TIE-SIMPLEX METHOD FOR
THERMAL-COMPOSITIONAL SIMULATION

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Abstract

Enhanced Oil Recovery (EOR) processes usually involve complex phase behaviors between the injected fluid (e.g., steam, hydrocarbon gas, CO₂) and the in-situ rock-fluid system. Equation-of-State (EoS) computations for complex mixtures than can form three, or more, phases at equilibrium poses significant challenges. In addition, computational issues related to proper coupling of the thermodynamic phase-behavior with multi-component transport across multiple fluid phases must be resolved in order to model the behaviors of large-scale EOR processes accurately and efficiently.

Here, we propose an EoS-based tie-simplex framework to deal with the thermodynamic phase behavior, in which an arbitrary number of phases can form. It is shown that our generalized negative-flash method yields the unique tie-simplex parameterization of the compositional space. Specifically, we show that the tie-simplexes change continuously as a function of temperature, pressure, and composition. In the course of a thermal-compositional simulation, the compositional space is tabulated adaptively using tie-simplexes. We also prove that the Gibbs free-energy analysis of this tie-simplex space is equivalent to conventional methods for equilibrium phase calculations. This multiphase tie-simplex method is integrated into Stanford’s General-Purpose Research Simulator (GPRS), and its application to thermal-compositional simulation is demonstrated here using several challenging thermal-compositional flows with complex phase behaviors.
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Chapter 1

Introduction

Enhanced Oil Recovery (EOR) processes, such as gas and steam injection, are expected to grow in importance over the next several decades. In order to obtain reliable predictions based on numerical simulation of such processes, thermal-compositional formulations are used, in which the mass, energy, and momentum conservation equations are solved together with the equations that describe thermodynamic equilibrium.

Several authors have discussed simulation techniques for compositional models where only two hydrocarbon phases are involved in the chemical equilibrium calculations (Coats, 1980; Cao, 2002). Thermal-compositional displacement processes often involve the formation of three, or more, fluid phases, and that poses serious difficulties for conventional methods.

To anchor this discussion, consider displacements including C\textsubscript{1}, C\textsubscript{6}, and CO\textsubscript{2}. The phase behavior of this system at $p = 17.5$ bar and two temperatures is shown in Figure (1.1). Note that displacement at higher temperatures involve two phases only (Figure 1.1-a). However, for colder conditions, or if the range of temperature variation is large, the assumption that a maximum of two phases can coexist at equilibrium would be wrong. Figure (1.1-b) shows that the system can form three different phases (one vapor, and two liquids) at equilibrium.

This thesis describes a framework to resolve the thermodynamics of subsurface displacement processes that involve such systems. Our framework is based on tie-simplex parameterization of the compositional space, so we start with an overview of
Figure 1.1: Changes in phase behavior as a function of temperature

tie-line representation of chemical equilibria. Figure (1.2) shows the loci of bubble and
dew points in the same ternary system as in Figure (1.1), but at increased temperature
and pressure conditions. A tie-line connects a pair of vapor and liquid phases at
equilibrium. Mathematically, the overall composition of any mixture, $\mathbf{z}$, along the
tie-line can be expressed as a linear combination of tie-line endpoints, $\mathbf{x}_j$:

$$
\mathbf{z} = \sum_{j=1}^{N_p} \nu_j \mathbf{x}_j,
$$

(1.1)

where $N_p = 2$, and

$$
\sum_{j=1}^{N_p} \nu_j = 1.
$$

(1.2)

In these equations, $\nu_j$ denotes the molar fraction of phase $j$. Eq. (1.1) indicates that
all the compositions on the extension of a tie-line can be parameterized using the
tie-line endpoints, and one scalar, $\nu_1$ or $\nu_2$.

This parameterization can be generalized for multi-component systems with an
arbitrary number of phases by using tie-simplexes. Figure (1.1-b) shows a tie-triangle. Note that all the mixtures marked with \( V+L_1+L_2 \) are parameterized by a unique tie-triangle. It is very important to note that different two-phase regions exist on the three sides of the tie-triangle. In this thesis, we will describe how these multiphase (one three-phase, and three two-phase) regions can be parameterized using tie-simplexes (one tie-triangle, and three sets of tie-lines).

Also, note that in Figure (1.2), the length of the tie-lines approaches zero as the critical point is reached. Tie-line parameterization is not possible beyond the critical tie-line. As we will show later, parameterization of the multiphase compositional space is more challenging due to the degeneration of tie-simplexes.
1.1 Multiphase Thermal-Compositional Formulation

A comprehensive review of the numerical considerations in general-purpose reservoir simulation models was presented by Aziz and Wong (1989). Here, we provide an overview of the multiphase simulator formulation. Neglecting capillarity, diffusion, chemical reactions, and interactions with the solid phase, and assuming instantaneous thermodynamic equilibrium, the governing conservation equations, and thermodynamic phase equilibrium relations can be expressed as:

\[
\frac{\partial}{\partial t} \left( \phi \sum_{j=1}^{N_p} x_{i,j} \rho_j S_j \right) - \nabla \cdot \left( \sum_{j=1}^{N_p} x_{i,j} \rho_j u_j \right) = -\sum_{j=1}^{N_p} x_{i,j} \rho_j q_j, \tag{1.3}
\]

\[
\frac{\partial}{\partial t} \left( \phi \sum_{j=1}^{N_p} S_j \rho_j e_j + (1-\phi) \rho_s e_s \right) = -\nabla \cdot \left( \sum_{j=1}^{N_p} \rho_j h_j u_j + \lambda_h \nabla T \right) + q_h, \tag{1.4}
\]

\[
u_j = \frac{k_{r_i,j}}{\mu_j} (\nabla p - \gamma_j \nabla D), \tag{1.5}
\]

\[
\hat{f}_{i,1}(p, T, x_1) = \hat{f}_{i,j}(p, T, x_j). \tag{1.6}
\]

The mass conservation equations (Eqs. 1.3) are written for all components, \(i = 1, \ldots, N_c\). Note that Darcy’s law (Eqs. 1.5) has been used to approximate the conservation of momentum.

Similarly, the conservation of energy, Eq. (1.4), indicates that the accumulation of thermal energy in existing fluid phases and rock equals net inflow of heat due to convection, conduction, and point source/sink. Note that other mechanisms of heat transfer such as viscous shear, and heat generation due to chemical reactions are neglected in this formulation (Aziz and Wong, 1989).

The last set of equations, Eqs. (1.6), describe the thermodynamic behavior of the multiphase multi-component system. It indicates that the chemical potential of component \(i\) in all phases, \(j\), must be equal (note that \(i = 1, \ldots, N_c\), and \(j = 2, \ldots, N_p\)). This is equivalent to the expression of chemical equilibrium (Michelsen and Mollerup, 2004). An important point to emphasize is that the conditions of chemical
equilibrium are necessary, but not sufficient, to describe the accurate thermodynamic state of the compositional model. We will clarify this subject in more detail in Chapter 5.

With the following constraints:

\[
\sum_{i=1}^{N_c} x_{i,j} = 1, \quad j = 1, \ldots, N_p, \quad (1.7)
\]

\[
\sum_{j=1}^{N_p} S_j = 1, \quad (1.8)
\]

the coupled set of \(N_p(N_c + 1) + 2\) equations is solved for the unknown variables of each gridblock (temperature, pressure, phase saturations, and phase compositions).

In recent years, several approaches have been proposed for the simultaneous solution of the governing conservation equations. The resulting nonlinear solution strategies are formulated using different sets of primary variables. One of the most common approaches is based on the natural-variables set, namely, temperature, pressure, phase saturations, and phase compositions (Coats, 1980). Another widely used formulation is based on the molar variables, where overall molar compositions are the primary variables (Young and Stephenson, 1983; Acs et al., 1985; Chien et al., 1985). Alternative formulations for multiphase multi-component displacement processes have been investigated by Aziz and Wong (1989). Voskov and Tchelepi (2012) compared nonlinear behaviors of different compositional formulations.

Coupling thermodynamics with the conservation equations is a major challenge in the development of a general-purpose thermal-compositional simulation framework. The partial differential equations are highly nonlinear, and they are tightly coupled to the phase equilibrium relations. In order to deal with thermal-compositional models of practical utility, accurate and consistent treatment of the thermodynamic phase behavior is crucial (Farouq-Ali and Abou-Kassem, 1988). Moreover, in many displacement processes, components partition into more than two fluid phases. This is common in steam injection processes and in systems that include CO\(_2\), or sour gas, over wide ranges of temperature and pressure. Modeling the phase behavior of such
systems is challenging even when all the phases are completely immiscible with each other. The complexity of the problem increases when multiphase regions approach the critical state.

Let us review some of the techniques that have been developed by different researchers for multiphase thermal-compositional simulation. Simultaneous solution of the energy and mass conservation equations was first demonstrated by Coats et al. (1974). Their numerical model solved the three-phase flow of oil, water, and steam for a steam-flooding problem. Their model assumed that only the water and steam phases exchange mass. Later, Coats (1976) extended this formulation by modeling steam distillation of oil and the release of solution gas. In his model, a fixed number of conservation equations is solved, in which oil is represented as a mixture of solution gas, a distillable portion, and nonvolatile heavy ends. Moreover, Coats (1976) assumed that the phase equilibrium ratios are functions of temperature and pressure only. The so-called natural variables were used in his formulation.

Simplified compositional (or modified black-oil) models have been developed in order to account for the thermodynamic phase behavior in reservoir flow simulation (Bolling, 1987; Whitson et al., 1988). One of the most common approaches is the ‘constant K-values’ method, where it is assumed that the component equilibrium factors, K-values, are functions of temperature and pressure only, and therefore, the thermodynamic equilibrium can be modeled efficiently using tables of K-values (see Aziz et al. (1987) for a practical example). However, the accuracy of the constant K-values approach is limited to effectively immiscible displacements at relatively low pressures, where the assumption of composition-independent K-values is valid.

Van-Quy et al. (1972) and Young and Stephenson (1983) proposed a methodology based on the Hand’s rule (Hand, 1930). They defined K-values that are functions of pressure and composition. Hand’s rule has also been applied in several applications, such as simulation of surfactant flooding. Limited-compositional models can be thermodynamically inconsistent, and they do not provide a continuous representation of the changes in the phase behavior (Coats, 1980). Consequently, such models may not be able to capture the complex physics in problems involving the development of miscibility, or interactions involving more than two fluid phases.
Chien et al. (1989) developed a three-phase thermal compositional simulator, in which they used vectorization to improve computational efficiency. Chien et al. (1989) represented the equilibrium phase behavior using an Equation of State (EoS). Their model used temperature, pressure, and overall component mole fractions as primary variables. Brantferger et al. (1991) proposed using enthalpy, in place of temperature, as a primary variable. Their formulation eliminates the need to use variable substitution when temperature and pressure become dependant as a result of component disappearance due to distillation. Because of the choice of the primary variables, Brantferger et al. (1991) implemented an isenthalpic flash procedure to model instantaneous phase equilibrium within each gridblock.

Different time approximation schemes are developed for solving the conservation equations. In partially explicit schemes, the time-step size is restricted by the Courant-Friedrichs-Lewy (CFL) condition (Coats, 2003a,b). This limit is not an issue for the fully implicit method (FIM); however, the computational cost associated with the fully implicit treatment of the variables can rise significantly with the number of components and gridblocks. The adaptive implicit method (AIM) uses the implicit formulation only when changes in the variables are significant (Cao, 2002). Sequential implicit formulation of the compositional reservoir flow equations have also been developed by Watts (1986).

Because we are interested in resolving the coupling of thermodynamic phase behavior with multiphase flow and multi-component transport in porous media, we will use an Equation of State approach in the fully implicit method to solve Eqs. (1.3) to (1.6). We note that our approach is not dependent on the specific EoS choice; empirical functions that calculate fugacities may also be used.

1.2 Conventional EoS Based Methods

Accurate and efficient phase-state identification for thermal-compositional simulation is a challenging problem. Here, we review the standard methods that are used to resolve the complex phase behaviors in compositional displacements.
In recent years, various approaches have been proposed to deal with the coupling of thermodynamic phase behavior with multiphase flow and multi-component transport in porous media. Recent developments include the use of reduced-variables (Michelsen, 1986; Pan and Tchelepi, 2011; Okuno et al., 2010), bypassing of phase stability analysis (Rasmussen et al., 2006; Pan and Tchelepi, 2011), and Gibbs energy minimization by Simulated Annealing (Pan and Firoozabadi, 1998), and Tunneling (Nichita et al., 2004).

In the development of a compositional simulation model, the maximum number of coexisting phases, \( N_{p}^{\text{max}} \), across the entire temperature and pressure ranges of interest is assumed to be known (Coats, 1980; Aziz and Wong, 1989; Cao, 2002). A particular challenge in multiphase compositional simulation is that the actual number of existing phases changes with location and time. As a result, \( N_{p} \) in Eqs. (1.3) to (1.6) is a strong function of space and time, but it is restricted to \( 2 \leq N_{p} \leq N_{p}^{\text{max}} \). Consequently, the set of equations has to be modified for the appropriate set of unknown variables in each gridblock. In a simulation model for displacements with a maximum of three phases, for example, the challenge is obvious because various combinations of two-phase mixtures, as well as, the three-phase region have to be considered. For this purpose, a thermodynamically consistent procedure is needed that accurately and efficiently determines the number of phases for a given mixture.

Let us consider Newton’s method to solve the system of equations described in the previous section. In a formulation based on the natural-variables set, if the saturation of a phase becomes negative at the end of a Newton iteration, then that phase is removed from the gridblock (phase disappearance). On the other hand, if the number of phases in a gridblock is smaller than \( N_{p}^{\text{max}} \), thermodynamic stability analysis is required. In the following, we review the two major kernels of conventional EoS based thermodynamic calculations:

- **Thermodynamic Stability Analysis** (Michelsen, 1982a). The purpose of the phase stability test is to determine if a given mixture is stable at the prevailing conditions of temperature and pressure. The second law of thermodynamics indicates that the state of the mixture must be such that its Gibbs free energy is at the global minimum. Several techniques (mostly based on optimization)
have been proposed to deal with this computational problem. The complexity of the conventional techniques increases considerably as $N^\text{max}_p$ increases. In Chapter 5, we will briefly review some of the standard approaches.

- **Flash (Phase Partitioning) Computations** (Michelsen, 1982b). If a single-phase mixture is not thermodynamically stable, it will form a new phase (phase appearance). Therefore, phase partitioning (flash) calculations are performed after the stability analysis. The purpose of the flash approach is to compute the amount and compositions of the multiple phases that coexist at equilibrium. Note that the number of existing phases must be known before flash calculations are performed. Chapter 2 discusses some of the previous work in this area.

If the value of $N^\text{max}_p$ is accurate across the composition, pressure, and temperature ranges during a simulation, then flash computations are not necessary for gridblocks in which the phase state is $N^\text{max}_p$. This is because the solution of the chemical equilibrium equations for such gridblocks, which are coupled with the nonlinear flow equations, already satisfies the second law of thermodynamics.

At the end of each Newton iteration, the set of the equations for all gridblocks are assembled based on the number of existing phases. Robust algorithms for stand-alone calculations of multiphase stability and flash procedures have been described by several authors (see Michelsen and Mollerup (2004)). However, previous developments for phase behavior computations coupled with flow and transport have basically focused on methods that are suitable for two-phase compositional simulation. As we will discuss in the following Chapters, thermodynamic phase behaviors become more complex when the compositional system forms three, or more, phases at equilibrium. Description of phase transitions is required for a robust nonlinear solver when the Fully Implicit Method is applied for the solution of flow and transport problem in such systems.
1.3 Tie-line Based Solution Techniques

In this section, we review previous work in the area of tie-line parameterization for compositional simulation. We start with an overview of analytical methods developed to solve the conservation equations, Eqs. (1.3) to (1.6).

In order to obtain analytical solutions for nonlinear compositional displacements, several assumptions are usually made (Orr, 2007); specifically, one-dimensional, homogeneous displacements with uniform and constant initial conditions, as well as, constant temperature/pressure conditions. Moreover, dispersion is neglected, and it is assumed that gas is injected with constant composition. The resulting Riemann problem is then solved with the Method of Characteristics (MoC) (Orr, 2007).

The first analytical solution for the three-component gas injection problem was presented by Welge et al. (1961). Their solution allowed for the volume changes of components upon mixing. Later, Helfferich (1981) described the mathematical theory of multi-component, multiphase displacements in porous media. This theory has been extensively developed by Lake (1989), and Orr (2007). Barenblatt et al. (1990) developed similar derivations for pseudo-ternary systems.

Monroe et al. (1990), Johns (1992), and Johns et al. (1993) presented analytical solutions of four-component displacements. Dindoruk (1992), and Dindoruk et al. (1992) considered four-component problems where they studied the effect of volume changes on mixing.

The MoC theory describing the development of miscibility in gas injection problems was presented by Orr et al. (1993). Assuming a fully self-sharpening displacement, Wang and Orr (1997, 1998) studied miscibility in systems with an arbitrary number of components. Systematic methods to solve the problem of multi-component models were presented by Jessen et al. (1999). They showed that the MoC solution must be constructed using the primary key tie-line. Moreover, they presented a method to determine if the solution across a key tie-line should be a rarefaction, or a shock.
CHAPTER 1. INTRODUCTION

Brusilovsky and Zazovsky (1991) showed that the thermodynamic and hydrodynamic problems can be split into two separate problems for two-phase three-component systems. Later, Bedrikovetsky and Chumak (1992) presented the tie-line based splitting of thermodynamics and hydrodynamics for multi-component systems with constant K-values. Their approach was extended for general hydrocarbon systems by Entov (1997, 1999). Recently, the tie-line based splitting method was used to develop analytical solutions for several practical problems (Pires et al., 2006).

These analytical solutions have significantly improved our knowledge of the underlying physics of multiphase flow, and multicomponent transport in porous media. One of the most important conclusions is that in an MoC solution, the single-phase compositions are connected to two-phase mixtures along the extension of a key tie-line (the Rankine-Hugoniot condition, Helfferich (1981); LaForce et al. (2008a,b); Voskov and Tchelepi (2009c)). Based on this theoretical development, tie-simplexes can be used to identify the phase-state of gridblocks in the numerical compositional simulation (Voskov and Tchelepi, 2009a,b). In order to eliminate the majority of redundant EoS computations, one can find the key tie-lines in a multi-dimensional numerical displacement problem, and parameterize the compositional space on their extensions.

The first practical implementation of the splitting approach was based on a parameterization strategy that decouples pressure dependencies of the tie-line parameterization (Voskov and Entov, 2001; Voskov, 2002). Later, Voskov and Tchelepi (2008) developed a tie-line based Compositional Space Parameterization (CSP) framework, and they reported improved performance and stability of EoS based phase-behavior calculations for two-phase compositional simulation.

An effective way of utilizing the concept of CSP for general-purpose simulation is the Compositional Space Adaptive Tabulation (CSAT) framework, where adaptive tie-line parameterization is used to accelerate the convergence of EoS-based calculations (Voskov and Tchelepi, 2009b). In the CSAT approach, one constructs and tabulates tie-lines adaptively. The tie-line tables are then used to identify the phase-state of compositions encountered in the course of the simulation. Linear interpolation in pressure is performed to obtain a tie-line for a composition at the pressure of interest.

The initial development of CSAT for immiscible (sub-critical) displacements has
been generalized for multi-contact miscible processes (Voskov and Tchelepi, 2009a). They showed that adaptive tabulation of the critical tie-lines improves the efficiency and accuracy of multi-contact miscible simulation significantly. Generalization of CSAT to thermal problems, where tabulation and interpolation as a function of temperature and pressure is performed, was proposed by Iranshahr et al. (2010). Voskov and Tchelepi (2009c) described an extension to multiphase parameterization using tie-simplexes. The wide range of examples presented in these references shows that CSAT is an effective method for phase behavior modeling in general-purpose compositional simulation.

1.4 Statement of the Problem

This work deals with modeling subsurface processes with complex phase behaviors. The problem, therefore, is to develop a phase behavior framework that:

1. models displacement processes with coexistence of three or more phases,
2. is accurate, and thermodynamically consistent,
3. is applicable across wide ranges of temperature, and pressure (models development of miscibility),
4. improves computational efficiency, and numerical stability of the multiphase simulator.

For this purpose, we will generalize the EoS based CSAT approach for multiphase problems. Moreover, we will assume that the accurate value of $N_{p}^{max}$ is known in our developments.

This thesis is organized as follows. In Chapter 2, a generalized negative-flash methodology is introduced, which serves as the main computational tool for multiphase CSAT. It is shown that, with the correct assumption of $N_{p}^{max}$, the negative-flash converges to the unique tie-simplex. Chapter 3 provides the theoretical basis for the continuity of CSP using tie-simplexes. These developments set the stage for designing the multiphase CSAT framework.
Chapter 4 describes the details of tie-simplex parameterization of multiphase (more than two phases) systems. It is shown that how interpolation with respect to temperature, pressure and composition in the discrete tie-simplex space yields the appropriate thermodynamic phase-state. Moreover, the Gibbs free-energy analysis of Chapter 5 gives insight into the application of CSAT to complex thermodynamic systems. Specifically, it is proved that CSAT is equivalent to conventional phase-state identification techniques. Finally, Chapter 6 presents several numerical examples of compositional simulation involving challenging multiphase systems.
Chapter 2

Generalized Negative-Flash Method

2.1 Introduction

In this Chapter, we describe a generalized negative-flash method that is applicable for systems with any number of phases. This negative-flash framework is a critical building block for employing the tie-simplex parameterization in general-purpose compositional flow simulation.

Similar to the conventional flash approach (Michelsen, 1982b), the negative-flash solves the thermodynamical equilibrium problem. The purpose of both approaches is to obtain the amounts and compositions of the equilibrium phases for a given mixture at known conditions of temperature and pressure. In order to perform the conventional flash, one needs to determine the number of coexisting phases for the given mixture. On the other hand, in the negative-flash approach, the maximum number of phases that can coexist anywhere in the compositional space for the given temperature and pressure conditions must be known. With this information, the negative-flash can be applied for any mixture (single- or multiphase), regardless of its phase-state.

The problem of how components partition among multiple phases at equilibrium was first formulated by Rachford and Rice (1952). Assuming constant partitioning
coefficients (K-values), they derived an objective function, which is solved for the phase fraction of a two-phase mixture. In their work, they considered positive phase ratios only. Later, Li and Nghiem (1982) showed that the formulation can be applied to negative phase-fractions, which allows phase-split calculations for mixtures in the single-phase, as well as, the two-phase region. They updated K-values in an iterative procedure to satisfy the equal fugacity constraints for each component. Whitson and Michelsen (1989) made significant contributions to the negative-flash problem. They bounded the range of the phase fractions of the Rachford-Rice problem, and they argued that application of two-phase negative-flash calculations for a single-phase mixture is as reliable as a conventional phase stability test.

An advantage of the negative-flash procedure is that the calculated tie-simplex may not enclose the given mixture (for example, tie-line on the extension of a single-phase mixture). Considering the maximum number of phases that can form in the displacement (see Chapter 4 for a discussion), the negative-flash can be used to determine the phase-state of a fluid mixture in a gridblock during flow simulation (Whitson and Michelsen, 1989). It also plays an important role in computing the Minimum Miscibility Pressure (MMP), a pressure value at which the given composition is on the extension of a critical tie-line (Wang, 1998). Wang and Orr (1997) derived a variant of the negative-flash for systems outside the compositional space (i.e., with negative compositions).

Several researchers have developed flash calculation methods of multiphase systems. Gautam and Seider (1979b) developed a phase splitting algorithm to test the stability of a mixture. The multiphase flash problem was tackled effectively by Michelsen (1994). In his work, Michelsen developed a procedure based on constrained minimization. The original method dealt with positive phase ratios, and it was later generalized to a negative-flash scheme by Leibovici and Nichita (2008).

Here, we study the generalized Rachford-Rice problem for mixtures that can form an arbitrary number of phases. The algorithm combines Successive Substitution Iteration (SSI) with Newton’s method (Michelsen, 1982b). During any SSI iteration, the K-values are assumed constant; therefore, a robust constant K-value negative-flash procedure (i.e., multiphase extension of the Rachford-Rice problem) is required
to obtain a stable SSI algorithm. Our experience indicates that a gradient based scheme to solve the multiphase flash problem is not guaranteed to find the global minimum (Michelsen and Mollerup, 2004). As we show later in this Chapter, the problem is amenable to a bracketing based scheme, such as bisection.

Accurate phase-state identification in systems that can form more than two fluid phases is challenging because any combination of phase-states is possible within the compositional space. Identification of the phase-state using a multiphase negative-flash is sufficient only if the mixture is inside the tie-simplex (assuming that the correct value of $N_p^{\text{max}}$ is known). For three-phase systems, for example, performing a three-phase negative-flash is not enough to confirm the phase-state of single- or two-phase mixtures. Additional two-phase negative-flash computations are required to identify the phase-state of such compositions. As a result, one can develop a negative-flash method that yields the correct phase-state, as well as, the compositions of the phases at equilibrium.

In this Chapter, we show the existence and uniqueness of the solution for the multiphase negative-flash problem with constant K-values. Then, we provide a nested bisection solution procedure for three-phase systems. This procedure is different from the two-dimensional bisection method to solve the three-phase Rachford-Rice equations (Haugen et al., 2007). The method proposed here is a general negative-flash procedure extended recursively to systems that can form any number of phases at equilibrium. We also perform convergence analysis of the SSI scheme. Finally, we demonstrate the effectiveness of the negative-flash procedure in resolving the equilibrium phase behavior of several challenging multiphase systems.

### 2.2 Multiphase Negative-Flash Framework

Here, we review the two-phase problem and formulate the negative-flash for systems with an arbitrary number of phases.
2.2.1 EoS Based Multiphase Negative-Flash

We start with an overview of the multiphase negative-flash framework based on an Equation of State (EoS). Let \( N_p \) be the maximum number of the phases that can coexist for a given system at the specified temperature and pressure conditions (\( N_p = N_p^{\text{max}} \)). Here, we consider the partitioning of a mixture made up of \( N_c \) components into \( N_p \) phases at equilibrium. The set of the equations can be written as

\[
\hat{f}_{i,0} - \hat{f}_{i,j} = 0, \quad i = 0, \ldots, N_c - 1, \quad j = 1, \ldots, N_p - 1, \tag{2.1}
\]

\[
z_i - \sum_{j=0}^{N_p-1} x_{i,j} \nu_j = 0, \quad i = 0, \ldots, N_c - 1, \tag{2.2}
\]

\[
\sum_{i=0}^{N_c-1} (x_{i,0} - x_{i,j}) = 0, \quad j = 1, \ldots, N_p - 1, \tag{2.3}
\]

\[
1 - \sum_{j=0}^{N_p-1} \nu_j = 0, \tag{2.4}
\]

where \( z_i \) denotes the overall composition of component \( i \). The fugacities in Eqs. (2.1), \( \hat{f}_{i,j} \), are computed using an EoS model (e.g., Peng and Robinson (1976)). The above \( N_p(N_c + 1) \) equations are solved for the fraction (\( \nu_j \)) and composition (\( x_{i,j} \)) of each phase. The pure phases define the vertices of a tie-simplex in compositional space. Noting that the actual number of phases at equilibrium may be smaller than \( N_p \), the phase fractions are not restricted to [0, 1].

Newton’s method can be used to solve Eqs. (2.1-2.4). Convergence of the Newton iterations depends on the quality of the initial guess. A good initial guess is usually obtained using a Successive Substitution Iterations (SSI) procedure (Whitson and Michelsen, 1989). During each SSI iteration, the component fugacities are held fixed, and Eqs. (2.2-2.4) are solved simultaneously. Here, we present a generalization of the two-phase negative-flash approach (Whitson and Michelsen, 1989). We note that a constrained optimization method can also be employed (Michelsen, 1994; Leibovici and Nichita, 2008).

Negative-flash iterations can be initiated using various techniques (Voskov and
Tchelepi, 2009c). Here, we describe a general procedure to obtain an initial guess for the \( N_c \)-component \( N_p \)-phase negative-flash problem. Consider an \( M_c \)-component system, where \( N_p \leq M_c \leq N_c \). The \( N_p \)-phase negative-flash iterations can start from a tie-simplex that lies on a face of the \( M_c \)-component space. The problem of solving for a tie-simplex in the \((M_c-1)\)-component system can be tackled in a similar way, and the procedure is recursively extended to all lower dimensional compositional spaces with \( M_c \geq N_p \). Performing an \( N_p \)-phase negative flash in an \( N_p \)-component system is straightforward, since a single tie-simplex parameterizes the entire compositional space.

At convergence, the \( N_p \)-phase negative-flash provides the phase state of the mixture only if the fractions of all \( N_p \) phases are positive (i.e., the mixture is in the \( N_p \)-phase region). Figure (2.1) shows an example where the three-phase negative-flash is not sufficient for identifying the phase-state of mixtures that are outside the tie-triangle. In Chapter 4, we show that all the \( M_p \)-phase regions with \( 1 \leq M_p \leq N_p \) can exist in the compositional space at the given temperature and pressure conditions. Lower-dimensional tie-simplexes parameterize the compositional space around a given tie-simplex. As a result, in order to identify the state of compositions that are outside the \( N_p \)-phase region, a multi-stage negative-flash framework is used. In general, an \((N_p-1)\)-stage negative-flash is required for a system that can form a maximum of \( N_p \) phases at equilibrium. At the \( i \)-th stage, a set of \((N_p+1-i)\)-phase negative-flash calculations is performed, where the initial guess is obtained from a face of the calculated tie-simplexes at stage \( i-1 \). The calculations are terminated once it is found that the mixture is inside a tie-simplex. The composition is single-phase if it is outside all the tie-simplexes calculated in the multi-stage procedure.

### 2.2.2 Overview of the Two-Phase Negative-Flash

In this section, we briefly review the two-phase negative-flash problem. Figure (2.2-a) shows the phase diagram of a three-component mixture with constant K-values. Every composition on the bubble-point locus \((x)\) is at equilibrium with only one composition on the dew-point locus \((y)\). A tie-line connects all the compositions that
Figure 2.1: Correct phase-state of a mixture is determined using a multi-stage negative-flash approach. Compositional system is from Figure (2.10).

share these two equilibrium mixtures. The same tie-line parameterizes all the single-phase compositions that lie on its extension (i.e., all compositions between $a$ and $b$ in Figure (2.2-a)). By performing a negative-flash, a tie-line is computed for a given overall composition ($z$), regardless of its location in the single- or two-phase region.

Allowing for negative equilibrium phase fractions with $\nu_0 + \nu_1 = 1$ (Whitson and Michelsen, 1989), and expressing the overall compositions in terms of two equilibrium phase compositions, we can write:

$$
    z_i = \nu_0 x_{i,0} + \nu_1 x_{i,1} \\
    = \ x_{i,0} + \nu_1 (x_{i,1} - x_{i,0}) \\
    = \ x_{i,0} m_i(\nu_1), \quad i = 0, \ldots, N_c - 1, \quad (2.5)
$$

where $m_i(\nu_1) = 1 + \nu_1 (K_i - 1)$, and $K_i = x_{i,1}/x_{i,0}$. With constant $K$-values (the Rachford-Rice problem (Rachford and Rice, 1952)), the objective function to be solved
for the single unknown phase fraction, $\nu_1$, is

$$f(\nu_1) = \sum_{i=0}^{N_c-1} (x_{i,0} - x_{i,1}) = \sum_{i=0}^{N_c-1} z_i (1 - K_i) = 0. \quad (2.6)$$

Figure (2.2-b) shows $f(\nu_1)$ in the space of physical phase fractions. From Eqs. (2.5), the physical domain of the problem is defined by

$$m_i(\nu_1) > 0, \quad i = 0, \ldots, N_c - 1. \quad (2.7)$$

Noting that,

$$\frac{\partial m_i}{\partial \nu_1} = g_i = K_i - 1, \quad i = 0, \ldots, N_c - 1, \quad (2.8)$$

the physical domain is a bounded set of phase fractions, $\nu_1$, if the K-values satisfy the following condition,

$$\exists i, j \text{ such that } g_i g_j < 0. \quad (2.9)$$

One can show that $f(\nu_1)$ is a monotonically increasing function of $\nu_1$, and that there is only one unique solution.

### 2.2.3 Multiphase Negative-Flash Formulation

We formulate the negative-flash procedure for multiphase systems with constant K-values. The overall mole fraction of a component, $z_i$, is given by:

$$z_i = x_{i,0} \nu_0 + \sum_{j=1}^{N_p-1} x_{i,j} \nu_j, \quad i = 0, \ldots, N_c - 1, \quad (2.10)$$
where we have arbitrarily chosen a phase as the ‘base’ phase, and we have denoted its index by 0. Using

\[
\nu_0 = 1 - \sum_{j=1}^{N_p-1} \nu_j, \quad (2.11)
\]

\[
x_{i,j} = K_{i,j} x_{i,0}, \quad i = 0, \ldots, N_c - 1; \quad j = 1, \ldots, N_p - 1, \quad (2.12)
\]

one obtains

\[
z_i = x_{i,0} \left( 1 + \sum_{j=1}^{N_p-1} \nu_j (K_{i,j} - 1) \right) = x_{i,0} m_i(\nu), \quad i = 0, \ldots, N_c - 1. \quad (2.13)
\]
In order to determine the equilibrium partitioning of all components among all phases, one must solve the following coupled \( N_p - 1 \) equations

\[
f_j(\nu) = \sum_{i=0}^{N_c-1} (x_{i,0} - x_{i,j}) = \sum_{i=0}^{N_c-1} \frac{z_i(1 - K_{i,j})}{m_i(\nu)} = 0, \quad j = 1, \ldots, N_p - 1, \tag{2.14}
\]

for \( N_p - 1 \) unknowns, \( \nu(\equiv \{\nu_j\}, j = 1, \ldots, N_p - 1) \).

Next, we define the domain of the full problem. For this purpose, let us assume that we have an admissible set of K-values (so that the domain of Eqs. (2.14) is bounded). From Eqs. (2.13), we conclude that \( m_i(\nu) \) must be strictly positive for each component (denoted by index \( i \)). Let

\[
\Omega = \{ \nu \in \mathbb{R}^{N_p-1} \mid 0 < m_i(\nu), i = 0, \ldots, N_c - 1 \}, \tag{2.15}
\]

represent the set of ‘physical’ phase fractions. Given an admissible set of K-values, \( \Omega \) is a full-dimensional bounded polytope in \( \mathbb{R}^{N_p-1} \) (Brøndsted, 1983). Let

\[
\Delta = \{ \nu \in \mathbb{R}^{N_p-1} \mid 0 \leq \nu_j \leq 1, j = 1, \ldots, N_p - 1 \}, \tag{2.16}
\]

define the bounded polytope representing the region where all \( N_p \) phases coexist. We note that

\[
m_i(e_j) = K_{i,j} > 0, \quad i = 0, \ldots, N_c - 1, \quad j = 1, \ldots, N_p - 1, \tag{2.17}
\]

where \( e_j \) is a unit-vector in \( \mathbb{R}^{N_p-1} \). As a result, \( \Delta \subset \Omega \).

We next show that \( \Omega \) is a convex polytope in \( \mathbb{R}^{N_p-1} \). Note that a line segment connecting any two arbitrary points in \( \Omega \) is itself within \( \Omega \). To see this, consider two points, \( \nu_1 \) and \( \nu_2 \), inside \( \Omega \); and let \( \nu_3 \) be a point on the line connecting \( \nu_1 \) and \( \nu_2 \):

\[
\nu_3 = \alpha \nu_1 + (1 - \alpha) \nu_2, \tag{2.18}
\]
where \( 0 < \alpha < 1 \). Since

\[
m_i(\nu_3) = 1 + \sum_j \nu_{3,j}(K_{i,j} - 1)
\]

\[
= 1 + \alpha \sum_j \nu_{1,j}(K_{i,j} - 1) + (1 - \alpha) \sum_j \nu_{2,j}(K_{i,j} - 1) + \alpha - \alpha
\]

\[
= \alpha m_i(\nu_1) + (1 - \alpha)m_i(\nu_2) > 0, \quad i = 0, \ldots, N_c - 1,
\]

\( \nu_3 \in \Omega \); and \( \Omega \) is convex.

2.2.4 Three-phase Negative-Flash for Steam-Hydrocarbon Systems

Throughout this work, we consider Equation-of-State based thermodynamic calculations. All components of a mixture may partition among all coexisting phases. Under certain conditions of temperature and pressure, the phase behavior of steam-hydrocarbon system can be simplified. Specifically, one can assume that the hydrocarbon components are not present in the water phase, and the water component is not present in the oil phase. Table (2.1) describes these assumptions.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Gas</th>
<th>Oil</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Component</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>( \times )</td>
<td>( \times )</td>
<td>( - )</td>
</tr>
<tr>
<td>Water</td>
<td>( \times )</td>
<td>( - )</td>
<td>( \times )</td>
</tr>
</tbody>
</table>

Table 2.1: Simplified distribution of components among phases

The mass balance for hydrocarbon components that partition in the oil, vapor, and water phases (with phase ratios denoted by \( L \), \( V \), and \( W \), respectively) is given by:

\[
z_i = x_i L + y_i V + w_i W.
\]

When a phase is not present, its phase ratio becomes negative. For hydrocarbon
components (with subscript $h$), we assume $w_h = 0$, therefore:

$$z_h = x_h L + y_h V,$$

which yields:

$$x_h = \frac{z_h}{L(1 - K_h) + K_h(1 - W)}, \quad (2.20)$$

where $K_h = y_h / x_h$. From the mass balance for the water component,

$$z_w = y_w V + W,$$

one obtains:

$$W = \frac{z_w + y_w (L - 1)}{1 - y_w}. \quad (2.21)$$

Substitution of $W$ from Eq. (2.21) into Eq. (2.20), yields:

$$x_h = \frac{z_h (1 - y_w)}{(1 - y_w - K_h) L + K_h (1 - z_w)}. \quad (2.22)$$

The objective function is:

$$f(L) = \sum_{i=1}^{N_i} (y_i - x_i) = \sum_{h=1}^{N_h} (y_h - x_h) + y_w = 0,$$

where $N_h$ represents the number of hydrocarbon components. Finally, from Eq. (2.22), we obtain:

$$f(L) = \sum_{h=1}^{N_h} z_h (1 - y_w) (K_h - 1) \frac{1 - y_w - K_h}{1 - y_w - K_h - K_h (1 - z_w)} + y_w = 0. \quad (2.23)$$

The problem is to solve $f(L) = 0$ in the physical region for $L$ given by $L_{\text{min}} < L <$
CHAPTER 2. GENERALIZED NEGATIVE-FLASH METHOD

$L_{\text{max}}$. $f(L)$ has $N_h$ asymptotes given by:

$$
\hat{L}_h = \frac{K_h(z_w - 1)}{1 - y_w - K_h}.
$$

(2.24)

Differentiating $f(L)$ yields:

$$
\frac{\partial f(L)}{\partial L} = \sum_{h=1}^{N_h} \frac{z_h(1 - y_w)(1 - K_h)(1 - y_w - K_h)}{[(1 - y_w - K_h)L + K_h(1 - z_w)]^2}.
$$

(2.25)

In the limit where $y_w$ approaches 1, $\partial f(L)/\partial L$ becomes zero between any two adjacent asymptotes. In this case, the simplified negative-flash problem does not have a unique solution. However, if $y_w$ is sufficiently small, $\partial f(L)/\partial L$ will be positive and consequently, $f(L)$ will be monotonically increasing between adjacent asymptotes. Therefore, a bisection-based algorithm can be used to solve for $f(L) = 0$.

Since $x_h > 0$ must be satisfied in Eq. (2.22), physical bounds on $L$ can be obtained from:

$$
L_{\text{min}} = \max (\hat{L}_h) \quad \text{if} \quad 1 - y_w - K_h > 0, \quad (2.26)
$$

$$
L_{\text{max}} = \min (\hat{L}_h) \quad \text{if} \quad 1 - y_w - K_h < 0, \quad (2.27)
$$

where $\hat{L}_h$ is defined in Eq. (2.24). Obviously, $f(L)$ will not have a solution if $L_{\text{max}} < L_{\text{min}}$. Otherwise, a bisection-based algorithm can be used to locate the solution to Eq. (2.23). Figure (2.3) compares the accuracy of this modified negative flash (against the three-phase negative-flash) for a 10-component mixture composed of 80% of the SPE3 mixture (Kenyon and Behie, 1987) and 20% water at various pressures and temperatures.

2.3 Physical Domain of the Problem

In this section, we show that the general negative-flash problem is recursive, and we describe the physical domain of the equations for a subproblem of the $N_p$-phase negative-flash. Then, we specialize our development for three-phase systems.
2.3.1 Solution Domain for the Recursive Subproblem

We show the existence and uniqueness of the general negative-flash problem by considering subproblems of the full problem. Suppose for an $N_p$-phase negative-flash problem, we want to solve for the first $M_p$ phase fractions assuming that the last $N_p - M_p - 1$ phase fractions are known:

$$\min \nu_{j,\Omega} < \nu_j < \max \nu_{j,\Omega}, \quad j = M_p + 1, \ldots, N_p - 1,$$

(2.28)

where $\nu_j$ is a value in the range of the $j$-th phase fraction for the full-dimensional $\Omega$.

The equations to be solved simultaneously for $\nu(\equiv \{\nu_j\}, j = 1, \ldots, M_p)$ are:

$$f_j(\nu) = \sum_{i=0}^{N_c-1} \frac{z_i (1 - K_{i,j})}{m_i(\nu) + n_i} = 0, \quad j = 1, \ldots, M_p,$$

(2.29)

where $n_i$ is a fixed number given by,

$$n_i = \sum_{j=M_p+1}^{N_p-1} \nu_j(K_{i,j} - 1), \quad i = 0, \ldots, N_c - 1.$$

(2.30)
We note that \( m_i(\mathbf{v}) \) is a function of the \( M_p \) phase fractions only. Let

\[
\Omega^{M_p} = \{ \mathbf{v} \in \mathbb{R}^{M_p} \mid m_i(\mathbf{v}) + n_i > 0, \ i = 0, \ldots, N_c - 1 \},
\]

represent the set of physical phase fractions for this subproblem. If \( \Omega \) is bounded, \( \Omega^{M_p} \) will be bounded. Moreover, \( \Omega^{M_p} \) is convex. In order to show this, pick two arbitrary points, \( \mathbf{v}_1, \mathbf{v}_2 \in \Omega^{M_p} \), and a point on the line segment between them: \( \mathbf{v}_3 = \alpha \mathbf{v}_1 + (1 - \alpha) \mathbf{v}_2 \), where \( 0 < \alpha < 1 \). Since

\[
m_i(\mathbf{v}_3) + n_i = 1 + \sum_{j} \nu_{3,j}(K_{i,j} - 1) + n_i \\
= 1 + \alpha \sum_{j} \nu_{1,j}(K_{i,j} - 1) + (1 - \alpha) \sum_{j} \nu_{2,j}(K_{i,j} - 1) \\
+ \alpha - \alpha + \alpha n_i + (1 - \alpha)n_i \\
= \alpha (m_i(\mathbf{v}_1) + n_i) + (1 - \alpha) (m_i(\mathbf{v}_2) + n_i) > 0,
\]

for \( i = 0, \ldots, N_c - 1 \), \( \Omega^{M_p} \) is convex. Therefore, the subproblem of solving for \( M_p \) phase fractions has all the properties of a full negative-flash problem, and a recursive procedure can be applied to solve the multiphase negative-flash problem.

### 2.3.2 Solution Domain for Three-phase Systems

For three-phase systems, \( \Omega \) is a convex polygon, and we solve for two phase fractions \( (\nu_1, \nu_2) \). Figure (2.4) describes the construction of \( \Omega \) for a four-component system with an admissible set of K-values. The three-phase behavior inside the compositional space is shown using tie-triangles (see Figure (2.4-a)). We choose an arbitrary composition and find the unique tie-triangle that parameterizes this composition (i.e., its extension intersects the composition). We extend this tie-triangle plane throughout the compositional space to include all the compositions that it parameterizes. The bounds of this plane are shown by the dashed blue lines in Figure (2.4-a). Since each composition on this plane is associated with a unique set of phase fractions, the set of independent phase fractions \( (\nu_1 \text{ and } \nu_2) \) is mapped into the phase-ratio space \( (\Omega) \). Note that \( \Omega \) is a convex bounded polygon (see Figure (2.4-b)).
Figure 2.4: (a) Three-phase region (wedge-shaped) inside the compositional space of a four-component system with constant K-values, (b) Space of the physical phase fractions (Ω), and the solution point associated with an arbitrary composition in (a). In this example, 
\( z = \{0.412, 0.155, 0.369, 0.063\} \), and 
\( K = \{0.938, 1.446, 0.543, 1.380; 0.713, 0.953, 0.549, 3.533\} \).

In order to define the conditions that must be satisfied by the K-values, consider the following set of K-values for a three-component system,

\[
K = \begin{bmatrix}
0.9 & 2 \\
1.2 & 1.5 \\
1.3 & 0.3
\end{bmatrix}.
\]

Figure (2.5-a) shows the three lines where \( m_i(\nu) = 0 \). Note that \( m_i \) is positive on one side of each line (represented by the arrows). Although for this example, \( \Delta \subset \Omega \), \( \Omega \) is obviously not bounded. However, the setup suggests a procedure to verify the validity of a given set of K-values. We choose a point inside \( \Omega \), \( \nu = 0 \), and calculate the directional derivatives of \( m_i(\nu) \) along \( N_{c - 1} \) lines through \( 0 \) that are parallel to each \( m_{j \neq i}(\nu) = 0 \). The equation of such a line is \((K_{j,1} - 1)\nu_1 + (K_{j,2} - 1)\nu_2 = 0\), and
the phase fractions along this line change as follows

$$
\left( \frac{\partial \nu}{\partial s} \right)_j = \frac{1}{\sqrt{(K_{j,1} - 1)^2 + (K_{j,2} - 1)^2}} \frac{K_{j,2} - 1}{1 - K_{j,1}},
$$

(2.33)

with respect to a parameter $s$. Moreover,

$$
\frac{\mathbf{d} m_i(\mathbf{\nu})}{\mathbf{d} \nu} = g_{i,j} = \sum_{k=1}^{2} \frac{\partial m_i(\mathbf{\nu})}{\partial \nu_k} \left( \frac{\partial \nu_k}{\partial s} \right)_j = \frac{(K_{i,1} - 1)(K_{j,2} - 1) - (K_{i,2} - 1)(K_{j,1} - 1)}{\sqrt{(K_{j,1} - 1)^2 + (K_{j,2} - 1)^2}},
$$

(2.34)

determines how $m_i(\mathbf{\nu})$ varies when another $m_j(\mathbf{\nu})$ is fixed. Here, $i$ and $j$ refer to the component indices, $i, j = 0, \ldots, N_c - 1$. For an unbounded $\Omega$, there exists an $m_j(\mathbf{\nu})$ along which all other $m_i(\mathbf{\nu})$'s are either increasing or decreasing. Therefore, we deduce that $\Omega$ is bounded if and only if

$$
\exists j, k \text{ such that } g_{j,i}g_{k,i} < 0, \quad i = 0, \ldots, N_c - 1.
$$

(2.35)

In this procedure, the number of constraints which must be honored is the number of components. Figure (2.5-b) shows an example of bounded $\Omega$ for a 25-component system with arbitrary K-values.

### 2.4 Existence and Uniqueness of Solution for Multiphase Negative-Flash

Here, we prove that a solution to the set of equations exists within the physical domain, $\Omega$, and that it is unique. We show this for the general multiphase case, and then we describe the developments for three-phase systems. In the following discussion, we assume that the maximum number of coexisting phases is known for EoS-based calculations.
2.4.1 Existence and Uniqueness of Solution for the Recursive Subproblem

We prove that by fixing some phase fractions (\( \nu_j \) with \( j = M_p + 1, \ldots, N_p - 1 \)), the negative-flash problem for the rest of the phase ratios (\( \nu_j \) with \( j = 1, \ldots, M_p \), Eqs. 2.29) has one and only one solution. Let us first show the existence of such a solution. Since

\[
\frac{\partial f_j}{\partial \nu_j} = \sum_{i=0}^{N_p-1} \frac{z_i(1 - K_{i,j})^2}{(m_i(\nu) + n_i)^2} > 0, \quad j = 1, \ldots, M_p, \quad (2.36)
\]

and given that \( f_j(\nu) \) is indefinite at the boundaries of \( \Omega^{M_p} \) (Eq. 2.31), the following equation has one and only one solution

\[
f_j(\nu) = 0, \quad \text{with fixed } \nu_k \neq j, \quad j = 1, \ldots, M_p, \quad (2.37)
\]

where the subscript \( k \neq j \) indicates that all the phase ratios, \( \nu_k \), except \( \nu_j \) are held constant. As a result, \( f_j(\nu) = 0 \) defines a surface which is extended over the range
of $\nu_j$ in $\Omega^{M_p}$. Since this is true for all of the equations ($j = 1, \ldots, M_p$), the surfaces defined by $f_j(\nu) = 0$ must intersect for at least one point, and a solution to Eqs. (2.29) exists. We next show the uniqueness of the solution.

The Jacobian of Eqs. (2.29) is

$$J_{i,j} = \frac{\partial f_i}{\partial \nu_j} = \sum_{k=0}^{N_c-1} \frac{z_k(1 - K_{k,i})(1 - K_{k,j})}{(m_k(\nu) + n_k)^2}, \quad i, j = 1, \ldots, M_p. \quad (2.38)$$

We note that $J$ is a symmetric matrix. First, we show that $J$ is positive definite. For this purpose, we need to prove:

1. $u^T Ju \geq 0, \quad \forall u \in \Omega^{M_p},$

2. $u^T Ju = 0$ implies $u = 0$.

We have,

$$u^T Ju = \sum_{j=1}^{M_p} \sum_{k=1}^{M_p} u_j u_k J_{j,k}$$

$$= \sum_{i=0}^{N_c-1} \frac{z_i}{(m_i(\nu) + n_i)^2} \sum_{j=1}^{M_p} (1 - K_{i,j}) u_j \sum_{k=1}^{M_p} (1 - K_{i,k}) u_k$$

$$= \sum_{i=0}^{N_c-1} \frac{z_i p_i^2}{(m_i(\nu) + n_i)^2}, \quad (2.39)$$

where,

$$p_i = \sum_{j=1}^{M_p} (1 - K_{i,j}) u_j. \quad (2.40)$$

Therefore, $u^T Ju \geq 0$. Moreover, since both $z_i$ and $m_i(\nu) + n_i$ are strictly positive, $u^T Ju = 0$ implies that $p = 0$. From Eq. (2.40), this is the case if and only if $u = 0$. As a result, $J$ is a symmetric positive definite matrix.

In order to show the uniqueness of the solution, we study how the value of $f_{M_p}(\nu)$
changes along the curve defined by

\[ f_j(\nu) = 0, \quad j = 1, \ldots, M_p - 1, \]  

(2.41)
in \( \Omega^{M_p} \). In order to prove the uniqueness of the solution, it is necessary and sufficient to show that the directional derivative of \( f_{M_p}(\nu) \) with respect to \( \nu_{M_p} \) is strictly positive along this trajectory. Differentiating Eqs. (2.41) yields:

\[ \frac{\partial f_j}{\partial \nu_{M_p}} = - \sum_{k=1}^{M_p-1} J_{j,k} \frac{\partial \nu_k}{\partial \nu_{M_p}}, \quad j = 1, \ldots, M_p - 1. \]  

(2.42)

We need to determine the value of

\[ \frac{df_{M_p}}{d\nu_{M_p}} = \sum_{k=1}^{M_p-1} \frac{\partial f_{M_p}}{\partial \nu_k} \frac{\partial \nu_k}{\partial \nu_{M_p}} + \frac{\partial f_{M_p}}{\partial \nu_{M_p}}, \]  

(2.43)
along the trajectory defined by Eqs. (2.42). Let

\[ \mathbf{J} = \mathbf{J}^{M_p} = \begin{pmatrix} \mathbf{J}^{M_p-1} & \mathbf{v} \\ \mathbf{v}^T \frac{\partial f_{M_p}}{\partial \nu_{M_p}} \end{pmatrix}, \]  

(2.44)

where

\[ \mathbf{J}^{M_p-1} = \begin{cases} \frac{\partial f_j}{\partial \nu_k}, \quad j, k = 1, \ldots, M_p - 1, \\
\end{cases} \]

\[ \mathbf{v} = \begin{cases} \frac{\partial f_j}{\partial \nu_{M_p}}, \quad j = 1, \ldots, M_p - 1. \\
\end{cases} \]

From the Sylvester’s criterion (Gilbert, 1991), both \( \mathbf{J}^{M_p} \) and \( \mathbf{J}^{M_p-1} \) have positive determinants. Noting that \( \mathbf{J}^{M_p-1} \) is invertible, Eqs. (2.42) can be written as

\[ - \mathbf{J}^{M_p-1} \mathbf{w} = \mathbf{v}, \]  

(2.45)
where
\[
\mathbf{w} = - (\mathbf{J}^{M_p-1})^{-1} \mathbf{v} = \left\{ \frac{\partial v_j}{\partial \nu_{M_p}} \right\}, \quad j = 1, \ldots, M_p - 1, \tag{2.46}
\]
defines how phase ratios change along the trajectory. Consequently, from Eq. (2.43),
\[
\frac{df_{M_p}}{d\nu_{M_p}} = \sum_{k=1}^{M_p-1} \frac{\partial f_k}{\partial \nu_{M_p}} \frac{\partial v_k}{\partial \nu_{M_p}} + \frac{\partial f_{M_p}}{\partial \nu_{M_p}}
\]
\[
= \mathbf{v}^T \mathbf{w} + \frac{\partial f_{M_p}}{\partial \nu_{M_p}}
\]
\[
= -\mathbf{v}^T (\mathbf{J}^{M_p-1})^{-1} \mathbf{v} + \frac{\partial f_{M_p}}{\partial \nu_{M_p}}
\]
\[
= \frac{\det \mathbf{J}^{M_p}}{\det \mathbf{J}^{M_p-1}}. \tag{2.47}
\]
We conclude from the Sylvester’s criterion that \( \frac{df_{M_p}}{d\nu_{M_p}} \) is strictly positive. Since the numbering of the first \( M_p \) phases is arbitrary,
\[
\frac{df_j}{d\nu_j} > 0, \quad \text{along } f_{k\neq j} = 0, \quad k, j = 1, \ldots, M_p, \tag{2.48}
\]
and the solution to the subproblem is unique.

### 2.4.2 Solution Existence for Three-Phase Systems

For the three-phase negative-flash problem, \( m_i(\nu) = 0 \) is represented by a line in the space of phase fractions. Each line is associated with one component. The corners of \( \Omega \) are determined from the intersection of such lines. Consider the intersection of the \( p^{th} \) and \( q^{th} \) lines. This intersection is considered to be a corner of \( \Omega \), if it satisfies:
\[
m_i(\nu) \geq 0, \tag{2.49}
\]
for all the component indices \((i = 0, \ldots, N_c - 1)\) except \( p \) and \( q \). Once all the corners of \( \Omega \) in the phase-ratio space have been computed, the minimum and maximum values
of $\nu_1$ and $\nu_2$ can be determined ($\Omega$ is a convex polygon). For a given $\nu_1$ such that $\nu_{1,\text{min}} < \nu_1 < \nu_{1,\text{max}}$, one can calculate the range of physical $\nu_2$. Let $j$ and $k$ represent subsets of component indices for which $K_{j,2} > 1$, and $K_{k,2} < 1$, respectively. The physical bounds of $\nu_2$ are obtained from,

$$
\max_j \left( \frac{\nu_1(1 - K_{j,1}) - 1}{K_{j,2} - 1} \right) \leq \nu_2 \leq \min_k \left( \frac{\nu_1(1 - K_{k,1}) - 1}{K_{k,2} - 1} \right). \tag{2.50}
$$

Similarly, the physical domain for $\nu_1$ can be calculated for a given $\nu_2 \in (\nu_{2,\text{min}}, \nu_{2,\text{max}})$. Figure (2.6) shows the physical boundaries of the two phase fractions ($\Omega$, shown by black lines), as well as, $\Delta$ for a 15-component mixture with an arbitrary set of $K$-values that satisfies Eqs. 2.35.

Figure 2.6: $\Omega$ for a 15-component mixture with random $K$-values. Zero loci of both functions are shown by dashed curves. Their intersection is the solution, which lies outside $\Delta$. 
From Eqs. (2.14), we have:

\[
\frac{\partial f_j(\nu)}{\partial \nu} = \sum_{i=0}^{N_c-1} \frac{z_i(1 - K_{i,j})^2}{m_i^2}, \quad j = 1, 2, \tag{2.51}
\]

\[
\frac{\partial f_1(\nu)}{\partial \nu_2} = \frac{\partial f_2(\nu)}{\partial \nu_1} = \sum_{i=0}^{N_c-1} \frac{z_i(1 - K_{i,1})(1 - K_{i,2})}{m_i^2}. \tag{2.52}
\]

From Eqs. (2.51), \(\frac{\partial f_1}{\partial \nu_1} > 0\) and \(\frac{\partial f_2}{\partial \nu_2} > 0\). Moreover, both \(f_1\) and \(f_2\) are indefinite at the boundaries of the compositional space. As a result, for a given \(\nu_2\), there is one and only one \(\nu_1\) such that \(f_1(\nu_1, \nu_2) = 0\). Similarly, for a given \(\nu_1\), there is one and only one \(\nu_2\), such that \(f_2(\nu_1, \nu_2) = 0\). Therefore, the loci of \(f_1(\nu) = 0\) and \(f_2(\nu) = 0\) are represented by two curves extending from \(\nu_{2,\text{min}}\) to \(\nu_{2,\text{max}}\) and from \(\nu_{1,\text{min}}\) to \(\nu_{1,\text{max}}\), respectively (see Figure 2.6). These curves intersect for at least one point, which is a solution to Eqs. (2.14). We note that the solution need not be inside the three-phase region (\(\Delta\)).

### 2.4.3 Solution Uniqueness for Three-Phase Systems

Here, we show that \(f_1 = 0\) and \(f_2 = 0\) intersect at one and only one point, i.e., Eqs. (2.14) have a unique solution. For this purpose, we need to show that the directional derivative of either function along the zero locus of another function is strictly positive (or negative). We have

\[
\frac{df_2(\nu_1, \nu_2)}{d\nu_2} = \frac{\partial f_2(\nu_1, \nu_2)}{\partial \nu_2} + \frac{\partial f_2(\nu_1, \nu_2)}{\partial \nu_1} \frac{\partial \nu_1}{\partial \nu_2}, \tag{2.53}
\]

where \(\partial \nu_1/\partial \nu_2\) is determined by the locus of \(f_1(\nu_1, \nu_2) = 0\). That is

\[
\frac{df_1(\nu_1, \nu_2)}{d\nu_2} = \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_2} + \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_1} \frac{\partial \nu_1}{\partial \nu_2} = 0, \tag{2.54}
\]

\[
\frac{\partial \nu_1}{\partial \nu_2} = -\frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_2} \left/ \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_1} \right. \tag{2.55}
\]
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Substituting Eq. (2.55) in Eq. (2.53) yields

\[
\frac{df_2(\nu_1, \nu_2)}{d\nu_2} = \frac{\partial f_2(\nu_1, \nu_2)}{\partial \nu_2} - \frac{\partial f_2(\nu_1, \nu_2)}{\partial \nu_1} \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_2} \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_1}
\]

\[
= \frac{\partial f_2(\nu_1, \nu_2)}{\partial \nu_2} - \left( \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_2} \right)^2 \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_1},
\] (2.56)

where the derivatives on the right hand side are given by Eqs. (2.51) and (2.52). Note that Eq. (2.56) can be obtained from Eq. (2.47) with \( N_p = 3 \) and \( M_p = 2 \).

Consider the following two vectors in \( N_c \)-dimensional space:

\[
v_i = \sqrt{z_i(1 - K_{i,1})} / m_i, \quad (2.57)
\]

\[
w_i = \sqrt{z_i(1 - K_{i,2})} / m_i. \quad (2.58)
\]

From the Cauchy-Schwarz inequality,

\[
\left( \sum_{i=0}^{N_c-1} v_i w_i \right)^2 \leq \left( \sum_{i=0}^{N_c-1} v_i^2 \right) \left( \sum_{i=0}^{N_c-1} w_i^2 \right). \quad (2.59)
\]

Therefore,

\[
\left( \sum_{i=0}^{N_c-1} \frac{z_i(1 - K_{i,1})(1 - K_{i,2})}{m_i^2} \right)^2 \leq \left( \sum_{i=0}^{N_c-1} \frac{z_i(1 - K_{i,1})^2}{m_i^2} \right) \left( \sum_{i=0}^{N_c-1} \frac{z_i(1 - K_{i,2})^2}{m_i^2} \right),
\]

\[
\left( \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_2} \right)^2 \leq \frac{\partial f_1(\nu_1, \nu_2)}{\partial \nu_1} \frac{\partial f_2(\nu_1, \nu_2)}{\partial \nu_2}. \quad (2.60)
\]

Moreover, since \( v_i \) and \( w_i \) are linearly independent, the equality in Eq. (2.60) does not hold. Therefore, \( df_2(\nu_1, \nu_2)/d\nu_2 \) (and similarly \( df_1(\nu_1, \nu_2)/d\nu_1 \)) is strictly positive (see Figure 2.7), and the solution to Eqs. (2.14) is unique.
Figure 2.7: $f_1(\nu)$ and $f_2(\nu)$ at zero loci of the other function. The problem is from Figure (2.6).

### 2.5 Convergence Analysis of SSI

In this section, we develop a convergence criterion for the Successive Substitution Iterations (SSI) of the multiphase negative-flash problem. This analysis is a generalization of the developments for the two-phase negative-flash problem (Michelsen, 1982b; Whitson and Michelsen, 1989). Consider the equality of fugacities for each component between every pair of fluid phases:

$$\hat{f}_{i,0} = \hat{f}_{i,j}, \quad i = 0, \ldots, N_c - 1, j = 1, \ldots, N_p - 1. \tag{2.61}$$

where the fugacity of component $i$ in phase $j$, $\hat{f}_{i,j}$, is a function of pressure, temperature, and the molar amounts of all the components present in phase $j$. In a
negative-flash problem, we solve Eqs. (2.61) for a mixture with fixed overall compositions, temperature, and pressure. Taking the molar amounts of the phases with \( j = 1, \ldots, N_p - 1 \) as independent variables, we differentiate Eqs. (2.61) for the negative-flash problem to obtain:

\[
\sum_{l=0}^{N_c-1} \left( \frac{\partial \ln \hat{f}_{i,0}}{\partial n_{l,0}} \right)_{p,T,n_{k\neq l,0}} \ dn_{l,0} = \sum_{l=0}^{N_c-1} \left( \frac{\partial \ln \hat{f}_{i,j}}{\partial n_{l,j}} \right)_{p,T,n_{k\neq l,j}} \ dn_{l,j},
\]

(2.62)

for \( i = 0, \ldots, N_c - 1, j = 1, \ldots, N_p - 1 \). The subscript \( n_{k\neq l,j} \) indicates that the molar amounts of all the components except \( l \) are held fixed in the \( j \)-th phase. Substituting

\[
dn_{l,0} = - \sum_{m=1}^{N_p-1} \ dn_{l,m}
\]

(2.63)

and

\[
dn_{l,j} = \sum_{m=1}^{N_p-1} \delta_{j,m} \ dn_{l,m}
\]

(2.64)

in Eqs. (2.62) yields

\[
\sum_{l=0}^{N_c-1} \sum_{m=1}^{N_p-1} \left[ \left( \frac{\partial \ln \hat{f}_{i,0}}{\partial n_{l,0}} \right)_{p,T,n_{k\neq l,0}} + \delta_{j,m} \left( \frac{\partial \ln \hat{f}_{i,j}}{\partial n_{l,j}} \right)_{p,T,n_{k\neq l,j}} \right] \ dn_{l,m} = 0,
\]

(2.65)

where \( i = 0, \ldots, N_c - 1, j = 1, \ldots, N_p - 1 \), and \( \delta_{j,m} \) is the Kronecker delta. Differentiating

\[
\ln \hat{f}_{i,j} = \ln n_{i,j} - \ln \sum_{i=0}^{N_c-1} n_{i,j} + \ln \hat{\varphi}_{i,j} + \ln p
\]

(2.66)

yields

\[
\left( \frac{\partial \ln \hat{f}_{i,j}}{\partial n_{l,j}} \right)_{p,T,n_{k\neq l,j}} = \frac{\delta_{i,l}}{n_{i,j}} - \frac{1}{\sum_{i=0}^{N_c-1} n_{i,j}} + \left( \frac{\partial \ln \hat{\varphi}_{i,j}}{\partial n_{l,j}} \right)_{p,T,n_{k\neq l,j}}
\]

(2.67)
As a result, the Jacobian of Eqs. (2.65) is obtained from

\[ J^E_{i,j,m} = \frac{\delta_{i,l}}{n_{i,0}} - \frac{1}{\sum_{i=0}^{N_c-1} n_{i,0}} \left[ \delta_{i,l} \left( \frac{\partial \ln \hat{\phi}_{i,0}}{\partial n_{i,0}} \right)_{p,T,n \neq l,0} + \delta_{j,m} \left[ \delta_{i,l} \left( \frac{\partial \ln \hat{\phi}_{i,j}}{\partial n_{i,j}} \right)_{p,T,n \neq l,j} + \left( \frac{\partial \ln \hat{\phi}_{i,j}}{\partial n_{i,j}} \right)_{p,T,n \neq l,j} \right] \right], \quad \text{(2.68)} \]

for \( i, l = 0, \ldots, N_c - 1 \), and \( j, m = 1, \ldots, N_p - 1 \). Noting that during each successive Substitution Iteration, the fugacity coefficients are composition-independent, an approximation of the exact Jacobian in Eqs. (2.68) is obtained as

\[ J^A_{i,j,m} = \frac{\delta_{i,l}}{n_{i,0}} - \frac{1}{\sum_{i=0}^{N_c-1} n_{i,0}} \left[ \delta_{i,l} \left( \frac{\partial \ln \hat{\phi}_{i,j}}{\partial n_{i,j}} \right)_{p,T,n \neq l,j} \right]. \quad \text{(2.69)} \]

It can be shown that the error vector for Eqs. (2.65) at iteration \( k+1 \), \( \mathbf{e}^{k+1} \), is related to \( \mathbf{e}^k \) by

\[ \mathbf{e}^{k+1} = \mathbf{M} \mathbf{e}^k = (\mathbf{J}^A)^{-1}(\mathbf{J}^A - \mathbf{J}^E)\mathbf{e}^k; \quad \text{(2.70)} \]

as a result, a necessary condition for the convergence of the iterations is that all the eigenvalues of \( \mathbf{M} \) must be smaller than one in magnitude (Michelsen and Mollerup, 2004). We demonstrate this using a numerical example (see Figure 2.8). We consider a three-phase negative-flash of a three-component mixture at fixed temperature and pressure. All the eigenvalues of \( \mathbf{M} \) are calculated using the negative-flash solutions. In the first example, we plot the eigenvalues as a function of pressure. Note that two sides of the tie-triangle converge at \( p = 211.05 \text{ bar} \), and consequently, the two largest eigenvalues of \( \mathbf{M} \) approach unity. However, for changes in temperature, the parameterizing tie-triangle degenerates (i.e., its area becomes zero). This is confirmed by the fact that all the eigenvalues of \( \mathbf{M} \) remain smaller than one. As we will discuss in Chapter 5, the number of phases exceeds the number of components in this case.
CHAPTER 2. GENERALIZED NEGATIVE-FLASH METHOD

Figure 2.8: Continuous variation of the parameterizing tie-triangles for \( \{C_1(0.2), NC_{10}(0.4), H_2O(0.4)\} \) at \( (a) \ T = 500 \text{ K} \), and \( (c) \ p = 75 \text{ bar} \) until degeneration. The largest eigenvalues of \( M \) for \( (b) \) constant temperature, and \( (d) \) constant pressure approach unity with increase in \( p \) and \( T \), respectively.

2.6 Numerical Results

In this section, we describe the implementation of the negative-flash procedure for three-phase problems. Then, we present numerical results for three- and four-phase systems.
2.6.1 Bisection Based Algorithm for Three-phase Systems

Based on the properties of the problem, a bisection based method is guaranteed to converge to the solution. In order to improve the convergence rate, the bisection strategy can be combined with a gradient based scheme. Here, we use a nested bisection scheme to solve for the two unknowns \( \nu_1 \), and \( \nu_2 \) in a three-phase negative flash problem. Algorithm 1 summarizes this procedure.

**Algorithm 1** Bisection-Based Three-Phase Negative-Flash

1: Check if Eqs. (2.35) hold
2: Find the boundaries of the physical plane using Eq. (2.49) (hence, \( \nu_{2,\text{min}} \), and \( \nu_{2,\text{max}} \))
3: \( \nu_{2,\text{mid}} \leftarrow (\nu_{2,\text{min}} + \nu_{2,\text{max}})/2 \)
4: Use bisection to solve \( f_1(\nu_1, \nu_{2,\text{min}}) = 0 \), and \( f_1(\nu_1, \nu_{2,\text{mid}}) = 0 \) for \( \nu_{1,\text{min}} \), and \( \nu_{1,\text{mid}} \), respectively
5: if \( f_2(\nu_{1,\text{min}}, \nu_{2,\text{min}}) \times f_2(\nu_{1,\text{mid}}, \nu_{2,\text{mid}}) > 0 \) then
6: \( \nu_{2,\text{min}} \leftarrow \nu_{2,\text{mid}} \)
7: else
8: \( \nu_{2,\text{max}} \leftarrow \nu_{2,\text{mid}} \)
9: end if
10: if \( \nu_{2,\text{max}} - \nu_{2,\text{min}} < \varepsilon \) then
11: Stop
12: else
13: Go to step 3
14: end if

Figure (2.9) illustrates the first iterations of the procedure for the 15-component system introduced previously (Figures 2.6 and 2.7). The SSI method for solving two-phase negative-flash problems can be generalized to three-phase systems by introducing this algorithm as a constant K-value flash solver at each iteration. An initial guess for the K-values is required for such an SSI procedure. For this purpose, we flash the overall composition, which yields the ‘largest’ tie-triangle at the given temperature and pressure conditions. The resulting tie-triangle is then used as an initial guess to flash the target overall composition. This method of computing an initial guess is applicable for systems with an arbitrary number of phases (Voskov and Tchelepi, 2009c).
2.6.2 Multi-Stage Three-Phase Negative-Flash

The three-phase negative-flash introduced in the previous section is not sufficient for determining the phase-state of a given composition. This is because the actual two-phase behavior outside the three-phase region may be different from the three-phase negative-flash results (the extension of the edges that define the tie-triangle, see Figure 2.7). These lower and upper bounds become closer as the iterations proceed.
as stable in the single-phase region; however, its Gibbs free energy might decrease by splitting into two phases. To avoid such problems, a second stage using two-phase negative-flash can be employed.

\[ \text{Figure 2.10: Complete parameterization of } \{C_1, C_2, H_2S\} \text{ at } T = 180 \text{ K, } p = 15 \text{ bar. The accurate two-phase behavior is shown by the solid curves outside the three-phase region.} \]

Consequently, in order to determine the number and compositions of the existing phases for a given overall composition at the specified temperature and pressure conditions, a multi-stage negative-flash algorithm can be used. In the first stage, a three-phase negative-flash is performed. If the composition is inside the tie-triangle (three-phase), its phase-state is confirmed. Otherwise, based on the results of the three-phase negative-flash, additional two-phase negative-flash computations are necessary. Here, we assume that the tie-lines are in the plane of the tie-triangle, even though real multicomponent systems show slight deviations from this behavior. The compositions of the tie-triangle edges provide good initial guesses for the two-phase negative-flashes. This is because tie-line compositions change continuously around a tie-triangle edge (see Chapter 3). A tie-line can eventually degenerate to a point (see Figure 2.10). Tie-simplexes also degenerate with increase in pressure, or temperature
(see Figure 2.11).

**Figure 2.11:** Complete parameterization of \( \{H_2O, C_1, C_{10}\} \) at \( T = 520 \text{K} \), (a) \( p = 100 \text{bar} \), (b) tie-triangle degeneration pressure, \( p = 170.53 \text{bar} \)

We present two examples to illustrate the parameterization of three-phase compositional spaces (see Figure 2.12). For each system, we choose two compositions for the initial oil and the injection gas. Using the multi-stage negative-flash strategy, we identify the phase-state, and we parameterize the tie-triangle/tie-line for the compositions along the dilution line (i.e., the line connecting the initial and injection compositions). One tie-triangle and two tie-lines are used to parameterize a single-phase composition. A two-phase composition is parameterized by one tie-triangle and one tie-line. Only a single tie-triangle is required to determine the state of a three-phase composition. In Figure (2.12), phase boundaries show where the phase-state changes along the dilution line between the injection and initial compositions.

The three-phase negative-flash procedure can also be used to generate phase diagrams (see Figure 2.13), and this is demonstrated using two examples: (1) a sour gas example, and (2) a Maljamar reservoir oil (Haugen et al., 2007). The accuracy of our numerical results is verified by a commercial simulator (CMG, 2010b) (For compositions and thermodynamic properties of these mixtures, refer to Appendix ??).
Figure 2.12: (a) Injection of CO$_2$ into \{C$_1$(0.1), C$_{10}$(0.4), H$_2$O(0.4), CO$_2$(0.1)\} at \(T = 500\) K and \(p = 140\) bar, (b) Injection of \{C$_1$(0.5), CO$_2$(0.5)\} into \{C$_6$(0.5), CO$_2$(0.2), C$_2$(0.3)\} at \(T = 180\) K and \(p = 4\) bar. Linear path includes compositions in gas-phase (●), oil-phase (●), two-phase (●), and three-phase (●) states.

We consider dilution of both mixtures with pure CO$_2$. That is, for every mixture which results from the addition of CO$_2$ to the initial feed, we increase the pressure and compute the three-phase behavior. The pressure is increased until the parameterizing tie-triangle degenerates to a tie-line. Figure (2.13) shows the locus of the three-phase boundary, as well as, the tie-triangle degeneration locus. We note that no phase-stability test is required, since the three-phase negative-flash is capable of determining the bounds of the three-phase region accurately.

### 2.6.3 Four-Phase Systems

Given that the negative-flash subproblem has a unique solution, and that all the subproblems of a multiphase negative-flash problem have similar properties, we employ a recursive methodology. For a four-phase system, for example, we solve for \(\nu_3\) at the highest level \((M_p = 3)\). During these iterations, once the values of \(\nu_3\) are obtained,
the first two equations are solved (for $\nu_1, \nu_2$) at the next (lower) level of the recursion ($M_p = 2$, see Eqs. 2.29).

Similar to the three-phase negative-flash problem, one can derive the conditions for admissible K-values of four-phase systems. Here, $\Omega$ is a three-dimensional convex polytope. In order to show that $\Omega$ is bounded, one needs to prove that the $N_c$ planes through $\nu = 0$ which are parallel to the $m_i(\nu) = 0$ planes, are bounded. This is very similar to verifying the validity of a set of K-values for the three-phase negative-flash problem.

Next, we consider the application of negative-flash to parameterize the compositional space of four-phase systems. Once the tie-tetrahedron, which encloses the four-phase region, is computed, we parameterize the lower-dimensional phase regions using tie-triangles and tie-lines. Figure (2.14) shows an example of the four-phase behavior. We note that since in these conditions, water is almost completely immiscible with the other three phases, one side of the tie-tetrahedron almost lies on the C$_2$-N$_2$-CO$_2$ face. Figure (2.15) shows an example for which three-phase space parameterization alone is not sufficient to describe the compositional phase behavior (Voskov and Tchelepi, 2009c).
We finally describe how the negative-flash methodology can be used to construct four-phase diagrams (see Figure 2.16). By decreasing the temperature of the sour gas example discussed before (Haugen et al., 2007), four-phase behavior is revealed for small injection fractions. From this example, we note that by increasing the pressure, it is possible for a single composition to experience the three- and four-phase regions more than once.
Figure 2.15: Four-phase compositional space parameterization at $T = 140$ K and $p = 200$ bar. Each figure shows the tie-tetrahedron and two sets of side tie-triangles.

Figure 2.16: Phase diagram for the four-phase region: sour gas example with $T = 123.15$ K.
Chapter 3

Continuity of Tie-Simplex Parameterization

In the previous Chapter, we showed the existence and uniqueness of the solution to the generalized negative-flash problem. In this Chapter, we prove that the resulting tie-simplexes change continuously with respect to the negative-flash parameters, namely, composition, temperature, and pressure. Continuity of the Compositional Space Parameterization (CSP) is a very important property, since it allows for discrete representation of complex thermodynamic phase behaviors using tie-simplexes.

Similar to the negative-flash developments, we assume that the correct value of $N_{p}^{max}$ for the compositional space across the temperature and pressure ranges of interest is known a-priori. As a result, the Jacobian matrix of the phase equilibrium equations is positive-definite (Michelsen and Mollerup, 2004).

Here, we will study the continuity of the negative-flash strategy in the multi-stage formulation described in the previous Chapter. Let

$$x_j = x_j(z, T, p), \quad j = 1, \ldots, M_p,$$

represent the endpoints of an $M_p$-phase tie-simplex ($2 \leq M_p \leq N_{p}^{max}$) calculated in a multi-stage negative-flash framework. Continuity indicates that bounded changes in the parameters yield well defined changes in the tie-simplex compositions. Note that
the phase-state of a mixture whose overall composition is \( z \) may change with varying flash parameters (\( z \) might be inside or outside \( x_j \)); however, the parameterizing tie-simplexes will change continuously.

We first prove the continuity of compositional space parameterization for two-phase systems (\( N_p^{\text{max}} = 2 \)). Specifically, we show that at constant temperature and pressure, tie-line parameterization of a continuous trajectory in the compositional space is continuous. Moreover, the tie-line that parameterizes a given composition changes continuously with pressure and temperature. Then, we show continuity for systems with \( N_p^{\text{max}} > 2 \).

### 3.1 Parameterization Along a Continuous Path

We start with parameterizing a continuous path in compositional space at constant temperature and pressure. Assuming that both phases are at chemical equilibrium, we write the equality of chemical potentials for each component:

\[
\mu_{i,1} = \mu_{i,2}, \quad i = 1, \ldots, N_c. \tag{3.1}
\]

Note that the chemical potential of component \( i \) in phase \( j \), \( \mu_{i,j} \), is a function of pressure, temperature, and the molar amounts of all the components present in that phase, so that:

\[
\mu_{i,j} = \mu_{i,j}(p, T, n_{1,j}, n_{2,j}, \ldots, n_{N_c,j}). \tag{3.2}
\]

In our discussions in this Chapter and the next, we will assume that the EoS-based negative-flash problem described by Eqs. (3.1) has a unique solution (and invertible Jacobian). The overall molar composition of a component, \( z_i \), is defined as:

\[
z_i = \frac{n_{i,\text{tot}}}{\sum_{l=1}^{N_c} n_{l,\text{tot}}}, \quad i = 1, \ldots, N_c, \tag{3.3}
\]

where \( n_{i,\text{tot}} \) represents the total molar amount of component \( i \). Here, we assume that \( 0 < n_{i,\text{tot}} \). Let \( \xi \) parameterize a continuous trajectory in compositional space, then
along \( \xi \), we have

\[
\frac{d n_{i, \text{tot}}}{d \xi} = \left( \frac{\partial n_{i, \text{tot}}}{\partial \xi} \right)_{p, T, n_{k \neq i, \text{tot}}}, \quad i = 1, \ldots, N_c,
\]

(3.4)

where the subscript \( n_{k \neq i, \text{tot}} \) indicates that the total molar amounts of all the components, \( k \), except \( i \) are held fixed. Differentiating Eqs. (3.3) with respect to \( \xi \) yields:

\[
\sum_{i=1}^{N_c} (\delta_{i,l} - z_i) \left( \frac{\partial n_{l, \text{tot}}}{\partial \xi} \right)_{p, T, n_{k \neq l, \text{tot}}} = \frac{dz_i}{d\xi} \sum_{i=1}^{N_c} n_{l, \text{tot}}, \quad i = 1, \ldots, N_c,
\]

(3.5)

where \( \delta \) represents the Kronecker delta. Therefore, if \( (\partial n_{l, \text{tot}}/\partial \xi)_{p, T, n_{k \neq l, \text{tot}}} \) is bounded, then \( dz_i/d\xi \) will also be bounded (Note that \( 0 < z_i < 1 \), and \( 0 < \sum_{l=1}^{N_c} n_{l, \text{tot}} \)). Similar results can be derived for the compositions of each phase. Since,

\[
\sum_{l=1}^{N_c} \frac{dz_l}{d\xi} = 0,
\]

(3.6)

only a subset of \( N_c - 1 \) equations from Eqs. (3.5) are linearly independent. As a result, there is not a unique set of changes in the molar amounts that corresponds to the given changes in the molar compositions. In the following, we will assume a set of continuous changes in the total molar amounts of components that satisfies Eqs. (3.5) for the given trajectory in compositional space. Here, we provide a formal proof for the first part of the Continuity Theorem:

**Continuity Theorem, Part 1.** At constant temperature and pressure, tie-line parameterization of a continuous path in compositional space is continuous.

**Proof.** First, we consider changes in the phase behavior along a continuous trajectory that is entirely inside the two-phase region. Differentiating Eqs. (3.1) with respect to \( \xi \) at fixed pressure and temperature yields

\[
\sum_{l=1}^{N_c} \left( \frac{\partial \mu_{i,1}}{\partial n_{l,1}} \frac{\partial n_{l,1}}{\partial \xi} \right)_{p, T, n_{k \neq l,1}} - \sum_{l=1}^{N_c} \left( \frac{\partial \mu_{i,2}}{\partial n_{l,2}} \frac{\partial n_{l,2}}{\partial \xi} \right)_{p, T, n_{k \neq l,2}} = 0, \quad i = 1, \ldots, N_c.
\]

(3.7)
CHAPTER 3. CONTINUITY OF TIE-SIMPLEX PARAMETERIZATION

Material balance for each component is:

\[ n_{i,\text{tot}} = n_{i,1} + n_{i,2}, \quad i = 1, \ldots, N_c. \] (3.8)

Along the path, we differentiate Eqs. (3.8) to obtain:

\[ \left( \frac{\partial n_{i,\text{tot}}}{\partial \xi} \right)_{p,T,n_k \neq i,\text{tot}} = \left( \frac{\partial n_{i,1}}{\partial \xi} \right)_{p,T,n_k \neq i,1} + \left( \frac{\partial n_{i,2}}{\partial \xi} \right)_{p,T,n_k \neq i,2}, \quad i = 1, \ldots, N_c. \] (3.9)

Combining Eqs. (3.7) and (3.9) yields:

\[ \sum_{l=1}^{N_c} \left[ J_{i,l}^1 + J_{i,l}^2 \right] \left( \frac{\partial n_{l,2}}{\partial \xi} \right)_{p,T,n_k \neq l,2} = \sum_{l=1}^{N_c} J_{i,l}^1 \left( \frac{\partial n_{l,\text{tot}}}{\partial \xi} \right)_{p,T,n_k \neq l,\text{tot}}, \quad i = 1, \ldots, N_c. \] (3.10)

where

\[ J_{i,l}^m = \left( \frac{\partial \mu_{i,m}}{\partial n_{l,m}} \right)_{p,T,n_k \neq l,m}, \quad i, l = 1, \ldots, N_c, m = 1, 2. \] (3.11)

From the Gibbs-Duhem equation we have:

\[ \sum_{l=1}^{N_c} n_l J_{i,l}^m = 0, \quad i = 1, \ldots, N_c, m = 1, 2. \] (3.12)

As a result, the right-hand-side of Eqs. (3.10) is bounded. We note that the solution of the nonlinear set of equations for the phase splitting problem (Eqs. 3.1), whose Jacobian is \( J^1 + J^2 \), is unique. Consequently, \( J^1 + J^2 \) is invertible, and the differential of \( n_{l,2} \) in Eqs. (3.10) is bounded. From Eqs. (3.5) written for the molar amounts and the compositions of each phase, we conclude that the tie-line compositions, \( x_{i,j} \), vary continuously along the trajectory.

Next, we generalize the continuity of parameterization along any trajectory. For this purpose, we consider a path, \( \mathcal{C} \), in the single-phase region. Since the parameterization of the entire compositional space is unique, we define a curve, \( \Gamma \), within the two-phase region that has an identical parameterization as \( \mathcal{C} \) (see Figure 3.1). \( \Gamma \) is also defined to be the midpoint locus of a set of tie-lines. We can demonstrate that
if $C$ is continuous, then $\Gamma$ will be continuous. For this purpose, consider two compositions along $C$, $z(\xi_1)$ and $z(\xi_1 + d\xi)$, that are infinitesimally apart from each other. We need to show that the distance between the corresponding compositions on $\Gamma$, $\gamma(\xi_1)$ and $\gamma(\xi_1 + d\xi)$, is finite. Starting from $\gamma(\xi_1)$, we parameterize the straight line between $\gamma(\xi_1)$ and $\gamma(\xi_1 + d\xi)$. Assuming that $d\xi$ is small enough, the line segment is entirely within the two-phase region, and therefore, it has a continuous parameterization. As a result, the midpoint of the parameterizing tie-lines changes continuously, and $\Gamma$ is continuous. Since the parameterizations of $C$ and $\Gamma$ are identical, the proof is complete.

\[\text{Figure 3.1: Parameterization continuity for a path, } C(\xi), \text{ in the single-phase region. } z \text{ and } \gamma \text{ are the corresponding points on } C \text{ and } \Gamma, \text{ respectively. In this example, } T = 450 \text{ K and } p = 180 \text{ bar.}\]
3.2 Parameterization in Pressure and Temperature

Next, we consider a mixture with a fixed overall composition, and we prove the second part of the Continuity Theorem:

**Continuity Theorem, Part 2.** At fixed temperature (or pressure), the tie-line that parameterizes a given composition changes continuously with pressure (or temperature).

*Proof.* Let us consider changes in pressure. First, we assume that when pressure is changing, the composition remains inside the two-phase region. For a mixture with given overall composition, changing the pressure (at fixed temperature) results in a redistribution of the components between the two phases. Consequently, the chemical potential of a component changes as a function of pressure and component molar amounts. Partial differentiation of Eqs. (3.1) with respect to pressure yields:

\[
\sum_{l=1}^{N_c} \left( \frac{\partial \mu_{i,1}}{\partial n_{l,1}} \right)_{p,T,n_k \neq l,1} \cdot \left( \frac{\partial n_{l,1}}{\partial p} \right)_{T,n_k \neq l,1} + \left( \frac{\partial \mu_{i,1}}{\partial p} \right)_{T,n_k,1} = 0,
\]

for \( i = 1, \ldots, N_c \). Considering that the overall composition (and \( n_{i,tot} \) for each component) is fixed, we differentiate Eqs. (3.8) to obtain:

\[
\left( \frac{\partial n_{i,1}}{\partial p} \right)_{T,n_k \neq i,1} + \left( \frac{\partial n_{i,2}}{\partial p} \right)_{T,n_k \neq i,2} = 0, \quad i = 1, \ldots, N_c.
\]

Combining Eqs. (3.13) and Eqs. (3.14) yields:

\[
\sum_{l=1}^{N_c} \left[ \left( \frac{\partial \mu_{i,1}}{\partial n_{l,1}} \right)_{p,T,n_k \neq l,1} + \left( \frac{\partial \mu_{i,2}}{\partial n_{l,2}} \right)_{p,T,n_k \neq l,2} \right] \cdot \left( \frac{\partial n_{l,2}}{\partial p} \right)_{T,n_k \neq l,2} = \left( \frac{\partial \mu_{i,1}}{\partial p} \right)_{T,n_k,1} - \left( \frac{\partial \mu_{i,2}}{\partial p} \right)_{T,n_k,2}, \quad i = 1, \ldots, N_c.
\]
CHAPTER 3. CONTINUITY OF TIE-SIMPLEX PARAMETERIZATION

Using Eqs. (3.11), Eqs. (3.15) simplify to:

\[
\sum_{l=1}^{N_c} \left[ J_{i,l}^1 + J_{i,l}^2 \right] \cdot \left( \frac{\partial n_{l,2}}{\partial p} \right)_{T,n_{k\neq l,2}} = \bar{V}_{i,1} - \bar{V}_{i,2}, \quad i = 1, \ldots, N_c, \quad (3.16)
\]

where \( \bar{V}_{i,j} \) denotes the partial molar volume of component \( i \) in phase \( j \). Similarly, the equilibrium phase amounts of a given mixture at fixed pressure change with temperature as follows:

\[
\sum_{l=1}^{N_c} \left[ J_{i,l}^1 + J_{i,l}^2 \right] \cdot \left( \frac{\partial n_{l,2}}{\partial T} \right)_{p,n_{k\neq l,2}} = \bar{S}_{i,2} - \bar{S}_{i,1}, \quad i = 1, \ldots, N_c, \quad (3.17)
\]

where the right-hand-side is the difference between the partial molar entropies of the \( i \)-th component. From

\[
M_j = \sum_{l=1}^{N_c} n_{l,j} \bar{M}_{l,j}, \quad j = 1, 2, \quad (3.18)
\]

we note that the partial molar property of each component (\( \bar{M}_{l,j} \)) has a finite value. As a result, the derivatives of the molar amounts in Eqs. (3.16) and Eqs. (3.17) are finite, and from Eqs. (3.5), the compositions of parameterizing tie-lines change continuously.

Next, we generalize the continuity of parameterization for a single-phase composition. For this purpose, we consider a curve, \( \Gamma \), in the two-phase region that (1) has an identical parameterization as the single-phase composition, \( z \), and (2) is the midpoint locus of a set of tie-lines. Since parameterization of the compositional space is unique at each pressure value, \( \Gamma \) is unique. We show that \( \Gamma \) is a continuous curve; and therefore, the pressure changes continuously along \( \Gamma \).

In order to show the continuity of \( \Gamma \), consider the midpoint, \( \gamma \), of the parameterizing tie-line at some pressure value, \( p_1 \). We need to demonstrate that \( \gamma(p_1 + dp) \) is at a finite distance from \( \gamma(p_1) \) if \( dp \) is small enough (see Figure 3.2). For this purpose, we first change pressure from \( p_1 \) to \( p_1 + dp \), then calculate the tie-line that parameterizes \( \gamma(p_1) \) at \( p_1 + dp \). Assuming that \( dp \) is small enough, \( \gamma(p_1) \) will remain within the two-phase region, and the midpoint of the resulting tie-line, \( \gamma' \), is at a
finite distance from \( \gamma(p_1) \). Next, at constant pressure, \( p_1 + dp \), we parameterize the straight line connecting \( \gamma' \) to the given mixture, \( z \). The parameterization of such a line is continuous, and therefore, \( \gamma(p_1 + dp) \) is at a finite distance from \( \gamma' \). As a result, \( \Gamma \) is a continuous curve (along which pressure changes continuously). Since the parameterizations of \( \Gamma \) and the single-phase composition are identical, the proof is complete. Using a similar argument, parameterization of a single-phase composition with temperature at constant pressure is continuous.

\[ \begin{align*}
&\text{CO}_2 \\
&\text{C}_1 \text{N}_10 \\
&x_2(p) \Gamma(p) x_1(p) \\
&z
\end{align*} \]

**Figure 3.2:** Parameterization in pressure for a single-phase mixture, \( z \). Numbers show the pressure (in bar) of the tie-lines; for this system, \( T = 450 \) K.

Using numerical experiments, we can show that for a given overall composition at fixed temperature, there is a Minimal Critical Pressure (MCP) value (Voskov and Tchelepi, 2009a) such that \( J^1 = J^2 \) holds. Noting that \( J^m \) is a singular matrix (see Eqs. 3.12), the tie-lines degenerate to a point. Similar arguments can be made for changes in temperature, or along a trajectory in the compositional space.

Figure (3.3) describes the parameterization continuity for two-phase, four-component...
 systems. In the first example (see Figure 3.3-a), we show an isothermal table of tie-lines \((T = 450 \text{ K})\) for a fixed composition. The mixture is initially in the two-phase region. As the pressure increases, the composition becomes single-phase, and the parameterizing tie-line degenerates at \(p = 175 \text{ bar}\). We also show how parameterization of the same composition changes with temperature at fixed pressure (see Figure 3.3-b). For this example, the composition is initially single-phase, and it enters the two-phase region as the temperature increases. The parameterizing tie-line becomes critical at \(T = 550 \text{ K}\).

![Figure 3.3: Continuity of compositional space parameterization for four-component two-phase systems](image)

(a) \(T = 450 \text{ K}, p = (10, 175) \text{ bar}\)  
(b) \(p = 100 \text{ bar}, T = (250, 550) \text{ K}\)

3.3 Parameterization Continuity for Systems with an Arbitrary Number of Phases

Next, we consider systems that can form a maximum of \(N_p\) phases at equilibrium, where \(N_p\) is a pre-defined number. Let us first consider a continuous trajectory inside the \(N_p\)-phase region, and study how the parameterizing tie-simplexes (denoted by \(\Delta^{N_p-1}\)) change along the path at constant temperature and pressure. The equality
Chapter 3. Continuity of Tie-Simplex Parameterization

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of chemical potentials for each component between every pair of phases defines a tie-simplex:

\[ \mu_{i,1} = \mu_{i,j}, \quad i = 1, \ldots, N_c; j = 2, \ldots, N_p. \] (3.19)

Differentiating Eqs. (3.19) with respect to a parameter along the path, \( \xi \), at constant temperature and pressure yields

\[ \sum_{l=1}^{N_c} J^1_{i,l} \left( \frac{\partial n_{i,1}}{\partial \xi} \right)_{p,T,n_{k \neq i,1}} = \sum_{l=1}^{N_c} J^j_{i,l} \left( \frac{\partial n_{i,j}}{\partial \xi} \right)_{p,T,n_{k \neq i,j}}, \quad i = 1, \ldots, N_c; j = 2, \ldots, N_p. \] (3.20)

where \( J_{i,j} \) for each phase \( j \) is defined by Eq. (3.11). We consider splitting of each component among all \( N_p \) phases:

\[ n_{i,tot} = \sum_{m=1}^{N_p} n_{i,m}, \quad i = 1, \ldots, N_c. \] (3.21)

Therefore,

\[ \left( \frac{\partial n_{i,tot}}{\partial \xi} \right)_{p,T,n_{k \neq i,tot}} = \left( \frac{\partial n_{i,1}}{\partial \xi} \right)_{p,T,n_{k \neq i,1}} + \sum_{m=2}^{N_p} \left( \frac{\partial n_{i,m}}{\partial \xi} \right)_{p,T,n_{k \neq i,m}}. \] (3.22)

Combining Eqs. (3.20) and Eqs. (3.22), and noting that

\[ \left( \frac{\partial n_{i,j}}{\partial \xi} \right)_{p,T,n_{k \neq i,j}} = \sum_{m=2}^{N_p} \delta_{j,m} \left( \frac{\partial n_{i,m}}{\partial \xi} \right)_{p,T,n_{k \neq i,m}}, \] (3.23)

we obtain

\[ \sum_{l=1}^{N_c} \sum_{m=2}^{N_p} \left[ J^1_{i,l} + \delta_{j,m} J^j_{i,l} \right] \left( \frac{\partial n_{i,m}}{\partial \xi} \right)_{p,T,n_{k \neq i,m}} = \sum_{l=1}^{N_c} J^1_{i,l} \left( \frac{\partial n_{i,tot}}{\partial \xi} \right)_{p,T,n_{k \neq i,tot}}, \] (3.24)

where \( i = 1, \ldots, N_c; j = 2, \ldots, N_p \). Since the multiphase flash problem for \( N_p \) phases (Eqs. 3.19) has a unique solution (\( N_p \)-phase tie-simplexes do not intersect), the Jacobian of Eqs. (3.24) is invertible. Moreover, because the right-hand-side of
Eqs. (3.24) is bounded, the partial derivatives of $n_{l,m}$ are bounded, and from Eqs. (3.5), the equilibrium compositions change continuously.

Next, let us consider a continuous trajectory, $\mathcal{C}$, that is outside the $N_p$-phase region. Since parameterization of the compositional space using $N_p$-phase tie-simplexes is unique, we can define a curve, $\Gamma$, inside the $N_p$-phase region that has an identical parameterization as $\mathcal{C}$. We also define $\Gamma$ to be the center of a set of $N_p$-phase tie-simplexes (hence, $\Gamma$ is unique). Similar to the two-phase case, one can conclude that $\Gamma$ is continuous if $\mathcal{C}$ is continuous, and consequently, parameterization along $\mathcal{C}$ (using $N_p$-phase tie-simplexes) is continuous.

Continuity of multiphase compositional space parameterization can be shown for changes in pressure or temperature. For this purpose, we consider a mixture with a fixed overall composition and determine how the parameterizing $N_p$-phase tie-simplexes change with pressure, or temperature. Initially, we assume that the mixture remains inside the $N_p$-phase region with changes in pressure or temperature. It can be shown that the molar amounts change with respect to $p$ or $T$ as follows:

\[
\sum_{l=1}^{N_c} \sum_{m=2}^{N_p} [J_{i,l}^j + \delta_{j,m}J_{i,l}^j] \left( \frac{\partial n_{l,m}}{\partial p} \right)_{T,n_{k\neq l,m}} = \bar{V}_{i,1} - \bar{V}_{i,j}, \tag{3.25}
\]

\[
\sum_{l=1}^{N_c} \sum_{m=2}^{N_p} [J_{i,l}^j + \delta_{j,m}J_{i,l}^j] \left( \frac{\partial n_{l,m}}{\partial T} \right)_{p,n_{k\neq l,m}} = \bar{S}_{i,j} - \bar{S}_{i,1}, \tag{3.26}
\]

for $i = 1, \ldots, N_c$, and $j = 2, \ldots, N_p$. Eqs. (3.25) and Eqs. (3.26) indicate that the partial derivatives of $n_{l,m}$ are bounded; as a result, the parameterizing tie-simplexes change continuously with $p$ or $T$.

Continuity of parameterization in pressure and temperature can be generalized to any composition. Consider a mixture, $z$, outside the $N_p$-phase region. Let $\Gamma$ be a curve within the $N_p$-phase region that (1) has an identical parameterization as $z$, and (2) is the center of a set of $N_p$-phase tie-simplexes. Since parameterization of the compositional space using $N_p$-phase tie-simplexes is unique at each pressure value, $\Gamma$ is unique. It can be shown that $\Gamma$ is a continuous curve (see the similar arguments for the two-phase case), and the parameterization of $z$ in $p$ (or $T$) is continuous. Figure
(3.4) shows the continuity of three-phase compositional space parameterization (in pressure and temperature) for a four-component system.

\[
\begin{align*}
C_1 & \quad C_6 & \quad CO_2 & \quad C_2 \\
C_2 & \quad C_6 & \quad & \quad & \quad
\end{align*}
\]

\[\text{(a) } T = 180 \text{ K}, \ p = (1, 18.5) \text{ bar} \]
\[\text{(b) } p = 5 \text{ bar}, \ T = (150, 202.9) \text{ K} \]

**Figure 3.4:** Continuity of compositional space parameterization for four-component three-phase systems

The above developments describe the continuity of parameterization in the multi-phase region with \(N_p\) (maximum) phases. One can generalize the continuity theorem for the rest of the compositional space with a fewer number of phases. In order to explain this, let us consider a system with \(N_p = 3\). As we will discuss in the next Chapter, one three-phase region and three two-phase regions can coexist inside the compositional space. Consider two-phase parameterization of a continuous curve at constant temperature and pressure. Depending on the location of the curve, tie-lines from different two-phase regions can be used for the parameterization. Moreover, a mixture can be parameterized by two tie-lines from different two-phase regions. However, for each two-phase region, the parameterization is governed by an equation similar to Eq. (3.10). We note that tie-lines in each region do not intersect, and therefore, the Jacobian is invertible. As a result, the parameterization in each two-phase region is continuous. Note that, although there may be different parameterizations for this curve, each parameterization is continuous and represented by a unique set.
of tie-lines.
Chapter 4

Compositional Space Adaptive Tabulation

From our discussions in the last two chapters, it is evident that tie-simplexes are perfectly suitable to parameterize the compositional space. In this Chapter, we describe the tie-simplex based Compositional Space Adaptive Tabulation (CSAT) framework for multiphase (three- or more phases) compositional simulation.

The development of CSAT for numerical simulation is motivated by theoretical findings from Method of Characteristics (MoC) solutions of gas injection problems (Orr, 2007). Previous work has shown that interpolation in the discretized tie-line space (with respect to temperature and pressure) can replace thermodynamic stability analysis, and significantly improve the efficiency of two-phase thermal-compositional simulation (Voskov and Tchelepi, 2008, 2009a,b; Iranshahr et al., 2010).

Similarly, tie-simplex tabulation is a promising strategy to perform thermodynamic calculations (stability and flash) in multiphase compositional simulation. This is because:

1. Performing negative-flash for all mixtures on the extension of a tie-simplex (inside or outside) yields the same result.

2. Tie-simplex parameterization is unique; tie-simplexes do not intersect inside multiphase regions.
3. Tie-simplex parameterization is continuous, which allows for discrete representation of the compositional space.

4. In numerical simulation, the composition of gridblocks that require thermodynamic stability analysis lie in the neighborhood of a few key tie-simplexes (Helfferich, 1981; Voskov and Tchelepi, 2009c).

Multiphase CSAT is a very efficient and robust approach to implement the idea of multi-stage negative-flash introduced in Chapter 2. Considering the above properties, CSAT uses negative-flash to tabulate the highest-dimensional tie-simplex, as well as, all multiphase regions on its extension. For this purpose, tabulation is performed in temperature, pressure and composition. Therefore, the setup is more complex than two-phase systems. In Chapter 5, we will show that this type of parameterization is necessary and sufficient to guarantee the global minimization of Gibbs free energy during the phase-state identification stage.

In our developments, we will assume that a non-degenerate base tie-simplex parameterization is associated with the compositional system of interest, and that the maximum number of phases, \( N_p^{\text{max}} \), that can coexist in the base parameterization is known. \( N_p^{\text{max}} \) is defined such that the extensions of \( N_p^{\text{max}} \)-phase tie-simplexes do not intersect inside the compositional space (see Voskov and Tchelepi (2009c) and Chapter 2). As we will discuss further, with changes in temperature and pressure, multiphase regions in the base parameterization become critical (degenerate to lower-dimensional multiphase regions), or they disappear from the compositional space. So, we assume that no new multiphase region will appear with changes in the \( T-p \) conditions. It is important to note that when the assumed \( N_p^{\text{max}} \) is wrong, tie-simplexes will actually intersect inside some multiphase regions (see Voskov and Tchelepi (2009c), for example). In this case, the value of \( N_p^{\text{max}} \) must be increased, and the parameterization must be repeated. So, the value of \( N_p^{\text{max}} \) can be determined adaptively, even though for most displacement problems of interest, \( N_p^{\text{max}} \) is usually known a-priori.

If critical tie-simplexes exist at the given conditions, the base parameterization is obtained by changing the temperature and pressure. Moreover, the number of phases may exceed the number of components in a degenerate compositional space. We will
describe the parameterization of such systems in Chapter 5.

The value of $N_p^{max}$ is estimated based on the preliminary knowledge of the system (e.g., existing hydrocarbon components, temperature, and pressure conditions). Further studies include parameterization of the compositional space between injection and initial compositions across the practical range of temperature and pressure (determined from the initial, injection, and production conditions). These primitive studies lead to an initial estimate of $N_p^{max}$, which is used to perform actual reservoir flow simulation. For this purpose, CSAT constructs base parameterizations in multiphase tables (as we will discuss further). According to the practical $T\text{-}p$ range, multiphase regions of the base parameterization might degenerate at further $T\text{-}p$ levels of the table. If any tie-simplexes intersect inside the multiphase regions, the simulation studies are performed with the modified value of $N_p^{max}$.

In this Chapter, we describe a generalization of the CSAT framework for systems with an arbitrary number of phases. Then, we describe the details of the three-phase CSAT, and present several numerical examples.

### 4.1 Multiphase CSAT

Phase behavior in systems that can form more than two fluid phases is complicated because a large number of regions with two or more phases may be present. (see Figure 4.1). Here, we describe construction of an $N_p$-phase base tie-simplex parameterization.

We consider an $N_p$-phase tie-simplex, $\Delta^{N_p-1}$, in a system that can form a maximum of $N_p$ phases at equilibrium ($N_p > 2$). Starting from each $(m-1)$-face of $\Delta^{N_p-1}$, where $m = 2, \ldots, N_p - 1$, an $m$-phase region is extended throughout the compositional space. Let $\Gamma_f^m$ represent a hyper-volume in the $m$-phase region that starts from the $f$-th $(m-1)$-face of $\Delta^{N_p-1}$. By definition, $\Gamma_f^m$ is parameterized by $\Delta^{N_p-1}$; that is, any composition on $\Gamma_f^m$ can be expressed as a linear combination of the vertices of $\Delta^{N_p-1}$. Moreover, $\Gamma_f^m$ is the locus of the geometric center of a set of tie-simplexes in the $m$-phase region. From the uniqueness of flash calculations in the $m$-phase region, $\Gamma_f^m$ is unique. Also, note that $\Gamma_f^m$ is a continuous hyper-volume, and its representation
requires an \((N_p - m)\)-dimensional parameterization.

The total number of \(\Gamma^m_j\)'s in an \(N_p\)-phase system is given by the binomial coefficient

\[
\binom{N_p}{m} = \frac{N_p!}{m!(N_p - m)!}.
\]  

(4.1)

In a three-phase system, for example, a \(\Gamma^2_j\) curve is connected to each edge of a tie-triangle (see Figure 4.1). Similarly, in a four-phase system, a \(\Gamma^3_j\) curve starts from each face of a tie-tetrahedron. Moreover, each edge of a tie-tetrahedron is connected to a \(\Gamma^2_j\) surface (see the Numerical Results section).

In the general CSAT framework, a multiphase table is constructed by parameterizing the multiphase regions around a given overall composition at discrete temperature and pressure values. For each level of the \(T - p\) grid, \(\Delta^{N_p-1}\) is calculated, and all the \(m\)-phase regions around \(\Delta^{N_p-1}\) are parameterized using \(\Gamma^m_j\)'s. The multi-stage approach for parameterization is designed such that \(\Gamma^{m-1}\) is calculated after all \(\Gamma^m_j\) hyper-volumes are constructed. Therefore, once the \(N_p\)-phase tie-simplex is calculated, the procedure starts with discretizing \(\Gamma^{N_p-1}\) and ends with tabulating tie-lines (\(\Gamma^2\)). The parameterization details at each stage are given in the next section. We use the multiphase negative-flash procedure to compute the parameterizing tie-simplexes. Since \(\Delta^{N_p-1}\) for a given mixture changes continuously with temperature and pressure, \(\Gamma^m_j\) is a continuous function of these parameters. Note that \(\Gamma^m_j\) is a continuous hyper-volume, and it is parameterized by \(\Delta^{N_p-1}\). Moreover, construction of \(\Gamma^m_j\) is still possible if \(\Delta^{N_p-1}\) has degenerated. As a result, parameterizing tie-simplexes for each \(\Gamma^m_j\) proves to be very robust in the general CSAT framework.

From extensive numerical experiments, we can show that the volume of the \(M_p\)-phase tie-simplex \(\Delta^{M_p-1}\), where \(M_p = 2, \ldots, N_p\) that parameterizes a given mixture approaches zero with changes in pressure or temperature (i.e., \(\Delta^{M_p-1}\) degenerates to \(\Delta^{M_p-2}\)). Next, we show that the critical tie-simplexes \(\Delta^{M_p-2}\)'s change continuously in the compositional space.

Consider a continuous curve, \(\mathcal{C}\), in a compositional space with constant temperature. Let \(v\) denote the volume of a tie-simplex, \(\Delta^{M_p-1}\) (Voskov and Tchelepi, 2009c).
Figure 4.1: Complete parameterization of \{C_1, C_{10}, H_2O\} at $T = 520$ K, and $p = 75$ bar using one tie-triangle (in red) and three sets of tie-lines (in blue). The three $\Gamma^2$ curves are shown in green.
We assume that $C$ can be parameterized with a set of tie-simplexes, $\Delta^{M_p-1}$, at different pressure values, such that the volume of each tie-simplex, $v$, is a fixed value, $\varepsilon$. Due to the continuity of parameterization, the set of the parameterizing tie-simplexes with volume $\varepsilon$ change continuously along $C$ (also, pressure changes continuously along $C$). Letting $\varepsilon$ be a value close to zero, we conclude the continuity of degenerate tie-simplexes inside the compositional space. For a majority of hydrocarbon systems (Voskov and Tchelepi, 2009a), the set of degenerate tie-simplexes is unique for the fixed temperature or pressure. In the following sections, we describe the details of tie-simplex parameterization and phase-state identification in the CSAT framework.

4.2 Discretization of $\Gamma^m_f$

Here, we describe the discretization of $\Gamma^m_f$ on the $f$-th ($m-1$)-face of an $N_p$-phase tie-simplex, $\Delta^{N_p-1}$ ($N_p$ represents the maximum number of coexisting phases). A similar approach is presented by Voskov and Tchelepi (2009c), but it is limited to the parameterization of a tie-triangle plane.

Starting from the center of an $m$-phase tie-simplex, $\Delta^{m-1}$, we solve for the new points that are farther by a given distance, $d$. We note that the center of $\Delta^{m-1}$, $a$, lies on $\Gamma^m_f$. Moreover, the vertices of $\Delta^{m-1}$ may not be parameterized by $\Delta^{N_p-1}$.

Let $x_j$ represent the compositions of the $j$-th vertex of $\Delta^{N_p-1}$, where $j = 1, \ldots, N_p$. We also use $y_j$ to represent the $j$-th vertex of $\Delta^{m-1}$, where $j = 1, \ldots, m$. The new composition, $b$,

1. is parameterized by $\Delta^{N_p-1}$,
2. satisfies $(b - a) . (y_1 - y_j) = 0$ for $j = 2, \ldots, m$,
3. satisfies $\|b - a\|_2 = d$, where $d$ is a measure of the separation between two adjacent $\Delta^{m-1}$s.

First, we express $b$ as a linear combination of the vertices of $\Delta^{N_p-1}$:

$$b = \sum_{j=1}^{N_p} \nu_j x_j = X\nu$$

(4.2)
CHAPTER 4. COMPOSITIONAL SPACE ADAPTIVE TABULATION

where $X$ is an $N_c \times N_p$ matrix of the vertices of $\Delta^{N_p-1}$, and $\nu$ is an $N_p \times 1$ vector of the phase fractions. From

$$(b - a) \cdot (y_1 - y_j) = 0, \quad j = 2, \ldots, m,$$  \hspace{1cm} (4.3)

we write,

$$Yb = Ya$$  \hspace{1cm} (4.4)

where $Y$ is an $(m - 1) \times N_c$ matrix:

$$Y = \begin{bmatrix}
y_{1,1} - y_{1,2} & y_{2,1} - y_{2,2} & \cdots & y_{N_c,1} - y_{N_c,2} \\
y_{1,1} - y_{1,3} & y_{2,1} - y_{2,3} & \cdots & y_{N_c,1} - y_{N_c,3} \\
\vdots & \vdots & \ddots & \vdots \\
y_{1,1} - y_{1,m} & y_{2,1} - y_{2,m} & \cdots & y_{N_c,1} - y_{N_c,m}
\end{bmatrix}.$$  \hspace{1cm} (4.5)

After combining Eqs. (4.2) and (4.4), and adding $\sum_j \nu_j = 1$ to the set of equations, we obtain

$$\underbrace{B}_{m \times N_p \ N_p \times 1} \underbrace{\nu}_{N_p \times 1} = \underbrace{v}_{m \times 1}$$  \hspace{1cm} (4.6)

where

$$B = \begin{bmatrix} YX \\ u \end{bmatrix}$$  \hspace{1cm} (4.7)

$$v = \begin{bmatrix} Ya \\ 1 \end{bmatrix}$$  \hspace{1cm} (4.8)
and \( \mathbf{u} \) is the \( 1 \times N_p \) vector of ones. We express \( \mathbf{B} \) and \( \mathbf{\nu} \) as:

\[
\mathbf{B} = \begin{bmatrix} \mathbf{B}_1 & \cdots & \mathbf{B}_{N_p-m} & \mathbf{B}' \end{bmatrix},
\]

(4.9)

\[
\mathbf{\nu} = \begin{bmatrix} \nu_1 \\ \vdots \\ \nu_{N_p-m} \\ \mathbf{\nu}' \end{bmatrix},
\]

(4.10)

where \( \mathbf{B}_j \) is the \( j \)-th column of \( \mathbf{B} \) \( (1 \leq j \leq N_p - m) \). Also, note that \( \mathbf{B}' \) is an \( m \times m \) matrix. Consequently, from Eq. (4.6)

\[
\mathbf{\nu}' = \mathbf{B}'^{-1} \mathbf{\nu} - \sum_{j=1}^{N_p-m} \mathbf{B}'^{-1} \mathbf{B}_j \nu_j
\]

(4.11)

We write \( \mathbf{X} \) as

\[
\mathbf{X} = \begin{bmatrix} \mathbf{X}_1 & \cdots & \mathbf{X}_{N_p-m} & \mathbf{X}' \end{bmatrix}.
\]

(4.12)

Similarly, \( \mathbf{X}_j \) is the \( j \)-th column of \( \mathbf{X} \) \( (1 \leq j \leq N_p - m) \), and \( \mathbf{X}' \) is an \( N_c \times m \) matrix. From Eqs. (4.2), and (4.11),

\[
\mathbf{b} = \mathbf{X}' \mathbf{B}'^{-1} \mathbf{\nu} + \sum_{j=1}^{N_p-m} \left( \mathbf{X}_j - \mathbf{X}' \mathbf{B}'^{-1} \mathbf{B}_j \right) \nu_j
\]

\[
= \mathbf{P} + \sum_{j=1}^{N_p-m} \mathbf{Q}_j \nu_j,
\]

(4.13)

which indicates that \( \mathbf{b} \) is a function of \( N_p - m \) phase fractions (\( \Gamma^m \) requires an \((N_p - m)\)-dimensional parameterization). Finally, from

\[
\| \mathbf{b} - \mathbf{a} \|_2 = d,
\]

(4.14)

one can obtain the governing equation for the set of solutions.
If \( m = N_p - 1 \), Eq. (4.14) has only two solutions (see Figure 4.2-a). When \( m < N_p - 1 \), there are an infinite number of solutions for the given \( d \). Only a limited number of them would be required for discrete parameterization (Figure 4.2-b). For this purpose, a generic multi-dimensional discretization technique can be applied. We use Algorithm 1 to obtain a composition that lies on \( \Gamma^m_f \).

**Algorithm 2 Solving for a composition on \( \Gamma^m_f \)**

1: Obtain \( b \) from Eq. (4.14)  
2: loop  
3: if \( b \) is inside higher-dimensional tie-simplex, or outside compositional space then  
4: return  
5: end if  
6: \( \Delta^{m-1} \leftarrow \) \( m \)-phase negative-flash for \( b \)  
7: if \( \Delta^{m-1} \) is critical then  
8: \( d \leftarrow d/2 \)  
9: Go to Step 1  
10: end if  
11: \( \gamma \leftarrow \) project geometric center of \( \Delta^{m-1} \) onto \( \Delta^{N_p-1} \)  
12: if \( \gamma \) is close enough to \( b \) then  
13: return \( \gamma \)  
14: end if  
15: \( b \leftarrow \gamma \)  
16: end loop

### 4.3 Parameterization of Three-Phase Compositional Space

We start with an overview of the two-phase CSAT Framework (Voskov and Tchelepi, 2009a). In the natural variable formulation for solving the conservation equations (Coats, 1980), CSAT provides the accurate number of co-existing phases, as well as, an initial guess for EoS-based computations. During iterations, the number of existing phases in each gridblock might change. If the saturation of a phase becomes negative, then the set of the equations are adapted to account for the disappearance of that phase. Furthermore, the phase-state of single-phase gridblocks is checked using the
CSAT framework. For multiphase gridblocks, the thermodynamic relations are solved simultaneously with the conservation equations, and upon convergence, the solution route in the compositional space is consistent with phase-state identification of CSAT. Due to this treatment of the equilibrium phase behavior, CSAT is particularly suitable for the natural variable formulation. Note that a limited number of tie-simplex tables are generated in this formulation.

Given the overall composition of a gridblock, all the tie-line tables are checked to determine if there is any tie-line that parameterizes the composition. The phase-state of the mixture is determined if its composition and the interpolated tie-line are close enough. Otherwise, a new tie-line table is parameterized and added to the list of tables. For multi-contact miscible displacements, critical tie-lines (at different pressure values) that parameterize the solution path are calculated adaptively and stored. An initial check in the table of critical tie-lines determines if the composition belongs to the super-critical or sub-critical regions.

For two-phase systems, a single tie-line parameterizes the two-phase region around
a given overall composition. However, for three-phase systems, the entire plane defined by a tie-triangle needs to be parameterized. In the next Chapter, we will show that this is necessary to guarantee the global minimization of the Gibbs free energy. Note that only a few tie-triangle planes parameterize the solution path in a three-phase compositional displacement (LaForce et al., 2008b; Voskov and Tchelepi, 2009c). Similar to the two-phase CSAT framework, parameterization is performed for mixtures that do not lie on the extension of existing tie-simplex tables. For a given overall composition, we calculate a tie-triangle ($\Delta^2$), and parameterize three curves: $\Gamma^2_1$, $\Gamma^2_2$, and $\Gamma^2_3$. Each one of the $\Gamma^2$ curves parameterizes the two-phase behavior on one of the tie-triangle sides.

Here, we demonstrate the construction of a general three-phase thermal-compositional table for a given composition. We assume that the starting pressure at each temperature level is below the minimal degeneration pressure for the three-phase region. For the smallest pressure, the tie-triangle that parameterizes the given composition is calculated and stored. Starting from each edge of the tie-triangle, we parameterize the two-phase region by solving for each $\Gamma^2_f$.

For the next pressure levels, side tie-lines can be calculated toward the tie-triangle. For this purpose, an iterative procedure is used to find the farthest composition on $\Gamma^2_f$ at the new pressure level. Parameterization of $\Gamma^2_f$ starts from this composition if the length of the farthest tie-line is greater than the length of the $f$-th edge of the tie-triangle (see Figure 4.3). This flexible parameterization framework has proven to be very robust for different three-phase systems over wide ranges of pressure.

As noted previously, the three-phase region degenerates with increase in pressure (see Figure 4.4). If the pressure is large enough, we solve for the minimal degeneration pressure of the tie-triangle that parameterizes the given composition. An iterative procedure is used to find a pressure value such that the area of the tie-triangle, $A$, satisfies:

$$\varepsilon_{\text{min}} < A < \varepsilon_{\text{max}}, \quad (4.15)$$

for some small values of $\varepsilon_{\text{min}}$ and $\varepsilon_{\text{max}}$. The plane of the degenerate tie-triangle
Figure 4.3: In this example, each $\Gamma^2_f$ is parameterized from the farthest composition.

is then parameterized at higher pressure values. We note that immediately after the degeneration of the tie-triangle, a two-phase region disappears from the plane (see Figure 4.4-a), or the length of a side of the tie-triangle becomes infinitesimal (see Figure 4.4-b). However, all the parameterization techniques developed for sub-critical pressures are applicable for higher pressure values.

Tie-lines on a tie-triangle side may also degenerate. For such systems, parameterization of $\Gamma^2_f$ is started from the non-degenerate end. Then, we determine how far the parameterization of the tie-lines along $\Gamma^2_f$ should proceed until the length of the critical tie-line, $\ell$, satisfies:

$$\varepsilon_{\text{min}} < \ell < \varepsilon_{\text{max}},$$

for some small values of $\varepsilon_{\text{min}}$ and $\varepsilon_{\text{max}}$. The calculated critical tie-line marks the boundary between the extendible and non-extendible regions on the $f$-th tie-triangle side. In order to obtain the parameterization for a thermal problem, these procedures are performed at discrete temperature levels.
4.4 Phase-State Identification in Parameterized Compositional Space

Based on theoretical considerations from the Method of Characteristics and extensive flow simulation computations, only a few tables of tie-simplexes are required for a single simulation run (LaForce et al., 2008b; Voskov and Tchelepi, 2009c). In the second stage of the CSAT framework, we use tabulated tie-simplexes to identify the phase-state of mixtures that require phase stability tests (Voskov and Tchelepi, 2008).

In the following developments, we assume that a side tie-line lies on the extension of a tie-triangle. The systems that we have considered in our studies exhibit this behavior. We note that CSAT still provides a very good initial guess for conventional phase-behavior calculations in systems that violate this assumption.

Let us consider a thermal three-phase table, and describe the procedures for identifying the state of a given composition, \( z \), at some temperature, \( T \), and pressure, \( p \),
CHAPTER 4. COMPOSITIONAL SPACE ADAPTIVE TABULATION

conditions:

\[ T_j \leq T \leq T_{j+1} \quad (4.17) \]
\[ p_{ij,j} \leq p \leq p_{ij+1,j} \quad (4.18) \]
\[ p_{ij+1,j+1} \leq p \leq p_{ij+1,j+1} \quad (4.19) \]

where \( j \) denotes the temperature index of the table, and \( i_j \) represents the pressure index at the \( j \)-th temperature level.

Consider parameterization of the three-phase region in Figure (4.1). Noting that a \( \Gamma \) curve can be expressed as a linear combination of the tie-triangle compositions, we parameterize \( \Gamma_f \) using fractions of the \( f \)-th phase, \( \nu_f \) (see the numbering in Figure 4.1). We first describe interpolation in tables with identical temperature values. Let \( N^f_i \) represent the set of the \( \nu_f \) values for the \( i \)-th pressure level. Since \( N^f_i \) is different from \( N^f_{i+1} \), we initially interpolate tie-lines in \( \nu_f \) to obtain two-phase parameterization for \( N^f_i \cup N^f_{i+1} \) at each pressure level. Noting that a composition on \( \Gamma_f \) with a fixed \( \nu_f \) changes continuously with pressure, we interpolate the two sets of side tie-lines in pressure. Performing these interpolations at each temperature level, \( T_j \) and \( T_{j+1} \), we finally interpolate in temperature (note that another unification of the \( \nu_f \) values is required). The same interpolation techniques are used after the tie-triangle degeneration pressure.

The tables of tie-simplexes are used to interpolate in temperature and pressure, then \( z \) is projected onto the closest tie-simplexes (see Voskov and Tchelepi (2009c) and Figure 4.5). In the general case, \( z \) is in \( M_p \)-phase state, if it is inside a \( \Delta^{M_p-1} \). Moreover, \( z \) is single-phase, if it is outside all tie-simplexes. These state identification rules are based on the fact that an \( M_p \)-phase negative-flash can only determine the state of a mixture in the \( M_p \)-phase region.

It is worthwhile to note that a single-phase mixture in a system with \( N_p^{\text{max}} = 3 \) can be on the extension of:

1. two tie-lines from the same two-phase region (see Figure 4.12, for example),
2. two tie-lines from different two-phase regions.
Consider the parameterization of such a mixture. Since $N_p^{\text{max}} = 3$, the parameterizing tie-triangle is unique. In the second stage, two-phase regions on the extension of the tie-triangle are parameterized. Unique tie-line parameterization of the $\Gamma^2$ curves is still possible because each curve is inside the respective two-phase region, and that tie-lines do not intersect inside the two-phase regions. Moreover, tie-line endpoints change continuously along each $\Gamma^2$ curve. This allows for discrete representation of each two-phase region on a side of the tie-triangle.

Next, consider phase-state identification of such a mixture. If it is on the extension of two different tie-lines from the same two-phase region, then the mixture does not lie inside that two-phase region (intersection is possible only outside the multiphase region). Note that for accurate phase-state identification, the boundaries of multiphase regions must be represented correctly. For this purpose, it is sufficient that tie-simplexes do not intersect inside the multiphase regions. Continuity of parameterization is crucial to handle cases with variable temperature and pressure. The boundaries of multiphase regions change continuously with temperature and pressure.
and this allows for interpolation in discrete tie-simplex tables.

As noted previously, tie-triangles degenerate differently in various systems. Here, we describe state identification procedures for degenerate steam systems. Consider a three-component steam example at $T = 550\, \text{K}$ (see Figure 4.6-a). The three-phase region becomes critical at $p = 110\, \text{bar}$. With further increase in pressure, the gas-oil region shrinks until it disappears completely from the plane at $p = 148.9\, \text{bar}$.

Figure 4.6: (a) Critical locus for $\{C_1, C_{10}, H_2O\}$ at $T = 550\, \text{K}$; the locus of critical oil-gas tie-lines is extended from $p = 110\, \text{bar}$ to $p = 148.9\, \text{bar}$. (b) Phase diagrams at $p = 137\, \text{bar}$

From the continuity of parameterization in degenerate space, the critical gas-oil tie-lines change continuously with pressure. We calculate and store the critical tie-lines at discrete pressure values between the minimal three-phase degeneration pressure and the gas-oil disappearance pressure. Note that the locus of the critical tie-lines is almost linear on the plane of the tie-triangle. The discretized locus of critical tie-lines as well as the critical tie-triangle is then used to identify if a single-phase mixture is gas- or oil-like. This technique is based on the fact that the phase-state of a composition on the extension of a critical tie-line does not change with an increase in pressure (Voskov and Tchelepi, 2009a). We use this critical boundary to separate water-oil and water-gas tie-lines with an intermediate tie-line, which connects the
water phase to a point on the critical tie-line locus (see Figure 4.6-b). If the water tie-lines shrink in size, the critical tie-triangle serves as the intermediate tie-line.

The procedures for phase-state identification in immiscible displacements are summarized in the following algorithm.

**Algorithm 3** Multiphase CSAT for Immiscible Displacements

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>for all existing tie-simplex tables do</td>
</tr>
<tr>
<td>2</td>
<td>$\Delta \leftarrow N_p^{\text{max}}$-phase tie-simplex estimate for $T$ and $p$</td>
</tr>
<tr>
<td>3</td>
<td>$d \leftarrow$ Euclidean distance between $z$ and $\Delta$ in compositional space</td>
</tr>
<tr>
<td>4</td>
<td>if $d &gt; \varepsilon$ then</td>
</tr>
<tr>
<td>5</td>
<td>{Construct tie-simplex table}</td>
</tr>
<tr>
<td>6</td>
<td>for all discrete levels of $T$ and $p$ do</td>
</tr>
<tr>
<td>7</td>
<td>Calculate $N_p^{\text{max}}$-phase tie-simplex for $z$</td>
</tr>
<tr>
<td>8</td>
<td>Calculate all lower-dimensional tie-simplexes on its extension</td>
</tr>
<tr>
<td>9</td>
<td>end for</td>
</tr>
<tr>
<td>10</td>
<td>Store table; go to Step 2</td>
</tr>
<tr>
<td>11</td>
<td>else</td>
</tr>
<tr>
<td>12</td>
<td>{Identify phase-state}</td>
</tr>
<tr>
<td>13</td>
<td>Project $z$ onto tie-simplex space (estimated for $T$ and $p$) in extension of $\Delta$</td>
</tr>
<tr>
<td>14</td>
<td>if projection lies inside an $M_p$-phase tie-simplex then</td>
</tr>
<tr>
<td>15</td>
<td>return $M_p$-phase state (where $2 \leq M_p \leq N_p^{\text{max}}$)</td>
</tr>
<tr>
<td>16</td>
<td>else</td>
</tr>
<tr>
<td>17</td>
<td>return single-phase state</td>
</tr>
<tr>
<td>18</td>
<td>end if</td>
</tr>
<tr>
<td>19</td>
<td>end if</td>
</tr>
<tr>
<td>20</td>
<td>end for</td>
</tr>
</tbody>
</table>

### 4.5 Numerical Examples

In this section, we first present several numerical examples to demonstrate the parameterization techniques for multiphase systems. Next, we show phase-state identification in parameterized steam systems. In Chapter 6, we will present the computational examples of three-phase thermal-compositional flow simulation.
4.5.1 Tie-Simplex Space Parameterization

We show that the generalized CSAT framework accurately captures degeneration of the multiphase regions across a wide pressure range. Parameterization of the three- or two-phase regions can be adaptively refined along pressure or $\Gamma$. Typically, this refinement is performed close to a critical tie-simplex (Voskov and Tchelepi, 2009a).

In an isothermal three-phase table, only two sets of tie-lines parameterize the plane of a degenerate tie-triangle. With further increase in pressure, a two-phase region disappears from the plane. We use an iterative procedure to calculate the pressure at which the two-phase region disappears. That is, we find a pressure value such that the disappearing two-phase region is represented by a trivial tie-line (the length of which satisfies Eq. 4.16). Figure 4.7 describes the general structure of an isothermal three-phase table. Note that the water tie-lines disappear from the compositional space if the upper bound of pressure (or temperature) is large enough.

Figure 4.7: General structure of an isothermal three-phase table. The three-component systems are calculated at $T = 520 \text{ K}$ and $p = 75, 180, 250 \text{ bar}$, respectively.

We validate the accuracy of our numerical results using a reliable commercial simulator (CMG, 2010b). Figure 4.8 shows the parameterization of a three-component steam system. Using different Equations of State, we also compare the degeneration
of the three-phase region (see Figure 4.9). Note that both equations predict similar three-phase degeneration characteristics.

![Figure 4.8: Full parameterization of \(\{C_1, C_{10}, H_2O\}\) at \(T = 550\) K and \(p = 100\) bar. Compare the phase diagrams in blue with the standard calculations (red tie-lines).](image)

We describe the three-phase space parameterization for \(\{C_1, CO_2, C_{10}, H_2O\}\) at \(T = 550\) K. We parameterize the multiphase region for the center of the space (see Figure 4.10). A three-phase region and three two-phase regions are parameterized for this mixture at \(p = 95\) bar. With increase in pressure, the gas-oil side of the tie-triangle becomes critical, and the tie-triangle degenerates to a tie-line at \(p = 105.8\) bar. At higher pressure values, the water tie-lines grow in length, and the gas-oil two-phase region shrinks. Here, \(\Gamma^2\) for the gas-oil region is parameterized from the \(\{C_1, C_{10}, CO_2\}\) face. As a result, the associated critical tie-line can be easily captured. Note that after the tie-triangle degeneration pressure, the plane of the degenerate tie-triangle is parameterized (see Figures 4.10-c,d). Also, these examples clearly indicate that the extension of the two-phase tie-lines may intersect inside the compositional space.
Figure 4.9: Parameterization of \( \{C_1, C_{10}, H_2O\} \) at \( T = 550 \text{ K} \) and \( p = 113.8 \text{ bar} \). Here, only two sets of tie-lines parameterize the space. The calculations are performed using (a) the SRK-EoS, tie-triangle degenerates at \( p = 106.8 \text{ bar} \) and the oil-gas region disappears at \( p = 163.5 \text{ bar} \), and (b) the PR-EoS, tie-triangle degenerates at \( p = 110.0 \text{ bar} \) and the oil-gas region disappears at \( p = 148.9 \text{ bar} \). Compare the phase diagrams in blue with the standard calculations (red tie-lines)
Figure (4.11) shows the full parameterization of the system at $T = 550 \text{ K}$ and $p = 105 \text{ bar}$. In this system, the three-phase region exists only in a part of the space, and the gas-oil region degenerates close to the $\{H_2O, CO_2, C_{10}\}$ face.

Next, we present three-phase compositional space parameterization for these systems: (1) a sour gas example: $\{C_1, C_2, H_2S\}$ at $T = 185 \text{ K}$, Figure (4.12), and (2) a cold CO$_2$ example: $\{C_1, C_2, C_6, CO_2\}$ at $T = 180 \text{ K}$, Figure (4.13).

Consider two features of the sour gas example. First, the degenerate tie-triangle has three distinct phases; that is, neither of its sides becomes critical. As a result, the Successive Substitution Iterations for the three-phase negative-flash converge faster near the degeneration pressure (see Chapter 2). Second, tie-lines on a side of the tie-triangle become critical before degeneration of the three-phase region. For this case, $\Gamma^2$ is parameterized from the side of the tie-triangle.

Parameterization of four-phase systems is significantly more complicated than three-phase problems. Figures (4.14), and (4.15) present the base parameterization of a four-component system with $N_p^{\text{max}} = 4$. Here, we first calculate the tie-tetrahedron that parameterizes a given composition. Four curves, $\Gamma^3$, parameterize the three-phase regions around the tie-tetrahedron (see Figure 4.14). Moreover, different two-phase regions in the system are calculated using six surfaces, $\Gamma^2$ (see Figure 4.15). This way, all the multiphase regions on the extension of the tie-tetrahedron are parameterized.

### 4.5.2 Phase-State Identification

Here, we demonstrate the accuracy of phase-state identification for several steam systems. Consider the three-component steam example in Figure (4.8). We choose two compositions and use CSAT to identify the state of the compositions along the dilution line (see Figure 4.16-a). For the first composition, CSAT constructs a three-phase table as described earlier. The phase-state of all the compositions are then determined using this table. Note that a single table parameterizes the entire three-component system. Two- or three-phase compositions are parameterized by a tie-line or tie-triangle, respectively. A single-phase composition is outside all tie-lines and
Figure 4.10: Parameterization of \( \{C_1(0.25), CO_2(0.25), C_{10}(0.25), H_2O(0.25)\} \) at \( T = 550 \text{ K} \). Tie-triangle degenerates at \( p = 105.8 \text{ bar} \).
Figure 4.11: Two views from the full parameterization of \{C_1, CO_2, C_{10}, H_2O\} at \(T = 550\) K and \(p = 105\) bar: (a) oil-gas tie-lines, and (b) water tie-lines. The three-phase region is enclosed by the blue tie-triangles.
Figure 4.12: Parameterization of \( \{C_1(0.33), C_2(0.33), H_2S(0.34)\} \) at \( T = 185 \text{ K} \). The parameterizing tie-triangle degenerates at \( p = 34.3 \text{ bar} \).
Figure 4.13: Parameterization of \{C_1(0.25), C_2(0.25), C_6(0.25), CO_2(0.25)\} at $T = 180$ K. The parameterizing tie-triangle degenerates at $p = 26.1$ bar.
Figure 4.14: Four $\Gamma^3$ curves (in green) that parameterize four different three-phase regions of \{C$_2$, N$_2$, CO$_2$, H$_2$S\} at $T = 200$ K, and $p = 140$ bar.
Figure 4.15: Six $\Gamma^2$ surfaces (in green) that parameterize six different two-phase regions of $\{C_2, N_2, CO_2, H_2S\}$ at $T = 200$ K, and $p = 140$ bar.
the tie-triangle. Additional two- or three-phase negative-flash calculations may be required in order to accurately identify the phase-state of mixtures that are too close to the phase boundaries (Voskov and Tchelepi, 2009a).

With increase in pressure, the three-phase region degenerates, and the gas-oil region exhibits critical behavior (see Figure 4.16-b). Here, we also use CSAT to determine the phase-state of a dilution line. Note that the locus of the critical tie-lines, which are at different pressures, separates single-phase gas and oil compositions (see Figure 4.6).

Figure 4.16: Phase state identification at $T = 550 \text{ K}$ for the dilution line between (a) \{C$_{1}$ (0.7), C$_{10}$ (0.29), H$_{2}$O (0.01)\} and \{C$_{1}$ (0.01), C$_{10}$ (0.19), H$_{2}$O (0.8)\} at $p = 100 \text{ bar}$, and (b) \{C$_{1}$ (0.65), C$_{10}$ (0.3), H$_{2}$O (0.05)\} and \{C$_{1}$ (0.1), C$_{10}$ (0.4), H$_{2}$O (0.5)\} at $p = 137 \text{ bar}$.

Next, we increase pressure for the example in Figure (4.11) to obtain a fully-degenerate steam system (see Figure 4.17-a; it can be considered as a stack of parameterized degenerate planes as shown in Figure 4.6-b). When $N_{c} > 3$, side tie-lines may not lie on the extensions of tie-triangle planes. This tilting of tie-lines is trivial for steam systems. Note that the gas-oil two-phase region exists only in a part of the compositional space. Similarly, we identify the phase-state of the compositions along a dilution line using three-phase CSAT (see Figure 4.17-b). As shown in the figure,
only a few parameterized planes are required for this purpose.

Figure 4.17: (a) Full parameterization of \{C_1, CO_2, C_{10}, H_2O\} at $T = 550$ K and $p = 137$ bar, (b) Phase state identification for the dilution line between \{C_1(0.05), C_{10}(0.45), CO_2(0.42), H_2O(0.08)\} and \{C_1(0.47), C_{10}(0.265), CO_2(0.04), H_2O(0.225)\}. 
Chapter 5

Gibbs Energy Analysis

In this Chapter, we show the Gibbs free energy minimization of the Compositional Space Parameterization (CSP) framework, given the correct value of $N_p^{\max}$. As we have discussed earlier, the maximum number of phases, $N_p^{\max}$, that can coexist for the temperature and pressure ranges of interest is assumed to be known in our developments. $N_p^{\max}$ is defined such that the extensions of $N_p^{\max}$-phase tie-simplexes do not intersect inside the compositional space (Voskov and Tchelepi, 2009c). It is important to note that when the $N_p^{\max}$ that we use is wrong, tie-simplexes intersect inside the multiphase regions. In this case, the value of $N_p^{\max}$ must be increased, and the parameterization must be repeated. Also note that if an $N_p^{\max}$-phase tie-simplex lies on the extension of a different $N_p^{\max}$-phase tie-simplex, the number of phases would exceed the number of components. In this Chapter, we will show how such degenerate systems can be modeled in the CSP framework.

Once the value of $N_p^{\max}$ is defined, CSAT parameterizes all the multiphase regions in the neighborhood of a given composition. When $N_p^{\max} = 3$, for example, one tie-triangle, and three sets of tie-lines at discrete temperature and pressure levels are computed for the given composition. Interpolation in the discretized tie-simplex space determines the phase-state of any other mixture of interest. This is possible because parameterization of the compositional space using tie-simplexes is continuous (see Chapter 3).

The phase-state identification in the CSP framework is of value only if the Gibbs
energy of the solution is at global minimum. As we will briefly discuss in the following section, the thermodynamically stable equilibrium configuration is unique if and only if the tangent plane distance function, \( tpd(z) \), is non-negative for any mixture, \( z \). A rigorous proof of this criterion was first presented by Baker et al. (1982). Computational techniques to locate the stationary points of the \( tpd \) function, as well as, second-order methods for Gibbs energy minimization were developed by Michelsen (1982a,b). Following the work of these authors, we provide an analysis of the Gibbs energy minimization in the parameterized tie-simplex space. Then, we present several examples to describe the global minimization of Gibbs free energy in the CSP framework.

### 5.1 An Overview of the Stability Criterion

First, we show that the tangent plane distance criterion is a necessary condition for phase behavior stability in the CSP framework. We note that CSP yields equilibrium conditions:

\[
\mu^*_{i,j} = \mu^*_{i,1} (= \mu^*_{i}), \quad i = 1, \ldots, N_c, \ j = 2, \ldots, N_p^*,
\]

where the superscript * indicates the CSP result. The Gibbs free energy of the mixture is given by:

\[
G^* = \sum_{i=1}^{N_c} \sum_{j=1}^{N_p^*} n^*_{i,j} \mu^*_{i,j} = \sum_{i=1}^{N_c} n_{i,tot} \mu^*_{i},
\]

which is applicable for \( N_p^* \geq 1 \). Let us consider the formation of an infinitesimal amount, \( dn^o \), of a trial phase represented by the superscript \( o \). At constant temperature and pressure, the Gibbs free energy of the system changes as follows:

\[
dG = \sum_{i=1}^{N_c} \left( \mu^o_i dn^o_i + \sum_{j=1}^{N_p^*} \mu^*_{i,j} dn^*_{i,j} \right).
\]
Since the system is closed,
\[ dn_i^o + \sum_{j=1}^{N_p^o} dn_{i,j}^* = 0, \quad i = 1, \ldots, N_c, \] (5.4)
and Eq. (5.3) simplifies to:
\[
\begin{align*}
\text{d}G &= \sum_{i=1}^{N_c} dn_i^o (\mu_i^o - \mu_i^*) \\
&= dn \sum_{i=1}^{N_c} z_i^o (\mu_i^o - \mu_i^*).
\end{align*}
\] (5.5)

If the CSP result corresponds to the global minimum of Gibbs free energy, \( \text{d}G/\text{d}n \) must be non-negative, and from Eq. (5.5),
\[
\text{tpd}(z^o) = \sum_{i=1}^{N_c} z_i^o (\mu_i^o - \mu_i^*) \geq 0,
\] (5.6)
which yields a necessary condition for stability in the CSP framework. The tangent plane distance function, \( \text{tpd}(z^o) \), measures the distance between the Gibbs free energy surface and its tangent plane at tie-simplex compositions. We note that the criterion is tested for any trial composition, \( z^o \).

It can be shown that the condition in Eq. (5.6) is sufficient for thermodynamic stability of the CSP result (Michelsen and Mollerup, 2004). Suppose a different (trial) distribution of phases satisfies the global minimum of Gibbs free energy. If such a mixture is multiphase, from the second law of thermodynamics we have (chemical equilibrium):
\[
\mu_{i,j}^o = \mu_{i,1}^o (= \mu_i^o), \quad i = 1, \ldots, N_c, \quad j = 2, \ldots, N_p^o.
\] (5.7)
Therefore, the global minimum of Gibbs energy is given by:

\[
G^\circ = \sum_{i=1}^{N_c} \sum_{j=1}^{N_p^\circ} n_{i,j}^\circ \mu_{i,j}^\circ = \sum_{i=1}^{N_c} n_{i,tot} \mu_i^\circ,
\]

which is valid for \(N_p^\circ \geq 1\) (\(N_p^\circ\) is not necessarily identical to \(N_p^*\)). Combining this relation with Eq. (5.2), and noting that:

\[
z_i = \sum_{j=1}^{N_p^\circ} \nu_j^\circ x_{i,j}^\circ,
\]

we obtain:

\[
G^\circ - G^* = \sum_{i=1}^{N_c} n_{i,tot}(\mu_i^\circ - \mu_i^*)
\]

\[
= n_{tot} \sum_{i=1}^{N_c} z_i(\mu_i^\circ - \mu_i^*)
\]

\[
= n_{tot} \sum_{i=1}^{N_c} \sum_{j=1}^{N_p^\circ} \nu_j^\circ x_{i,j}^\circ (\mu_i^\circ - \mu_i^*)
\]

\[
= n_{tot} \sum_{j=1}^{N_p^\circ} \nu_j^\circ tpd(x_j^\circ).
\]

(5.10)

Since \(\nu_j^\circ > 0\), CSP yields the global minimum of Gibbs free energy if and only if Eq. (5.6) holds for any mixture in the compositional space. For computational purposes, it is more convenient to work with fugacities. Therefore, we will use:

\[
\frac{tpd(z^\circ)}{RT} = \sum_{i=1}^{N_c} z_i^\circ (\ln \hat{f}_i^\circ - \ln \hat{f}_i^*),
\]

(5.11)

instead of Eq. (5.6) to represent the tangent plane distance function.

Noting that the \(N_p^{\text{max}}\)-phase tie-simplexes (and their extensions) do not intersect inside the compositional space, the stability analysis is not required for an \(N_p^{\text{max}}\)-phase mixture (it splits into a unique set of phases). However, the stability analysis
is needed if \( N_p^* < N_p^{\text{max}} \). In this case, the formation of a new trial phase must be rejected by confirming that Eq.(5.6) holds. This is a common practice in conventional reservoir simulation (Coats, 1980; Cao, 2002).

## 5.2 Gibbs Energy Analysis of Tie-Simplex Space

Here, we analyze the thermodynamic stability criterion in the parameterized tie-simplex space. Note that the correct value of \( N_p^{\text{max}} \) is assumed to be known in the following developments.

We start by describing the relation between a tie-line based approach, and the conventional \( tpd \) analysis. For this purpose, we consider a simple binary mixture of C\(_1\) and C\(_6\) at \( T = 410 \) K. Figure (5.1-a) shows the \( px \) (pressure-composition)-phase diagram of this simple system. The bubble and dew points converge to the critical point at \( p = 165 \) bar (Minimal Critical Pressure). The figure also shows a discrete CSAT representation of the \( px \)-phase diagram with only four tie-lines. Note that linear interpolation in the discretized tie-simplex space is used for phase-state identification. For mixtures that are close to phase boundaries, additional negative-flash computations with initial guess obtained from CSAT are performed. Figure (5.1-b) shows the \( tpd \) function for two-phase mixtures in the pressure range of interest. Note that the zero locus of \( tpd \) corresponds to the \( px \)-phase diagram of the system; the \( tpd \) is strictly positive elsewhere in the \( px \) domain. This binary case demonstrates the equivalence of tie-line based parameterization and Gibbs energy minimization for phase-state identification.

### 5.2.1 Local Condition for CSP-Based Gibbs Energy

In the thermal-compositional flow simulation framework, the thermodynamic constraints of chemical equilibrium are expressed as:

\[
\mu_{i,j} = \mu_{i,1}, \quad i = 1, \ldots, N_c, \quad j = 2, \ldots, N_p,
\]  

(5.12)
CHAPTER 5. GIBBS ENERGY ANALYSIS

Figure 5.1: \{C_1, C_6\} at \(T = 410\, \text{K}\). (a) continuous (CSP) and discrete (CSAT) representations of the \(px\)-phase diagram. (b) contours of \(tpd\) for two-phase mixtures where \(N_p \leq N^\text{max}_p\). Any Equation-of-State (EoS) can be used to compute the equilibrium chemical potentials; the only condition is that the EoS must yield a unique solution for the equilibrium problem (Eqs. 5.12). The Gibbs energy of the CSP tie-simplex that represents this equilibrium satisfies the following condition:

**Lemma 1.** Let \(G(n)\) represent the Gibbs free energy of a multiphase mixture, \(n\), determined by CSP (temperature and pressure are constant). It can be shown that \(G(n + \Delta n) > G(n)\), where \(\|\Delta n\|\) is sufficiently small.

**Proof.** The Gibbs energy of the mixture is given by:

\[
G(n) = \sum_{i=1}^{N_c} \sum_{j=1}^{N_p} n_{i,j} \mu_{i,j},
\]  

(5.13)
where the extensive parameters, \( n_{i,j} \), are constrained by the mass balance equations:

\[
\sum_{j=1}^{N_p} n_{i,j} = n_{i,tot}, \quad i = 1, \ldots, N_c.
\]  

(5.14)

Choosing the first phase, \( j = 1 \), as reference, we obtain the first and second derivatives of \( G(n) \):

\[
J_{i,j} = \frac{\partial G}{\partial n_{i,j}} = \mu_{i,j} - \mu_{i,1},
\]

(5.15)

\[
H_{i,l;j,m} = \frac{\partial J_{i,j}}{\partial n_{l,m}} = \frac{\partial \mu_{i,j}}{\partial n_{l,j}} \delta_{j,m} + \frac{\partial \mu_{i,1}}{\partial n_{l,1}},
\]

(5.16)

where \( i, l = 1, \ldots, N_c \), and \( j, m = 2, \ldots, N_p \). The derivatives in Eqs. (5.16) can be calculated using:

\[
\frac{\partial \mu_{i,j}}{\partial n_{l,j}} = RT \left( \frac{\delta_{i,l}}{n_{i,j}} - \frac{1}{\sum_{i=1}^{N_c} n_{i,j}} + \frac{\partial \ln \hat{\phi}_{i,j}}{\partial n_{l,j}} \right).
\]

(5.17)

A Taylor series expansion of \( G(n) \) around the CSP tie-simplex, \( n \), yields:

\[
G(n + \Delta n) = G(n) + J(n)\Delta n + \frac{1}{2} \Delta n^T H(n) \Delta n,
\]

(5.18)

for some small \( \|\Delta n\| \) (Michelsen, 1982b; Gautam and Seider, 1979a). The elements of the Jacobian, \( J \), and the Hessian, \( H \), are provided by Eqs. (5.15) and (5.16), respectively. \( J(n) \) and \( H(n) \) correspond to the residual and Jacobian of the multi-stage flash problem in CSP (see Chapter 2). Since the CSP solution, \( n \), represents an equilibrium condition, \( J(n) = 0 \), and \( n \) is a stationary point of \( G \).

Let \( \mathbf{H}^A \) represent an approximation of \( \mathbf{H} \), where the derivatives of fugacity coefficients, \( \partial \ln \hat{\phi}_{i,j}/\partial n_{l,j} \), are set to zero. If \( N_p^{\max} \) is correct, it can be shown that the magnitude of all the eigenvalues of \( \mathbf{H}^A(n)^{-1}(\mathbf{H}^A(n) - \mathbf{H}(n)) \) is smaller than unity (see Chapter 2). As a result, \( \mathbf{H}(n) \) is positive definite (Michelsen, 1982b), and from Eq. (5.18), \( G(n + \Delta n) > G(n) \).

\[
\text{If the assumption of } N_p^{\max} \text{ is wrong, tie-simplexes will intersect inside multiphase}
\]


regions, and \( H(n) \) will be singular. Eq. (5.18) shows that \( G(n + \Delta n) \) can be identical to \( G(n) \) for some non-trivial \( \Delta n \). Since \( G \) is a continuous function, one can find a mixture, \( m \), in the neighborhood of the tie-simplex, \( n \), such that \( G(m) < G(n) \). In such a case, the tie-simplex parameterization is not unique, and it does not represent the global minimum of Gibbs energy.

Figure (5.2) shows examples where the phase-state of a mixture is determined inaccurately (i.e., the assumed \( N_p^{\text{max}} \) is wrong). Here, a three-component, three-phase mixture is considered, and the tangent plane distance function, \( tpd(z) \), is shown for cases where the mixture is misidentified as single-phase (Figure 5.2-a), or two-phase (Figures 5.2-b,c). Note that using different initial guesses, the two-phase flash converges to two different tie-lines, and the parameterization is not unique. In all three cases, \( tpd(z) \) is negative in parts of the space, and the given phase-state is not stable.

### 5.2.2 Gibbs Energy Function Convexity

In this section, we show that the Gibbs energy function, \( G(n) \), is strictly convex in the tie-simplex space. The Gibbs energy surface, \( F(z) \), is computed for a homogeneous phase with composition \( z \), regardless of the actual phase-state (Baker et al., 1982):

\[
F(z) = \sum_{i=1}^{N_c} z_i \mu_i. \tag{5.19}
\]

To perform the stability analysis, the tangent plane of the Gibbs energy surface is constructed. We express the molar Gibbs energy of a multiphase mixture with overall composition \( z \) as:

\[
G(z; x_j) = \frac{G(n)}{n_{\text{tot}}} = \sum_j \nu_j \sum_i x_{i,j} \mu_{i,j} = \sum_j \nu_j F(x_j). \tag{5.20}
\]

The following Lemma describes the behavior of \( F(z) \) in the single-phase regions.

**Lemma 2.** At constant temperature and pressure, the Gibbs energy surface is strictly convex in single-phase regions and along the loci of tie-simplex endpoints.
**Proof.** First, we consider single-phase regions. \( F(z) \) over a convex domain, \( \Omega \), is strictly convex if

\[
F(\nu z_1 + (1 - \nu)z_2) < \nu F(z_1) + (1 - \nu)F(z_2),
\]

(5.21)

for any \( 0 < \nu < 1 \), and \( z_1, z_2 \in \Omega \).

Consider a convex set of compositions, \( \Omega \), in a small neighborhood around the mixture, \( z \). Let \( \Omega \) be inside a single-phase region. Suppose \( z \) is enclosed by a hypothetical tie-line, \( x_j \):

\[
z = \nu x_1 + (1 - \nu)x_2,
\]

(5.22)

where \( 0 < \nu < 1 \), and \( x_1, x_2 \in \Omega \) are arbitrary compositions. From the thermodynamic stability of \( z \), we obtain:

\[
F(z) < G(z; x_1, x_2) = \nu F(x_1) + (1 - \nu)F(x_2).
\]

(5.23)

Since \( z \) can be any composition in the single-phase region, and \( F(z) \) is continuous, the Gibbs energy surface is strictly convex throughout the single-phase region. Note that this is true for mixtures on the boundaries of single- and multi-phase regions.

Convexity of the Gibbs energy surface along the loci of tie-simplex endpoints can also be explained using Lemma 1. Consider a mixture with composition \( x_1 \) that corresponds to a corner of an \( M_p \)-phase tie-simplex (\( 2 \leq M_p \leq N_p^{\text{max}} \)). From the equality of chemical potentials for tie-simplex endpoints, the change in Gibbs energy, \( dG \), for the formation of an infinitesimal amount of a phase with composition \( x_j \) (another endpoint of the tie-simplex with index \( j = 2, \ldots, M_p \)) is zero (see Eq. 5.5 of the Appendix). From Lemma 1, \( dG \) for the formation of any other mixture in the neighborhood of \( x_j \) is positive. We conclude from Eq. (5.5) that both \( tpd(z) \) and \( F(z) \) are strictly convex around \( x_j \). Assuming a correct value for \( N_p^{\text{max}} \), tie-simplex parameterization of the compositional space is unique, and the analysis is valid for all the tie-simplexes that parameterize the same \( M_p \)-phase region. As a result, \( F(z) \) is strictly convex along the loci of \( M_p \)-phase tie-simplex endpoints.
Next, we consider a mixture, \( z \), in the multiphase region. Since \( z \) is not stable as a single-phase state, we have \( F(z) > G(z; x_j) \), where \( G(z; x_j) \) is calculated using the parameterizing tie-simplex. Note that the inequality is valid for all mixtures inside the tie-simplex. As a result, the Gibbs energy surface must be concave over a subset of the domain enclosed by any tie-simplex. Moreover, \( F(z) \) may have two, or more, separate concave regions inside a tie-simplex (for example, see Figure 3 of Baker et al. (1982)). In this case, adjacent concave lobes are separated by a convex region. Since \( F \) is a continuous function of temperature and pressure, one can find a set of conditions such that a composition inside the tie-simplex lies on the tangent plane to the Gibbs energy surface, and a new phase is formed. As a result, a corner of the new tie-simplex is on the extension of the other corners. This is possible when the number of phases exceeds the number of components (Baker et al., 1982).

Such systems can be treated as part of the degenerate compositional space for a higher-dimensional problem with more components. In order to explain this, consider a binary mixture of \( \{NC_{10}, H_2O\} \) at \( T = 544 \) K, and \( p = 75 \text{ bar} \). Figure (5.3-a) shows \( tpd(z) \) for a two-phase mixture. Here, only one tie-line exists throughout the compositional space. Note that \( F(z) \) is represented by two concave lobes inside the two-phase region. This binary mixture can also be considered as a side of a ternary system, for example \( \{C_1, NC_{10}, H_2O\} \). Figure (5.3-b) shows that the compositional space is close to the degeneration of the three-phase region. The tie-triangle degenerates (disappears) at \( T = 548.1 \) K (Figure 5.3-d). Note from Figure (5.3-c) that a composition from the convex region of \( F(z) \) inside the tie-line is now in equilibrium with two other mixtures. As the temperature increases to 555 K, only two sets of tie-lines parameterize the ternary compositional space (Figure 5.4-b). Note that \( \{NC_{10}, H_2O\} \) is represented by two distinct tie-lines on the side of the ternary space. Figure (5.4-a) shows \( tpd(z) \) functions for two-phase mixtures inside different tie-lines. As discussed above, the convex region of the Gibbs energy surface within the tie-line in Figure (5.3-a) has formed a new single-phase region.

Finally, we describe \( F(z) \) for a multi-component system with \( N_p^{\text{max}} = 3 \). The description can be generalized for systems with more phases. At constant temperature
and pressure, CSP calculates the unique tie-triangle for a given composition. Then, all the two-phase regions on the extension of the tie-triangle are parameterized by three sets of tie-lines. In the parameterized tie-simplex space (tie-triangle and three sets of tie-lines), the Gibbs energy surface is:

1. strictly convex in the single-phase regions,
2. strictly convex along the loci of tie-line and tie-triangle endpoints,
3. greater than $G(z; x_j)$ for all the multiphase mixtures, $z$, enclosed by a tie-simplex, $x_j$. As a result, the tangent plane distance function, $tpd(z)$, is positive inside the tie-simplexes.

Consequently, $F(z)$ is strictly convex in the solution domain of the CSP framework. Moreover,

$$
G(z) = \begin{cases} 
F(z) & \text{single-phase } z, \\
\sum_j \nu_j F(x_j) & \text{multiphase } z \text{ inside tie-simplex } x_j,
\end{cases} 
$$

is convex. From Lemma 1, we conclude the global minimization of Gibbs free energy for the CSP tie-simplex (local minimum corresponds to the global minimum of $G(z)$).

## 5.3 Numerical Examples

In this section, we show several examples to demonstrate the correspondence of the global Gibbs energy minimization techniques with the solution in tie-simplex space. We consider the following systems:

1. $\{C_2, N_2, CO_2\}$ at $T = 140$ K, and $p = 200$ bar, Figures (5.5) and (5.6);

2. $\{C_1, NC_{10}, H_2O\}$ at $T = 540$ K, and $p = 150$ bar, Figure (5.7);

3. $\{C_2, N_2, CO_2, H_2S\}$ at $T = 140$ K, and $p = 200$ bar, Figure (5.8), also presented in Chapter 2.
In the first case, we consider mixtures at all possible phase-states when $N_p^{\text{max}} = 3$ (see Figure 5.5-a). The $tpd(z)$ for each case is shown in Figures (5.5) and (5.6), and the states of these mixtures are identified by CSP. Note that in all cases, $tpd(z)$ is non-negative throughout the compositional space, and that its global minimum (zero) corresponds to tie-simplex endpoints, or the mixture’s composition.

A degenerate steam system, where only two sets of tie-lines exist inside the compositional space, is shown in Figure (5.7). Finally, we consider a four-component system with $N_p^{\text{max}} = 4$. Two mixtures that form three (Figure 5.8-a,b) and four phases (Figure 5.8-c,d) are considered. The parameterizing tie-simplexes from the CSP framework are then used to construct $tpd(z)$ throughout the compositional space. Noting that $tpd(z)$ is non-negative globally, we conclude the accuracy of the state identification.
Figure 5.2: \{C_2, N_2, CO_2\} at $T = 140$ K and $p = 200$ bar. Plots of $tpd(z)$ when the mixture represented by $\times$ is identified as (a) single-phase, and (b,c) two-phase. The value of $tpd(z)$ is negative in the regions enclosed by $tpd(z) = 0$, and it increases from the blue to red contour lines. The correct state of the mixture is three-phase, for which the parameterizing tie-triangle is shown in each figure (see Figure 5.6-d). The red tie-lines also represent (inaccurate) two-phase states.
Figure 5.3: Figures in the left column show tangent plane distance functions for two-phase mixtures in \{NC_{10}, H_2O\}. The right column shows full parameterization of \{C_1, NC_{10}, H_2O\}. Pressure equals 75 bar in all the figures. Moreover, \(T_a = T_b = 544\) K, and \(T_c = T_d = 548.1\) K.
Figure 5.4: Continued from Figure (5.3). Here, $T_a = T_b = 555$ K.
Figure 5.5: (a) Full parameterization of \{C_2, N_2, CO_2\} at $T = 140 \text{ K}$ and $p = 200 \text{ bar}$. The figure shows the test compositions (in red), and their parameterizing tie-simplexes. $tpd(\mathbf{z})$ for the test mixtures in single-phase regions: (b) $L_1$, (c) $L_2$, and (d) $L_3$. In all cases, $tpd(\mathbf{z}) > 0$, and its value increases from blue to red contour lines.
Figure 5.6: Continued from Figure (5.5). $tpd(z)$ for the test mixture in (a) $L_1L_2$, (b) $L_1L_3$, (c) $L_2L_3$, and (d) three-phase regions. The figures also show the parameterizing tie-simplexes in red. In all cases, $tpd(z) > 0$, and its value increases from blue to red contour lines.
Figure 5.7: (a) Full parameterization of \( \{C_1, NC_{10}, H_2O\} \) at \( T = 540 \text{ K} \) and \( p = 150 \text{ bar} \). The figure shows the test compositions (in red), and their parameterizing tie-simplexes. \( tpd(z) \) for the test mixtures in (b) gas-oil, and (c) oil-water regions. In all cases, \( tpd(z) > 0 \), and its value increases from blue to red contour lines.
Figure 5.8: \( \{C_2, N_2, CO_2, H_2S\} \) at \( T = 140 \) K and \( p = 200 \) bar. Figures (a) and (b) show two views of \( tpd(z) \) for a three-phase mixture. \( tpd(z) \) equals 0.02 and 0.1 along the blue and red surfaces, respectively. Similarly, Figures (c) and (d) show \( tpd(z) \) for a four-phase mixture. Blue and red surfaces are plotted for \( tpd(z) = 0.01 \) and \( tpd(z) = 0.1 \), respectively. In both cases, \( tpd(z) > 0 \), and the parameterizing tie-simplexes are shown in red.
Chapter 6

Multiphase Simulation Examples

The generalized CSAT approach is integrated with Stanford’s Automatic Differentiation based General-Purpose Research Simulator (AD-GPRS, Younis (2011); Voskov (2011)). In this Chapter, we present several thermal-compositional simulations where three fluid phases coexist at equilibrium.

Our main focus is to represent the complex thermodynamic phase behaviors associated with degenerate steam systems accurately and efficiently. For this purpose, we consider super-critical steam injection, as well as, displacements in the neighborhood of three- and two-phase degeneration conditions. In the CSAT framework, all components are allowed to partition among the existing fluid phases. The examples that we present in this Chapter include models where the fraction of H$_2$O in both the gas and oil phases is considerable.

For simplicity, we model heat transfer by convection only. Moreover, we assume constant rock heat-capacity in our thermal simulations.

6.1 MoC-like Displacements

In order to mimic the Method of Characteristics (MoC) solutions, we consider three- and four-component displacements in a one-dimensional homogeneous reservoir ($50 \times 1 \times 1$). In these models, the temperature is constant, and the pressure drop is small (2 bar).
In order to show the solution routes for three-component steam systems, two sets of injection and initial mixtures are considered (see Table 6.1). In the first example, we displace INIT1 by INJ1 at $T = 550$ K. Note that INJ1 is a mixture of undersaturated steam and gas. We consider two pressures: one below and one above the tie-triangle degeneration pressure (see Figures 6.1-a,b). The solution path is similar in both cases; a leading rarefaction in the gas-oil region is followed by a shock along a gas-water tie-line. Since the solution path enters critical regions, accurate phase-state identification in these models requires a robust treatment of the phase behavior close to the degeneration conditions.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$C_1$</th>
<th>$NC_{10}$</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>INJ1</td>
<td>0.1</td>
<td>0.01</td>
<td>0.89</td>
</tr>
<tr>
<td>INJ2</td>
<td>0.72</td>
<td>0.01</td>
<td>0.27</td>
</tr>
<tr>
<td>INIT1</td>
<td>0.395</td>
<td>0.595</td>
<td>0.01</td>
</tr>
<tr>
<td>INIT2</td>
<td>0.01</td>
<td>0.5</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 6.1: Molar compositions of the three-component mixtures used in MoC-like displacements

Next, we model the injection of INJ2 (a mixture of super-saturated steam and gas at injection conditions) into INIT2 at $T = 520$ K. For the fully immiscible displacement (Figure 6.1-c), the solution path enters the three-phase region, as well as, the gas-water and oil-water regions. When pressure is increased to slightly above the tie-triangle degeneration pressure, the three-phase region disappears (Figure 6.1-d). Note that another path through the gas-oil region is also possible for this case. Generally, the solution path for gas-phase steam injection (with a fraction of the lighter hydrocarbon component) models enters the gas-water region first. This is due to the conditions of temperature and pressure which result in the condensation of the injected steam to a liquid water phase as the steam front moves through the reservoir.
Figure 6.1: Immiscible and miscible three-component displacements; phase envelopes surrounding the three-phase and multiple two-phase regions are shown using dashed black lines. The tie-triangles and tie-lines that parameterize three- and two-phase mixtures along the solution path are shown in red and blue, respectively. Mixtures are color-coded as follows: gas (○), oil (○), gas-oil (○), gas-water (○), oil-water (○), and three-phase (●).

Figure (6.2) shows four-component MoC-like displacements for the systems described in Table (6.2). A four-component solution path is parameterized by more
than one table of tie-simplexes. In the first example, the solution consists of a rarefaction in the gas-oil region (on the extension of a single tie-triangle), followed by a rarefaction in the three-phase region. For Case 2, gas-oil mixtures lie on the extensions of several tie-triangles. Note that this example is similar to the three-component cases shown in Figure (6.1-a,b), and that the parameterizing tie-triangles degenerate along the solution path.

<table>
<thead>
<tr>
<th>Case</th>
<th>C&lt;sub&gt;1&lt;/sub&gt;</th>
<th>NC&lt;sub&gt;10&lt;/sub&gt;</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>T (K)</th>
<th>p (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>0.09</td>
<td>0.88</td>
<td>0.01</td>
<td>530</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.01</td>
<td>0.88</td>
<td>0.01</td>
<td>530</td>
<td>145</td>
</tr>
</tbody>
</table>

Table 6.2: Summary of four-component simulation cases; injection and initial compositions are shown in red and blue, respectively.
Figure 6.2: Four-component displacements. Case 1 (top), the three-phase region inside the compositional space is shown by two limiting tie-triangles, which are on the \{H_2O, C_{10}, C_1\} and \{H_2O, C_{10}, CO_2\} faces. Case 2 (bottom), the largest tie-triangle lies on the \{H_2O, C_{10}, C_1\} face. Tie-triangles degenerate inside the space as shown by the bounds of the three-phase region. The tie-triangles and tie-lines that parameterize three- and two-phase mixtures along the solution path are shown in red and blue, respectively. Mixtures along the solution path are color-coded as in Figure (6.1).
6.2 Heterogenous Models

In this section, we consider thermal-compositional displacements in two-dimensional heterogenous models. The permeability distributions are obtained from different layers of the tenth SPE solution project (Christie and Blunt, 2001).

6.2.1 Cold CO$_2$ Injection

First, we consider the injection of \{C\(_1\)(0.05), CO$_2$(0.95)\} at $T = 235K$ and $p = 17.5$ bar into \{C\(_1\)(0.2), C\(_6\)(0.8)\} at $T = 170$ K and $p = 15$ bar. Figure (6.3) shows the phase behavior of this ternary system at the injection and initial conditions. In this case, three phases (V, L\(_1\), and L\(_2\)) exist inside the compositional space. Note that C\(_6\) is almost missing from the vapor phase. Moreover, the displacement is immiscible for the given pressure and temperature.

![Figure 6.3: Full parameterization of the cold CO$_2$ system at (a) initial, and (b) injection conditions.](image)

Figure (6.4) shows the MoC-like solutions of this system. The solution path at initial conditions of temperature and pressure enters the L\(_1\)L\(_2\) region only. However,
at injection conditions, the solution consists of gridblocks in the VL$_2$, three-phase, and VL$_1$ states.

**Figure 6.4:** MoC-like solutions for the cold CO$_2$ injection problem at (a) initial, and (b) injection conditions. Tie-triangles and tie-lines represent the compositions of multiphase gridblocks.

Figure (6.5) shows this multiphase displacement across the seventh layer of the SPE10 problem. Here, the solution path mainly consists of gridblocks in the VL$_2$ and VL$_1$L$_2$ states. This is expected considering the parameterization of the dilution line between the injection and initial mixtures.
6.2.2 Thermal Steam Injection

In this section, we present several examples of thermal steam injection in heterogeneous reservoirs.

We start by describing the phase behavior of steam injection in a one-dimensional homogeneous model. Here, steam is injected into a binary mixture of \( C_1 \) and \( C_{10} \).
Since one table of tie-simplexes is sufficient to parameterize a ternary displacement problem, the \( p-T \) conditions of multiphase degeneration can be represented in a single plot. These critical conditions for the degeneration of tie-triangles, as well as, disappearance of the gas-oil and water tie-lines are shown in Figure (6.6). Note that the ternary compositional space has degenerated completely (no tie-simplexes) for temperature and pressure conditions to the right of the red curve. Moreover, it is non-degenerate (no critical tie-simplexes) to the left of the blue curve.

In this figure, we also show the temperature and pressure conditions of the gridblocks for a particular time-step in the simulation. Note that the injection condition is super-critical and that the initial mixture is far below the degeneration conditions. The plot indicates that the thermodynamic state of the displacement changes in the neighborhood of various degeneration conditions.

\[\text{Figure 6.6: One-dimensional solution of a thermal steam injection problem in the } p-T \text{ domain. The dots represent } p-T \text{ conditions of the gridblocks.}\]

Figure (6.7) shows a one-dimensional solution of the thermal steam injection problem (flow is from left to right). In the first 60 gridblocks, conditions of temperature and pressure are such that the compositional space is in the critical state; the phase-state at these gridblocks is single-phase gas. Then, the saturation of the gas phase drops considerably as the solution path enters the gas-water region (some of the injected steam condenses to liquid water phase). Farther into the reservoir, all three phases move together. Note that the water phase saturation in the water bank is non-zero in all the gridblocks from 60 to 140. Profiles of the overall compositions...
show that the in-situ components have been swept ahead of the water bank.

![Figure 6.7: One-dimensional solution of a thermal steam injection problem: (top) saturations, (bottom) overall compositions.](image)

Next, we consider steam injection in a heterogeneous model. We simulate the injection of \( \{C_1(0.01), H_2O(0.99)\} \) at \( T = 610 \text{ K} \) and \( p = 135 \text{ bar} \) into \( \{C_1(0.2), C_{10}(0.8)\} \) at \( T = 410 \text{ K} \) and \( p = 105 \text{ bar} \) (see Figure 6.8). As in the 1D case, the compositional space is fully critical at injection conditions (i.e., all the tie-simplexes have degenerated), and it is far below the critical state at initial conditions (phase behavior changes as described in Figure 4.7). Figure (6.8-c) shows that the temperature front has developed, and it is close to the displacement front.
Chapter 6. Multiphase Simulation Examples

Layer 7, \( \log_{10}(k_{\text{max}}/k_{\text{min}}) = 6.388 \)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{example.png}
\caption{Solution of the three-component thermal steam injection model. From top to bottom: phase-state map, temperature, and \( z_{H_2O} \).}
\end{figure}

Steam injection in four-component systems show similar phase behaviors. Figure (6.9) presents a one-dimensional \((500 \times 1 \times 1)\) displacement process in a four-component system. Here, a mixture of \( \{H_2O (0.9), CO_2 (0.05), C_1 (0.05)\} \) at \( T = 610 \text{K} \) and \( p = 130 \text{bar} \) is injected into \( \{NC_{10} (0.7), CO_2 (0.2), C_1 (0.1)\} \) at \( T = 410 \text{K} \) and \( p = 110 \text{bar} \). The four-component phase behavior is similar to those presented in Figure (4.10). Note that more than one table of tie-simplexes parameterize the
compositional space between the injection and initial mixtures.

Figure 6.9: Solution of the one-dimensional four-component thermal steam injection problem.

In this example, the solution path approaches the water component in the compositional space (note the water bank in the gas-water region). Furthermore, two banks of C\textsubscript{1} and CO\textsubscript{2} form just downstream of the water bank. Figure (6.10) presents the results for the displacement in a heterogeneous two-dimensional model (layer 31 of the SPE10 problem). Due to complex thermodynamic interactions between the injected steam and the in-situ oil, five different phase-states exist across the reservoir model.
Finally, we consider a model with both steam and gas injection. Here, we inject \{C_1(0.9), NC_{10}(0.05), H_2O(0.05)\} (from bottom left at $T = 510$ K and $p = 130$ bar), and \{C_1(0.1), H_2O(0.9)\} (from top left at $T = 610$ K and $p = 135$ bar) into \{C_1(0.2), NC_{10} (0.8)\} at $T = 410$K and $p = 110$ bar (see Figures 6.11, and 6.12). Note that the sequence of phase-states from the steam injector to the in-situ oil is G→GW→GOW, and from the gas injector the sequence is G→GO. As a result, the patterns of phase
appearance/disappearance are quite complex when fronts from different injectors interact with each other.

The phase-state maps also show the gridblocks that are in critical and non-degenerate phase states. This identification is based on the pressure and temperature of the gridblock only (since the compositional system is ternary, note Figure 6.6). Gridblocks at critical state are close to the steam injector (they have $p$-$T$ conditions that are beyond the red curve in Figure 6.6). A narrow region separates this critical region from the rest of the reservoir in the non-degenerate state.
Figure 6.11: Steam-gas co-injection model, solution at an early time-step. From top to bottom: permeability map, temperature, phase-state, and $z_{NC_{10}}$. 
Figure 6.12: Steam-gas co-injection model, solution at breakthrough. From top to bottom: permeability map, temperature, phase-state, and $z^{NC}_{10}$.

6.2.3 Thermal Injection into Heavy Oil

Here, we use the description of the heavy oil provided by Characterization I in Table (6) of Krejbjerg and Pedersen (2006). The 21-component system is lumped into two pseudo-components (denoted by PC$_1$ and PC$_2$), where PC$_1$ is made up of CO$_2$ and
C₁, only.

Figure (6.13) shows the full parameterization of compositional space when water is included in the system. Note that the single-phase oil region is considerably larger than the gas region. Moreover, with increasing temperature at constant pressure, the water tie-lines disappear before the gas-oil region disappears (this is different from the pattern presented in Figure 4.7).

![Diagram of compositional space](image)

**Figure 6.13:** Full parameterization for water-heavy-oil system at (a) initial, (b) an intermediate, and (c) injection conditions.

We consider thermal steam injection of composition \{PC₁(0.05), H₂O(0.95)\} at \( T = 650 \) K and \( p = 340 \) bar into \{PC₁(0.2016), PC₂(0.7984)\} at \( T = 450 \) K and \( p = 210 \) bar. Figure (6.14) shows the numerical solution at breakthrough. Note that some gridblocks between the single-phase gas and the two-phase gas-water are single-phase water. In this case, the equilibrium composition of PC₁ in the water phase is not negligible, and the solution path (which usually approaches the H₂O corner in a thermal steam injection problem) enters the slightly larger single-phase water region.
6.3 Comparison with STARS (CMG, 2010a)

In this section, we present a comparison of our numerical solutions with a commercial flow simulator, STARS (CMG, 2010a). For this purpose, tie-simplex tables of CSAT are used to generate the table of K-values required by the STARS simulator. In the following examples, we chose the coefficients of fluid enthalpy calculations such that the temperature front moves close to the regions of phase appearance/disappearance.

In the first model, we consider an immiscible displacement. Here, a mixture of
\{C_1(0.8), H_2O(0.2)\} at \( T = 420 \text{ K} \) and \( p = 14 \text{ bar} \) is injected into oil made up of \{C_{20}(0.3), H_2O(0.7)\} at \( T = 360 \text{ K} \) and \( p = 10 \text{ bar} \). Compositional spaces for the initial and injection conditions are shown in Figure (6.15). Note that the fraction of H_2O in the oil phase is small at these conditions. Here, the tie-triangle compositions at different temperatures and pressures are used to construct the K-value tables.

Figure 6.15: Parameterization of \{C_1, C_{20}, H_2O\} at initial and injection conditions.

For this system, the solution path is similar to that presented in Figure (6.1-c,d). Figures (6.16) and (6.17) compare the solutions of both simulators for temperature and \( z_{H_2O} \) at breakthrough. Note the formation of the water bank in the gas-water and three-phase regions.
CHAPTER 6. MULTIPHASE SIMULATION EXAMPLES

Figure 6.16: Solutions of temperature by GPRS (top) and STARS (bottom)

Figure 6.17: Phase-state map, as well as, solutions of $z_{H_2O}$ by GPRS (top) and STARS (bottom)
In the second example, \( \{ C_1(0.4), H_2O(0.6) \} \) at \( T = 600 \) K and \( p = 135 \) bar is injected into \( \{ C_{10}(0.9), H_2O(0.1) \} \) at \( T = 410 \) K and \( p = 110 \) bar. In this case, the temperature and pressure conditions vary across the critical states of the compositional system. Therefore, the K-value tables are generated using the compositions of the farthest side tie-lines (instead of the tie-triangle) at each \( p-T \) level.

We consider the displacement in a \( 60 \times 60 \times 1 \) reservoir model from the fifteenth layer of the SPE10 problem (Figure 6.18). Figures (6.19) and (6.20) compare the solutions of GPRS and STARS. The results of both simulators match closely. Note that the water component is mainly present in the gas-water and three-phase regions that are formed between the injected mixture and in-situ fluid phases. Furthermore, the temperature front moves closely with the regions of phase appearance/disappearance. Figure (6.21) shows that the injected mixture is just below the conditions for full disappearance of all tie-simplexes from the compositional space.

Figure 6.18: The permeability map for the second comparison model
Figure 6.19: Phase-state maps at breakthrough

Figure 6.20: Maps of temperature and $z_{H_2O}$ at breakthrough
Figure 6.21: Pressure-temperature domain before breakthrough. The blue and red curves represent, respectively, the conditions for degeneration of the three-phase regions, and disappearance of the two-phase regions. Pressure and temperature conditions of each gridblock is shown by black dots.
Chapter 7

Conclusions

Thermodynamic systems that are used to model complex Enhanced Oil Recovery processes can form three or more phases at equilibrium. Resolving the coupling of thermodynamics with the equations of flow and transport poses a significant challenge in the development of a numerical simulation framework. Furthermore, various multiphase regions appear/disappear, or degenerate as a function of temperature, pressure and composition. Clearly, a consistent, robust, and efficient phase behavior modeling framework is required for the simulation of large-scale thermal-compositional flows.

Previous work on the application of tie-lines for two-phase simulation has shown that an adaptive tabulation strategy is an efficient and accurate alternative to standard Equation-of-State computations. This dissertation described the development of a generalized tie-simplex method for numerical modeling of multiphase (three or more phases) thermal-compositional displacements. Theoretical advances in this work are summarized as follows:

1. Convexity of the tie-simplex space. We start our developments with a known value of $N_p^{\text{max}}$, the maximum number of equilibrium phases in the displacement. If the value of $N_p^{\text{max}}$ is correct, the Gibbs energy surface is strictly convex in the tie-simplex space. Therefore, phase-state identification in the tie-simplex space is equivalent to conventional thermodynamic stability techniques based on global minimization of Gibbs free energy. Our numerical experiments have shown that a wrong estimate of $N_p^{\text{max}}$ results in an intersection
of tie-simplexes, and this provides a criterion to determine the value of \( N_{p}^{\text{max}} \) adaptively.

2. **Parameterization of the multiphase compositional space.** Once the value of \( N_{p}^{\text{max}} \) is known, a non-degenerate base parameterization is associated with the given compositional system. With \( N_{p}^{\text{max}} = 3 \), for example, the base parameterization includes one set of tie-triangles, and three sets of tie-lines. We developed a generalized negative-flash strategy for tie-simplex parameterization. It is shown that the negative-flash is guaranteed to converge to the unique parameterization if the value of \( N_{p}^{\text{max}} \) is correct.

3. **Continuity of parameterization.** We developed the Continuity Theorem for compositional space parameterization. This analysis describes the continuous variations of tie-simplexes as a function of temperature, pressure, and composition. Therefore, it allows for discrete representation of the multiphase thermodynamics using tables of tie-simplexes.

These ideas are integrated in the Compositional Space Adaptive Tabulation (CSAT) framework. Given the composition of a gridblock, CSAT constructs a base tie-simplex parameterization. For this purpose, the negative-flash method calculates the \( N_{p}^{\text{max}} \)-phase tie-simplex that parameterizes the given mixture. Then, all the multiphase regions on its extension are parameterized using lower-dimensional tie-simplexes. The resulting base parameterization is used as an initial guess for EoS computations in the next levels of temperature and pressure. We described how the degeneration and disappearance of tie-simplexes can be captured accurately in this parameterization framework.

Interpolation in the discrete tie-simplex table is used for phase-state identification. Theoretical developments based on the Method of Characteristics, as well as, an extensive set of numerical examples have shown that CSAT generates a limited number of tie-simplex tables in the course of a numerical compositional simulation. We integrated CSAT with Stanford AD-GPRS, and applied it to several challenging thermal problems including super-critical steam injection. We also demonstrated reasonable match between our results and the solutions of a widely used thermal flow
Modeling complex thermal-compositional displacements is a rich research topic with several potential future directions. An obvious candidate is to enable CSAT for cases where the number of phases exceeds the number of components. More research is also needed to find practical solutions for determining the correct value of $N_{p}^{max}$. As briefly discussed in Chapter 4, an adaptive strategy is the easiest approach. $N_{p}^{max}$ can also be determined from an efficient pre-processing analysis. An ideal technical design for CSAT will not depend on $N_{p}^{max}$, or the specific degeneration pattern.

Another interesting direction is investigating the nonlinear behaviors of the multiphase thermal-compositional simulator. This includes research on nonlinear solvers based on flux functions (Voskov and Tchelepi, 2011), and developing different formulations such as molar, and the so-called $\Gamma$ variables (Zaydullin et al., 2011). Furthermore, studying the coupling of various physics (e.g., energy equation, and counter-current flows in gravity-dominated displacements) is an open research challenge.
Bibliography


