqrt{2} \rho_t b_m} - \frac{a_m b_i}{2 \sqrt{2} b_m^2} \right) - \ln \frac{E_m}{S_m} \left( \frac{\sum_j (a_{ij} \rho_j)}{\sqrt{2} \rho_t b_m} - \frac{a_m b_i}{2 \sqrt{2} b_m^2} \right) \]

(2.16)

The expression of the first derivative of the chemical potential to density is presented as follows:

\[
\frac{\partial \mu_i}{\partial \rho_j} = \frac{\partial \mu_i^{id}}{\partial \rho_j} + \frac{\partial \mu_i^{res}}{\partial \rho_j} ,
\]

(2.17)

in which,

\[
\frac{\partial \mu_i^{id}}{\partial \rho_j} = \begin{cases} 
RT/\rho_i & \text{for } j = i \\
0 & \text{for } j \neq i 
\end{cases}
\]

(2.18)

\[
\frac{\partial \mu_i^{res}}{\partial \rho_j} = \frac{RT b_j}{1 - \rho_t b_m} + \frac{RT b_i (1 - \rho_t b_m + \rho_t b_j)}{(1 - \rho_t b_m)^2} - \frac{2(\sum_k a_{jk} \rho_k)b_j}{\rho_t b_m E_m S_m} \left( \frac{\rho_t a_m b_i}{b_m E_m S_m} + \frac{\sum_k a_{ik} \rho_k b_m}{\sqrt{2} \rho_t b_m} \right) \\
- \ln \frac{E_m}{S_m} \left( \frac{\rho_t a_{ij} b_m - (\sum_k a_{ik} \rho_k)b_j}{\sqrt{2} \rho_t b_m^2} - \frac{(\sum_k a_{jk} \rho_k)b_m^2 - \rho_t a_m b_i b_j}{\sqrt{2} \rho_t b_m^2} \right) - \frac{2\sqrt{2} b_j}{E_m S_m} \left( \frac{\sum_k a_{ik} \rho_k}{\sqrt{2} \rho_t b_m} - \frac{a_m b_i}{2 \sqrt{2} b_m^2} \right) + \frac{a_m b_i [b_j E_m S_m + 2 \rho_t b_m b_j (1 - \rho_t b_m)]}{b_m E_m^2 S_m^2} 
\]

(2.19)

In some cases, the performance of PR EoS is less satisfactory in liquid density predictions. To improve it, the volume-translated PR (VTPR) EoS was developed by introducing a volume translation parameter \(V_c\) to the volume term. The parameter \(V_c\) serves as a correction term to shift the liquid density while not affecting the phase equilibrium [91, 92, 93].

2.2.2 SAFT equation of state

The cubic EoS models each molecule as a hard-sphere, which works quite well for simple molecules, such as low-carbon-number hydrocarbons and inorganic gases.
However, the hard-sphere approximation in the cubic EoS is less accurate for systems containing molecules that have heterogeneous chain structures or associating interactions [89]. For example, the hydrogen bond between water molecules is a kind of associating interaction, which greatly affect the fluid structures and thus water properties.

In a series of papers [39, 40, 41], Chapman et al. introduced a novel EoS called the statistical associating fluid theory (SAFT). SAFT was developed by extending Wertheim’s thermodynamic perturbation theory of first order (TPT1) [94, 95, 96, 97] to mixtures of associating molecules. According to SAFT, a system in which only hard sphere segments exist is defined as a reference fluid. The polyatomic molecules are modeled by forcing a mixture of associating spheres to form chains, and by adding perturbations of the association interactions. The SAFT EoS has so far been applied in many complex fluids systems with good accuracy, including water, electrolytes, polymers, surfactants and liquid crystals [89].

In the past three decades, the original SAFT EoS has been studied and further developed by many groups. Among these different SAFT versions, the perturbed chain-SAFT (PC-SAFT) developed by Gross and Sadowski [98, 99] is one of the most popular and successful one. In the PC-SAFT model, the contribution from long range attractions (dispersion) in SAFT is revisited and improved. A system with hard chain repulsion force is defined as a reference fluid and the perturbation theory of Baker and Henderson [100] is introduced to the reference system.

For each component, there are five PC-SAFT parameters: $m_i$ [1], the effective number of segments which represents the chain length; $\sigma_i$ [m], the segment diameter; $\epsilon_i/k_B$ [K], the depth of pair potential energy; $\epsilon^{A_i,B_i}/k_B$ [K], the association energy of interaction; and $\kappa^{A_i,B_i}$ [1] the effective volume of interaction between site A and site B.
on molecule $i$. For component with no association sites, $\epsilon^{A_iB_i} = \kappa^{A_iB_i} = 0$. PC-SAFT parameters of pure components used in this work are listed in Table 2.1.

For mixtures, the following mixing rules apply to $\sigma_{ij}$ and $\epsilon_{ij}$:

\[
\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j),
\]
\[
\epsilon_{ij} = (1 - k_{ij})\sqrt{\epsilon_i \epsilon_j},
\]

where $k_{ij}$ is the binary interaction parameter. Cross-association parameters $\epsilon^{A_iB_j}$ and $\kappa^{A_iB_j}$ are determined using the mixing rule suggested by Wolbach and Sandler [101]:

\[
\epsilon^{A_iB_j} = \frac{1}{2}(\epsilon^{A_iB_i} + \epsilon^{A_jB_j}),
\]
\[
\kappa^{A_iB_j} = \sqrt{\kappa^{A_iB_i}\kappa^{A_jB_j}}\left(\frac{\sqrt{\sigma_{ii}\sigma_{jj}}}{(\sigma_{ii} + \sigma_{jj})/2}\right)^3.
\]
Table 2.1: PC-SAFT parameters of pure components.

<table>
<thead>
<tr>
<th>Component</th>
<th>$M_i$</th>
<th>$m_i$</th>
<th>$\sigma_i$</th>
<th>$\epsilon_i/k_B$</th>
<th>$\kappa_{A,B_i}$</th>
<th>$\epsilon^{A,B_i}/k_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>16.043</td>
<td>1.000</td>
<td>3.7039</td>
<td>150.03</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ethane</td>
<td>30.070</td>
<td>1.6069</td>
<td>3.5206</td>
<td>191.42</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Propane</td>
<td>44.096</td>
<td>2.0020</td>
<td>3.6184</td>
<td>298.11</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Butane</td>
<td>58.123</td>
<td>2.3316</td>
<td>3.7086</td>
<td>222.88</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pentane</td>
<td>72.146</td>
<td>2.6896</td>
<td>3.7729</td>
<td>231.20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hexane</td>
<td>86.177</td>
<td>3.0576</td>
<td>3.7983</td>
<td>236.77</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Heptane</td>
<td>100.203</td>
<td>3.4831</td>
<td>3.8049</td>
<td>238.40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Octane</td>
<td>114.231</td>
<td>3.8176</td>
<td>3.8373</td>
<td>242.78</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nonane</td>
<td>128.25</td>
<td>4.2079</td>
<td>3.8448</td>
<td>244.51</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Decane</td>
<td>142.285</td>
<td>4.6627</td>
<td>3.8384</td>
<td>243.87</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Undecane</td>
<td>156.312</td>
<td>4.9082</td>
<td>3.8893</td>
<td>248.82</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dodecane</td>
<td>170.338</td>
<td>5.3060</td>
<td>3.8959</td>
<td>249.21</td>
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<td>0</td>
</tr>
<tr>
<td>Toluene</td>
<td>92.141</td>
<td>2.8149</td>
<td>3.7169</td>
<td>285.69</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>44.010</td>
<td>2.0729</td>
<td>2.7852</td>
<td>169.21</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>28.010</td>
<td>1.2053</td>
<td>3.3130</td>
<td>90.96</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Water</td>
<td>18.015</td>
<td>1.0656</td>
<td>3.0007</td>
<td>366.51</td>
<td>0.034868</td>
<td>2500.7</td>
</tr>
<tr>
<td>$C_1E_1$</td>
<td>76.090</td>
<td>3.9560</td>
<td>2.9580</td>
<td>187.69</td>
<td>0.49750</td>
<td>1698.3</td>
</tr>
</tbody>
</table>

*Parameters of methane to carbon dioxide are taken from [98], water parameters are taken from [102], and $C_1E_1$ parameters are from [103].
The Helmholtz free energy of the PC-SAFT EoS has five parts of contributions:

\[ a_0 = a_{0}^{id} + a_{0}^{hs} + a_{0}^{hc} + a_{0}^{disp} + a_{0}^{assoc}, \]  

(2.20)

where \( a_{0}^{id} \) is the ideal gas Helmholtz free energy given in Eqn. 2.13, \( a_{0}^{hs} \) and \( a_{0}^{hc} \) are Helmholtz free energy of hard spheres and the formation of hard chains respectively, \( a_{0}^{disp} \) is the Helmholtz free energy of dispersion attraction and \( a_{0}^{assoc} \) accounts for the associating energy between molecules.

1. Hard sphere contribution \( a_{0}^{hs} \)

The expression of the Helmholtz free energy for hard-sphere fluid is:

\[ \frac{a_{0}^{hs}}{RT} = \frac{6}{\pi N_A} \left[ \frac{3 \zeta_1 \zeta_2}{1 - \zeta_3} + \frac{\zeta_3^3}{\zeta_3(1 - \zeta_3)^2} + \left( \frac{\zeta_3^3}{\zeta_3^2} - \zeta_0 \right) \ln(1 - \zeta_3) \right], \]  

(2.21)

where \( N_A \) is the Avogadro constant, and \( \zeta_n \) is defined as:

\[ \zeta_n = \frac{\pi N_A}{6} \sum_{i=1}^{N} \rho_i m_i d_i^n \quad n \in \{0, 1, 2, 3\}, \]  

(2.22)

in which, the temperature-dependent segment diameter \( d_i \) is given by:

\[ d_i = \sigma_i \left[ 1 - 0.12 \exp \left( -\frac{3\epsilon_i}{k_B T} \right) \right]. \]  

(2.23)

2. Hard chain contribution \( a_{0}^{hc} \)

The expression of the Helmholtz free energy due to chain formation is:

\[ \frac{a_{0}^{hc}}{RT} = \sum_{i=1}^{N} \rho_i (1 - m_i) \ln g_{ii}^{hs}, \]  

(2.24)

where \( g_{ij}^{hs} \) is the radial distribution function of the hard-sphere fluids:

\[ g^{hs}_{ij} = \frac{1}{1 - \zeta_3} + \left( \frac{d_i d_j}{d_i + d_j} \right) \frac{3 \zeta_2}{(1 - \zeta_3)^2} + \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2 \zeta_3^2}{(1 - \zeta_3)^3}. \]  

(2.25)
3. Dispersion contribution $a_{0}^{\text{disp}}$

The dispersion contribution to the Helmholtz free energy is given as:

$$a_{0}^{\text{disp}} = -\pi N_A R T \left( 2\rho^2 I_1 \bar{m}^2 \epsilon \sigma^3 + \rho^2 \bar{m} C_1 I_2 \bar{m}^2 \epsilon^2 \sigma^3 \right),$$  \hspace{1cm} (2.26)

where $\bar{m}$ is the mean segment number in the mixture:

$$\bar{m} = \sum_{i=1}^{N} x_i m_i,$$

(2.27)

and $I_1$ and $I_2$ are the integrals in the perturbation theory, which can be substituted by simple power series of density:

$$I_1 = \sum_{i=0}^{6} a_i \eta^i,$$

$$I_2 = \sum_{i=0}^{6} b_i \eta^i,$$

(2.28)

in which, $\eta = \zeta_3$ is the packing fraction.

Coefficients $a_i$ and $b_i$ are functions of mean segment number $\bar{m}$:

$$a_i = a_{0i} + \frac{\bar{m} - 1}{\bar{m}} a_{1i} + \frac{(\bar{m} - 1)(\bar{m} - 2)}{\bar{m}^2} a_{2i},$$

$$b_i = b_{0i} + \frac{\bar{m} - 1}{\bar{m}} b_{1i} + \frac{(\bar{m} - 1)(\bar{m} - 2)}{\bar{m}^2} b_{2i},$$  \hspace{1cm} (2.29)

where $a_{0i}, a_{1i}, a_{2i}, b_{0i}, b_{1i}$, and $b_{2i}$ for $i = 0, \ldots, 6$ are universal model constants reported in [98].

The two abbreviations $\bar{m}^2 \epsilon \sigma^3$ and $\bar{m}^2 \epsilon^2 \sigma^3$ are defined as:

$$\bar{m}^2 \epsilon \sigma^3 = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j m_i m_j \left( \frac{\epsilon_{ij}}{k_B T} \right) \sigma_{ij}^3,$$

$$\bar{m}^2 \epsilon^2 \sigma^3 = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j m_i m_j \left( \frac{\epsilon_{ij}}{k_B T} \right)^2 \sigma_{ij}^3,$$

(2.30)

In Eqn. 2.26, $C_1$ is an abbreviation for the compressibility expression, which is defined as:

$$C_1 = \left( 1 + \bar{m} \frac{8\eta - 2\eta^2}{(1 - \eta)^4} + (1 - \bar{m}) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1 - \eta)(2 - \eta)]^2} \right)^{-1}.$$  \hspace{1cm} (2.31)
4. Association contribution $a^\text{assoc}_0$

The Helmholtz free energy contribution due to the association interaction is:

$$a^\text{assoc}_0 = RT \sum_{i=1}^{N} \rho_i \left[ \sum_{A_i} \left( \ln X_{A_i} - \frac{X_{A_i}^2}{2} \right) + \frac{M_i}{2} \right] ,$$  \hspace{1cm} (2.32)

where $M_i$ is the number of association sites on molecule $i$, $\sum_{A_i}$ is the summation of all association sites on component $i$, $X_{A_i}$ is the fraction of component $i$ that is NOT bonded at site $A_i$. $X_{A_i}$ can be calculated by solving the following nonlinear equations:

$$X_{A_i} = \left( 1 + N_i \sum_{j=1}^{N} \rho_j \sum_{B_j} X_{B_j} \Delta_{A_iB_j} \right)^{-1} ,$$  \hspace{1cm} (2.33)

in which, the association strength $\Delta_{A_iB_j}$ is given by:

$$\Delta_{A_iB_j} = d_{ij}^3 k_{A_iB_j} g^{hs}_{ij} \left[ \exp\left( \frac{\epsilon_{A_iB_j}}{k_B T} \right) - 1 \right] ,$$  \hspace{1cm} (2.34)

where $d_{ij}$ is the crossing segment diameter: $d_{ij} = (d_{ii} + d_{jj})/2$.

Based on the Helmholtz free energy expression of the PC-SAFT EoS, the expressions of chemical potential $\mu_i$ and the derivative of chemical potential to density $\partial \mu_i / \partial \rho_j$ are derived and documented in Appendix B. The major difference between our expressions and those documented in the original PC-SAFT paper is that all energy and chemical potential expressions in this work are based on molar densities $\rho_i$, instead of mole fraction $x_i$.

2.3 Influence parameter

The influence parameter $v_i$ is an unique and important parameter in the DGT model, as it determines the interface width as well as IFT results. According to Bongiorno et al. [104], the chemical potential difference $\Delta \mu_i = \mu_{i,\text{bulk}} - \mu_i$ is the cause of inhomogeneity of a system, and the density gradient is the response of that.
influence parameter determines how much response is required per unit of cause. In other words, the influence parameter actually measures how much extra energy is associated locally with a given density gradient.

The theoretical expression of $v_i$ as derived in Appendix A is:

$$v_{ij} = -\frac{1}{6} \int_{V} (r - r')^2 g_{ij}(|r - r'|, \bar{\rho}) u_{ij}(|r - r'|) \, dr', \quad (2.35)$$

where $g_{ij}$ is the pair-correlation function of homogeneous fluid and $u_{ij}$ is the inter-particle potential between particle $i$ and $j$. However, due to the lack of the information about the pair-correlation function $g_{ij}$, it is hard to apply this theoretical expression in practical calculations.

Another way to determine the influence parameter of certain component is by fitting with the IFT data $\gamma^{\text{exp}}$ using the following equation:

$$v = \frac{1}{2} \left( \gamma^{\text{exp}} \int_{\rho_v}^{\rho_l} \sqrt{(a_0 - \rho \mu_{\text{bulk}} + P_0) \, d\rho} \right)^2, \quad (2.36)$$

where $\rho_v$ and $\rho_l$ are bulk densities of vapor and liquid phases respectively, and $P_0$ is the equilibrium bulk pressure.

To use Eqn. 2.36 for $v$ calculations, first conduct the phase equilibrium calculation to obtain $\rho_v$, $\rho_l$ and $\mu_{\text{bulk}}$ at the same temperature of $\gamma^{\text{exp}}$ measurement. Then, interpolate $M$ points in-between bulk densities, and calculate $a_0$ on each point. Finally, calculate the integration numerically, and plug the integration in Eqn. 2.36 to obtain $v$. We use $M = 500$ in most cases.

For mixtures, the crossing influence parameter is evaluated using the geometric mixing rule:

$$v_{ij} = (1 - \beta_{ij}) \sqrt{v_i v_j}, \quad (2.37)$$

where $\beta_{ij}$ is the binary interaction parameter for influence parameters.
The fitting method is an accurate way to determine \( v_i \), since it links the influence parameter directly to experimentally measured IFT. However, IFT data is not always available for specific component or temperature. More importantly, DGT is expected to be a predictive model for IFT, instead of taking experimentally measured IFT data as a feed. Therefore, correlation functions that relate the influence parameter with temperature, carbon number or other easily assessed properties have been developed based on the EoS used in the DGT model.

1. Influence parameter with PR EoS

The influence parameter with PR EoS tends to have strong temperature-dependency. Zuo and Stenby [105] in their work found that the ratio of the influence parameter to \( a_i \) and \( b_i \) increases rapidly when approaching the critical temperature. Therefore, they proposed a correlation expression based on the reduced temperature \( T_r \):

\[
\frac{v}{ab^{2/3}} = A(1 - T_r)^B, \tag{2.38}
\]

where parameters \( A \) and \( B \) are correlated to the acentric factor \( \tilde{\omega} \):

\[
A = e_1 + e_2\tilde{\omega},
\]

\[
B = e_3 + e_4 + e_5\tilde{\omega}^2, \tag{2.39}
\]

in which, constants \( e_1 \sim e_5 \) are determined by fitting with the interfacial tension experimental data of pure hydrocarbons.

Miqueu et al. presented another correlation function with reduced temperature in their work [17]:

\[
\frac{v}{ab^{2/3}} = A(1 - T_r) + B, \tag{2.40}
\]

in which, the parameter \( A \) and \( B \) are obtained by fitting with experimental data for alkanes, aromatics, cyclic alkanes, refrigerants and some other pure fluids. They also
provided nonlinear regressions for these two parameters:

\[
A = \frac{-10^{-16}}{1.2326 + 1.3757\omega},
\]

\[
B = \frac{-10^{-16}}{0.9051 + 1.5410\omega}.
\]  

(2.41)

Lin et al. [34] proposed their correlation function for influence parameter as:

\[
\frac{v_i}{ab^{2/3}N_{i,A}^{2/3}} = \exp\left(\kappa_0 + \kappa_1 \ln(1 - T_r) + \kappa_2 (\ln T)^2\right),
\]  

(2.42)

where \(\kappa_0, \kappa_1, \kappa_2\) are component’s characteristic parameters. The values of \(\kappa_0 \sim \kappa_2\) for more than 80 different components and their generalized correlation functions are listed in the paper [34].

Figure 2.1: Influence parameters of butane at different temperatures: the black solid line are fitted \(v_i\), and markers are PR EoS correlation function results.

The performances of different correlation functions are tested and compared with fitting results. In the first test, the influence parameters of butane at different temperatures are calculated. In Figure 2.1, the black solid line indicates fitted \(v_i\) values
using Eqn. 2.36, and other makers are correlation function results. It can be observed that the results of Lin’s correlation function match with the fitting results very well at low temperature, while at high temperature Zuo’s correlation function has a better performance. Miqueu’s correlation functions does not perform well for this system.

In another test, the correlation functions are used to calculate the influence parameters for different hydrocarbons at 298.15 K, and results are presented in Figure 2.2. When the carbon number $\leq 8$, Miqueu, Lin, and Zuo’s correlation functions give pretty accurate predictions compared with the fitting results. When the carbon number $> 8$, Zuo’s results matches with the dash line better. According to the two tests, we recommend Zuo’s correlation method for PR EoS, which has good performances for different temperatures as well as for different carbon numbers.

![Figure 2.2 : Influence parameters of hydrocarbons with different carbon numbers at 298.15 K: the black solid line shows fitting results, and markers are PR EoS correlation function results.](image)
2. Influence parameter with PC-SAFT EoS

For the PC–SAFT EoS, we observe weak temperature dependency of the influence parameter away from the critical temperature. For example, Figure 2.3 shows the fitted influence parameters of hexane and water at different temperatures. The influence parameters of both components do not change much over a large temperature range. Therefore in the calculation with the PC-SAFT EoS, we fit the influence parameter of each component at one temperature (normally in room temperature), and use it as a constant in other calculations. This feature of the PC-SAFT EoS makes DGT a more predictive tool since no extra correlation function is required. The fitted influence parameters with the PC-SAFT EoS are listed in Table 2.2.

![Graphs showing influence parameters for hexane and water](image)

(a) Hexane.  
(b) Water.

Figure 2.3 : Fitted influence parameters using the PC-SAFT EoS for hexane and water.
Table 2.2: List of fitted influence parameters using the PC-SAFT EoS

<table>
<thead>
<tr>
<th>Component</th>
<th>T [K]</th>
<th>IFT [mN/m]</th>
<th>$v_i$ [Jm$^5$mol$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>131.97</td>
<td>9 [106]</td>
<td>1.9949e-20</td>
</tr>
<tr>
<td>Ethane</td>
<td>149.73</td>
<td>22.12 [107]</td>
<td>5.2765e-20</td>
</tr>
<tr>
<td>Propane</td>
<td>332.92</td>
<td>3.09 [108]</td>
<td>1.0460e-19</td>
</tr>
<tr>
<td>Butane</td>
<td>247.15</td>
<td>18.18 [108]</td>
<td>1.7731e-19</td>
</tr>
<tr>
<td>Pentane</td>
<td>249.34</td>
<td>20.42 [109]</td>
<td>2.4779e-19</td>
</tr>
<tr>
<td>Hexane</td>
<td>181.52</td>
<td>31.03 [109]</td>
<td>3.5575e-19</td>
</tr>
<tr>
<td>Heptane</td>
<td>183.21</td>
<td>32.28 [109]</td>
<td>4.3864e-19</td>
</tr>
<tr>
<td>Octane</td>
<td>279.52</td>
<td>23.25 [109]</td>
<td>6.3815e-19</td>
</tr>
<tr>
<td>Nonane</td>
<td>283.15</td>
<td>23.79 [110]</td>
<td>7.6202e-19</td>
</tr>
<tr>
<td>Decane</td>
<td>283.15</td>
<td>24.75 [110]</td>
<td>9.4036e-19</td>
</tr>
<tr>
<td>Dodecane</td>
<td>303.15</td>
<td>24.47 [110]</td>
<td>1.3554e-18</td>
</tr>
<tr>
<td>Toluene</td>
<td>332.15</td>
<td>23.88 [111]</td>
<td>3.2152e-19</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>107.76</td>
<td>2.66 [106]</td>
<td>1.1049e-20</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>280</td>
<td>3.33 [106]</td>
<td>2.4175e-20</td>
</tr>
<tr>
<td>Water</td>
<td>323.15</td>
<td>67.93 [112]</td>
<td>1.5293e-20</td>
</tr>
<tr>
<td>$C_1E_1$</td>
<td>298.15</td>
<td>30.84 [113]</td>
<td>1.6880e-19</td>
</tr>
</tbody>
</table>
Chapter 3

The stabilized density gradient theory algorithm

With an EoS and influence parameters as inputs, the objective functions (2.4) are ready to be solved, the results of which are equilibrium density profiles $\rho_i(z)$ in space. However, solving this boundary value problem (BVP) directly is challenging due to the uncertainty in boundary conditions: although theoretically the domain size $D$ can be any value that is larger than the interface width $L_w$, a stable convergence is achieved only when a close estimation of $D$ to $L_w$ is given. With an over or underestimated $D$ value, Eqn. 2.4 becomes ill-conditioned, and singularity happens in the solution process. Nevertheless, estimating the accurate interface width $L_w$ of certain system before the calculation is not possible, and using the try & error method to get a good estimation is dramatically time-consuming.

To handle the numerical challenges encountered in the solution process, different algorithms have been developed. In this chapter, we first review the reference fluid (RF) algorithm in Section 3.1, which was proposed by Carey [14], and it is so far the most widely used algorithm for DGT equations. After realizing the limitations of the RF algorithm, we develop a novel and robust algorithm in Section 3.2, which is called the stabilized density gradient theory (SDGT) algorithm. The DGT model together with the SDGT algorithm is applied in many pure and mixed systems, the results of which are presented in Section 3.3.
3.1 The reference fluid algorithm

Despite that a more advanced algorithm is developed in our work, we review the RF algorithm in details at the beginning of this chapter for the following three reasons:

- The RF algorithm is by far the most widely used one, and it works great for pure systems, as the only component naturally becomes the reference fluid.
- The equation manipulation process in the RF algorithm is also used in the surface free energy development in Chapter 6.
- Understanding the basics of the RF algorithm will help realize its limitations, and therefore better accept the SDGT algorithm introduced in Section 3.2.

3.1.1 DGT equation manipulations

The first step of the RF algorithm is to manipulate the objective function. Rewriting Eqn. 2.4 by expressing the chemical potential as the first derivative of the free energy to density gives:

\[
\frac{\partial \omega[\rho(z)]}{\partial \rho_i} - \sum_{j=1}^{N} v_{ij} \frac{d^2 \rho_j}{dz^2} = 0, \tag{3.1}
\]

where \( \omega[\rho(z)] = a_0[\rho(z)] - \sum_i \rho_i(z) \mu_{i,\text{bulk}} \). Multiplying Eqn. 3.1 by \( d\rho_i/dz \) and then summarizing over \( i \) produces:

\[
\frac{d\omega[\rho(z)]}{dz} - \sum_{i=1}^{N} \sum_{j=1}^{N} v_{ij} \frac{d^2 \rho_j}{dz^2} \frac{d\rho_i}{dz} = 0. \tag{3.2}
\]

Integrating Eqn. 3.2 over \( z \) yields:

\[
\omega[\rho(z)] - \omega_0 - \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{2} v_{ij} \frac{d\rho_j}{dz} \frac{d\rho_i}{dz} = 0, \tag{3.3}
\]
where \( \omega_0 = -P_0 \) is the constant of integration.

For mixtures, choose one component with monotonic equilibrium density profile as a reference fluid, and mark its density as \( \rho_{\text{ref}} \). Multiplying Eqn. 3.3 by \( (dz/d\rho_{\text{ref}})^2 \) produces:

\[
(\omega[\rho(z)] - \omega_0) \left( \frac{dz}{d\rho_{\text{ref}}} \right)^2 - \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{1}{2} v_{ij} \frac{d\rho_i}{d\rho_{\text{ref}}} \frac{d\rho_j}{d\rho_{\text{ref}}} = 0. \tag{3.4}
\]

Reorganizing Eqn. 3.4 leads to:

\[
dz = \sqrt{\frac{C_{\text{ref}}}{2(\omega - \omega_0)}} d\rho_{\text{ref}}, \tag{3.5}
\]

with \( C_{\text{ref}} \) defined as:

\[
C_{\text{ref}} = \sum_{i=1}^{N} \sum_{j=1}^{N} v_{ij} \frac{d\rho_i}{d\rho_{\text{ref}}} \frac{d\rho_j}{d\rho_{\text{ref}}}. \tag{3.6}
\]

Integrating Eqn. 3.5 from the density of bulk phase \( A \) to that of position \( z \) generates the density profiles:

\[
z = z_0 + \int_{\rho_{\text{ref}, A}}^{\rho_{\text{ref}}} \sqrt{\frac{C_{\text{ref}}}{2(\omega - \omega_0)}} d\rho_{\text{ref}}, \tag{3.7}
\]

in which, \( z_0 \) marks the left boundary of the interface, which is often set on the origin point, and \( \rho_{\text{ref}, A} \) is the bulk density of the reference fluid in phase \( A \).

The IFT expression calculation can be rewritten by plugging Eqn. 3.3 in Eqn. 2.7:

\[
\gamma = \int_0^{D} \left( \omega[\rho(z)] - \omega_0 + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} \right) dz
\]

\[
= \int_0^{D} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} dz, \tag{3.8}
\]

or \( \gamma = \int_0^{D} 2 \{\omega[\rho(z)] - \omega_0\} dz \).

Eqn. 3.8 can be further modified by the change of variables from \( dz \) to \( d\rho_{\text{ref}} \) using Eqn. 3.5:

\[
\gamma = \int_{\rho_{\text{ref}, B}}^{\rho_{\text{ref}, A}} \sqrt{2C_{\text{ref}}(\omega - \omega_0)} d\rho_{\text{ref}}. \tag{3.9}
\]
3.1.2 Mathematical model

In the density profile (Eqn. 3.7) and IFT (Eqn. 3.9) calculations, the density relationship of each non-reference fluid to the reference fluid \( \frac{d \rho_i}{d \rho_{\text{ref}}} \) is required. This relationship can be obtained by solving the following differential equations [18, 26, 47]:

\[
\sum_{i=1}^{N} \sum_{j=1}^{N} v_{ij} \frac{d \rho_i}{d \rho_{\text{ref}}} \frac{d \rho_j}{d \rho_{\text{ref}}} \left( A_{\text{ref}} \frac{d \rho_i}{d \rho_{\text{ref}}} - A_i \right) + 2(\omega - \omega_0) \frac{d^2 \rho_i}{d \rho_{\text{ref}}^2} = 0, \tag{3.10a}
\]

subjected to the boundary conditions:

\[
\rho_i = \rho_{i,A}, \text{ at } \rho_{\text{ref}} = \rho_{\text{ref},A}, \tag{3.10b}
\]

\[
\rho_i = \rho_{i,B}, \text{ at } \rho_{\text{ref}} = \rho_{\text{ref},B},
\]

with

\[
A = \begin{pmatrix}
A_1 \\
A_2 \\
\vdots \\
A_N
\end{pmatrix} = v_{ij}^{-1} \begin{pmatrix}
\Delta \mu_1 \\
\Delta \mu_2 \\
\vdots \\
\Delta \mu_N
\end{pmatrix}, \tag{3.10c}
\]

where \( v_{ij}^{-1} \) is the inverse of the influence parameter matrix, and \( \Delta \mu_i = \mu_i - \mu_{i,\text{bulk}} \).

As the first step, phase equilibrium calculation is required to produce the bulk densities \( \rho_{i,\text{bulk}} \) for \( i = 1, 2, \ldots, N \) as boundary conditions. After selecting a reference fluid, the system of equations (3.10) can be discretized using the finite difference scheme. Let \( \rho_i^V := \rho_i^0 < \rho_i^1 < \cdots < \rho_i^{M+1} := \rho_i^L \) for \( i \neq \text{ref} \) denote equidistant nodes on a grid with mesh size \( \Delta \rho_{\text{ref}} := (\rho_{\text{ref},L} - \rho_{\text{ref},V})/(M + 1) \). We therefore approximated the first and the second derivative using:

\[
\frac{d \rho_i}{d \rho_{\text{ref}}} (\rho_{\text{ref}}^k) \approx \frac{\rho_i^{k+1} - \rho_i^{k-1}}{2 \Delta \rho_{\text{ref}}},
\]

\[
\frac{d^2 \rho_i}{d \rho_{\text{ref}}^2} (\rho_{\text{ref}}^k) \approx \frac{\rho_i^{k-1} - 2 \rho_i^k + \rho_i^{k+1}}{\Delta \rho_{\text{ref}}^2}. \tag{3.11}
\]
The nonlinear equations (3.10a) after discretization have \( M(N - 1) \) unknowns and the system can be solved using Newton’s iteration. After obtaining \( \rho_i \) for every \( \rho_{\text{ref}} \), \( d\rho_i/d\rho_{\text{ref}} \) can be evaluated using Eqn. 3.11.

Eqn. 3.10 is a general equation for \( \rho_i \) calculations based on \( \rho_{\text{ref}} \). When the geometric mixing rule is applied for the crossing influence parameters (\( \beta_{ij} = 0 \)), the system of differential equations can be reduced to the following set of algebraic equations on each grid point [18]:

\[
\sum_{j=1}^{N} \left[ \left( \sqrt{v_i} \frac{\partial \mu_{\text{ref}}}{\partial \rho_j} - \sqrt{v_{\text{ref}}} \frac{\partial \mu_i}{\partial \rho_j} \right) \frac{d\rho_j}{d\rho_{\text{ref}}} \right] = \sqrt{v_{\text{ref}}} \frac{\partial \mu_i}{\partial \rho_{\text{ref}}} - \sqrt{v_i} \frac{\partial \mu_{\text{ref}}}{\partial \rho_{\text{ref}}} \quad \text{for } i \neq \text{ref}. \tag{3.12}
\]

Eqn. 3.12 can be solved to obtain \( d\rho_i/d\rho_{\text{ref}} \) using the \( LU \) decomposition. The density needed in the calculation of \( \partial \mu_i/\partial \rho_j \) can be obtained by solving the following nonlinear equations using Newton’s method:

\[
\sqrt{v_i} \Delta \mu_{\text{ref}}(\rho^k) - \sqrt{v_{\text{ref}}} \Delta \mu_i(\rho^k) = 0 \quad \text{for } i \neq \text{ref}, \tag{3.13}
\]

in which, the initial guess of \( \rho_i \) on point \( k \) can be estimated using the density and density derivatives from last point:

\[
\rho_i^k = \rho_i^{k-1} + \left( \frac{d\rho_i}{d\rho_{\text{ref}}} \right)^{k-1} \Delta \rho_{\text{ref}}, \tag{3.14}
\]

\[
\rho_{\text{ref}}^{k} = \rho_{\text{ref}}^{k-1} + \Delta \rho_{\text{ref}}.
\]

The overall procedures of using either the general approach or the simplified approach of the RF algorithm to solve DGT equations are summarized in the flowchart at Figure 3.1. The generated \( d\rho_i/d\rho_{\text{ref}} \) on each density point \( \rho_{\text{ref}}^k \) are used in Eqn. 3.7 and Eqn. 3.9 to calculate the density profiles and IFT.

By reformulating the original DGT equations, the integration variable is changed from \( z \) to \( \rho_{\text{ref}} \) in the RF algorithm such that no interface thickness estimation is required. The new boundary conditions can be easily obtained from phase equilibrium calculations.
Figure 3.1: The reference fluid algorithm flowchart.

1. **Phase equilibrium calculations for** \( \rho_i^Y \) and \( \rho_i^L \) for \( i = 1,2,...,N \)

2. **Choose a reference fluid** \( \rho_{ref} \)
3. **Discretize its bulk densities by interpolating M points:**
   \[ \rho_{ref}^0 < \rho_{ref}^1 < ... < \rho_{ref}^{M+1} = \rho_{ref}^v \]
   \[ \Delta \rho_{ref} = \frac{\rho_{ref}^L - \rho_{ref}^v}{M+1} \]

4. **Setup initial guess of non-reference fluid density:**
   \[ \rho_i^0(k) = \rho_i^Y + \Delta \rho_i k \]
   where \( \Delta \rho_i = \frac{\rho_i^L - \rho_i^Y}{M+1} \)

5. **Solve the system of equations (3.10) using finite difference scheme and Newton’s method**

6. **Obtain** \( \rho_i(k) \) for \( i \neq \text{ref}, k = 1,...,M \)

7. **Initialization**
   \[ \rho_i(k) = \rho_i^Y, \frac{d \rho_i}{d \rho_{ref}}(k) = 1 \]
   for \( i \neq \text{ref}, k = 1 \)

8. **Update** \( k = k + 1 \)

9. **Update reference fluid density**
   \[ \rho_{ref}(k) = \rho_{ref}(k - 1) + \Delta \rho_{ref} \]

10. **Setup initial guess of non-reference fluid density at point k:**
    \[ \rho_i^0(k) = \rho_i(k - 1) + \frac{d \rho_i}{d \rho_{ref}}(k - 1) \Delta \rho_{ref} \]

11. **Solve the system of equations (3.13) using Newton’s method to obtain** \( \rho_i(k) \)

12. **Solve system of equations (3.13) using the LU decomposition to obtain** \( \frac{d \rho_i}{d \rho_{ref}}(k) \)

13. **Check** \( k = M + 1 ? \)

14. **Finished**
3.1.3 Limitations of the RF algorithm

The RF algorithm has been successfully applied to solved DGT equations in many pure and mixed systems. Through our implementations of the RF algorithm, however, we found several limitations that make it a less general algorithm for some complex systems.

First, a reference fluid is required in the RF algorithm. The main requirement of the reference fluid is that its density needs to vary monotonically through the interface. If the monotonicity of a preselected reference fluid changes, it must be switched to a different component based on the density function behavior, and this procedure will be repeated if the new reference fluid becomes non-monotonic again. This is a time-consuming process. More importantly, the failure to select a suitable reference fluid will lead to numerical errors, and some interfacial phenomena such as surface accumulations can not be described correctly.

In most cases, the determination of the reference fluid is based on experience or a try & error approach, which introduces another factor of uncertainty to the model. Recently, a mathematical basis [114] was developed to help select the reference fluid for VLE systems. According to the basis, component $i$ is a good choice of reference fluid if the relationship $d\mu_{j,\text{bulk}}/dn_i > 0$ holds for every component $j$ in the system. In two other papers [115, 116], a path function algorithm was proposed within the framework of the RF algorithm, in which a weighted molar density is defined, and the reference fluid is not needed. However, both approaches are valid only when the geometric-mean of the influence parameter ($\beta_{ij} = 0$) can be applied. In the case of $\beta_{ij} \neq 0$, a reference fluid is still needed, and there is no clear strategy for the selection of proper reference fluid.

Second, the manipulation process in the RF algorithm is no longer valid if addi-
tional terms are added to the DGT function. As we have reviewed, the BVPs solved in the RF algorithm is transformed from the original DGT equations (2.4) by the change of variables. Noticeably, the prerequisite of this manipulation process is that the original DGT functional form must be strictly followed. In other words, the RF algorithm, if applicable, works exclusively for one specific DGT functional form. Any extensions of DGT functions are not allowed, or the manipulation process will not work. This feature of the RF algorithm prevents the extension of the DGT model to systems like surfactant mixtures, in which molecules are considered to have more complex structures that require additional energy terms in DGT equations.

3.2 The stabilized density gradient theory algorithm

3.2.1 Modified DGT equations

Due to the two major drawbacks of the RF algorithm, a new algorithm is developed for DGT type of equations in this section. We revisit the original Euler-Lagrange equations (2.4). Recall that solving these equations directly requires a good estimation of the interface width $L_w$, or severe numerical issues happen. To avoid this, an evolution term $d\rho_i/ds$ is added to Eqn. 2.4, such that the ordinary differential equation (ODE) becomes a time-dependent partial differential equation (PDE):

$$\frac{\partial \rho_i}{\partial s} + \mu_i(\rho) - \mu_{i,\text{bulk}} - \sum_{j=1}^{N} v_{ij} \frac{\partial^2 \rho_j}{\partial z^2} = 0 \quad \text{for } i = 1, \ldots, N, \quad (3.15a)$$

subjected to the following boundary conditions:

$$\rho_i(s,0) = \rho_{i,A}, \quad \rho_i(s,D) = \rho_{i,B}, \quad (3.15b)$$

for all time levels $s$. An easy and good initial condition for this system of PDEs is linear density distribution of each component across the domain by interpolating the
boundary values:

\[ \rho_i(0, z) = \rho_{i,A} + \frac{\rho_{i,B} - \rho_{i,A}}{D} z. \]  

(3.15c)

In Eqn. 3.15a, the time derivative \( \partial \rho_i/\partial s \) serves as a stabilizing term to ensure a stable convergence, and we name the new algorithm the stabilized density gradient theory (SDGT) algorithm. With given boundary and initial conditions, the system of PDEs (3.15) is solved with a time marching scheme until a stationary state is reached. This system has been proved to be more well-posed than the original ODE system. Similar idea was used by Qiao and Sun [117] for one component systems, and we further develop and generalize this algorithm to multiphase multicomponent systems.

### 3.2.2 Mathematical model

#### Time discretization

In order to apply the SDGT algorithm more efficiently, a convex–concave splitting scheme of the nonlinear function is employed, cf. [118, 119]. In Eqn. 3.15a, the nonlinear function is the chemical potential \( \mu_i \) expression. It is simple to prove that the ideal gas chemical potential \( \mu_{i}^{id} \) is a convex function with respect to \( \rho_i \). For the excess chemical potential, the splitting is based on the type of the molecular interactions: as justified by Qiao and Sun in their work [117], the repulsion force between molecules must result in a convex contribution while the attraction force should have a concave contribution so as to have phase splitting.

For the PR EoS, the residual Helmholtz free energy is naturally constructed by an attraction term and a repulsion term, cf. Eqn. 2.15. Therefore, the convex-concave
splitting reads:

\[
a_0^{\text{convex}} = a_0^{\text{id}} - \rho_t RT \ln(1 - \rho b_m), \\
a_0^{\text{concave}} = -\frac{\rho_t a_m}{2\sqrt{2} b_m} \ln \frac{E_m}{S_m}.
\]  

(3.16)

Consequently, the chemical potential splits into \( \mu_i^{\text{convex}} = \partial a_0^{\text{convex}} / \partial \rho_i \) and \( \mu_i^{\text{concave}} = \partial a_0^{\text{concave}} / \partial \rho_i \).

For the PC-SAFT EoS, the hard sphere \( \mu_i^{\text{hs}} \) and hard chain \( \mu_i^{\text{hc}} \) chemical potential are results of repulsion forces, while the association \( \mu_i^{\text{assoc}} \) and dispersion \( \mu_i^{\text{disp}} \) contributions are results of attraction forces. Therefore the convex-concave splitting for the PC-SAFT EoS reads:

\[
\mu_i^{\text{convex}} = \mu_i^{\text{id}} + \mu_i^{\text{hs}} + \mu_i^{\text{hc}}, \\
\mu_i^{\text{concave}} = \mu_i^{\text{disp}} + \mu_i^{\text{assoc}}.
\]  

(3.17)

There are several advantages of using the convex–concave splitting scheme:

- The concave part is treated time-explicitly with the forward Euler method, which speeds up the overall computation.

- The convex–concave splitting makes the time discretization unconditionally stable, i.e. there is no restriction in time step size. However, large time step implies a large condition number in the linear system that has to be solved in every Newton iteration.

- The convex–concave splitting ensures a monotonic dissipation of free energy with respect of time.

Discretizing Eqn. 3.15 in time while applying the convex–concave splitting yields:

\[
\frac{\rho_{i}^{t+1} - \rho_{i}^{t}}{\Delta S_t} + \mu_i^{\text{convex}}(\rho_i^{t+1}) + \mu_i^{\text{concave}}(\rho_i^{t}) - \mu_{i,\text{bulk}} = \sum_{j=1}^{N} v_{ij} \frac{d^2 \rho_j^{t+1}}{d z^2} = 0,
\]  

(3.18)
for \( i = 1, \ldots, N, t = 1, 2, \ldots \). The term \( \Delta s_t \) denotes the time step size from time level \( t \) to \( t + 1 \). The discretized equations (3.18) are subjected to the B.C.: \( \rho_i^{t+1}(0) = \rho_i,A \), \( \rho_i^{t+1}(D) = \rho_i,B \) for all time level \( t \), and I.C.: \( \rho_i^0(z) = \rho_i(0, z) \) for \( z \in [0, D] \).

**Space discretization**

Finite difference scheme is used to discretize Eqn. 3.18 in space. Let \( 0 =: z_0 < z_1 < \ldots < z_{M+1} := D \) denote equidistant nodes on a grid with mesh size \( \Delta z := \frac{D}{M+1} \), cf. Figure 3.2. We therefore approximate the second derivative \( \frac{d^2 \rho_i}{dz^2} \) by a central difference quotient:

\[
\frac{d^2 \rho_i}{dz^2}(z_k) \approx \frac{\rho_{i,k-1} - 2\rho_{i,k} + \rho_{i,k+1}}{\Delta z^2}.
\]

![Figure 3.2: Space discretization of the domain [0,D].](image)

For every time step \( t + 1 \), Eqn. 3.18 can be discretized on space as:

\[
\frac{\rho_{i,k}^{t+1} - \rho_{i,k}^t}{\Delta s_t} + \mu_i^{\text{convex}}(\rho_k^{t+1}) + \mu_i^{\text{concave}}(\rho_k^t) - \mu_i^{\text{bulk}} + \sum_{j=1}^{N} v_{ij} \left( \frac{\rho_{j,k-1}^{t+1} - 2\rho_{j,k}^{t+1} + \rho_{j,k+1}^{t+1}}{(\Delta z)^2} \right) = 0,
\]

for \( k = 1, \ldots, M, i = 1, \ldots, N \).

Reorganize Eqn. 3.19 in a format of “linear function of \( \rho_{i,k}^{t+1} \) + nonlinear function of \( \rho_{i,k}^{t+1} \) + constant part”, and we have:

\[
\rho_{i,k}^{t+1} - \Delta s_t \sum_{j=1}^{N} v_{ij} \left( \frac{\rho_{j,k-1}^{t+1} - 2\rho_{j,k}^{t+1} + \rho_{j,k+1}^{t+1}}{(\Delta z)^2} \right) + \Delta s_t \mu_i^{\text{convex}}(\rho_k^{t+1}) + \Delta s_t \mu_i^{\text{concave}}(\rho_k^t) - \Delta s_t \mu_i^{\text{bulk}} - \rho_{i,k}^t = 0,
\]

(3.20)
with B.C.: \( \rho_{i,0}^t = \rho_{i,A} \), \( \rho_{i,M+1}^t = \rho_{i,B} \) for all time level, and I.C.: \( \rho_{i,k}^0 = \rho_i(0, z_k) \) for \( k = 0, \ldots, M + 1 \).

**Newton’s method**

For each component \( i \), there are \( M \) unknowns in space. Therefore for a mixture of \( N \) components, the nonlinear system (3.20) has in total \( MN \) unknowns on each time level \( t+1 \). We store all the unknowns in a vector \( X^{t+1} \) such that

\[
[X^{t+1}]_{M(i-1)+k} := \rho_{i,k}^{t+1}
\]

for \( k = 1, \ldots, M, \ i = 1, \ldots, N \).

Using the above index order, system (3.20) is equivalent to

\[
F(X^{t+1}) := (I + \Delta s_t A)X^{t+1} + \Delta s_t M^{\text{convex}}(X^{t+1})
\]

\[
+ \Delta s_t M^{\text{concave}}(X^t) - \Delta s_t M^{\text{bulk}} - X^t = 0, \quad (3.21)
\]

with \( I \) denoting a \( MN \times MN \) unit matrix, and \( A \) being a \( MN \times MN \) block matrix:

\[
A := \frac{1}{(\Delta z)^2}
\begin{bmatrix}
  v_{11}H & \cdots & v_{1N}H \\
  \vdots & \ddots & \vdots \\
  v_{N1}H & \cdots & v_{NN}H
\end{bmatrix},
\]

where \( H \) is the matrix of size \( M \times M \) with 2 on its diagonal and \(-1\) on both of the minor diagonals, and with the following vectors of size \( MN \):

\[
\begin{align*}
  [M^{\text{convex}}(X^{n+1})]_{M(i-1)+k} &:= \mu_i^{\text{convex}}(\rho_{i,k}^{t+1}), \\
  [M^{\text{concave}}(X^n)]_{M(i-1)+k} &:= \mu_i^{\text{concave}}(\rho_{i,k}^t), \\
  [M^{\text{bulk}}]_{M(i-1)+k} &:= \mu_i,\text{bulk},
\end{align*}
\]

for \( k = 1, \ldots, M, \ i = 1, \ldots, N \).

The Newton’s iteration scheme on each time level \( t + 1 \) reads:
1. Initialize the iteration by setting $Y^0 = X^t$ as an initial guess of $X^{t+1}$.

2. Construct the Jacobian matrix of the system:

$$J(Y^\kappa) := \frac{\partial F(Y^\kappa)}{\partial X} = [\partial F_j/\partial X_i]_{ij}.$$  \hfill (3.22)

3. Calculate the Newton step length:

$$\Delta Y^\kappa = -J(Y^\kappa)/F(Y^\kappa).$$  \hfill (3.23)

4. Calculate the new $Y^{\kappa+1}$:

$$Y^{\kappa+1} = Y^\kappa + \lambda \Delta Y^\kappa.$$  \hfill (3.24)

where $\lambda \leq 1$ is a parameter to damp the Newton step length.

5. $\kappa = \kappa + 1$.

6. Iterate from step 2 to step 5 until the $L^2$ norm of the residual functions $F(Y^{\kappa+1})$ meets the stopping criteria:

$$\|F(Y^{\kappa+1})\|_{L^2} \leq \varepsilon_{\text{abs}} + \varepsilon_{\text{rel}} \|F(Y^1)\|_{L^2},$$  \hfill (3.25)

where the discrete $L^2$ norm $\|\cdot\|_{L^2}$ is defined as $\|F\|_{L^2} := (\sum_{j=1}^{MN} F_j^2)^{1/2}$.

Tolerances $\varepsilon_{\text{abs}} = \varepsilon_{\text{rel}} = 1e^{-6}$ are used in our work. If the stopping criteria is met, we accept the results as solutions of the current time step, i.e. $X^{t+1} := Y^{\kappa+1}$, and move to the calculation of the next time step.

**Armijo algorithm for $\lambda$**

The parameter $\lambda$ in Eqn. 3.24 is used to damp the Newton step length in order to guarantee a decreasing residual and to enlarge the area of convergence. To start, $\lambda = 1$ is used as an initial value. If the $L^2$ norm of the residual functions is not
smaller than that of the last iteration, the Armijo rule [120] will be used to reduce \( \lambda \) by certain amount, and then the calculation at step 4 will be restarted with the new \( \lambda \). More details about applying the Armijo rule can be found in Kelley’s book [121]. The MATLAB code is also provided in his book.

**Time adaptation scheme**

During the calculation, the time step length \( \Delta s_t \) is not a constant, and it is adjusted by a time adaptation scheme on each time step to either accelerate or stabilize the calculation. The scheme reads as:

- If the Armijo rule is called more than \( p \) times on the same time step, the time step length \( \Delta s_t \) will be reduced by half, and then the Newton’s iteration starts over again on the same time level.

- If the Armijo rule is not called on this time step, which means the Newton’s method converges quite smoothly, the time step length \( \Delta s_t \) will be increased by a factor of \( q \) for the next time step.

In our work, \( p = 5 \) is used, and \( q \) varies from 1.03 to 1.1. The time step adaptation scheme ensures stable convergence by time step refining, and also accelerates the overall computation by time step coarsening.

**Stationary state**

The stationary state of the system is reached when one of the following absolute stopping criteria is satisfied: \( \| X^n - X^{n+1} \|_{L^2} \leq \varepsilon_{\text{diff}} \) or \( |(\Omega^{t+1} - \Omega^t) / \Omega^t| \leq \varepsilon_{\text{nrg}} \) or \( \Delta s_t \geq \varepsilon_t \). The first stopping criteria means that the \( L^2 \) norm of the density differences between the two time steps is smaller than the tolerance \( \varepsilon_{\text{diff}} \), and the second one
means the relative change of the grand potential energy between the two time steps is smaller than the tolerance $\varepsilon_{\text{nrg}}$, and the third one means that the time step length $\Delta s_t$ is greater than the tolerance $\varepsilon_t$. For most calculations, we use $\varepsilon_{\text{diff}} = 1e^{-3}$, $\varepsilon_{\text{nrg}} = 1e^{-6}$ and $\varepsilon_t = 1e4$. The tolerance can also be raised or lowered depending on needs. The obtained equilibrium density profile $\rho^{t+1}_{i,k}$ is an approximation of the solution of the original DGT model (2.4).

### 3.2.3 Boundary conditions and initial conditions

The SDGT equations have the same boundary conditions as the original DGT model, cf. Eqn. 2.5 and Eqn. 3.15b. But the SDGT algorithm does not require that the domain size $D$ be close to the interface thickness $L_w$. Instead, $D$ can be any values, and the algorithm can still handle the BVPs very well. For example, Figure 3.3 shows the equilibrium density profiles of propane/hexane mixture on different domain sizes. For $D = 5, 10, 20$ nm, the equilibrium density profiles have same interface shapes, while larger bulk regions appear on wider domains. For $D = 1$ nm (Figure 3.3a), the domain size is smaller than the interface thickness $L_w$. Therefore, no bulk phase appears in the density profile, and the entire domain is inside the interface region. In this case, a larger domain size is needed to redo the calculation. Since the SDGT algorithm works well for overestimated domain size, it is recommended to start with a large value of $D$, and switch to more proper values accordingly.

The SDGT algorithm is also quite flexible with the initial conditions. Figure 3.4 shows the density profiles convergence history of methane/propane mixture with different initial conditions. From linear function (Figure 3.4a), step function (Figure 3.4b), to random initial density distributions (Figure 3.4c), the SDGT algorithm drives the density profiles to their equilibrium state steadily. Although a shift of the
Figure 3.3: Equilibrium density profiles of propane/hexane mixture at 300 K, 1 bar on domain size $D = 1$ nm, 5 nm, 10 nm and 20 nm.

The interface region happens in Figure 3.4c, that does not change the interface shape, neither does that affect the system’s interfacial properties. In practice, we recommend using linear distributions as initial conditions for systems forming vapor-liquid equilibrium (VLE), and step function distributions for systems forming liquid-liquid equilibrium (LLE).
Figure 3.4: Density profiles convergence history of methane/propane mixture at 303 K, 50 bar with different initial conditions.

3.3 DGT model results with the SDGT algorithm

3.3.1 Phase equilibrium calculations

The phase equilibrium calculation is required to generate the bulk densities as boundary conditions in DGT calculations. For systems with planar interfaces, the equilibrium state is reached when the pressures and chemical potential are equal in each phase: $P_A(\rho) = P_B(\rho), \mu_{i,A}(\rho) = \mu_{i,B}(\rho)$ for $i = 1, 2, \ldots, N$. Figure 3.5 shows equilibrium bulk densities of hydrocarbons, $CO_2$ and $CO_2$/hydrocarbon mixtures us-
ing the PC-SAFT EoS at different temperatures and pressures. Excellent agreement is achieved between the model predictions and the experimental data. For more information about phase equilibrium calculations schemes, readers can refer to Michelsen’s book [122].

![Propane](image1)

(a) Propane

![Hexane](image2)

(b) Hexane

![Carbon dioxide](image3)

(c) Carbon dioxide

![Butane/Carbon dioxide](image4)

(d) Butane/Carbon dioxide

Figure 3.5: Equilibrium bulk densities of pure and mixed systems: dots are experimental data from literatures [123, 124] and lines are PC-SAFT calculation results.
3.3.2 One component VLE system

In the first test, the DGT model is applied to the pure hexane system at 313 K, and the density profile convergence history is shown in Figure 3.6 with a linear initial density distribution on a 6 nm domain. Starting from $\Delta s_0 = 1\text{e-5}$, the system has a stable but slow convergence as the density profile does not change much after 130 time steps. Meanwhile, the time step adaptation scheme keeps accelerating the calculation, and the density profile converges faster as shown from Figure 3.6b to Figure 3.6c. The equilibrium state is reached after 210 time steps when the stopping criteria is fulfilled.

![Density profile convergence history of hexane at 313 K.](image)

Figure 3.6: Density profile convergence history of hexane at 313 K.
The density profile calculations are also carried out for other hydrocarbons. Figure 3.7 shows the equilibrium density profiles of seven different pure hydrocarbons, from ethane to octane. At the same temperature (273 K), hydrocarbons with lower carbon numbers have more diffusive interfaces. This is because the smaller-chain hydrocarbons have lower critical temperatures, and thus have higher reduced temperatures at the same system temperature, which leads to more diffusive interfaces.

![Equilibrium density profiles of seven pure hydrocarbons at 273 K.](image)

The IFT of several one component systems are calculated using Eqn. 3.8 based on the equilibrium density profiles, the results of which are displayed in Figure 3.8. It can be seen that the DGT model gives excellent IFT predictions for pure hydrocarbons compared with experimental data in a wide range of temperatures. For molecules having association interactions, such as water, the DGT model gives great IFT predictions compared with experimental data as well. Also, it can be observed that system’s IFT decreases as the temperature increases. This is due to the decreasing of
the cohesive forces between molecules with the increase of system’s thermal energy, which reduces the IFT between phases.

Figure 3.8: IFT results of pure hydrocarbons and water at different temperatures: dots are experimental measured IFT data from literatures [106, 107, 109, 110, 112, 125, 126], and the dash lines are DGT calculation results.
3.3.3 Multicomponent VLE system

We use the natural gas as an example to test the performance of the DGT model in multicomponent VLE systems. Natural gas is a mixture of mainly methane and other heavier hydrocarbons, and it is one of the most important product in the Oil & Gas industry. Natural gas has served as the energy source for heating, electricity generation and also has been used as vehicle fuel and raw materials in chemical productions.

Table 3.1: Feed composition of the mixture with seven hydrocarbons.

<table>
<thead>
<tr>
<th>Component</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
<th>Butane</th>
<th>Pentane</th>
<th>Hexane</th>
<th>Heptane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar composition</td>
<td>0.348</td>
<td>0.174</td>
<td>0.174</td>
<td>0.087</td>
<td>0.043</td>
<td>0.130</td>
<td>0.043</td>
</tr>
</tbody>
</table>

In the test calculation, we use a mixture with seven different hydrocarbons from methane to heptane to model the natural gas. System conditions are set at 313 K, 5 bar, and the feed compositions are shown in Table 3.1. The DGT equations of the seven-component mixture are handled by the SDGT algorithm smoothly, and the equilibrium density profiles are depicted in Figure 3.9. It can be observed that heavier hydrocarbons, such as pentane, hexane and heptane, have monotonic density profiles through the interface, while lighter hydrocarbons have surface accumulations. For this mixture, the RF algorithm would fail if either methane, ethane, propane or butane was chosen as the reference fluid. The SDGT algorithm, on the other hand, is not affected by the different density profile behaviors, which makes the SDGT algorithm a more general and robust algorithm for DGT type of equations.

Pugachevich and Beglyarov [127] reported in their work the experimental mea-
Figure 3.9: Equilibrium density profiles of a mixture containing seven hydrocarbons from methane to heptane at 313.15 K, 5 bar.

We measured IFT data of several binary hydrocarbon mixtures, including hexane/octane, hexane/decane, and heptane/decane. We perform IFT calculations for these systems, and binary interaction parameters $k_{ij} = 0$ and $\beta_{ij} = 0$ are used between different hydrocarbons. Calculation results are displayed in Figure 3.10. The model results and experimental data has great agreement, which indicates that the DGT model produces great IFT predictions for hydrocarbon mixtures. Also, by comparing the IFT results in each mixture, we can see that IFT increases as the composition of the heavy hydrocarbon increases. And among different mixtures, the one containing heavier hydrocarbon tends to have a higher IFT at the same mole fraction.

Besides hydrocarbons, natural gas contains a small percentage of inorganic gases such as nitrogen and carbon dioxide. Therefore, we also perform IFT calculations
Figure 3.10: IFT results of binary hydrocarbon mixtures at 313.15 K and different mole fractions: the markers are experimentally measured IFT from literature [127] and the dash lines are DGT calculation results.

for nitrogen/hydrocarbon mixtures and carbon dioxide/hydrocarbon mixtures using the DGT model. Figure 3.11a shows the IFT results of nitrogen mixed with five different hydrocarbons at 313 K. From pressure as low as 5 bar to pressure up to 400 bar, great agreement is achieved between the prediction results and the experimental data [128]. Figure 3.11b depicts IFT of carbon dioxide/butane mixtures at different temperatures. In most cases, the DGT model results match with IFT data [124] very well, and only small deviations happen at 319.3 K and low carbon dioxide compositions.
(a) IFT results of binary mixtures of nitrogen with five different hydrocarbons at 313 K.

(b) IFT results of carbon dioxide/butane mixtures.

Figure 3.11 : IFT results of binary nitrogen/hydrocarbon and \( CO_2 \)/hydrocarbon mixtures: markers are experimentally measured IFT from literature [124, 128] and dash lines are DGT calculation results.
3.3.4 Multicomponent LLE system

In the oil recovery process, water is commonly used as the injection fluid to drive the oil through the rock pores. Due to the strong molecular interactions between water molecules and weak interactions between water and oil molecules, water and oil have very low mutual solubilities, and they tend to form LLE system at room conditions as well as reservoir conditions.

Figure 3.12: Density profiles convergence history of water/hexane mixture at 300 K, 1 bar.

The ultra low mutual solubilities pose challenges to the DGT model. For example,
the mole fraction of hexane in water can be lower than 1e-6 at room temperatures. When using the RF algorithm for water/hexane mixtures, the system cannot be solved as a whole. Instead, it needs to be split into two parts: water is chosen as the reference fluid in the water rich phase, and in the oil rich phase, the reference fluid is switched to hexane. This is a time consuming process, and the connecting point of the two parts can lead to inconsistency. The SDGT algorithm saves the game.

Figure 3.12 shows the density profile convergence history of a water/hexane mixture at 300 K, 1 bar. We use a combination of linear function and constant densities as the initial conditions. Without splitting the system nor choosing a reference fluid, the SDGT algorithm drives the system to its equilibrium state steadily after 370 time steps, and the overall computational time is only 219 seconds. With equilibrium density profiles, the IFT of various water/hydrocarbon mixtures are calculated and compared with experimental data in Figure 3.13, in which very good agreement is achieved between predictions and IFT data for different water/hydrocarbon mixtures.

In November 2016, we participated in the 9th Industrial Fluid Properties Simulation Challenge (IFPSC). The challenge topic is to predict the water/oil IFT at elevated temperature and pressure for three different oils: n-dodecane, toluene and 50:50 (wt/wt %) mixture of n-dodecane and toluene. The pressure for all state points is 250 psig (18.25 bar), and temperatures are 110, 130, 150 and 170 °C. In the challenge, we used DGT with PC-SAFT EoS and the SDGT algorithm for the IFT prediction. For example, Figure 3.14 shows the equilibrium density profiles of the three mixtures at 110 °C. In the ternary mixture, toluene has surface accumulation as shown in Figure 3.14c.

The IFT calculation results are summarized in Figure 3.15. The experimental data marked in the figures are from the IFPSC committee. Good agreements be-
Figure 3.13: IFT results of binary water/hydrocarbon mixtures at 1 bar and different temperatures: markers are experimentally measured IFT from literature [129] and dash lines are DGT calculation results.

(a) Water/dodecane. (b) Water/toluene. (c) Water/toluene/dodecane.

Figure 3.14: Equilibrium density profiles of water/dodecane, water/toluene, and water/toluene/dodecane mixtures at 110 °C, 250 psig.

The discrepancies between the prediction results and experimental data are achieved for water/toluene and water/toluene/dodecane system at low temperature, while deviations happen at
high temperature, as the prediction results have a weaker temperature dependence compared with the data. This could be a result of using a temperature-independent influence parameter. As discussed in Section 2.3, the influence parameter $v_i$ with PC-SAFT EoS can be treated as a constant at away from the critical temperature, while $v_i$ starts to become a stronger function of temperature when approaching the critical point. Therefore, prediction errors are amplified at higher temperatures when using a constant $v_i$ in calculations. The prediction results for water/dodecane mixture are less satisfying compared with the data. In fact, the temperature dependence of the water/dodecane IFT data is not even consistent with the other two data sets, which makes it questionable. Experimental data from other sources for water/dodecane mixture at high temperature might be necessary for further validations.

Figure 3.15 : IFT results of binary and ternary water/hydrocarbon mixtures: markers are experimentally measured IFT data from the IFPSC committee, and dash lines are DGT calculation results.
3.3.5 Free energy analysis

In many mixtures, surface accumulations are observed in the equilibrium density profiles, such as methane in Figure 3.16a. Similar behaviors are also observed in molecular simulations [130]. This phenomena can be explained using the free energy analysis. Figure 3.16b shows the grand potential energy surface of the methane/propane mixture at 303 K, 60 bar. The surface is generated by subtracting the tangent plane from the Helmholtz free energy surface [1]. On the grand potential energy surface, the two minimum spots are corresponding to the equilibrium bulk densities of the binary mixture. The grand potential energy contour is obtained by displaying the energy surface from a top angle, as shown in Figure 3.16c. The surface accumulation is well explained when we overlap the equilibrium density profiles on top of the contour (white line): in order to minimize the total free energy along the path from the vapor phase to the liquid phase, the density of methane must increase toward the saddle point of the energy surface so as to avoid the high energy hills, and then drop down to its liquid density. As a result, methane has a higher density at the interface region than that in both the liquid and vapor phases.

The low miscibility between water and oil can also be explained by the free energy analysis. Figure 3.17 shows the density profiles, grand potential energy surface and grand potential contour of water/hexane mixture at 293 K, 1 bar. It can be seen that the mixture would have very high energy level on the upper right or lower left corner of the energy contour, which indicate high mutual solubilities of the two components in liquid and vapor phase respectively. On the other hand, the mixture has energy minimum points on the upper left and lower right corner, which are corresponding to the low mutual solubilities of the two liquid phases.
Figure 3.16: Free energy analysis of the surface accumulation: (a) Equilibrium density profiles of methane/propane mixture at 303 K, 60 bar, (b) Grand potential energy surface, (c) Grand potential energy contour with density profiles (white line).
Figure 3.17: Free energy analysis of low mutual solubilities between water and oil:
(a) Equilibrium density profiles of water/hexane at 293 K, 1 bar, (b) Grand potential energy surface, (c) Grand potential energy contour with density profiles (white line).
Chapter 4

The mass-conserved density gradient theory model

The conventional DGT model established in open systems is incapable to generate a stable droplet with finite radius. This is because the grand potential energy in an open system has a saddle point, which corresponds to the droplet with the so-called critical nucleation radius $R_c$. When the droplet radius is smaller than $R_c$, the droplet keeps evaporating until no liquid phase is left; when the droplet radius is larger than $R_c$, it will grow until the entire system becomes liquid phase. Nevertheless, giving an exact critical nucleation radius is not practical in calculation, plus any small perturbation on the metastable system will lead to droplet growth or shrinkage.

A closed system with no mass exchange, on the other hand, can help stabilize the droplet. One example of a closed system is the canonical ensemble system, in which the number of particles $N$, volume $V$, and temperature $T$ are fixed. In this chapter, we develop a mass-conserved DGT model that works in canonical ensemble systems by introducing a mass-conservation term $\lambda_i$ and subjecting the model equations to no-flux boundary conditions. The new DGT model is applied in IFT calculations of both planar interface and spherical interface systems, the results of which are compared with those of the conventional DGT model and other theories.
4.1 The mass-conserved DGT model

4.1.1 DGT equations in closed systems

In a canonical ensemble system, the Helmholtz free energy $A$ is the characteristic energy that is minimized at equilibrium. The minimization of $A$ leads to

$$\frac{\delta A}{\delta \rho_i} = \mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \nabla^2 \rho_j ,$$

where $\delta A/\delta \rho_i$ is the functional derivative of the Helmholtz free energy $A$ with respect to molar density $\rho_i$. The term $\mu_i(\rho) := \partial a_0(\rho)/\partial \rho_i$ is the homogeneous chemical potential of component $i$ given by a bulk EoS. In this work, the perturbed chain statistical association fluid theory (PC-SAFT) EoS [41, 98] is employed for $\mu_i(\rho)$. With fixed number of particles in the system, the following constraint holds for each component $i$:

$$\int_V \rho_i = N_i ,$$

where $N_i$ is the total molar amount of component $i$ in the closed system.

In order to enforce this mass constraint to the energy minimization process, a mass-conservation term $\lambda_i$ as well as an evolution term [131] is introduced to the Euler–Lagrange equation such that:

$$\frac{1}{M_o} \frac{\partial \rho_i}{\partial t} + \frac{\delta A}{\delta \rho_i} + \lambda_i(t) = 0 \quad \text{for } i = 1, 2, \ldots, N ,$$

where $M_o > 0$ is a phenomenological mobility coefficient, which is assumed constant and equal for every component. The mass-conservation term $\lambda_i(t)$ is assumed to depend on time only (not on space) and is motivated by Rubinstein and Sternberg [132] in the context of the Allen–Cahn equation [133].

Since $V$ is assumed closed, there is no mass flux across the boundary $\partial V$, i.e., the
homogeneous Neumann boundary condition holds:
\[
\nabla \rho_i \cdot \mathbf{n} = 0, \quad (4.4)
\]
on the boundary \( \partial V \) with \( \mathbf{n} \) denoting the unit normal outward of the domain.

In previous works of classical DFT calculations [77, 78], the density profile \( \rho_i(\mathbf{r}) \) with mass-conservation is computed by
\[
\rho_i(\mathbf{r}) = \frac{N_i \exp \left( \frac{\mu_{ex}^i(\mathbf{r})}{RT} \right)}{\int_V \exp \left( \frac{\mu_{ex}^i(\mathbf{r})}{RT} \right) d\mathbf{r}}, \quad (4.5)
\]
where \( \mu_{ex}^i \) is the excess chemical potential. Equation 4.5 implies mass conservation, but it does not enforce the closed boundary of the system. In other words, the system is still a grand canonical ensemble with an open boundary, while the mass enters the system equal to the mass exists all the time. In the mass-conserved DGT model, by enforcing mass conservation and no-flux boundary conditions, we achieve a canonical ensemble, instead of a grand canonical ensemble with conserved mass.

4.1.2 Mass-conservation term \( \lambda_i \)

In Eqn. (4.3), the term \( \lambda_i \) is supposed to enforce mass conservation of the system. The closed-form expression of \( \lambda_i \) can be derived analytically. With the mass conservation assumption (4.2), the total mass of component \( i \) does not change over time, i.e.
\[
\frac{dN_i}{dt} = \frac{d}{dt} \int_V \rho_i = \int_V \frac{\partial \rho_i}{\partial t} = 0. \quad (4.6)
\]
Substituting Eqn. 4.3 into Eqn. 4.6 yields:
\[
-M_o \int_V \left( \frac{\delta A}{\delta \rho_i} + \lambda_i(t) \right) = 0. \quad (4.7)
\]
Since \( \lambda_i \) is only a function of time, it follows:
\[
\lambda_i(t) = -\frac{1}{|V|} \int_V \frac{\delta A}{\delta \rho_i}, \quad (4.8)
\]
where $|V|$ is the measure of the volume $V$. Eqn. 4.8 is the general expression of $\lambda_i$ for any formulations of inhomogeneous Helmholtz free energy. Within the DGT framework, this integral can be expanded and simplified:

$$
\lambda_i(t) = -\frac{1}{|V|} \left( \int_V \mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \int_V \nabla^2 \rho_j \right)
= -\frac{1}{|V|} \left( \int_V \mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \int_{\partial V} \nabla \rho_j \cdot n \right),
$$

(4.9)

where Gauss’ theorem is used to convert the volume integral to the surface integral. Due to the boundary condition (4.4), the surface integral in Eqn. 4.9 vanishes, hence:

$$
\lambda_i(t) = -\frac{1}{|V|} \int_V \mu_i(\rho).
$$

(4.10)

Substituting $\lambda_i$ back into Eqn. 4.3 leads to the mass-conserved DGT model (4.16a) for canonical ensemble systems.

### 4.1.3 Physical justification of $\lambda_i$

To justify the mass-conservation term $\lambda_i$ physically, we start from the concept of diffusion due to the differences in chemical potentials. Consider an inhomogeneous system at time $t$ with density distribution of $\rho(r)$ in the domain as shown in Figure 4.1, where $r$ is the position vector. In the diffusion process, the cell at position $r_0$ can only have mass exchange with its neighboring cells, i.e., cell at $r_1$. The density of component $i$ at $t + \Delta t$ in the cell $r_0$ equals to the current density plus the amount of mass diffused into the cell during $\Delta t$:

$$
\rho_i^{t+\Delta t}(r_0) = \rho_i^t(r_0) + \Delta t M_o \left( \mu_i(r_1) - \mu_i(r_0) \right).
$$

(4.11)

Eqn. 4.11 represents the change of density distribution due to the driving force of chemical potential differences. In the DGT model, we focus on the equilibrium state,
not on the process that the system takes to reach equilibrium. Therefore, we relax the constraint that mass exchange only occurs with neighbors, and let the cell have mass exchange with the outside reservoir, which has a constant chemical potential $\mu_i,\text{bulk}$. Equation (4.11), which describes diffusion, then becomes:

$$\rho_i^{t+\Delta t}(r_0) = \rho_i^t(r_0) + \Delta t M_o \left( \mu_i,\text{bulk} - \mu_i(r_0) \right).$$ (4.12)

By reorganizing Eqn. 4.12, we have:

$$\frac{1}{M_o} \frac{\partial \rho_i}{\partial t} + \mu_i(r_0) - \mu_i,\text{bulk} = 0,$$ (4.13)

which is exactly the familiar objective function of conventional DGT in grand canonical ensemble system [131].

With a closed boundary, let the cell at $r_0$ have mass exchange with every other cell inside the system instead of the outside reservoir, which is a process of redistributing the mass inside the system to achieve equilibrium. Therefore, Eqn. 4.13 becomes:

$$\frac{1}{M_o} \frac{\partial \rho_i}{\partial t} + \mu_i(r_0) - \frac{1}{|V|} \int_{V'} \mu_i(r')dr' = 0.$$ (4.14)
Mass conservation follows by integrating Eqn. 4.14 over $V$:

$$\frac{1}{M_o} \int_V \frac{\partial \rho_i}{\partial t} = \int_V \left( \frac{1}{|V|} \int_V \mu_i(r') dr' - \mu_i(r) \right) dr = 0,$$

(4.15)

i.e., there is no change of mass in time.

### 4.2 Mathematical model

#### 4.2.1 Model equations

With the mass-conserved DGT model, we propose the following system of partial differential equations, whose stationary state solutions are the molar density distributions that satisfy the energy-minimum equation (4.3) and the mass-balance constraint (4.2) for given molar amounts $N_i$:

For component $i = 1, \ldots, N$, we seek density distributions $\rho_i = \rho_i(t, x)$ as a function of time variable $t \in J$ and space variable $x \in V$ such that:

$$\frac{1}{M_o} \frac{\partial \rho_i}{\partial t} + \mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \nabla^2 \rho_j - \frac{1}{|V|} \int_V \mu_i(\rho) = 0,$$

(4.16a)

subjected to boundary conditions:

$$\nabla \rho_i \cdot n = 0 \quad \text{for } t \in J, x \in \partial V,$$

(4.16b)

and initial conditions:

$$\rho_i = \rho_i^0 \quad \text{for } t = 0, x \in V,$$

(4.16c)

where the time interval $J := (0, t_s)$ is assumed large enough such that the system reaches a stationary state at time $t_s$, and the initial data $\rho_i^0$ is chosen to satisfy (4.2).

System (4.16) is an extension of the system used by the SDGT algorithm [131], which introduced an artificial time dependence term in order to approach the stationary state steadily instead of attempting to solve the stationary state equations.
directly. In this work, we made several modifications to the SDGT algorithm. Firstly, system (4.16) is formulated for the NVT setting, and thus prescribes Neumann boundary conditions (4.16b) instead of having Dirichlet boundary conditions. Secondly, the time evolution term in (4.16a) is physically consistent by having the mobility coefficient $M_o$. Furthermore, it replaces $\mu_{i,\text{bulk}}$ with the term $\lambda_i = -\frac{1}{|V|} \int_V \mu_i(\rho)$ that guarantees mass-conservation (4.2) of each component over time.

### 4.2.2 Energy dissipation

In this section, we prove that solutions of system (4.16) satisfy the following energy dissipation law:

$$\frac{dA(t)}{dt} = -\sum_{i=1}^{N} \int_V \frac{1}{M_o} \left( \frac{\partial \rho_i}{\partial t} \right)^2 \leq 0 \quad \text{for } t \in J ,$$

i.e, the Helmholtz free energy $A$ dissipates over time in the NVT setting.

**Proof** Multiplying (4.16a) by $\partial \rho_i / \partial t$, integrating over $V$, and summing up over $i$ yields:

$$-\sum_{i=1}^{N} \int_V \frac{1}{M_o} \left( \frac{\partial \rho_i}{\partial t} \right)^2 = \sum_{i=1}^{N} \int_V \mu_i(\rho) \frac{\partial \rho_i}{\partial t} - \sum_{i,j=1}^{N} v_{ij} \int_V \nabla^2 \rho_j \frac{\partial \rho_i}{\partial t} - \sum_{i=1}^{N} \frac{1}{|V|} \int_V \mu_i(\rho) \int_V \frac{\partial \rho_i}{\partial t} \quad (4.18)$$

$$=: \Gamma_1 + \Gamma_2 + \Gamma_3 .$$

Using the definition of $\mu_i$, term $\Gamma_1$ is equivalent to

$$\sum_{i=1}^{N} \int_V \frac{\partial a_0(\rho)}{\partial \rho_i} \frac{\partial \rho_i}{\partial t} = \int_V \frac{\partial a_0(\rho)}{\partial t} = \frac{d}{dt} \int_V a_0(\rho) .$$
For term $\Gamma_2$, we use the identity

$$
\frac{d}{dt} \left( \frac{1}{2} \sum_{i,j=1}^{N} v_{ij} \int_{V} \nabla \rho_i \cdot \nabla \rho_j \right) = \sum_{i,j=1}^{N} v_{ij} \int_{V} \nabla \rho_j \cdot \nabla \left( \frac{\partial \rho_i}{\partial t} \right)
$$

$$
= \sum_{i,j=1}^{N} v_{ij} \left( \int_{\partial V} \nabla \rho_j \cdot n \frac{\partial \rho_i}{\partial t} - \int_{V} \nabla^2 \rho_j \frac{\partial \rho_i}{\partial t} \right)
$$

$$
= \sum_{i,j=1}^{N} v_{ij} \int_{V} \nabla^2 \rho_j \frac{\partial \rho_i}{\partial t}.
$$

(4.19)

Term $\Gamma_3$ vanishes due to mass conservation (4.6). Adding $\Gamma_1$, $\Gamma_2$, and $\Gamma_3$ leads to $dA(t)/dt$ according to Eqn. 2.1. Therefore, the energy dissipation law (4.17) holds.

### 4.2.3 Planar interface case

For the planar interface case, the system is homogeneous in $x$ and $y$ direction, and the density only varies along the $z$ direction. Assume a domain of size $D$ in $z$ direction is large enough that the boundary $\partial V$ locates in the two bulk phases. Eqn. 4.16 simplifies to:

For $i = 1, \ldots, N$, we seek $\rho_i = \rho_i(t, z)$ such that

$$
\frac{1}{M_o} \frac{\partial \rho_i}{\partial t} + \mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \frac{\partial^2 \rho_j}{\partial z^2} - \frac{1}{D} \int_{0}^{D} \mu_i(\rho) \, dz = 0,
$$

(4.20a)

with the boundary conditions for each component $i$:

$$
\frac{\partial \rho_i}{\partial z}(t, 0) = 0, \quad \frac{\partial \rho_i}{\partial z}(t, D) = 0,
$$

(4.20b)

and the initial condition $\rho_i(0, z)$ is chosen to satisfy the mass-constraint:

$$
A_s \int_{0}^{D} \rho_i(0, z) \, dz = N_i.
$$

(4.20c)

where $A_s$ is the surface area.
4.2.4 Spherical interface case

Without loss of generality, assume that $V$ is a sphere with radius $R$ and with its origin at the center of the droplet. In this setting, the density $\rho_i$ is only a function of the radial distance $r$ to the origin. The problem given in (4.16) then reads:

For $i = 1, \ldots, N$, we seek $\rho_i = \rho_i(t, r)$ such that

\[
\frac{1}{M_o} \frac{\partial \rho_i}{\partial t} + \mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \left( \frac{\partial^2 \rho_j}{\partial r^2} + \frac{2}{r} \frac{\partial \rho_j}{\partial r} \right) - \frac{3}{R^3} \int_0^R r^2 \mu_i(\rho) \, dr = 0, \quad (4.21a)
\]

with the following boundary conditions for each component $i$:

\[
\frac{\partial \rho_i}{\partial r}(t, 0) = 0, \quad \frac{\partial \rho_i}{\partial r}(t, R) = 0, \quad (4.21b)
\]

The initial conditions $\rho_i(0, r)$ are chosen to satisfy (4.2), which simplifies to

\[
4\pi \int_0^R r^2 \rho_i(0, r) \, dr = N_i. \quad (4.21c)
\]

4.3 Discretization

4.3.1 Space discretization

The system of time-dependent boundary value problems (BVPs) (4.20) and (4.21) is solved with a time-marching scheme until a stationary state is reached. On every time level, a finite difference scheme is used to discretize equations in space. By interpolating $M$ points in-between the boundaries, $0 = z_0 < z_1 < \ldots < z_{M+1} := D$ denote equidistant nodes on a grid with mesh size $\Delta z := \frac{D}{M+1}$. We approximate the first and second derivatives by central difference quotients:

\[
\frac{d \rho_i}{dz}(z_k) \approx \frac{\rho_i,k+1 - \rho_i,k-1}{2\Delta z},
\]

\[
\frac{d^2 \rho_i}{dz^2}(z_k) \approx \frac{\rho_i,k-1 - 2\rho_i,k + \rho_i,k+1}{\Delta z^2}.
\]
At the boundary, the first derivative $\frac{d\rho_i}{dz}$ vanishes due to the homogeneous Neumann boundary condition, and the second derivative can be simplified as:

$$\frac{d^2\rho_i}{dz^2}(z_k) \approx \frac{2\rho_{i,k-1} - 2\rho_{i,k}}{\Delta z^2} \text{ or } \frac{2\rho_{i,k+1} - 2\rho_{i,k}}{\Delta z^2}.$$  

4.3.2 Time discretization

Let $\Delta t_n$ denote the time step size between time level $t^{n+1}$ and $t^n$, which may vary from step to step according to a time step adaptation scheme [131]. The time derivative is approximated by:

$$\frac{\partial \rho_i}{\partial t} \approx \frac{\rho_i^{n+1} - \rho_i^n}{\Delta t_n}. \quad (4.22)$$

A convex–concave splitting [131] is applied to the nonlinear part of the equation, which is the expression of the homogeneous chemical potential:

$$\mu_i = \mu_i^+ (\rho_i^{n+1}) + \mu_i^- (\rho_i^n). \quad (4.23)$$

where $\mu_i^+$ is associated with the convex part of the energy and $\mu_i^-$ with the concave part.

4.3.3 Fully discretized equations

Discretizing Eqn. 4.20a and Eqn. 4.21a in time and space, while applying the convex–concave splitting (4.23) yields the fully discrete problem. For every time level $n + 1$, we seek $\rho_i^{n+1}$ such that for $k = 1, \ldots, M$, $i = 1, \ldots, N$, the residual equations equal zero:
Planar interface case

\[
\frac{\rho_{i,k}^{n+1} - \rho_{i,k}^n}{M_o \Delta t_n} + \mu_i^+ (\rho_k^{n+1}) + \mu_i^- (\rho_k^n) - \sum_{j=1}^{N} v_{ij} \frac{\rho_{j,k-1}^{n+1} - 2 \rho_{j,k}^{n+1} + \rho_{j,k+1}^{n+1}}{\Delta z^2} \\
- \frac{1}{D} \int_0^D \left( \mu_i^+ (\rho_k^{n+1}) + \mu_i^- (\rho_k^n) \right) dz = 0,
\]

subjected to the boundary conditions

\[
\frac{\partial \rho_{j,0}^{n+1}}{\partial z} = 0, \quad \frac{\partial \rho_{j,M+1}^{n+1}}{\partial z} = 0.
\]

Spherical interface case

\[
\frac{\rho_{i,k}^{n+1} - \rho_{i,k}^n}{M_o \Delta t_n} + \mu_i^+ (\rho_k^{n+1}) + \mu_i^- (\rho_k^n) - \sum_{j=1}^{N} v_{ij} \left( \frac{\rho_{j,k-1}^{n+1} - 2 \rho_{j,k}^{n+1} + \rho_{j,k+1}^{n+1}}{\Delta r^2} \\
+ \frac{2 \rho_{j,k+1}^{n+1} - \rho_{j,k-1}^{n+1}}{2 \Delta r} \right) - \frac{3}{R^3} \int_0^R r^2 \left( \mu_i^+ (\rho_k^{n+1}) + \mu_i^- (\rho_k^n) \right) dr = 0,
\]

subjected to the boundary conditions

\[
\frac{\partial \rho_{j,0}^{n+1}}{\partial r} = 0, \quad \frac{\partial \rho_{j,M+1}^{n+1}}{\partial r} = 0.
\]

The fully discretized equations (4.24) and (4.25) can be linearized and solved using Newton’s method to obtain the density distribution \( \rho^{n+1} \) on each time level. More details about using Newton’s method for DGT equations can be found in [131].

The stationary state of the system is reached when either of the following stopping criteria is satisfied: \( \sum_{k=1}^{M} |\rho_k^n - \rho_k^{n+1}| \leq \varepsilon_d \), or \( |(A^n - A^{n+1})/A^n| \leq \varepsilon_e \), or \( \Delta t_n \geq \varepsilon_t \). The first stopping criteria means that the density difference between the two time levels is smaller than the tolerance \( \varepsilon_d \), the second one means that the relative change of the Helmholtz free energy between two time levels is smaller than the tolerance \( \varepsilon_e \), and the third one means that the time step length \( \Delta t_n \) is larger than the tolerance \( \varepsilon_t \). We use \( \varepsilon_d = 1e-3, \varepsilon_e = 1e-6 \) and \( \varepsilon_t = 1e4 \) in this work. The obtained equilibrium density distribution is an approximation of the solution of the original mass-conserved DGT model.
4.4 Applications of the mass-conserved DGT model

4.4.1 Results for planar interface cases

Before applying the mass-conserved DGT model in a closed system, we first conduct conventional DGT calculations in open systems, of which the grand potential energy is minimized at equilibrium. Figure 4.2(a) shows the density profile convergence history of pure hexane at 293.15 K in an open system. Stating from the linear density distribution (red solid line), the density profile converges to its equilibrium state (blue solid line) in 110 time steps using the SDGT algorithm. At equilibrium, the system’s total molar amount per unit area $N_i/A_s$ is calculated by integrating the equilibrium density profile along the $z$ direction, which equals to $1.989605028 \times 10^{-5}$ mol/m$^2$ on a 5 nm domain.

![Figure 4.2](image)

(a) Open system. (b) Closed system.

Figure 4.2: Density profile convergence history of hexane at 293.15 K in (a) an open system and (b) a closed system.

Same amount of hexane is used as the mass input to the mass-conserved DGT model. The density profiles are obtained by solving Eqn. 4.24 on each time level, and the convergence history is displayed in Figure 4.2(b). From a linear density
distribution (red solid line), the system evolves to its equilibrium state (blue solid line) in 130 time steps. At equilibrium, the system’s total molar amount per unit area is $1.98960518 \times 10^{-5}$ mol/m$^2$, which is less than $1 \times 10^{-13}$ mol/m$^2$ mass loss compared with the initial condition. This means that the mass has been conserved accurately during the calculation.

![Density profile comparison](image)

**Figure 4.3**: Comparison of hexane’s equilibrium density profiles ($293.15$ K) of DGT models in open and closed systems.

By comparing the two density profile convergence histories in Figure 4.2, we demonstrate the differences of density profile behaviors in $\mu VT$ and $NVT$ systems. The conventional DGT model in $\mu VT$ system fixes boundary densities, which guarantees constant bulk chemical potentials during the calculation. At the same time, the system is allowed to have mass exchange with the environment, which leads to the change of the overall mass (area under the density profile) from time to time. The mass-conserved DGT model in $NVT$ system, on the other hand, retains the area under density profile as a constant on every time step, while the density values on each
position, including boundaries, are subjected to change. Since the mass-conserved DGT model used the same amount of mass from equilibrium state of the open system case, the two models produce identical equilibrium density profiles as shown in Figure 4.3.

When applying the conventional DGT model in open systems, the phase equilibrium calculation is required. The obtained bulk densities are used to set up boundary conditions for DGT equations. For the mass-conserved DGT model, no phase equilibrium calculation is required, and the bulk properties as well as the interfacial properties can be obtained from equilibrium density profiles. The work-flows of the two models are compared and summarized in Figure 4.4. To verify the accuracy of the bulk densities calculations from the mass-conserved DGT model, we compare the results with those from the phase equilibrium calculations at different temperatures in Figure 4.5. The comparison proves that the mass-conserved DGT model reproduces the bulk densities accurately without explicitly performing phase equilibrium calculations.

From the phase envelope in Figure 4.5, it can be concluded that the vapor–liquid phase splitting occurs when the average density $\rho_{\text{avg}}$ falls inside the phase equilibrium curve: $\rho_V < \rho_{\text{avg}} < \rho_L$, where $\rho_{\text{avg}} = N_i/(A_s D)$. Otherwise, only one vapor or liquid phase would exist. For example, the equilibrium bulk densities of hexane at 293.15 K are $\rho_V = 6.7$ and $\rho_L = 7588.1 \text{ mol/m}^3$. Figure 4.6 shows the equilibrium density profiles with different input $\rho_{\text{avg}}$ as marked on the dash line of Figure 4.5. For $\rho_{\text{avg}} = 3000$ (diamond-marked line), 4000 (circle-marked line), and 5000 (triangle-marked line) mol/m$^3$, the vapor–liquid phase split takes place. The volume of the liquid phase increases as more hexane is added to the system, while the interface shape and bulk densities do not change. If $\rho_{\text{avg}} < \rho_V$ or $\rho_{\text{avg}} > \rho_L$, such as when $\rho_{\text{avg}} = 5$
Conventional DGT in open systems:
Inputs: T (for pure system)
        T, P, z_i (for mixed system)
Phase equilibrium calculation for bulk properties
DGT calculation
Interfacial properties

Mass-conserved DGT in closed systems:
Inputs: T, V, N_i
DGT calculation

Figure 4.4: Comparison of workflows of conventional DGT model and the mass-conserved DGT model.

Figure 4.5: The phase envelope of hexane generated by the phase equilibrium calculation (solid line) and the mass-conserved DGT model (square markers). Markers on the dash line indicate the average input densities in Figure 4.6.
(star-marked line) or 10000 (square-marked line) mol/m$^3$, no phase splitting occurs, and thus no interface appears.

Figure 4.6: Equilibrium density profiles of hexane at 293.15 K with different mass in the system.

4.4.2 Results for spherical interface cases

As discussed in the introduction, it is technically impossible to obtain a stable droplet in an open system due to the saddle point on the grand potential energy surface. In this section, we study the droplet formation by applying the mass-conserved DGT model in a closed spherical system. Figure 4.7 shows the formation of the hexane droplet in a system of radius $R = 10$ nm. A step function is used as initial density distribution (red solid line), which is equivalent to having a 5 nm homogeneous liquid droplet surrounded by homogeneous vapor phase. The total molar amount is 1.595424691e–21 mol at initial time. The dash lines depict the convergence history of the density profiles. After 210 time steps the stopping criteria is met which in-
dicates a thermodynamically stable state. The mass measured at the equilibrium is $1.59538217 \times 10^{-21}$ mol, which indicates the mass loss of less than $7 \times 10^{-26}$ mol. Compared with the planar interface cases, finer grids are required here since numerical errors are amplified at nodes that are close to $R$.

![Graph](image)

Figure 4.7: Density profile convergence history of hexane droplet at 293.15 K.

From the equilibrium density profile (blue solid line), it can be observed that the hexane forms a droplet with a radius of about 4 nm, and it has an interface thickness of about 2 nm, which is comparable to the droplet radius. At such a small scale with a diffusive interface, the traditional thermodynamic approaches such as Young–Laplace equation lose their accuracy, while DGT is more suitable for this scenario.

The mass-conserved DGT calculation is also carried out at different temperatures using the same initial setup. The equilibrium density profiles are shown in Figure 4.8. As the temperature increases, the radius of the liquid droplet decreases and the interface becomes more diffusive. At the same time, the liquid density decreases while the vapor density increases at a higher temperature. This is because molecules
are energized at higher temperatures, and more liquid vaporizes into the vapor phase. These temperature-related behaviors are consistent with density functional theory calculations [78].

![Equilibrium density profiles of hexane droplet at different temperatures.](image)

Figure 4.8: Equilibrium density profiles of hexane droplet at different temperatures.

In a system with a planar interface, pressures are equal everywhere at equilibrium. Otherwise the pressure difference will lead to fluid flow until the pressure balance is achieved. In a system with spherical interface, however, there is a pressure difference across the interface region. Equilibrium liquid and vapor pressures are calculated on different radius droplets, and the results are displayed in Figure 4.9. The solid line shows the pressure as a function of the droplet radius at 293.15 K, and the dash line marks the pressure of a planar interface system at the same temperature, which is 0.1618 bar as computed by PC-SAFT EoS. For a droplet with small radius, both the liquid and vapor pressures are much higher than the planar interface pressure. As the droplet radius grows, the liquid and vapor pressures decrease, and will eventually drop to the same level as the planar interface pressure at infinitely large radius (infinitely
small curvature).

The reason that the pressure difference exists is because the IFT on the curved surface tends to contract the droplet, and therefore, the inner pressure increases to balance the force. With the equilibrium density profile, the IFT of a droplet can be calculated using the following equation:

\[ \gamma = \frac{\Omega + P_A V_A + P_B V_B}{A_s} , \]

where \( \Omega \) is the grand potential energy of the system, \( P_A V_A \) and \( P_B V_B \) are products of the bulk pressure with the bulk volume in the vapor and liquid phases respectively. For a spherical interface, a dividing surface is required to determine \( V_A, V_B \) and \( A_s \). In this work, we use the Gibbs dividing surface \( [1] \), which is the position where the surface excess number of particles \( \Gamma_s \) equals to zero. For a spherical system, the zero adsorption is defined as:

\[ \Gamma_s = 4\pi \int_0^{R_e} r^2 \left( \rho(r) - \rho_A \right) dr + 4\pi \int_{R_e}^R r^2 \left( \rho(r) - \rho_B \right) dr = 0 \] (4.26)

from which, the position of the Gibbs dividing surface \( R_e \) can be determined by

\[ R_e^3 = \frac{3 \int_0^R r^2 \left( \rho(r) - \rho_B \right) dr}{\rho_A - \rho_B} . \] (4.27)

The IFT of the hexane droplet at 293.15 K with different radii are calculated and displayed as the blue solid line in Figure 4.10. The black dot line marks the IFT on a planar interface. From infinitely small radius, the system’s IFT increases rapidly to a maximum value. After that, the IFT starts to decrease, and will eventually drops to the same value as the planar interface IFT at an infinitely large radius.

We recall below the Tolman equation that has been widely used as a macroscopic thermodynamic approach to describe the relationship between the droplet IFT and
Figure 4.9: Liquid and vapor phase pressures at different radius calculated by the mass-conserved DGT model.

Figure 4.10: IFT results of hexane droplet at 293.15 K using the mass-conserved DGT model (blue solid line) and Tolman equation (red dash line).

droplet radius:
\[
\frac{\gamma(r)}{\gamma_{\infty}} = \frac{1}{1 + 2\delta/r},
\]

in which, \(\gamma_{\infty}\) is the IFT on the planar interface, and \(\delta\) is the so-called Tolman length,
which by definition is:

\[ \delta = R_e - R_s, \]  

where \( R_s \) is called the surface of tension, at which the formal derivative of the IFT to the radius equals to zero:

\[ \left. \frac{d\gamma}{dr} \right|_{r=R_s} = 0. \]  

(4.30)

According to the Tolman equation, the droplet’s IFT is a monotonic function of the droplet radius, and the sign of the Tolman length \( \delta \) has a significant effect on the behavior of the IFT function: with growing radius, the IFT increases if Tolman length is positive, and the IFT decreases if Tolman length is negative. Figure 4.10 shows that IFT decreases with growing radius, which suggests a negative Tolman length.

We determine the value of \( \delta \) at the point where the IFT reaches its maximum in DGT calculations, so that the monotonicity can be best captured [73]. For hexane at 293.15 K, \( R_e = 2.9585 \) nm at IFT maximum, and \( R_s = 3 \) nm. Therefore \( \delta = -0.0415 \) nm. The red dash line in Figure 4.10 shows the Tolman equation results. It can be seen that the two approaches have excellent agreement at radius \( r > 10 \) nm. For smaller droplets, however, the Tolman equation results deviate from DGT results, and the sharp drop of IFT at very small radii could not be described by the Tolman equation. In general, Tolman equation is a fast and reasonably accurate approach to determine the \( \gamma - r \) relationship for large droplet, and DGT can serve as a reliable helper tool to calculate the Tolman length. For very small droplets, DGT is significantly a more suitable approach for the calculation.
Chapter 5

The modified density gradient theory model for surfactants

As discussed in the introduction, surfactants are widely used in many industrial processes to alter system’s IFT [50]. In an early attempt [131], we applied the conventional DGT model in a water/hexane/2-methoxyethanol mixture, in which 2-methoxyethanol (C$_1$E$_1$) is a surfactant [103] with the molecular structure shown in Figure 5.1. Using the SDGT algorithm introduced in Section 3.2, the equilibrium density profiles were calculated and displayed in Figure 5.2a. Although an enrichment of the surfactant molecule at the interface is observed, the conventional DGT model fails to describe the structure of the surfactant molecule: the surface active nature of surfactant is due to its amphiphilic structure, which consists of a hydrophilic group and a hydrophobic group. The conventional DGT model simply treats every molecule in the system as occupying a single point in space regardless of its structure, and it approximates the free energy using the component’s local density and the density gradient [14]. This single-point model works fairly well for those nearly spherical molecules or homonuclear chain molecules, such as alkanes, nitrogen, water etc., as discussed in Chapter 3. But much of the physics are missing when using the conventional DGT model for surfactant systems, in which the surfactant molecule would span multiple positions in space as shown in Figure 5.2b.

To overcome this limitation, we develop a modified DGT model for surfactant systems by introducing a chain formation energy term. The derivations of the mod-
(a) Line structure.  
(b) 3-D ball structure.

Figure 5.1: Molecular structure of 2-methoxyethanol.

Figure 5.2: In the conventional DGT model, the surfactant molecule is modeled to occupy a single point in space as shown in (a). The surfactant molecule would actually span multiple positions with a heterogeneous chain structure formed by hydrophilic segments (black circles) and hydrophobic segments (gray circles) as shown in (b).

ified DGT model are introduced in Section 5.1. Section 5.2 presents the numerical methods used in the solution process of model equations. The results of applying the modified DGT model in surfactant systems are discussed in Section 5.3.
5.1 The modified DGT model for surfactant systems

The conventional DGT model fails to describe surfactant molecules properly due to the lack of molecular structure information in the model. To improve this, we turned to the SAFT [39, 40, 41] formalism, which describes molecules as chains of spherical segments. The chain formation contribution added to the current Helmholtz free energy expression produces:

\[ A[\rho] = A^{\text{segment}}[\rho] + A^{\text{chain}}[\rho]. \]  \hspace{1cm} (5.1)

where \( A^{\text{segment}}[\rho] \) is the conventional DGT free energy expression as given in Eqn. 2.1, and \( A^{\text{chain}}[\rho] \) is the new energy term that accounts for the chain formation effect.

Eqn. 5.1 is a general form of the modified DGT free energy functional for heterogeneous chain molecules. One option of the chain formation energy term \( A^{\text{chain}} \) is to use the modified iSAFT model of Jain et al. [134], Bymaster and Chapman [135]. In iSAFT, the chain term is a natural extension of the associating free energy functional in the limit of complete bonding. The associating free energy functional can capture the detailed structure of associating molecules at an interface. According to iSAFT, the contribution to the inhomogeneous chemical potential of segment \( \beta \) due to the chain formation is (Eqn. 21 in Jain et al. [134]):

\[
\frac{1}{k_B T} \frac{\delta A^{\text{chain}}}{\delta \rho_\beta} = \sum_{A \in \Gamma^{(\beta)}} \ln X_A^\beta(r_\beta) - \frac{1}{2} \sum_{\gamma=1}^{N} \sum_{\gamma'} \int \rho_{\gamma}(r) \frac{\delta \ln y_{\gamma\gamma'}^{\text{contact}}[\rho_{\text{seg}}(r)]}{\delta \rho_\beta^{\text{seg}}(r_\beta)} dr. \]  \hspace{1cm} (5.2)

In the first term of Eqn. 5.2, \( \Gamma^{(\beta)} \) is the set of all bonding sites on segment \( \beta \). \( X_A^\beta \) denotes the fraction of segment \( \beta \) that does not form a chain bonding to site \( A \). We will take the limit \( X_A^\beta \to 0 \) for covalent bonding sites. This part is essential to account for the chain connectivity between chemically distinctive segments and to enforce stoichiometry.
The second term is similar to the chain contribution in the original SAFT [39, 40, 41], which takes into account the necessary work to bring two different chemical segments into contact. The first summation is over all the bonding segments, and the second summation is over all segments $\gamma'$ that are bonded to segment $\gamma$. $y_{\gamma'\gamma}^{\text{contact}}$ is the cavity correlation function for inhomogeneous hard spheres at contact. Its form for a bulk fluid is known from the Carnahan-Starling EoS [136]. The inhomogeneous version of this function is not known in a tractable form, and here, we follow the approach in the development of the iSAFT model [134] that the cavity function is approximated by a simple geometric average of its bulk forms at different positions in the interface [61, 136]:

$$
y_{\gamma'\gamma}^{12, \text{contact}}[\bar{\rho}_{\text{seg}}(r)] = \frac{1}{1 - \bar{\varsigma}_3} + \frac{3\sigma_1\sigma_2}{\sigma_1 + \sigma_2} \left( \bar{\varsigma}_2 \right)^2 + 2 \left( \frac{\sigma_1\sigma_2}{\sigma_1 + \sigma_2} \right)^2 \frac{(\bar{\varsigma}_2)^2}{(1 - \bar{\varsigma}_3)^3}, \tag{5.3}
$$

where $\bar{\varsigma}_i$ is given by:

$$
\bar{\varsigma}_i = \frac{\pi}{6} \sum_{\beta=1}^{N_i} \bar{\rho}_{\beta}^{\text{seg}}(r)(\sigma_\beta)^i, \tag{5.4}
$$

and $\bar{\rho}_{\beta}^{\text{seg}}(r)$ is the weighted density of segment $\beta$ at position $r$ which is evaluated by [61]:

$$
\bar{\rho}_{\beta}^{\text{seg}}(r) = \frac{3}{4\pi(\sigma_\beta)^3} \int_{|r - r_1| < \sigma_\beta} \rho_{\beta}^{\text{seg}}(r_1) dr_1. \tag{5.5}
$$

The chain formation free energy term in iSAFT has been applied to model branched chain connectivity of star polymers and dendrimers. In this work, we use it for the two-group surfactant molecule: the amphiphilic surfactant molecule is modeled by having a head group (H) and a tail group (T) bonded together, as illustrated in Figure 5.3. Although we illustrate the surfactant molecule as having one head group and one tail group, each group is polyatomic with multiple segments: the head group is formed by hydrophilic segments, and the tail group is formed by hydrophobic segments. The head and tail groups, while sitting on different positions in space, are
connected by a rigid chain bond to form the surfactant molecule \((H_1T_1)\). In the model illustration, we use water for the head group and hexane for the tail group. The length of the rigid chain bond is \(\sigma_{12} = (\sigma_H + \sigma_T)/2\), in which \(\sigma_H\) and \(\sigma_T\) are diameters of segments in the head and tail groups respectively.

\[ \text{water} \quad \text{hexane} \]

Figure 5.3: The two-group surfactant molecule model: the surfactant is formed by bonding a water-like head group and a hexane-like tail group together.

According to iSAFT, Eqn. 5.2 is a general expression for molecules with any number of segments and any orientations in the space. In the modified DGT model, the surfactant molecule has only one bonding site on each group as illustrated in Figure 5.3. Therefore, Eqn. 5.2 for surfactant components can be simplified to:

\[
\frac{\mu_{\text{chain}}^\beta(r_\beta)}{k_B T} = \ln X_A^\beta(r_\beta) - \Psi_\beta(r_\beta), \tag{5.6a}
\]

in which \(\Psi_\beta(r_\beta)\) is the abbreviation for the summation of the integral:

\[
\Psi_\beta(r_\beta) = \frac{1}{2} \sum_{\gamma=1}^{2} \int \rho^\gamma_{\text{seg}}(r) \frac{\delta \ln y_{\text{contact}}^{12}[p^\gamma_{\text{seg}}(r)]}{\delta \rho^\beta_{\text{seg}}(r_\beta)} \, dr. \tag{5.6b}
\]
Non-surfactant components have no bonding sites, which is equivalent to $X_A^\beta(r_\beta) = 1$, and therefore the chain chemical potential for water and oil simplifies to:

$$\frac{\mu_{\text{chain}}(r_\beta)}{k_B T} = -\Psi_\beta(r_\beta). \quad (5.6c)$$

The system of equations (5.6) gives the chain formation chemical potential of surfactant and solvents based on the current surfactant model. In Eqn. 5.6a, the fraction of unbounded group $X_A^\beta(r)$ is calculated by:

$$X_A^1(r_1) = \frac{1}{I_{2,1}(r_1) \exp(\mu_{2,\text{bulk}}/k_B T)};$$

$$X_A^2(r_2) = \frac{1}{I_{1,2}(r_2) \exp(\mu_{1,\text{bulk}}/k_B T)}, \quad (5.7)$$

where the recursive integral $I_{2,1}$ and $I_{1,2}$ are given by:

$$I_{2,1}(r_1) = \int \exp(D_2(r_2)) \Delta^{(1,2)}(r_1, r_2) dr_2,$$

$$I_{1,2}(r_2) = \int \exp(D_1(r_1)) \Delta^{(1,2)}(r_1, r_2) dr_1, \quad (5.8)$$

in which, $D_\beta(r_\beta)$ is:

$$D_\beta(r_\beta) = -\frac{1}{k_B T} \frac{\delta A^{\text{res}}}{\delta \rho_\beta^{\text{seg}}(r_\beta)} + \Psi_\beta(r_\beta). \quad (5.9)$$

The first term in Eqn. 5.9 is the functional derivative of the inhomogeneous residual Helmholtz free energy to density, which is given in DGT as:

$$\frac{\delta A^{\text{res}}}{\delta \rho_\beta^{\text{seg}}(r_\beta)} = \mu_\beta^{\text{res}}(r_\beta) - \sum_{j=1}^N v_{3j} \frac{d^2 \rho_j}{dz^2}(r_\beta), \quad (5.10)$$

where $\mu_\beta^{\text{res}}(r_\beta)$ is the homogeneous residual chemical potential evaluated at position $r_\beta$, and the second term is the gradient term.

The function $\Delta^{(1,2)}(r_1, r_2)$ in Eqn. 5.8 can be evaluated by:

$$\Delta^{(1,2)}(r_1, r_2) = K F^{(1,2)}(r_1, r_2)y^{(1,2)}(r_1, r_2), \quad (5.11)$$
where $K$ is a constant geometric factor which accounts for the entropic cost associated with the orientations of the two segments to form the bond [137]. $y^{(1,2)}(r_1, r_2)$ is the inhomogeneous cavity correlation function approximated by $y^{(1,2)}(r_1, r_2) = \sqrt{y^{12}(r_1)y^{12}(r_2)}$. $F^{(1,2)}(r_1, r_2)$ is the association Mayer-$f$ function that defines the bonding length and orientation angle of the chain bond. When added into a water/oil mixture, the surfactant molecules tend to partition to the interface with a fixed bond length $\sigma_{12}$ as well as the surfactant’s orientation in space $\theta_0$ and $\varphi_0$ as shown in Figure 5.4. Thus, the association Mayer-$f$ function in a spherical coordinates is expressed as:

$$F = \delta(\theta - \theta_0)\delta(\varphi - \varphi_0) \frac{\delta(r - \sigma_{12})}{4\pi\sigma_{12}^2}.$$  \hspace{1cm} (5.12)

![Figure 5.4: Surfactant molecules present in the interface with average orientation $\theta_0$.](image)

With the help of coordinate transformation, $I_{2,1}$ and $I_{1,2}$ can be integrated analytically. Figure 5.5 shows the coordinate transformation for one surfactant molecule in space. In the rectangular coordinate (the black solid line axes), positions of the surfactant head group and the tail group are determined by vector $r_1$ and $r_2$. For a head group, the relative position of the bonded tail group is described in the spherical coordinates (the gray dash line axes) by the fixed bond length $\sigma_{12}$ and fixed angles $\theta_0$, $\varphi_0$. By assuming that the densities are symmetric in the $x – y$ plane, $I_{2,1}$ and $I_{1,2}$
in Eqn. 5.8 become (here we use $I_{2,1}$ as an example):

$$I_{2,1}(\mathbf{r}_1) = \int \exp \left( D_2(\mathbf{r}_2) \right) \Delta^{(1,2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2$$

$$= \int \exp \left( D_2(\mathbf{r}_2) \right) K F^{(1,2)}(\mathbf{r}_1, \mathbf{r}_2) y^{(1,2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2$$

$$= \int \int \int \exp \left( D_2(z_2) \right) K y^{(1,2)}(z_1, z_2) \delta(\theta' - \theta_0) \delta(\phi' - \phi_0) \delta(r' - \sigma_{12})$$

$$\times \frac{\delta(r' - \sigma_{12})}{4\pi \sigma^2_{12}} d\phi' d\theta' dr'$$

$$= \frac{K \sqrt{y^{12}(z_1)} y^{12}(z_1 + z_0)}{4\pi \sigma^2_{12}} \exp \left( D_2(z_1 + z_0) \right),$$

where $z_1$ is the position of the head group along the $z$ direction in the rectangular coordinate, and $z_0$ is the projected bond length to the $z$ direction: $z_0 = \sigma_{12} \cos \theta_0$.

![Figure 5.5: Coordinate transformation from rectangular to spherical coordinate.](image)

Plugging Eqn. 5.9 and 5.13 back to the expression of $X_A^1$ (5.7) produces:

$$\ln X_A^1(z_1) = -\frac{\mu_{2,\text{bulk}}}{k_B T} - K_C - \frac{1}{2} \ln \left( y^{12}(z_1) y^{12}(z_2) \right) + \frac{\mu_{0,2}^{\text{res}}(z_2)}{k_B T}$$

$$- \sum_j \frac{v_{2j}}{k_B T} \frac{d^2 \rho_j}{dz^2}(z_2) - \Psi_2(\mathbf{r}_2),$$

(5.14)

in which, $K_C = \ln(K/4\pi \sigma^2_{12})$ is a constant.
With Eqn. 5.14, Eqn. 5.6a for surfactant groups can be expanded as:

\[
\frac{\mu^\text{chain}_{\beta}(r_\beta)}{k_B T} = -K_C - \frac{1}{2} \ln \left( y_{\text{contact}}^{12}(r_1) y_{\text{contact}}^{12}(r_2) \right) + \frac{\mu^\text{res}_{\alpha}(r_\alpha)}{k_B T} - \frac{\mu^\text{bulk}_{\alpha}}{k_B T} - \sum_j v_{\alpha j} \frac{d^2 \rho_j}{dz^2}(r_\alpha) - \Psi_1(r_1) - \Psi_2(r_2).
\] (5.15)

In bulk phases, the chain chemical potential expression for surfactant groups can be reduced to:

\[
\frac{\mu^\text{chain}_{\beta,\text{bulk}}}{k_B T} = -\frac{1}{2} \left( K_C + \ln y^{12}_{\text{bulk,contact}} + \frac{\mu^\text{id}_{\alpha,\text{bulk}}}{k_B T} + \frac{1}{2} \sum_{i,\gamma} \rho_{\gamma,\text{bulk}} \left( \frac{\partial \ln y^{12}_{\text{bulk,contact}}}{\partial \rho^\text{seg}_{i}} \right) \right).
\] (5.16a)

And for non-surfactant components:

\[
\frac{\mu^\text{chain}_{\beta,\text{bulk}}}{k_B T} = -\frac{1}{2} \sum_{\gamma=1}^2 \rho_{\gamma,\text{bulk}} \left( \frac{\partial \ln y^{12}_{\text{bulk,contact}}}{\partial \rho^\text{seg}_{\beta}} \right).
\] (5.16b)

The bulk Helmholtz free energy due to the chain formation is:

\[
a^\text{chain}_0 \frac{k_B T}{k_B T} = \frac{1}{2} \sum_{\gamma=1}^2 \rho_{\gamma,\text{bulk}} \left( 1 - K_C - \ln y^{12}_{\text{bulk,contact}} - \frac{\mu^\text{id}_{\gamma,\text{bulk}}}{k_B T} \right).
\] (5.17)

5.2 Numerical methods for modified DGT equations

5.2.1 SDGT algorithm for modified DGT equations

With the modified DGT model, we can write down the grand potential energy \( \Omega[\rho] \) of the system as:

\[
\Omega[\rho] = \int \left( a_0[\rho(r)] + \sum_{i=1}^N \sum_{j=1}^N \frac{1}{2} v_{ij} \nabla \rho_i(r) \cdot \nabla \rho_j(r) + a^\text{chain} - \sum_{i=1}^N \rho_i \mu_i^\text{bulk} \right) d^3 r. \] (5.18)

Minimizing the grand potential energy in an open system while applying the time evolution term \[131\] leads to the Euler-Lagrange equations on a planar interface as:

\[
\frac{\partial \rho_i}{\partial t} + \mu_{0,i}(\rho) + \mu_i^\text{chain}(\rho) - \sum_{j=1}^N v_{ij} \frac{d^2 \rho_j}{dz^2} - \mu_i^\text{bulk} = 0 \quad \text{for } i = 1, \ldots, N,
\] (5.19)
subjected to the following initial conditions and boundary conditions on a domain of size $D$:

$$\begin{aligned}
I.C. : & \quad \rho_i(0, z) = \rho_{i,A} + \frac{\rho_{i,B} - \rho_{i,A}}{D} z, \\
B.C. : & \quad \rho_i(s, 0) = \rho_{i,A}, \quad \rho_i(s, D) = \rho_{i,B} \quad \text{for } i = 1, \ldots, N.
\end{aligned}$$

(5.20)

Since the density profiles of the head group and the tail group are symmetric with a shift of $z_0 = \sigma_{12} \cos \theta_0$ in space, one differential equation for either head or tail group needs to be solved instead of two. The differential equation for the head group (1) is chosen as an example in the following illustrations.

Let $\Delta s_t$ denote the time step size from time level $t$ to $t + 1$. Discretizing Eqn. 5.19 for head group in time while applying the convex–concave splitting (3.17) yields:

$$\begin{aligned}
\frac{\rho_{1}^{t+1} - \rho_{1}^{t}}{\Delta s_t}(z) & + \mu_{0,1}^{\text{convex}}[\rho_{1}^{t+1}(z)] + \mu_{0,1}^{\text{concave}}[\rho_{1}^{t}(z)] \\
& + \mu_{1}^{\text{chain}}[\rho_{1}^{t+1}(z + z_0), \rho_{1}^{t}(z + z_0), \rho_{1}^{t}(z)] - \mu_{1,\text{bulk}} - \sum_{j=1}^{N} v_{1j} d^2 \rho_{1}^{t+1} dz(2)(z) = 0,
\end{aligned}$$

where $z$ represents the position of the head group in the interface, and $z + z_0$ represents the position of the tail group. $\mu_{1}^{\text{chain}}$ is given by:

$$\begin{aligned}
\mu_{1}^{\text{chain}}[\rho_{1}^{t+1}(z + z_0), \rho_{1}^{t}(z + z_0), \rho_{1}^{t}(z)] \\
= -\frac{1}{2} k_B T \ln \left( y_{12}(z) y_{12}(z + z_0) \right) - \mu_{2,\text{bulk}} + \mu_{0,2}^{\text{convex, res}}[\rho_{1}^{t+1}(z + z_0)] \\
& + \mu_{0,2}^{\text{concave}}[\rho_{1}^{t}(z + z_0)] - \sum_{j=1}^{N} v_{2j} d^2 \rho_{j}^{t+1} dz(2)(z + z_0) - k_B T \left( \psi_{1}^{t}(z) + \psi_{1}^{t}(z + z_0) \right).
\end{aligned}$$

(5.21b)

For non-surfactant components, the time discretization leads to:

$$\begin{aligned}
\frac{\rho_{\beta}^{t+1} - \rho_{\beta}^{t}}{\Delta s_n}(z) & + \mu_{0,\beta}^{\text{convex}}[\rho_{\beta}^{t+1}(z)] + \mu_{0,\beta}^{\text{concave}}[\rho_{\beta}^{t}(z)] - k_B T \psi_{\beta}^{t}(z) \\
& - \mu_{\beta,\text{bulk}} - \sum_{j=1}^{N} v_{\beta j} d^2 \rho_{j}^{t+1} dz(2)(z) = 0.
\end{aligned}$$

(5.21c)
The finite difference method as illustrated in Section 3.2.2 is used to discretize Eqn. 5.21a and Eqn. 5.21c in space. For surfactant head group, we have for every time step $t+1$:

$$\frac{\rho_{1,k}^{t+1} - \rho_{1,k}^t}{\Delta s_t} + \mu_{0,1}^{\text{convex}} [\rho_k^{t+1}] + \mu_{0,1}^{\text{concave}} [\rho_k^t] + \mu_1^{\text{chain}} [\rho_{k+m}^{t+1}, \rho_{k+m,1}^{t+1}, \rho_k^t] - \mu_{1,\text{bulk}} - \sum_{j=1}^{N} v_{1j} \frac{\rho_{j,k-1}^{t+1} - 2\rho_{j,k}^{t+1} + \rho_{j,k+1}^{t+1}}{(\Delta z)^2} = 0,$$  

(5.22a)

in which

$$\mu_1^{\text{chain}} [\rho_{k+m}^{t+1}, \rho_{k+m,1}^{t+1}, \rho_k^t]$$

$$= -k_B T K_C - \frac{1}{2} k_B T \ln(y_{k}^{12} y_{k+m}^{12}) + \mu_{0,2}^{\text{convex, res}} [\rho_{k+m}^{t+1}] + \mu_{0,2}^{\text{concave}} [\rho_{k+m}^t]$$

$$- \mu_{2,\text{bulk}} - \sum_{j=1}^{N} v_{2j} \frac{\rho_{j,k+m-1}^{t+1} - 2\rho_{j,k+m}^{t+1} + \rho_{j,k+m+1}^{t+1}}{(\Delta z)^2} - k_B T (\Psi_{1,k}^{t} + \Psi_{2,k}^{t}),$$

(5.22b)

where $m$ is the number of grid points that the chain spans over: $m = z_0/\Delta z$.

For non-surfactant component $\beta$, discretizing Eqn. 5.21c on space produces:

$$\frac{\rho_{\beta,k}^{t+1} - \rho_{\beta,k}^t}{\Delta s_t} + \mu_{0,\beta}^{\text{convex}} [\rho_k^{t+1}] + \mu_{0,\beta}^{\text{concave}} [\rho_k^t] - \mu_{\beta,\text{bulk}} - k_B T \Psi_{\beta,k}^{t}$$

$$- \sum_{j=1}^{N} v_{\beta j} \frac{\rho_{j,k-1}^{t+1} - 2\rho_{j,k}^{t+1} + \rho_{j,k+1}^{t+1}}{(\Delta z)^2} = 0,$$  

(5.22c)

subjected to the initial conditions $\rho_{\beta,k}^1 = \rho_{\beta}(0,z_k)$ for $k = 0, \ldots, M+1$, and boundary conditions $\rho_{\beta,0}^{t+1} = \rho_{\beta,A}$, $\rho_{\beta,M+1}^{t+1} = \rho_{\beta,B}$ for all time level.

Due to the symmetric structure of the surfactant molecule, the head group density at position $M-m+1 < k \leq M+1$ is equal to the density of its connected tail group, which locates in the bulk phase as illustrated in Figure 5.6. Therefore, the densities of the head group in this area are constants:

$$\rho_{1,k} = \rho_{2,\text{bulk}} \quad \text{for} \quad k = M-m+2, \ldots, M+1.$$  

(5.23)
Figure 5.6: The head group densities are constants in the region where $M - m + 1 < k \leq M + 1$.

On each time step, the fully discretized equations (5.22) can be solved using Newton’s method to generate $\rho_{i,k}^{t+1}$ for $i = 1, 2, ..., N$ and $k = 0, 1, ..., M + 1$. The system reaches an equilibrium state when either of the following stopping criteria is satisfied: $\sum_i ||\rho_i^n - \rho_i^{n+1}||_{L^2} \leq \varepsilon_{\text{diff1}}$ or $|{(\Omega^n - \Omega^{n+1})/\Omega^n}| \leq \varepsilon_{\text{diff2}}$. We use $\varepsilon_{\text{diff1}} = 1e^{-2}$ mol/m$^3$ and $\varepsilon_{\text{diff2}} = 1e-6$ in this work. Detailed discussions about the Newton’s method as well as the stopping criteria could be found in Section 3.2.2.

### 5.2.2 Fast Fourier transform for convolution integrals

When solving the modified DGT equations, the integrals in the expression of the weighted density (5.5) as well as in $\Psi_\beta(r_\beta)$ (5.6b) need to be evaluated. By converting the boundary of integration involved, the weighted density expression can be transformed to a linear convolution between the density profile and the Heaviside step function:

$$\rho_{\text{seg}}^\beta(r) = \frac{3}{4\pi(\sigma_\beta)^3} \int_{|r - r_1| < \sigma_\beta} \rho^\text{seg}_\beta(r_1) dr_1$$

$$= \frac{3}{4\pi(\sigma_\beta)^3} \int \Theta(|r - r_1| - \sigma_\beta) \rho^\text{seg}_\beta(r_1) dr_1.$$  \hfill (5.24)

The integrals $\Psi_\beta(r_\beta)$ can be expanded using the chain rule as:

$$\Psi_\beta(r_\beta) = \int \rho^\text{seg}_\gamma(r) \frac{\partial \ln y_{12}^{\text{contact}}}{\partial \rho^\text{seg}_\beta(r)} \frac{\delta \rho^\text{seg}_\beta(r)}{\delta \rho^\text{seg}_\beta(r_\beta)} dr,$$  \hfill (5.25)

in which, the functional derivative of the weighted density to local density results in
a Heaviside step function:

\[ \frac{\delta \rho_{\beta}^{seg}(r)}{\delta \rho_{\beta}^{seg}(r_1)} = \frac{3}{4\pi(\sigma_{\beta})^3} \Theta(|r - r_1| - \sigma_{\beta}). \] (5.26)

Plugging Eqn. 5.26 back to the expression of \( \Psi_{\beta}(r_{\beta}) \) yields:

\[ \Psi_{\beta}(r_{\beta}) = \frac{3}{4\pi(\sigma_{\beta})^3} \int \Theta(|r - r_1| - \sigma_{\beta}) \rho_{\gamma}^{seg}(r) \frac{\partial \ln y_{\text{contact}}^{12}(r)}{\partial \rho_{\beta}^{seg}(r_{\beta})} \, dr. \] (5.27)

The convolution integrals Eqn. 5.24 and Eqn. 5.27 can be computed efficiently using the fast Fourier transform (FFT). We use the weighted density calculation as an example here to explain the FFT process.

Applying FFT to the two terms in the integral of Eqn. 5.24 gives:

\[ \Theta(|r - r_1| - \sigma_{\beta}) \xrightarrow{FFT} \hat{\Theta}(k) \quad (A), \]
\[ \rho_{\beta}^{seg}(r_1) \xrightarrow{FFT} \hat{\rho}_{\beta}^{seg}(k) \quad (B), \] (5.28)

where the Fourier transform of the Heaviside function (A) has an analytical expression [138]:

\[ \hat{\Theta}(k) = \frac{4\pi}{|k|^3} \sin(|k|\sigma_{\beta}) - \sigma_{\beta}|k| \cos(|k|\sigma_{\beta}). \] (5.29)

Performing the inverse FFT to the product of 5.28 (A) and (B) generates the results of the convolution integration directly:

\[ \frac{3}{4\pi(\sigma_{\beta})^3} \cdot \hat{\Theta}(k) \cdot \hat{\rho}_{\beta}^{seg}(k) \xrightarrow{iFFT} \tilde{\rho}_{\beta}^{seg}(r). \] (5.30)

The FFT package in MATLAB is used to conduct the FFT and inverse FFT calculations. FFT can significantly speedup the convolution integral calculations: for \( N \) mesh points, the time complexity of regular quadrature method for computing convolution is \( O(N^2) \), whereas the time complexity for FFT is \( O(N \log N) \). Further speedup is obtained by realizing that the Heaviside step function has a closed form in Fourier space as given by Eqn. 5.29. Therefore the overall speedup in time complexity is larger than \( O(N/\log N) \).
5.3 Applications of the modified DGT model

5.3.1 Density profile calculations

In this section, the modified DGT model is implemented for interfacial property calculations of a water/hexane/surfactant mixture system. The surfactant molecule, as illustrated in Figure 5.3, is a toy model that is constructed by bonding a water head to a hexane tail.

In the first test system, water and hexane form a liquid-liquid equilibrium system at 293.15 K, 1.01 bar, and the mole fraction of surfactant in the aqueous phase is set to be $5 \times 10^{-6}$. The setup of the systems initial condition is shown in Figure 5.7a. To make sure the boundary conditions do not change after the weighted density evaluation, bulk densities are extended outward by $m$ points, which form the flat density profiles on both sides. Starting from a small time step $\Delta s = 1 \times 10^{-5}$, the calculation is accelerated by the “time adaptation scheme” (Section 3.2.2), which increases the time step length based on Newton solver’s performance. It can be observed that slight changes of density profiles from Figure 5.7a to Figure 5.7b take a rather long time (150 time steps), and the time step length increases quickly from $s = 180$, which dramatically accelerates the calculation as shown from Figure 5.7c to Figure 5.7f.

In the equilibrium density profiles (Figure 5.7f), the surfactant has relatively low concentrations in both bulk phases, while it has significant accumulations in the interface. Instead of having a single surfactant density profile as given by the conventional DGT model, the modified DGT model generates density profiles for the surfactant head group (red dash line) and the tail group (green dot line) respectively. The amphiphilic character of the surfactant is also well described that its head group prefers the water rich phase, while the tail group preferring the oil rich phase.
Figure 5.7: Density profiles convergence history of the water/hexane/$H_1T_1$ surfactant system at 293.15 K, 1.01 bar.

5.3.2 The surfactant concentration effect

In the second test, different amounts of surfactant are added into the aqueous phase such that the mole fraction $x_s=1e-8, 1e-7, 1e-6$ and $5e-6$. The equilibrium density profiles are calculated and displayed in Figure 5.8. From extra low to relatively high surfactant concentrations, the interfacial accumulation of the surfactant is enhanced as the density profile peak grows higher. This is because more surfactant molecules move to the interface as the bulk concentration increases.

On the basis of the equilibrium density profiles, the system interfacial tension
Figure 5.8: Equilibrium density profiles of the water/hexane/surfactant system at 293.15 K, 1.01 bar with different surfactant mole fraction in the water phase.

(IFT) can be evaluated using the following equation:

$$\gamma = \frac{\Omega - \Omega_{\text{bulk}}}{A_s}$$

$$= k_B T \sum_{\beta=1}^{N} \int_0^D \rho_\beta(z) \left( D_\beta(z) + \frac{n(\Gamma(\beta))}{2} - 1 \right) dz + \int_0^D (a^{\text{res}} + P_0) dz,$$

(5.31)

in which, $A_s$ is the surface area, $n(\Gamma(\beta))$ is the total number of bonding sites on segment $\beta$, $P_0$ is the system pressure, and $a^{\text{res}}$ is the inhomogeneous residual Helmholtz.
free energy:

\[ a^\text{res} = a_0^\text{res} + \sum_{i,j=1}^{N} \frac{1}{2} v_{ij} \nabla \rho_i \cdot \nabla \rho_j. \]  

(5.32)

Figure 5.9: IFT results of the water/hexane/\(H_1T_1\) surfactant system as a function of the surfactant concentration at 293.15 K, 1.01 bar. Blue square is the experimentally measured IFT of water/hexane mixture without surfactant [129].

The selection of the domain size \(D\) will not affect the IFT calculation results as long as it is larger than the interface thickness, since the surface excess grand potential energy equals to zero in the bulk region. The IFT calculation results at 293.15 K, 1.01 bar are depicted in Figure 5.9. The system IFT decreases as more surfactant molecules are added into the system. This can be explained in combination with the density profile behaviors: more surfactant molecules move to the interface at higher surfactant bulk concentrations, and they squeeze the solvent molecules away, reducing the effective contact area for water and oil interactions while increasing water/head
group and oil/tail group interactions. As a result, the IFT of the system decreases [64]. At ultra low surfactant concentration, the modified DGT model reproduces the IFT of water/hexane system without surfactant (the blue square in Figure 5.9), which matches with the experimental data [129].

![Figure 5.10](image)

Figure 5.10: The tail length effect on surfactant performances: the surfactant is more effective with a longer tail.

5.3.3 Tail length effect

In previous calculations, segment number $m_i=3.0576$ (same as hexane) is assigned to the tail group. To study the impact of different tail lengths, segment number $m=1, 2, 3$ and 4 are assigned to the tail group, which is equivalent to having $C_1$, $C_3$, $C_6$ and $C_9$ as tail groups in the surfactant. The IFT results of adding surfactants with varying tail length are displayed in Figure 5.10. In order to achieve the same level
of IFT reduction, a lower bulk concentration is needed for a longer tail surfactant. This behavior indicates that the surfactant with longer tail length tends to be more effective in reducing IFT, and this is qualitatively consistent with experimental measurements [139, 140].

According to Traube’s rule [141], the surface activity of the surfactant triples for every extra $CH_2$ group. This is reflected in Figure 5.10 where the four curves have roughly equal distances on the logarithmic axis. The successful description of the tail length impact makes the modified DGT model a promising tool to guide the selection of surfactant for different chemical processes.
Chapter 6

Surface free energy and wetting boundary conditions

When a solid wall appears in the system, the interactions between the solid and liquid would affect fluids’ properties, and thus results in surface phenomena, such as adsorption [142], wetting & non-wetting [143] and so on.

In the classical DFT model [142, 144, 145], the solid-liquid interaction has been extensively studied by having an external potential energy $V_{\text{ext}}$ in the grand potential energy functional:

$$\Omega = A - \int_V \sum_i \rho_i (\mu_i,_{\text{bulk}} + V_{\text{ext}}).$$  \hspace{1cm} (6.1)

Minimizing the grand potential energy leads to the Euler-Lagrange equation:

$$\frac{\delta \Omega}{\delta \rho_i} = \frac{\delta A}{\delta \rho_i} - \mu_i,_{\text{bulk}} - V_{\text{ext}} = 0,$$  \hspace{1cm} (6.2)

the solution of which is the density profile of component $i$ close to a solid wall.

For homogeneous wall, the external potential is a function of the distance to the wall and the fluids’ densities. Models such as the 9-3 potential model proposed by Steele [146] have been widely accepted. In other cases, the wall could be inhomogeneous due to the geometric heterogeneity resulting from the shape, or the energetic heterogeneity resulting from the appearance of active sites that can associate with the fluid molecules. More advanced potential models have been developed to accurately describe the complex solid-fluids interactions in DFT calculations [142].

Teletzke et al. [36] is the only group we find in literature that used the DGT
model to study fluids’ interfacial behaviors near a wall. According to them, the DGT model qualitatively predicted the features of adsorption isotherms, wetting transitions and the contact angle behavior of fluids on solids. However due to the local density approximation, DGT was not able to generate the density profile oscillations like those reported by the classical DFT model.

Using an external potential to describe the solid effects on fluids’ properties has been a standard approach in the DFT model. In fact, other approaches have been developed outside the DFT field, and one example is in the phase field theory. Andreas Carlson in his Ph.D. thesis [143] proposed a surface free energy approach which could be used to represent the energy effect due to the presence of the solid wall. In the phase field theory, a binary system with two incompressible and immiscible phases has the Helmholtz free energy expression as:

\[
A = A_{\text{fluid}} + A_{\text{surface}}
\]

\[
= \int \left( \beta \psi(C) + \frac{\alpha}{2} |\nabla C|^2 \right) dV + \int \left( \gamma_{\text{sg}} + (\gamma_{\text{sl}} - \gamma_{\text{sg}}) g(C) \right) dS,
\]

where

\[
\psi(C) = \frac{1}{4}(C + 1)^2(C - 1)^2
\]

is the double-well potential energy, and

\[
|\nabla C|^2
\]

is the gradient term, where \( C \) is the order parameter varying from -1 to 1. \( \beta \approx \gamma/\epsilon \) and \( \alpha \approx \gamma\epsilon \) are positive phase field parameters which depend on the IFT \( \gamma \) and the interface thickness \( \epsilon \). This part of the Helmholtz free energy is similar to what we have in the DGT model (2.1).

The second term in Eqn. 6.3 accounts for the Helmholtz free energy in contact with the solid wall, in which \( g(C) \) is the surface free energy varying from 0 to 1, and \( \gamma_{\text{sg}} \) and \( \gamma_{\text{sl}} \) are IFTs on the solid–gas and solid–liquid interfaces respectively. In this expression, \( g(C) \) acts as an energy switch between the solid-liquid and solid-gas interfaces: when \( g(C) = 0 \), \( \gamma_{\text{sg}} \) is reproduced while \( \gamma_{\text{sl}} \) is obtained for \( g(C) = 1 \).
The significance of this surface free energy approach is that it provides an easy way to describe the surface effects such as adsorption, contact angle and wetting boundary conditions in the 2D or 3D fluid simulator. Inspired by Carlson, we derive the surface free energy and the corresponding equilibrium wetting boundary conditions based on the DGT model. Compared with the double-well potential model used in the phase field theory, bulk EoS is used in the DGT model, and therefore the model can be applied to multicomponent systems instead of just binary systems. More importantly, the DGT model could produce physical properties of solid-fluid systems that are comparable to real systems.

6.1 Equilibrium wetting boundary conditions

Following the surface free energy approach, the system’s grand potential energy in contact with a solid surface is:

$$\Omega = A_{\text{fluid}} + A_{\text{surface}} - \int \sum_{i} \rho_{i} \mu_{i,\text{bulk}} dV,$$

(6.4)
in which, the DGT free energy function (2.1) is used for the fluid free energy $A_{\text{fluid}}$, and $A_{\text{surface}}$ given as:

$$A_{\text{surface}} = \int \left( \gamma_{sg} + (\gamma_{sl} - \gamma_{sg}) g(\rho) \right) dS,$$

(6.5)
where the surface free energy $g(\rho)$ is the function of each component’s density $\rho_{i}$, instead of the order parameter $C$.

At equilibrium, the grand potential energy is minimized, which leads to Euler-Lagrange equation on a planar surface as:

$$\frac{\delta \Omega}{\delta \rho_{i}} = \mu_{i}(\rho) - \sum_{j=1}^{N} v_{ij} \nabla^{2} \rho_{j} - \mu_{i,\text{bulk}} + (\gamma_{sl} - \gamma_{sg}) \frac{\partial g(\rho)}{\partial \rho_{i}} = 0.$$

(6.6)
According to Young's law [147], the contact angle $\theta$ of a liquid droplet sitting on the solid surface is related to the IFT between different interfaces as:

$$\cos \theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{gl}}.$$  \hspace{1cm} (6.7)

Substituting Eqn. 6.7 into Eqn. 6.6 produces:

$$\mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \nabla^2 \rho_j - \mu_{i,\text{bulk}} - \gamma_{gl} \cos \theta \frac{\partial g(\rho)}{\partial \rho_i} = 0.$$  \hspace{1cm} (6.8)

Integrating the Euler-Lagrange equation over volume [143] produces:

$$\int \left( \mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \nabla^2 \rho_j - \mu_{i,\text{bulk}} - \gamma_{gl} \cos \theta \frac{\partial g(\rho)}{\partial \rho_i} \right) dV = 0,$$  \hspace{1cm} (6.9)

since the surface free energy only contributes on the surface.

The divergence term in the volume integral can be converted to a surface integral using Gauss's theorem:

$$\int \left( - \sum_{j=1}^{N} v_{ij} \nabla \rho_j \right) dV = \int \left( \sum_{j=1}^{N} v_{ij} \nabla \rho_j \cdot n \right) dS,$$  \hspace{1cm} (6.10)

where $n$ is the inward normal vector on the surface. Plugging it back to Eqn. 6.9 yields:

$$\int \left( \mu_i(\rho) - \sum_{j=1}^{N} v_{ij} \nabla^2 \rho_j - \mu_{i,\text{bulk}} \right) dV$$

$$+ \int \left( \sum_{j=1}^{N} v_{ij} \nabla \rho_j \cdot n - \gamma_{gl} \cos \theta \frac{\partial g(\rho)}{\partial \rho_i} \right) dS = 0.$$  \hspace{1cm} (6.11)

At equilibrium, the two integrals equal to 0, and therefore for the surface integral:

$$\sum_{j=1}^{N} v_{ij} \nabla \rho_j \cdot n - \gamma_{gl} \cos \theta \frac{\partial g(\rho)}{\partial \rho_i} = 0.$$  \hspace{1cm} (6.12)
Consider a two-phase fluid in contact with a solid surface as shown in Fig. 6.1. The dash lines mark the diffusive interface region where densities only vary along the $\xi$ direction. Therefore:

$$\nabla \rho_i \cdot n = \left( \frac{\partial \rho_i}{\partial \xi} n_\xi + \frac{\partial \rho_i}{\partial \kappa} n_\kappa \right) \cdot n = \frac{\partial \rho_i}{\partial \xi} n_\xi \cdot n = \frac{\partial \rho_i}{\partial \xi} \cos \theta. \tag{6.13}$$

Plugging Eqn. 6.13 back to Eqn. 6.12 produces the equilibrium wetting boundary condition for a multicomponent system on a 2-D domain as:

$$\sum_{j=1}^{N} v_{ij} \frac{\partial \rho_j}{\partial \xi} - \gamma_g \frac{\partial g(\rho)}{\partial \rho_i} = 0. \tag{6.14}$$

This equilibrium wetting boundary condition defines the contact line of two-phase fluids on a solid substrate. By enforcing this wetting boundary condition, the equilibrium contact angle is imposed between the fluid-fluid interface at the solid boundary.
6.2 Surface free energy

Based on the equilibrium wetting boundary condition, we derive the expression of the surface free energy \( g(\rho) \) in a multicomponent system. In the derivation process, similar ideas from the function manipulation process of the reference fluid algorithm (Section 3.1) are used.

Multiplying Eqn. 6.14 by \( \frac{d\rho_i}{d\xi} \) and summing over \( i \) produces:

\[
\sum_{i=1}^{N} \sum_{j=1}^{N} v_{ij} \frac{d\rho_i}{d\xi} \frac{d\rho_i}{d\xi} - \gamma_{gl} \frac{dg(\rho)}{d\xi} = 0.
\]

In the mixture system, choose one component as the reference fluid and multiply Eqn. 6.15 by \( (d\xi/d\rho_{\text{ref}})^2 \):

\[
\frac{d\rho_{\text{ref}}}{d\xi} C_{\text{ref}} - \gamma_{gl} \frac{dg(\rho)}{d\rho_{\text{ref}}} = 0,
\]

where \( C_{\text{ref}} \) is defined as:

\[
C_{\text{ref}} = \sum_{i=1}^{N} \sum_{j=1}^{N} v_{ij} \frac{d\rho_j}{d\rho_{\text{ref}}} \frac{d\rho_i}{d\rho_{\text{ref}}}.
\]

Substituting the expressions of \( d\rho_{\text{ref}}/d\xi \) from Eqn. 3.5 and \( \gamma \) from Eqn. 3.9 into Eqn. 6.16 generates:

\[
\frac{dg(\rho)}{d\rho_{\text{ref}}} = \frac{\sqrt{2(\omega - \omega_0)}C_{\text{ref}}}{\int_{\rho_{\text{ref}}^A}^{\rho_{\text{ref}}^B} \sqrt{2(\omega - \omega_0)}C_{\text{ref}} d\rho_{\text{ref}}},
\]

in which, \( \omega =: a_0 - \sum_i \rho_i \mu_{i,\text{bulk}} \) and \( \omega_0 = -P_0 \).

Integrating Eqn. 6.18 over the density of the reference fluid \( \rho_{\text{ref}} \) produces the expression of the surface free energy for multicomponent systems:

\[
g(\rho) = \frac{\int_{\rho_{\text{ref}}^A}^{\rho_{\text{ref}}^B} \sqrt{2(\omega - \omega_0)}C_{\text{ref}} d\rho_{\text{ref}}}{\int_{\rho_{\text{ref}}^A}^{\rho_{\text{ref}}^B} \sqrt{2(\omega - \omega_0)}C_{\text{ref}} d\rho_{\text{ref}}},
\]
Chapter 7

DGT software package
7.1 Overview of the PMFS Helper Tool

With the faith that new technology is developed to serve the society, we integrate different DGT models developed in this thesis into a software package with an user-friendly interface. The software is called the PMFS Helper Tool as it was originally designed to generate parameters and IFT information for the Pore-scale Multiphase Fluid Simulator (PMFS). In the later development, the PMFS Helper Tool has been upgraded and optimized so that it can serve as an independent software for phase equilibrium calculations and interfacial property calculations.

The PMFS Helper Tool is programmed in the way that only several easily-assessed parameters as inputs are required from users, and the software would conduct the calculations and detect possible errors automatically. It can be used by engineers to perform fast and accurate calculations for various fluids without requiring much thermodynamics background. The key features of this software include:

1. PC-SAFT EoS and PR EoS for phase equilibrium calculations;
2. The SDGT algorithm for DGT model equations;
3. The DGT model for one and multicomponent systems;
4. The DGT model in open systems and closed systems;
5. The DGT model for systems with planar or spherical interfaces;
6. The modified DGT model for surfactant systems;
7. Free energy plotting and analysis;
8. Computational progress monitoring and plotting;
9. Automatic video and report generation;
10. Automatic warning and error detection and report.
7.2 User interface of the PMFS Helper Tool

7.2.1 Start page

In the start page, user chooses components in the computational system. The software supports calculations for one component as well as multicomponent systems. User could also choose to add surfactant into the systems by clicking the “Add surfactant” button. With selected components in the system, the calculation can be conducted in an “open system”, where the mass exchange is allowed with the outside reservoir, or in a “closed system”, where the total mass in the system is conserved. The two systems would require different inputs in the next step.

Figure 7.1: Start page of the PMFS Helper Tool.
In the next step, system inputs such as system conditions and feed compositions are required. Different systems might require different inputs to initiate the calculation. In the first example (Figure 7.2), methane/ethane/propane/butane/pentane are added into an open system. System conditions including temperature, pressure and domain size are needed. We recommend to use the default domain size given by the software to conduct the first calculation, and adjust the size according to the results. For example, if the calculated interface width is wider than the given domain size, user could input a larger domain size and re-run the calculation. User can also choose the EoS for the calculation. Currently, PC-SAFT EoS and PR EoS are available for
selection.

The DGT calculation would be activated when the “Interfacial Properties” box is checked. Otherwise, only phase equilibrium calculation will be performed. The “Free Energy Analysis” checkbox is for free energy contour plotting as discussed in Section 3.3.5. This feature is available for pure systems or binary mixtures only.

For mixtures, feed compositions of each component are needed. The input compositions need to be added up to 1, or the software would normalize the numbers. Binary interaction parameters $k_{ij}$ and $\beta_{ij}$ are needed for mixtures. Default values are given by the software, and user can also modify these values.

Figure 7.3: Input page of the PMFS Helper Tool: example 2.

In the second example (Figure 7.3), methane/propane are added into a closed system. For this system, user can choose the type of interfaces (planar or spherical).
Besides domain size, user can also specify the number of grids for discretization, which provides more flexibility in the calculation. For a closed system, it is required to specify the total mass of each component instead of just the feed composition. Table 7.1 summarizes the input requirements for all different systems available in the software.

Figure 7.4 : Result page of the PMFS Helper Tool.
Table 7.1: Input requirements of the PMFS Helper Tool.

<table>
<thead>
<tr>
<th>System type</th>
<th>Interface type</th>
<th>Temperature</th>
<th>Pressure</th>
<th>Feed composition</th>
<th>Domain size</th>
<th>Grid points</th>
<th>Average density</th>
<th>Left boundary density</th>
</tr>
</thead>
<tbody>
<tr>
<td>One component, Open</td>
<td>Planar</td>
<td>√</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Multicomponent, Open</td>
<td>Planar</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>One component, Closed</td>
<td>Planar</td>
<td>√</td>
<td>–</td>
<td>–</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Multicomponent, Closed</td>
<td>Planar</td>
<td>√</td>
<td>–</td>
<td>–</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>One component, Closed</td>
<td>Spherical</td>
<td>√</td>
<td>–</td>
<td>–</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Multicomponent, Closed</td>
<td>Spherical</td>
<td>√</td>
<td>–</td>
<td>–</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
</tr>
<tr>
<td>Surfactant system, Open</td>
<td>Planar</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
7.2.3 Results page

In the results page (Figure 7.4), user could check the system setups, and may modify them by clicking the “Back” button to previous pages. If all inputs are confirmed, click the “Calculate” button, and the software will run the calculations. The computational progress and any warnings/errors messages will be displayed in the information panel.

Figure 7.5 : Density profiles and computational progresses displayed during the calculation.

During the calculation, density profiles and the performance of the numerical algorithm will be monitored and displayed in a figure. For example, Figure 7.5 shows
the convergence history of a mixture with C1 to C5 in an open system. The top left panel displays the density profiles of each component. The rest three plots are corresponding to the three iteration stopping criteria as introduced in Section 3.2: the top right panel shows the Newton iteration times (blue line) and the time step length (green line) on each time level. The bottom left panel displays the energy dissipating process during the convergence, and the bottom right panel indicates the density differences between two time steps. The figure on each time level will be automatically collected, and written into a video file.

At the end of the calculation, results will be displayed in the right section of the results page. Also, the software would export all inputs, results and figures to an Excel file for future references.

7.3 Applications of the PMFS Helper Tool

One practical application of this software was during 2017 American Institute of Chemical Engineers (AIChE) Annual conference. Dr. Ross Taylor from Clarkson University brought his research interest about modeling the distillation process, in which the IFT is a key property that needs to be calculated frequently. Therefore, a fast and accurate IFT model is required for the distillation process modeling. Dr. Taylor presented the IFT prediction results using correlation functions, which are very fast in computation, but have quite bad accuracy. He also showed MD simulation results, which is quite accurate, but would take hundreds of years to finish all the repeating calculations in one distillation tower.

We used the PMFS Helper Tool to conduct IFT calculations for two systems that he had data for, which are nitrogen/methane mixture at 91 K, and methane/propane mixture at 303.15 K, and the IFT calculation results were compared with experi-
mental data in Figure 7.6. Without further tuning or parameter fitting, the software produced excellent IFT predictions for both mixtures. More importantly, each calculation took roughly 20 seconds, which is much shorter compared with the MD simulation. The excellent performance of the PMFS Helper Tool in these calculations makes it a potential choice for applications in the distillation calculations.

Figure 7.6: IFT results of nitrogen/methane and methane/propane mixtures: dash lines are PMFS Helper Tool calculation results, and markers are experimental data from Dr. Ross Taylor, Clarkson University.
Chapter 8

Concluding remarks

8.1 Summary

In this work, we presented our extensions and applications of the density gradient theory (DGT) model in many different ways to meet various IFT calculation requirements.

Firstly, by realizing the limitations of the established reference fluid (RF) algorithm, we developed the stabilized density gradient theory (SDGT) algorithm, in which an evolution term was introduced to the original Euler-Lagrange equation so that it can be solved steadily with a time marching scheme. The performance of the DGT model with the SDGT algorithm was investigated by comparing the IFT calculations results with experimentally measured IFT data in many pure and mixed systems. Remarkable agreements were achieved in a wide temperature and pressure range. The numerical stability of the SDGT algorithm was tested by using extreme boundary and initial conditions such as random initial guesses and overestimated/underestimated domain sizes, which are potential risks of failing calculations in practice. Compared with the RF algorithm, the SDGT algorithm was proved to be a more general and straightforward approach to solve the DGT type of equations, and it paved the way for the next-step DGT model extensions.

Secondly, we extended the conventional DGT model from open systems to closed systems, in which the number of particles are fixed. By implementing a mass con-
ervation term $\lambda_i$ and no-flux boundary condition, we were able to enforce a rigorous canonical ensemble system in simulations. The mass-conserved DGT model has been proved to conserve mass while dissipating the Helmholtz free energy over time. With this new model, we have successfully calculated the interfacial properties in closed systems, in particular a spherical system in which nucleation process takes place. From the calculation results, we: (I) validated the mass conservation feature of the new model; (II) demonstrated that no explicit phase equilibrium calculations were needed in the new model, while it still delivered accurate equilibrium bulk density predictions; (III) showed that the pressure in the droplet is much higher than that in the planar interface system at the same condition, and will reduce to the same level at sufficiently large droplet radius; (IV) showed that the droplet IFT would increase sharply and then decrease as the radius grows from infinitely small to infinitely large, which indicated a negative Tolman length.

Thirdly, we developed a modified DGT model with an additional chain formation free energy term which can be used to describe surfactant systems. The chain formation free energy, derived based on the iSAFT work, served as the free energy contribution to describe the heteronuclear chain structure of surfactant molecules. With the help of the SDGT algorithm and the PC-SAFT EoS, the modified DGT model has been successfully applied in a water/hexane/surfactant system, in which the surfactant molecule is modeled by bonding a water-like head group with a hexane-like tail group. The density profiles as well as IFT of the surfactant system were calculated and compared with theories and experimental data at different conditions. The surfactant bulk concentration effect and the surfactant tail length effect on surfactant effectiveness were studied as well.

Fourthly, we derived a surface free energy function, which could replace the exter-
nal potential approach in describing the free energy contribution at close to the solid wall. The corresponding equilibrium wetting boundary condition could help define the contact angle on the wall for a 2D or 3D fluid flow model.

Fifthly, we introduced the PMFS Helper Tool, which is a software that combined different DGT models developed in our work. The software was designed for easy operations by engineers. In the current version, 14 different components and surfactant are available in the database, and the calculations can be conducted in open or closed systems, on planar or spherical interfaces.

8.2 Future work

Based on the progress of the model development and model application, we propose several topics that could be built upon the current work.

8.2.1 Nucleation of multicomponent systems

In Chapter 4, we developed the mass-conserved DGT model for IFT calculations in the nucleation process, and have applied it to one component systems. For the next step research, we are interested in applying this model to multicomponent nucleation processes, since droplet of mixtures are frequently encountered in industrial and experimental processes. For example, Braun et al. [148] used MD simulation to model the nucleation process of binary methane/nonane mixture. They observed the enrichment of methane molecules at the interface region, and they also found that the mole fraction of methane in the cluster is a lot higher than that in the bulk liquid phase at the same temperature and pressure. These microscopic details have great effect on the system IFT and hence affect the nucleation rate. The mass-conserved DGT model could be used to study the multicomponent nucleation process.
8.2.2 Verification of the droplet IFT calculation results

The IFT results for droplet were only qualitatively discussed in the current work. In the future work, we plan to quantitatively verify the IFT calculation results. Due to the difficulties of obtaining experimentally measured IFT data for nano-scale droplet, we would expect the comparison with calculation results from DFT model or MD simulations.

8.2.3 Verification of the surfactant IFT calculation results

In Chapter 5, the modified DGT model was developed for surfactant systems. In the test phase, we used a toy model for surfactant molecule which is formed by bonding a water molecule with a hexane molecule. In the next step research, we plan to apply the modified DGT model in a real nonionic surfactant system. One example of surfactant molecule is nonylphenol as shown in Fig. 8.1. According to the modified DGT model, the nonylphenol molecule can be constructed by bonding a phenol molecule (head group) with an iso-nonane molecule (tail group). With the PC-SAFT parameters of phenol and iso-nonane, as well as the binary interaction parameters, this surfactant molecule should readily be modeled by the modified DGT model.

8.2.4 Extensions of the surfactant model

In the development of the modified DGT model for surfactant, we made several assumptions that could be relaxed in the future model development:

- The current surfactant molecule is formed by bonding one head group and one tail group. This assumption can be relaxed to have more groups bonded together.
• The orientation of the surfactant molecule in the interface region is fixed in the current model. This assumption can be relaxed to let each surfactant molecule rotate in space to find its best orientation.

8.2.5 Micelle formation

When added into water/oil mixtures, surfactant molecules would participate at the interface region. As the concentration rises, surfactant would eventually self-assemble to form micelles [149]. The surfactant concentration at which micelles start to form is called the critical micelle concentration (CMC). After this concentration, the system’s IFT would not decrease with more surfactant being added into the system. Studying the micelle formation has been a challenging topic. In the past, Wang et al. made a progress in this field by using the iSAFT model in micelle modeling [65]. In our work, the modified DGT model makes it possible to study surfactant systems, and the mass-conserved DGT model could handle spherical systems. By combing these two DGT models together, we could study the micelle system, especially to capture the CMC point in a surfactant system.
# List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$</td>
<td>J</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>$A_s$</td>
<td>$m^2$</td>
<td>Surface area</td>
</tr>
<tr>
<td>$a_i$</td>
<td>$Jm^3/mol^2$</td>
<td>Peng-Robinson parameter $a_i$</td>
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<td>$a_0$</td>
<td>$J/m^3$</td>
<td>Homogeneous Helmholtz free energy density</td>
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<td>Ideal gas contribution to $a_0$</td>
</tr>
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<td>Residual free energy contribution to $a_0$</td>
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<td>$D$</td>
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<td>$\Delta^{(1,2)}$</td>
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</tr>
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<td>$M_o$</td>
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<td>Mobility coefficient</td>
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<td>Ideal gas chemical potential of comp. $i$</td>
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<td>$n$</td>
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<td>$P_c$</td>
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<td>An integral abbreviation defined in Eqn. 5.6b</td>
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<tr>
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<td>J/(mol K)</td>
<td>Gas constant</td>
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<td>$R_e$</td>
<td>m</td>
<td>Radius of the Gibbs dividing surface</td>
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<td>$R_s$</td>
<td>m</td>
<td>Radius of the surface of tension</td>
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<td>$\rho$</td>
<td>mol/m$^3$</td>
<td>Density vector of all components</td>
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<td>$s$</td>
<td>mol$^2$/(J m$^3$)</td>
<td>Pseudo time</td>
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\( \sigma_i \)  \( m \)  Segment diameter of comp. \( i \)  
\( T \)  \( K \)  Temperature  
\( T_c \)  \( K \)  Critical temperature  
\( T_r \)  \( 1 \)  Reduced temperature  
\( t \)  \( s \)  Time variable  
\( V \)  \( m^3 \)  Volume domain  
\( \partial V \)  \( m^2 \)  Boundary of domain \( V \)  
\( V_c \)  \( m^3/mol \)  Volume translation parameter in VTPR EoS  
\( V^{\text{ext}} \)  \( J/mol \)  External potential between solid and fluid  
\( V_m \)  \( m^3/mol \)  Molar volume  
\( v_i \)  \( Jm^5/mol^2 \)  Influence parameter of comp. \( i \)  
\( v_{ij} \)  \( Jm^5/mol^2 \)  Influence parameter matrix  
\( X^{A_i} \)  \( 1 \)  Fraction of comp. \( i \) that is not bonded at site \( A_i \)  
\( x_i \)  \( 1 \)  Mole fraction of comp. \( i \)  
\( y_{\text{contact}} \)  \( 1 \)  Cavity correlation function at contact  
\( z \)  \( m \)  Distance

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
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<tbody>
<tr>
<td>AIChE</td>
<td>American Institute of Chemical Engineers</td>
</tr>
<tr>
<td>APACT</td>
<td>Associated Perturbed Anisotropic Chain Theory</td>
</tr>
<tr>
<td>AAD</td>
<td>Average absolute deviation</td>
</tr>
<tr>
<td>B.C.</td>
<td>Boundary condition</td>
</tr>
<tr>
<td>BVP</td>
<td>Boundary value problem</td>
</tr>
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<td>CNT</td>
<td>Classical nucleation theory</td>
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<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>C$_1$E$_1$</td>
<td>2-methoxyethanol</td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DGT</td>
<td>Density gradient theory</td>
</tr>
<tr>
<td>EOR</td>
<td>Enhanced oil recovery</td>
</tr>
<tr>
<td>EoS</td>
<td>Equation of state</td>
</tr>
<tr>
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<td>Fast Fourier transform</td>
</tr>
<tr>
<td>iFFT</td>
<td>Inverse Fast Fourier transform</td>
</tr>
<tr>
<td>I.C.</td>
<td>Initial condition</td>
</tr>
<tr>
<td>IFT</td>
<td>Interfacial tension</td>
</tr>
<tr>
<td>IFPSC</td>
<td>Industrial Fluid Properties Simulation Challenge</td>
</tr>
<tr>
<td>iSAFT</td>
<td>Inhomogeneous statistical associating fluid theory</td>
</tr>
<tr>
<td>LLE</td>
<td>Liquid-liquid equilibrium</td>
</tr>
<tr>
<td>MD</td>
<td>Molecular dynamics</td>
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<tr>
<td>MVDW</td>
<td>Modified van der Waals</td>
</tr>
<tr>
<td>ODE</td>
<td>Ordinary differential equation</td>
</tr>
<tr>
<td>PDE</td>
<td>Partial differential equation</td>
</tr>
<tr>
<td>PC-SAFT</td>
<td>Perturbed-chain statistical associating fluids theory</td>
</tr>
<tr>
<td>PCP-SAFT</td>
<td>Perturbed-chain polar statistical associating fluids theory</td>
</tr>
<tr>
<td>PR</td>
<td>Peng-Robinson</td>
</tr>
<tr>
<td>RF</td>
<td>Reference fluid</td>
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<td>SRK</td>
<td>Soave–Redlich–Kwong</td>
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<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>SAFT</td>
<td>Statistical associating fluid theory</td>
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<td>SAFT VR-Mie</td>
<td>SAFT of variable range employing a Mie potential</td>
</tr>
<tr>
<td>SDGT</td>
<td>Stabilized density gradient theory</td>
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<tr>
<td>TPT1</td>
<td>Thermodynamic perturbation theory of first order</td>
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<td>vdw</td>
<td>van der Waals</td>
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<td>VLE</td>
<td>Vapor-liquid equilibrium</td>
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<td>VTPR</td>
<td>Volume translated Peng-Robinson</td>
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Appendix A

Derivations of density gradient theory

In this section, we document the derivations to the DGT free energy functions based on the modified van der Waals (MVDW) model. The derivations are summarized from the work of Davis [84] and Carey [14].

In thermodynamics, the Helmholtz free energy $A$ is defined as:

$$A = U - TS$$

$$= \int_V (u - Ts)dr,$$

(A.1)

where $U$ is the internal energy of the system, $T$ is the temperature, $S$ is the entropy of the system, and $r$ is the position vector.

In the MVDW model, there are two important assumptions:

Assumption 1: The entropy of an inhomogeneous fluid can be approximated by:

$$S = \int_V s_0[\rho(r)]dr,$$

(A.2)

where $s_0$ is the entropy density of a homogeneous fluid at density $\rho$.

Assumption 2: The pair correlation function $g(r, r')$ can be approximated by that of a homogeneous fluid $\bar{\rho}$ related to the local densities in the vicinity of the correlated pair. Therefore, the internal energy of the inhomogeneous fluid becomes:

$$u[\rho(r)] = u_{0}^{id}[\rho(r)] + \frac{1}{2} \int_{V'} \rho(r)\rho(r')g_0(|r - r'|, \bar{\rho})u_{\text{inter}}(|r - r'|)dr',$$

(A.3)

where $u_{0}^{id}$ is the homogeneous thermodynamic contributions from an ideal gas, $g_0(|r - r'|, \bar{\rho})$ is the pair-correlation function of homogeneous fluid at density $\bar{\rho}$, and $u_{\text{inter}}(|r - r'|)$ is the inter-particle potential.
For a homogeneous fluid, in which \( \rho(r) = \rho(r') \), the internal energy can be simplified to:

\[
    u_0[\rho(r)] = u_0^{id}[\rho(r)] + \varpi(r),
\]

where \( \varpi(r) \) is defined as:

\[
    \varpi(r) = \frac{1}{2} n^2 \int_V g_0(|r - r'|, \bar{\rho}) u_{\text{inter}}(|r - r'|) \, dr' ,
\]

in which, \( n = \int_V \rho(r) \, dr \) is the total number of particles in the system.

With the expression of \( S \) and \( u \) from Eqn. A.2 and A.3, the inhomogeneous Helmholtz free energy can be written as:

\[
    A = \int_V (u - Ts) \, dr
    = \int_V \left( u_0^{id}[\rho(r)] + \frac{1}{2} \int_{V'} \rho(r) \rho(r') g_0(|r - r'|, \bar{\rho}) u_{\text{inter}}(|r - r'|) \, dr' - Ts_0 \right) \, dr
    = \int_V \left( u_0^{id}[\rho(r)] + \varpi(r) - \varpi(r) - Ts_0 \right) \, dr
    \quad + \frac{1}{2} \int_V \int_{V'} \rho(r) \rho(r') g_0(|r - r'|, \bar{\rho}) u_{\text{inter}}(|r - r'|) \, dr' \, dr
    = A_0 + \frac{1}{2} \int_V \int_{V'} \left[ \rho(r) \rho(r') - \rho^2(r) \right] g_0(|r - r'|, \bar{\rho}) u_{\text{inter}}(|r - r'|) \, dr' \, dr,
\]

where \( A_0 = \int_V a_0[\rho(r)] \, dr = \int_V (u_0[\rho(r)] - Ts_0) \, dr \) is the homogeneous Helmholtz free energy.

Inside the integration of Eqn. A.6, \( \rho \) and \( \rho' \) are exchangeable. Therefore we rewrite the inhomogeneous Helmholtz free energy \( A \) such that:

\[
    A = A_0 + \frac{1}{2} \int_V \int_{V'} \left[ \rho(r) \rho(r') - \frac{1}{2} \rho^2(r) - \frac{1}{2} \rho^2(r') \right] g_0(|r - r'|, \bar{\rho}) u_{\text{inter}}(|r - r'|) \, dr' \, dr .
\]
For multicomponent systems, the inhomogeneous Helmholtz free energy becomes:

\[ A = A_0 + \sum_{i,j} \frac{1}{2} \int_V \int_{V'} \left[ \rho_i(r) \rho_j(r') - \frac{1}{2} \rho_i(r) \rho_j(r) - \frac{1}{2} \rho_i(r') \rho_j(r') \right] \times g_{ij}(|r - r'|, \bar{\rho}) u_{ij}(|r - r'|) \, dr \, dr' \]

\[ = A_0 - \frac{1}{4} \sum_{i,j} \int_V \int_{V'} \left[ \rho_i(r) - \rho_i(r') \right] \left[ \rho_j(r) - \rho_j(r') \right] \times g_{ij}(|r - r'|, \bar{\rho}) u_{ij}(|r - r'|) \, dr \, dr' \]  \hspace{1cm} (A.8)

If density varies slowly over the order of the range of \( u_{ij} \), we can expand the density \( \rho_i(r') \) in Taylor series around \( \rho_i(r) \) till the third order:

\[ \rho_i(r') = \rho_i(r) + (r' - r) \nabla \rho_i(r) + \frac{1}{2} (r' - r)^2 \nabla^2 \rho_i(r) + O(\nabla^3 \rho_i) . \]  \hspace{1cm} (A.9)

Plugging the Taylor expansion of the density back to the Helmholtz free energy expression (A.8) gives:

\[ A = A_0 - \frac{1}{4} \sum_{i,j} \int_V \int_{V'} \left[ (r' - r) \nabla \rho_i(r) + \frac{1}{2} (r' - r)^2 \nabla^2 \rho_i(r) + O(\nabla^3 \rho_i) \right] \times \left[ (r' - r) \nabla \rho_j(r) + \frac{1}{2} (r' - r)^2 \nabla^2 \rho_j(r) + O(\nabla^3 \rho_j) \right] \times g_{ij}(|r - r'|, \bar{\rho}) u_{ij}(|r - r'|) \, dr' \, dr \]

\[ = A_0 - \frac{1}{4} \sum_{i,j} \int_V \int_{V'} \left[ (r' - r)^2 \nabla \rho_i(r) \nabla \rho_j(r) + \frac{1}{2} (r' - r)^3 \nabla^2 \rho_i(r) \nabla \rho_j(r) \right. \]

\[ + \nabla \rho_i(r) \nabla^2 \rho_j(r) ) + \frac{1}{4} (r' - r)^4 \nabla^2 \rho_i(r) \nabla^2 \rho_j(r) \]

\[ + O(\nabla^3 \rho_i) O(\nabla^3 \rho_j) \] \times g_{ij}(|r - r'|, \bar{\rho}) u_{ij}(|r - r'|) \, dr' \, dr' \, dr . \]

Since \( u_{ij}(|r - r'|) \) is an even function of \( r - r' \), the following term vanishes:

\[ \frac{1}{2} (r - r')^3 u_{ij}(|r - r'|) = 0 . \]  \hspace{1cm} (A.11)

In a Cartesian coordinate:

\[ (r - r')(r - r') = \frac{1}{3} |r - r'|^2 , \]  \hspace{1cm} (A.12)
where $\mathbf{1}$ is the unit tensor.

Thus to the order of $\nabla^4 \rho$, the Helmholtz free energy expression (A.10) becomes:

$$
A = A_0 - \frac{1}{4} \sum_{i,j} \int_V \int_{V'} \left( \frac{1}{3} |\mathbf{r} - \mathbf{r}'|^2 \nabla \rho_i(\mathbf{r}) \cdot \nabla \rho_j(\mathbf{r}) + O(\nabla^4 \rho) \right)
\times g_{ij}(|\mathbf{r} - \mathbf{r}'|, \bar{\rho}) u_{ij}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' d\mathbf{r}
$$

(A.13)

where $v_{ij}$ is the influence parameter, which is defined as:

$$
v_{ij} = -\frac{1}{6} \int_{V'} (|\mathbf{r} - \mathbf{r}'|^2 g_{ij}(|\mathbf{r} - \mathbf{r}'|, \bar{\rho}) u_{ij}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}'.
$$

(A.14)

Neglecting the fourth and higher order of the density gradient, Eqn. A.13 is the inhomogeneous Helmholtz free energy expression of the DGT model.
Appendix B

PC-SAFT derivatives

In section 2.2, the Helmholtz free energy given by PC-SAFT EoS is introduced. In many calculations, the chemical potential expression or the first derivative of the chemical potential to density are needed. In this appendix, the PC-SAFT derivatives of these expressions are documented.

In PC-SAFT, the chemical potential expression of component $i$ has five parts of contributions:

$$
\mu_i = \frac{\partial a^{\text{id}}}{\partial \rho_i} + \frac{\partial a^{\text{hs}}}{\partial \rho_i} + \frac{\partial a^{\text{hc}}}{\partial \rho_i} + \frac{\partial a^{\text{disp}}}{\partial \rho_i} + \frac{\partial a^{\text{assoc}}}{\partial \rho_i}.
$$

And the second derivative of the Helmholtz free energy to the molar density, which is also the first derivative of the chemical potential to density, is:

$$
\frac{\partial^2 a}{\partial \rho_i \partial \rho_j} = \frac{\partial \mu_i}{\partial \rho_j} = \frac{\partial \mu_i^{\text{id}}}{\partial \rho_j} + \frac{\partial \mu_i^{\text{hs}}}{\partial \rho_j} + \frac{\partial \mu_i^{\text{hc}}}{\partial \rho_j} + \frac{\partial \mu_i^{\text{disp}}}{\partial \rho_j} + \frac{\partial \mu_i^{\text{assoc}}}{\partial \rho_j}.
$$

In the following discussion, we will present the PC-SAFT expressions based on the five contributions separately.

Ideal gas term

The chemical potential expression for ideal gas is known from thermodynamics, and does not depend on the EoS:

$$
\frac{\mu_i^{\text{id}}}{RT} = \log(\rho_i).
$$

(B.1)

The first derivative of the chemical potential to density $\partial \mu_i^{\text{id}}/\partial \rho_i$ is the same as Eqn. 2.18.
### Hard sphere term

The hard sphere contribution to the chemical potential is:

\[
\frac{\mu_{i}^{hs}}{RT} = m_i \left[ \frac{3(d_i \zeta_2 + d_i^3)}{1 - \zeta_3} + \frac{3\zeta_1 \zeta_2 d_i^3}{(1 - \zeta_3)^2} + \frac{3\zeta_2^2 d_i^3}{\zeta_3 (1 - \zeta_3)^2} + \frac{\zeta_3^3 (3\zeta_3 - 1) d_i^3}{\zeta_3^2 (1 - \zeta_3)^3} \right. 
\]

\[
+ \left. \left( \frac{3\zeta_2^2 \zeta_3 d_i^3 - 2\zeta_3^2 d_i^5}{\zeta_3^3} - 1 \right) \ln(1 - \zeta_3) + \left( \zeta_0 - \frac{\zeta_3^3}{\zeta_3^2} \right) \frac{d_i^4}{1 - \zeta_3} \right],
\]

where \( \zeta_n \) is given in Eqn. 2.22, and \( d_i \) is given in Eqn. 2.23.

The derivative of the hard sphere chemical potential to density is:

\[
\frac{\partial \mu_{i}^{hs}}{\partial \rho_j} = RT \frac{\pi N_A}{6} m_i m_j \left\{ \frac{3(d_i d_j^2 + d_i^2 d_j)}{1 - \zeta_3} + \frac{3(d_i \zeta_2 + d_i^3)}{(1 - \zeta_3)^2} + \frac{6\zeta_1 \zeta_2 d_i^3 d_j}{(1 - \zeta_3)^3} + \frac{6\zeta_2 d_i^3}{\zeta_3 (1 - \zeta_3)^2} + \frac{3\zeta_2^2 (3\zeta_3 - 1) d_i^3 d_j^2}{\zeta_3^2 (1 - \zeta_3)^3} \right. 
\]

\[
+ \frac{3\zeta_2^2 d_i^3 d_j^2 (3\zeta_3 - 1) + \zeta_2 d_i^5}{\zeta_3^2 (1 - \zeta_3)^3} + \frac{\zeta_2^3 (3\zeta_3 - 1)(5\zeta_3 - 2) d_i^3}{\zeta_3^2} + \frac{\zeta_3^3 (1 - \zeta_3)^4}{\zeta_3^2} \} 
\]

\[
+ \ln(1 - \zeta_3) \left[ \frac{3\zeta_2 d_i^2 (2\zeta_3 d_j^2 + \zeta_2 d_j^3)}{\zeta_3^2} - 6\zeta_2 d_j^2 d_i^2 - 3d_j^3 \right] 
\]

\[
+ \left( 1 - \frac{3\zeta_2^2 \zeta_3 d_i^3 - 2\zeta_3^2 d_i^5}{\zeta_3^3} \right) \frac{d_j^4}{1 - \zeta_3} + \left( 1 - \frac{\zeta_2^2 (3\zeta_3 d_j^2 - 2\zeta_2 d_j^3)}{\zeta_3^3} \right) \frac{d_i^4}{1 - \zeta_3} 
\]

\[
+ \left( \zeta_0 - \frac{\zeta_3^3}{\zeta_3^2} \right) \frac{d_i^4 d_j^4}{(1 - \zeta_3)^2} \right\}.
\]

The compressibility factor due to the hard sphere contribution is:

\[
Z^{hs} = \frac{\zeta_3}{1 - \zeta_3} + \frac{3\zeta_1 \zeta_2}{\zeta_0 (1 - \zeta_3)^2} + \frac{3\zeta_3^3 - \zeta_3 \zeta_2^3}{\zeta_0 (1 - \zeta_3)^3}.
\]

### Hard chain term

The hard chain contribution to the chemical potential is:

\[
\frac{\mu_{i}^{hc}}{RT} = (1 - m_i) \ln(g_{ii}) + \sum_k \rho_k (1 - m_k) \frac{\partial \ln g_{kk}}{\partial \rho_i},
\]

where \( g_{ij} \) is given by Eqn. 2.25.
The derivative of the hard chain chemical potential to density is:

$$\frac{\partial \mu_{hc}^i}{RT \partial \rho_j} = (1 - m_i) \frac{\partial \ln g_{ii}}{\partial \rho_j} + (1 - m_j) \frac{\partial \ln g_{jj}}{\partial \rho_i} + \sum_{k=1}^{N} \rho_k (1 - m_k) \frac{\partial^2 \ln g_{kk}}{\partial \rho_i \partial \rho_j},$$  \hspace{1cm} (B.6)

in which,

$$\frac{\partial \ln g_{ij}}{\partial \rho_k} = \frac{1}{g_{ij}} \frac{\partial g_{ij}}{\partial \rho_k},$$  \hspace{1cm} (B.7)

$$\frac{\partial^2 \ln g_{ij}}{\partial \rho_k \partial \rho_l} = \frac{1}{g_{ij}} \frac{\partial^2 g_{ij}}{\partial \rho_k \partial \rho_l} - \frac{1}{g_{ij}^2} \frac{\partial g_{ij}}{\partial \rho_k} \frac{\partial g_{ij}}{\partial \rho_l},$$  \hspace{1cm} (B.8)

$$\frac{\partial g_{ij}^{hs}}{\partial \rho_k} = \frac{\pi N_A}{6} m_k \left[ \frac{d_k^3}{(1 - \zeta_3)^2} + 3 \left( \frac{d_i d_j}{d_i + d_j} \right) \left( \frac{d_k^2}{(1 - \zeta_3)^2} + \frac{2d_k^3 \zeta_2}{(1 - \zeta_3)^3} \right) \right]$$

$$+ 2 \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \left( \frac{2d_k^2 \zeta_2}{(1 - \zeta_3)^3} + \frac{3d_k^3 \zeta_2^2}{(1 - \zeta_3)^4} \right),$$  \hspace{1cm} (B.9)

$$\frac{\partial^2 g_{ij}^{hs}}{\partial \rho_k \partial \rho_l} = \left( \frac{\pi N_A}{6} \right)^2 m_k m_l \left[ \frac{d_k^3}{(1 - \zeta_3)^3} + 3 \left( \frac{d_i d_j}{d_i + d_j} \right) \left( \frac{2d_k^2 d_l^2}{(1 - \zeta_3)^3} + \frac{2d_k d_l}{(1 - \zeta_3)^3} \right) \right]$$

$$+ \frac{6d_k^3 d_l^3 \zeta_2}{(1 - \zeta_3)^4} + 2 \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \left( \frac{2d_k^2 d_l^2}{(1 - \zeta_3)^3} + \frac{6d_k^3 d_l^3 \zeta_2}{(1 - \zeta_3)^4} + \frac{6d_k^3 d_l^3 \zeta_2}{(1 - \zeta_3)^4} \right)$$

$$+ \frac{12d_k^3 d_l^3 \zeta_2^2}{(1 - \zeta_3)^5} \right].$$  \hspace{1cm} (B.10)

The compressibility factor due to the hard chain contribution is:

$$Z_{hc} = \bar{M} Z_{hs} - \sum_{i=1}^{N} x_i (m_i - 1) \frac{1}{g_{ii}} g_i,$$  \hspace{1cm} (B.11)

where

$$\bar{g}_i = \frac{\zeta_3}{(1 - \zeta_3)^2} + \frac{d_i}{2} \left( \frac{3\zeta_2}{(1 - \zeta_3)^2} + \frac{6\zeta_2 \zeta_3}{(1 - \zeta_3)^3} \right) + \frac{d_i^2}{4} \left( \frac{4\zeta_2^2}{(1 - \zeta_3)^3} + \frac{6\zeta_2^2 \zeta_3}{(1 - \zeta_3)^4} \right).$$  \hspace{1cm} (B.12)

**Association term**

The association contribution to the chemical potential is:

$$\frac{\mu_{assoc}^i}{RT} = \sum_{A} \ln X_{Ai} - \frac{1}{2} N_A \sum_{j=1}^{N} \sum_{k=1}^{N} \rho_j \rho_k \sum_{B} \sum_{C} X_{Bj} X_{Ck} \frac{\partial \Delta_{BjCk}}{\partial \rho_i},$$  \hspace{1cm} (B.13)
where the expression of \( \Delta^{A,B_j} \) is given by Eqn. 2.34, and the first derivative of \( \Delta^{A,B_j} \) with respect to density is:

\[
\frac{\partial \Delta^{A,B_k}}{\partial \rho_i} = d^{A,B_k}_{jk} \kappa^{A,B_k} \left( \exp(\epsilon^{A,B_k}/k_B T) - 1 \right) \left( \frac{\partial g_{jk}}{\partial \rho_i} \right) .
\] (B.14)

The derivative of the association chemical potential to density is:

\[
\frac{\partial \mu_i^{\text{assoc}}}{RT \partial \rho_j} = \sum_{A_i} \frac{1}{X^{A_i}} \frac{\partial X^{A_i}}{\partial \rho_j} - N_A \sum_{k=1}^{N} \rho_k \sum_{b_j} X^{b_j} X^{C_k} \frac{\partial \Delta^{b_j,C_k}}{\partial \rho_i} \\
- N_A \sum_{k=1}^{N} \rho_k \rho_l \sum_{C_k} \sum_{D_l} \frac{\partial X^{C_k}}{\partial \rho_j} X^{D_l} \frac{\partial \Delta^{C_k,D_l}}{\partial \rho_i} \\
- \frac{1}{2} N_A \sum_{k=1}^{N} \rho_k \rho_l \sum_{C_k} \sum_{D_l} X^{D_l} X^{C_k} \frac{\partial^2 \Delta^{C_k,D_l}}{\partial \rho_i \partial \rho_j} ,
\] (B.15)

where

\[
\frac{\partial X^{A_i}}{\partial \rho_j} = -(X^{A_i})^2 \left[ N_A \sum_{k=1}^{N} \rho_k \sum_{C_k} \left( \Delta^{A_i,C_k} \frac{\partial X^{C_k}}{\partial \rho_j} + X^{C_k} \frac{\partial \Delta^{A_i,C_k}}{\partial \rho_j} \right) \\
+ N_A \sum_{b_j} X^{b_j} \Delta^{A_i,B_j} \right],
\] (B.16)

and

\[
\frac{\partial^2 \Delta^{A,B_j}}{\partial \rho_k \partial \rho_l} = d^{A,B_j}_{jk} \kappa^{A,B_j} \left( \exp(\epsilon^{A,B_j}/k_B T) - 1 \right) \left( \frac{\partial^2 g_{jk}}{\partial \rho_i \partial \rho_l} \right) .
\] (B.17)

The compressibility factor of the association contribution is:

\[
Z^{\text{assoc}} = \sum_{i=1}^{N} \left( \frac{x_i \mu_{i}^{\text{assoc}}}{RT} \right) - \frac{a^{\text{assoc}}}{\rho RT} .
\] (B.18)

**Dispersion term**

The dispersion contribution to the chemical potential is:

\[
\frac{\mu_{\text{disp}}}{RT} = - \left[ 2 \rho I_1 m^2 \epsilon \sigma^3 + \rho \left( \frac{\partial I_1}{\partial \rho_i} m^2 \epsilon \sigma^3 \right) \frac{\partial \rho}{\partial \rho_i} I_1 + \frac{1}{2} \rho^2 \tilde{m} C_1 I_2 \frac{\partial m^2 \epsilon \sigma^3}{\partial \rho_i} I_1 \\
+ \frac{1}{2} \tilde{m} \epsilon^2 \sigma^3 \left( 2 \rho \tilde{m} C_1 I_2 + \rho \left( \frac{\partial \tilde{m}}{\partial \rho_i} C_1 I_2 + \rho \left( \frac{\partial C_1}{\partial \rho_i} \tilde{m} I_2 + \rho \left( \frac{\partial I_2}{\partial \rho_i} \tilde{m} C_1 \right) \right) \right) \right] 2 \pi N_A ,
\] (B.19)
where

\[
\frac{\partial I_1}{\partial \rho_i} = \sum_{k=0}^{6} \left( a_k \eta^{k-1} \frac{\partial \eta}{\partial \rho_i} + \frac{\partial a_k}{\partial \rho_i} \eta^k \right),
\]

(B.20)

\[
\frac{\partial I_2}{\partial \rho_i} = \sum_{k=0}^{6} \left( b_k \eta^{k-1} \frac{\partial \eta}{\partial \rho_i} + \frac{\partial b_k}{\partial \rho_i} \eta^k \right),
\]

(B.21)

\[
\frac{\partial m^2 \epsilon^3}{\partial \rho_i} = \frac{2 m_i}{\rho} \sum_{k=1}^{N} x_k m_k \left( \frac{\epsilon_{ik}}{kT} \right)^3 \sigma_{ik}^3 - \frac{2 m^2 \epsilon^3}{\rho},
\]

(B.22)

\[
\frac{\partial m^2 \epsilon^2 \sigma^3}{\partial \rho_i} = \frac{2 m_i}{\rho} \sum_{k=1}^{N} x_k m_k \left( \frac{\epsilon_{ik}}{kT} \right)^2 \sigma_{ik}^3 - \frac{2 m^2 \epsilon^2 \sigma^3}{\rho},
\]

(B.23)

\[
\frac{\partial C_1}{\partial \rho_i} = C_2 \frac{\partial \zeta_3}{\partial \rho_i} - C_1^2 \left( \frac{8 \eta - 2 \eta^2}{(1 - \eta)^4} - \frac{20 \eta - 27 \eta^2 + 12 \eta^3 - 2 \eta^4}{[(1 - \eta)(2 - \eta)]^2} \right) \frac{\partial \bar{m}}{\partial \rho_i},
\]

(B.24)

\[
C_2 = - C_1^2 \left( \frac{m - 4 \eta^2 + 20 \eta + 8}{(1 - \eta)^5} + (1 - \bar{m}) \frac{2 \eta^3 + 12 \eta^2 - 48 \eta + 40}{[(1 - \eta)(2 - \eta)]^3} \right),
\]

(B.25)

\[
\frac{\partial a_k}{\partial \rho_i} = \left( \frac{1}{m^2} a_{1k} + \frac{1}{m^2} (3 - \frac{4}{m}) a_{2k} \right) \frac{\partial \bar{m}}{\partial \rho_i},
\]

(B.26)

\[
\frac{\partial b_k}{\partial \rho_i} = \left( \frac{1}{m^2} b_{1k} + \frac{1}{m^2} (3 - \frac{4}{m}) b_{2k} \right) \frac{\partial \bar{m}}{\partial \rho_i},
\]

(B.27)

\[
\frac{\partial \bar{\eta}}{\partial \rho_i} = \frac{\pi}{6} N_A m_i d_i^3,
\]

(B.28)

\[
\frac{\partial \bar{m}}{\partial \rho_i} = \frac{m_i - \bar{m}}{\rho},
\]

(B.29)
The derivative of the dispersion chemical potential to density is:

\[
\frac{\partial \mu_{\text{disp}}}{RT \partial \rho_j} = -2\pi N_A \left( 2I_1 \bar{m}^2 \epsilon \sigma^3 + 2\rho \frac{\partial I_1}{\partial \rho_i} \frac{\partial \bar{m}^2 \epsilon \sigma^3}{\partial \rho_j} + 2\rho I_1 \frac{\partial \bar{m}^2 \epsilon \sigma^3}{\partial \rho_j} \right) + 2\rho \frac{\partial I_1}{\partial \rho_i} \frac{\partial \bar{m}^2 \epsilon \sigma^3}{\partial \rho_j} + \rho^2 I_1 \frac{\partial \bar{m}^2 \epsilon \sigma^3}{\partial \rho_i} + \rho^2 \frac{\partial I_1}{\partial \rho_i} \frac{\partial \bar{m}^2 \epsilon \sigma^3}{\partial \rho_i} \right) - \pi N_A \left[ \rho^2 \bar{m} C_1 I_2 \frac{\partial \bar{m}^2 \epsilon \sigma^3}{\partial \rho_i} \right] + \left[ 2\rho \frac{\partial \bar{m}}{\partial \rho_i} C_1 I_2 + 2\rho \frac{\partial \bar{m}}{\partial \rho_i} C_1 I_2 + 2\rho \frac{\partial \bar{m}}{\partial \rho_i} C_1 I_2 + 2\rho \frac{\partial \bar{m}}{\partial \rho_i} C_1 I_2 \right) \left( \frac{\partial \bar{m}^2 \epsilon \sigma^3}{\partial \rho_i} \right),
\]

where

\[
\frac{\partial I_1}{\partial \rho_i} \rho_i \rho_j = \sum_{k=0}^{6} \left( \frac{\partial a_k}{\partial \rho_j} \frac{\partial \eta}{\partial \rho_i} + \frac{a_k \eta}{\partial \rho_i} \frac{\partial \eta}{\partial \rho_j} \right) + \frac{\partial a_k}{\partial \rho_i} \frac{\partial \eta}{\partial \rho_j} + \frac{\partial a_k}{\partial \rho_i} \frac{\partial \eta}{\partial \rho_j} \right), \tag{B.31}
\]

\[
\frac{\partial I_2}{\partial \rho_i} \rho_i \rho_j = \sum_{k=0}^{6} \left( \frac{\partial b_k}{\partial \rho_j} \frac{\partial \eta}{\partial \rho_i} + \frac{b_k \eta}{\partial \rho_i} \frac{\partial \eta}{\partial \rho_j} \right) + \frac{\partial b_k}{\partial \rho_i} \frac{\partial \eta}{\partial \rho_j} + \frac{\partial b_k}{\partial \rho_i} \frac{\partial \eta}{\partial \rho_j} \right), \tag{B.32}
\]

\[
\frac{\partial a_k}{\partial \rho_i} \rho_i \rho_j = \left( \frac{-2}{\bar{m}^3} a_{1k} + \frac{6}{\bar{m}^3} (2\bar{m} - 1) a_{2k} \right) \frac{\partial \bar{m}}{\partial \rho_i} \frac{\partial \bar{m}}{\partial \rho_j} + \left( \frac{1}{\bar{m}} a_{1k} + \frac{1}{\bar{m}^2} (3 - \frac{4}{\bar{m}}) a_{2k} \right) \frac{\partial \bar{m}}{\partial \rho_i} \frac{\partial \bar{m}}{\partial \rho_j}, \tag{B.33}
\]
\[
\frac{\partial b_k}{\partial \rho_i \partial \rho_j} = \left( -\frac{2}{m^3} b_{1k} + \frac{6}{m^3} \left( \frac{2}{m} - 1 \right) b_{2k} \right) \frac{\partial \bar{m}}{\partial \rho_i} \frac{\partial \bar{m}}{\partial \rho_j} + \left( \frac{1}{\bar{m}} b_{1k} + \frac{1}{\bar{m}^2} \left( 3 - \frac{4}{\bar{m}} \right) b_{2k} \right) \frac{\partial \bar{m}}{\partial \rho_i \partial \rho_j}, \quad (B.34)
\]

\[
\frac{\partial (m^2 \epsilon^3 \sigma^3)}{\partial \rho_i \partial \rho_j} = \frac{2 m_i m_j}{\rho^2} \left( \frac{\epsilon_{ij}}{kT} \right) \frac{\sigma_{ij}^3}{\rho^2} - \frac{4 m_i}{\rho^2} \sum_{k=1}^{N} x_k m_k \frac{\epsilon_{ik}}{kT} \sigma_{ik}^3 + \frac{2 m^2 \epsilon^3 \sigma^3}{\rho^2} - \frac{2 m^2 \epsilon^2 \sigma^3}{\rho \partial \rho_j}, \quad (B.35)
\]

\[
\frac{\partial (m^2 \epsilon^3 \sigma^3)}{\partial \rho_i \partial \rho_j} = \frac{2 m_i m_j}{\rho^2} \left( \frac{\epsilon_{ij}}{kT} \right)^2 \frac{\sigma_{ij}^3}{\rho^2} - \frac{4 m_i}{\rho^2} \sum_{k=1}^{N} x_k m_k \left( \frac{\epsilon_{ik}}{kT} \right)^2 \sigma_{ik}^3 \\
+ \frac{2 m^2 \epsilon^3 \sigma^3}{\rho^2} - \frac{2 m^2 \epsilon^2 \sigma^3}{\rho \partial \rho_j}, \quad (B.36)
\]

\[
\frac{\partial C_1}{\partial \rho_i \partial \rho_j} = \frac{\partial C_2}{\partial \rho_j} \frac{\partial C_2}{\partial \rho_i} - 2 C_1 \frac{\partial C_1}{\partial \rho_j} \left( \frac{8 \eta - 2 \eta^2}{(1 - \eta)^4} - \frac{20 \eta - 27 \eta^2 + 12 \eta^3 - 2 \eta^4}{[(1 - \eta)(2 - \eta)]^2} \right) \frac{\partial \bar{m}}{\partial \rho_i} \\
- C_1^2 \left( \frac{-4 \eta^2 + 20 \eta + 8}{(1 - \eta)^5} - \frac{2 \eta^3 + 12 \eta^2 - 48 \eta + 40}{[(1 - \eta)(2 - \eta)]^3} \right) \frac{\partial \eta}{\partial \rho_j} \frac{\partial \bar{m}}{\partial \rho_i}, \quad (B.37)
\]

\[
\frac{\partial C_2}{\partial \rho_i} = -2 C_1 C_1 \left( \frac{m - 4 \eta^2 + 20 \eta + 8}{(1 - \eta)^5} + (1 - m) \frac{2 \eta^3 + 12 \eta^2 - 48 \eta + 40}{[(1 - \eta)(2 - \eta)]^3} \right) \\
- C_1^2 \left( \frac{-4 \eta^2 + 20 \eta + 8}{(1 - \eta)^5} - \frac{2 \eta^3 + 12 \eta^2 - 48 \eta + 40}{[(1 - \eta)(2 - \eta)]^3} \right) \frac{\partial \bar{m}}{\partial \rho_i} \\
- C_1^2 \frac{\partial \eta}{\partial \rho_i} \left( \frac{m - 12 \eta^2 + 72 \eta + 60}{(1 - \eta)^6} + (1 - m) \frac{-6 \eta^4 - 48 \eta^3 + 288 \eta^2 - 480 \eta + 264}{[(1 - \eta)(2 - \eta)]^4} \right), \quad (B.38)
\]

\[
\frac{\partial \bar{m}}{\partial \rho_i \partial \rho_j} = \frac{\bar{m} - m_i}{\rho^2} - \frac{1}{\rho} \frac{\partial \bar{m}}{\partial \rho_j}, \quad (B.39)
\]
The compressibility factor due to the dispersion contribution is:

\[ Z_{\text{disp}} = -2\pi \rho N_A \frac{\partial(\eta I_1)}{\partial \eta} \frac{m^2 \epsilon \sigma^3}{\bar{m}} - \pi \rho N_A \bar{m} \left( C_1 \frac{\partial(\eta I_2)}{\partial \eta} + C_2 \eta I_2 \right) \frac{m^2 \epsilon^2 \sigma^3}{\bar{m}} , \]  

(B.40)

where

\[ \frac{\partial(\eta I_1)}{\partial \eta} = \sum_{j=0}^{6} a_j (j + 1) \eta^j , \]  

(B.41)

\[ \frac{\partial(\eta I_2)}{\partial \eta} = \sum_{j=0}^{6} b_j (j + 1) \eta^j . \]  

(B.42)