## RICE UNIVERSITY

Simulations of Partially Miscible Two-Component Two-Phase Flow at the Pore-Scale Using Discontinuous Galerkin Methods

## By

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## A THESIS SUBMITTED <br> IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

## Master of Science

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#### Abstract

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In this dissertation, an effective numerical algorithm is developed for establishing simulation for the two-component two-phase flow with partial miscibility at the pore scale. Many studies in the rock-fluid interaction have been done for immiscible flow, whose components do not mix and separate instantaneously. This paper extends the study to miscible flow, whose components will mix with certain pressure and temperature, and exploits the potential of simulating complex real-life fluid interactions. The mathematical model consists of a set of Cahn-Hilliard equations and a realistic equation of state (i.e. Peng-Robinson equation of state). The numerical challenges lie in the fact that these are highly coupled, fourth-order, nonlinear partial differential equations. For solving the proposed PDEs, a discontinuous Galerkin (DG) method is used for space discretization, and a combination of backward Euler method and convex-concave splitting method is used for time discretizition. The resulting simulation can extract essential characteristics of the digital rock sample, agreeing with conventional lab-based tests but with only a fraction of cost in time and resources. Practically, the proposed algorithm and simulation can help engineers to make more informed decisions, for example in oil industry for enhancing oil recovery.

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## Chapter 1

## Introduction

Simulation of two-component flow with partial misciblily at the pore scale has been gaining attention over years in chemical and reservoir engineering. This simulation can extract essential characteristics of the fluids in the rock sample, and thus can help engineers to make more informed decisions, for example in oil industry for optimizing hydrocarbon production. As an inexpensive alternative to the conventional lab-based core tests, a robust rock-fluid simulation should have the following properties. First, the desired simulation must be governed by physics laws of conservation, for example conservation of mass, conservation of momentum, etc. Second, the simulation should be stable enough so that no small perturbation in input argument would lead to large error in the simulation result. The first property is inherent within the selected mathematical model, while the second properties is inherent within the selected numerical scheme.

In this chapter, we present a brief literature review for simulating the flows at the pore scale. Next, we summarize the popular choice of mathematical model and numerical scheme for the immiscible/partially miscible two-component two-phase flow. Finally, we conclude this chapter by presenting the outline of this dissertation.

### 1.1 Literature Review

### 1.1.1 Pore Scale Flows

Due to the advance in technology and the increased computing capacity in recent years, numerical simulation has become more and more competitive, compared to the traditional lab-based tests approach, in the systematic analysis of the pore scale flow. The two main branches in numerical simulation for pore scale flow are the pore network models [1] and the family of direct-numerical-simulation (DNS). The network models use an artificial network as a simplified representation of the rock geometry in the construction of the model, whereas the direct simulation approaches use a realistic digital rock sample that is captured by micro-CT scans and then reconstructed by a 3D imaging software. The pore network model is less numerically expensive due to the simplification of the rock geometry. This empowers it the capacity to reach larger length scale. But the lack of the complexity of the rock geometry in pore network models also impairs the credibility of the result, making it less reliable in the production applications.

Popular choices for direct simulating multi-phase flow in actual porous media include lattice Boltzmann methods (LBM) [2], and phase-field methods [3]. These two methods describe the mechanics of fluid flow in mesoscopic level and continuum level respectively. In continuum level, the fluid is described in terms of space-filing fields, such as density, velocity, which change smoothly over time and space. Whereas in mesoscopic level, the fluid is described in terms of the probability at a point of finding a given fictive particle ensemble, whose motions are refined in a space-time lattice. LBM is highly localized, which allows for efficient parallelization. However compared with phase field method, LBM has a much larger degree of freedom, which is
numerically unfavourable in memory consumption. Both of these approaches belong to the family of diffuse-interface methods. In this dissertation, phase-field method is used in the modeling of the two-component two-phase flow system.

### 1.1.2 Immiscible Two-Phase Flow

As an essential characteristic of two-component flow, miscibility describes the mixing level of two components with a given pressure and temperature. Substances are said to be miscible if they mix in all proportions. On the contrary, substances are said to be immiscible if they do not mix at all and separate into two homogeneous phases instantaneously [4].

One of the most cited mathematical models for characterizing the process of phase separation of an immiscible binary flow is Cahn-Hilliard (CH) equation, named after J.W. Cahn and J. E. Hilliard. In [5], they determined and formulated the Helmholtz free energy of a flat interface between two coexisting phases, which is expressed as follows:

$$
\begin{equation*}
f(c)=f_{0}(c)+\kappa(\boldsymbol{\nabla} c)^{2} \tag{1.1}
\end{equation*}
$$

where $c$ is called the order parameter, which is the difference between the mass fraction of the two components. Equation (1.1) states that the Helmholtz free energy density of a two-component fluid is the sum the two contributions: the contribution from the two homogeneous bulk phases, $f_{0}$, and the contribution from the diffusive interface, $\kappa(\boldsymbol{\nabla} c)^{2}$. According to thermodynamics [6], chemical potential, which is determined by $\mu=\frac{\partial f}{\partial c}$, must be in equilibrium spatially for each component. Coupling the homogeneous chemical potnetial and the conservation of the order parameter yields
the following classical CH equation (without advection).

$$
\begin{align*}
& \frac{\partial c}{\partial t}-\nabla \cdot(M(c) \nabla \mu)=0  \tag{1.2}\\
& \mu=\frac{\partial f_{0}(c)}{\partial c}-\kappa \Delta c \tag{1.3}
\end{align*}
$$

where the coefficient $M(c) \geq 0$ is called mobility. The CH equation is a fourth-order, nonlinear partial differential equation, which has numerical challenges.

### 1.1.3 Partially Miscible Two-Phase Flow

Both miscible and immiscible fluids have been heavily studied in porous media, for example, $[7,8]$. However, many fluids are only partially miscible, whose components will mix only in a limited range of proportion, for example, mixing of water and phenol. In fact, miscibility and immiscibility can be viewed as two extreme cases of partial miscibility according to thermodynamics. At the end of the mixing process, two homogeneous phases, consisting of one or more components, are formed in both immiscible flow and partially miscible flow.
J. Kou and S. Sun extended the classical CH equation from immiscible flow to partially miscible flow [9]. The main unknown is now extended from the order parameter, $c$, to two parameters $\rho_{1}, \rho_{2}$, which are the molar densities corresponding to the two components. This not only doubles the unknowns and the number of coupled equations but also increases the numerical challenging to solve such a complicated system.

The $f_{0}$ contribution in equation (1.1) can be determined based on a double-well potential or an realistic equation of state. Popular choices are Ginzburg-Landau potential [10] and Peng-Robinson equation of state [11]. The first choice is easy to implement, while the second choice is more accurate but computationally more
challenging. In this dissertation, Peng-Robinson equation of state is adopted in our mathematical model.

### 1.1.4 Numerical Schemes

The vast applications of the CH equation stimulate the development of numerical schemes for solving it accurately and efficiently. There are many efforts devoted to numerical methods both in terms of spatial and temporal approximation. For spatial discretization of CH equation, popular numerical methods includes finite difference [12], finite volume (FV)[13], finite element (FE) [14], and spectral methods [15]. For temporal discretization, the Euler method is most employed, followed by Runge-Kutta method.

In the dissertation, I adopt the discontinuous Galerkin (DG) method for spatial discretization. The DG method has many positive features, which makes it suitable for this problem. First, the DG method can be parallelized very easily. Similar to the FV and the FE method, the DG method decomposes the domain into small subdomains. Second, the DG method preserves mass locally. If one simulates a bubble in a 3D domain by using the DG method, then the size of the bubble will be preserved as time marches on, which is not always true for the case of applying other methods. Last but not least, the user has the freedom to choose any order of polynomial for the DG basis. This dissertation is currently using a linear basis, but it can be extended to a higher order.

As for the temporal discretization, I adopt the backward Euler method and convexconcave splitting [16]. The molar densities terms in the generalized CH model are approximated implicitly in time using backward Euler method, whereas the nonlinear chemical potential terms need to be decomposed into a convex and a concave part
first. The convex part would be approximated implicitly, and the concave part would be approximated explicitly. Adopting the convex-concave splitting for the nonlinear chemical potential terms ensures dissipation of energy. The combination of these two methods makes time-stepping unconditionally stable.

The key contribution of this dissertation is to establish an effective simulation based on the DG method in space, backward Euler and convex-concave splitting in time for the modified CH equations for the two-component two-phase flow with partial miscibility at the pore scale.

### 1.2 Thesis Outline

The rest of this dissertation is organized as follows. In Chapter 2, we formulate the mathematical problem and describe the boundary conditions and initial conditions. In Chapter 3, we discretize the proposed problem in space by the discontinuous Galerkin (DG) method, discretize it in time using a classic convex-concave splitting method for energy terms, and derive the matrix formulation of the proposed problem. In Chapter 4, numerical simulations are carried out for demonstrating accuracy and numerical robustness of the proposed numerical algorithm. Finally concluding remarks are provided in Chapter 5.

## Chapter 2

## Mathematical Model

In this chapter, we introduce a system of generalized Cahn-Hilliard equations for the two-component partially miscible flow problem, present the boundary conditions and initial conditions, and finally non-dimensionalize the system of equations.

### 2.1 Mass Conservation

Let $\Omega \in \mathbb{R}^{3}$ denote an open bounded domain. Let $\partial \Omega$ denote the boundary of $\Omega$. Let $(0, T)$ denote the time interval. Mass conservation of the two-component flow can be described by the following two equations:

$$
\begin{array}{ll}
\frac{\partial \rho_{1}}{\partial t}+\nabla \cdot J_{1}=0, & \text { in } \Omega \times(0, T), \\
\frac{\partial \rho_{2}}{\partial t}+\nabla \cdot J_{2}=0, & \text { in } \Omega \times(0, T),
\end{array}
$$

where $\rho_{1}, \rho_{2}$ represent the molar density of the two components of the flow. The parameters $J_{1}, J_{2}$ represent the diffusive fluxes of those two components.

The diffusive flux is driven by the sum of the gradient of chemical potentials of all components. The mathematical formulation for the diffusive fluxes $J_{1}, J_{2}$ is given by

$$
\begin{aligned}
& J_{1}=-M_{11} \boldsymbol{\nabla} \mu_{1}-M_{12} \boldsymbol{\nabla} \mu_{2}, \\
& J_{2}=-M_{21} \boldsymbol{\nabla} \mu_{1}-M_{22} \boldsymbol{\nabla} \mu_{2},
\end{aligned}
$$

where $M_{i, j}, i, j=1,2$, is referred to as mobility coefficient. The quantities $\mu_{1}, \mu_{2}$ are chemical potentials with respect to component 1 and 2 .

Let us recall the definition of the chemical potential

$$
\mu_{i}=\frac{\partial f}{\partial \rho_{i}}
$$

where $f$ denotes the Helmholtz free energy density of the given system. In a sharp interface method, $f$ equals to the bulk phase contribution $f_{b}$. However, in a diffuse interface method, we need to introduce an additional diffuse interface contribution $f_{\nabla}$, to account for the molar density change of those two components in the transition phase. That is

$$
f=f_{b}+f_{\nabla}
$$

Let us define

$$
f_{\nabla}\left(\rho_{1}, \rho_{2}\right):=\frac{1}{2} \sum_{i, j=1}^{2} c_{i j} \nabla \rho_{1} \cdot \nabla \rho_{2}
$$

where the parameters $c_{i j}, i, j=1,2$, are called cross influence parameters. Then the chemical potential of the two components can be calculated as

$$
\begin{aligned}
& \mu_{1}\left(\rho_{1}, \rho_{2}\right)=\mu_{b 1}\left(\rho_{1}, \rho_{2}\right)-c_{11} \Delta \rho_{1}-c_{12} \Delta \rho_{2}, \\
& \mu_{2}\left(\rho_{1}, \rho_{2}\right)=\mu_{b 2}\left(\rho_{1}, \rho_{2}\right)-c_{21} \Delta \rho_{1}-c_{22} \Delta \rho_{2},
\end{aligned}
$$

where the functions $\mu_{b 1}, \mu_{b 2}$ are the bulk phase chemical potential contributions, $\mu_{b i}:=\frac{\partial f_{b}}{\partial \rho_{i}}$. In the next section, we will explain in detail how to use the PengRobinson equation of state to derive these bulk phase chemical potential $\mu_{b 1}, \mu_{b 2}$, and the influence parameters $c_{i j}$.

If the mobility coefficients $M_{12}$ and $M_{21}$ are negligible compared to $M_{11}, M_{22}$, then
the mathematical model for mass conservation can be further simplified as follows:

$$
\begin{align*}
\frac{\partial \rho_{1}}{\partial t}-\nabla \cdot M_{11} \nabla \mu_{1}=0, & \text { in } \Omega \times(0, T),  \tag{2.1}\\
\frac{\partial \rho_{2}}{\partial t}-\nabla \cdot M_{22} \nabla \mu_{2}=0, & \text { in } \Omega \times(0, T),  \tag{2.2}\\
\mu_{1}=\mu_{b 1}\left(\rho_{1}, \rho_{2}\right)-c_{11} \Delta \rho_{1}-c_{12} \Delta \rho_{2}, & \text { in } \Omega \times(0, T),  \tag{2.3}\\
\mu_{2}=\mu_{b 2}\left(\rho_{1}, \rho_{2}\right)-c_{21} \Delta \rho_{1}-c_{22} \Delta \rho_{2}, & \text { in } \Omega \times(0, T) . \tag{2.4}
\end{align*}
$$

### 2.2 Peng-Robinson Equation of State

Peng-Robinson equation of state is a cubic thermodynamic equation relating the state variables. In this section, we introduce the pressure-temperture-mole form of PengRobinson equation of state, $\mathcal{F}(P, T, \rho)=0$, which is a cubic function of molar density $\rho$. Then we use it to recover the Helmholtz free energy density. More details of the derivation can be found in ([16] [9]).

### 2.2.1 Peng-Robinson equation of state

In a two-component system, one form of the Peng-Robinson equation of state, which is written in terms of the molar densities of the flow components, is formulated as

$$
P(\rho)=\frac{\rho R T}{1-b \rho}-\frac{a \rho^{2}}{1+2 b \rho-b^{2} \rho^{2}}
$$

where $P$ is the pressure. The variable $\rho$ is the total molar density, $\rho=\rho_{1}+\rho_{2}$. The parameter $R$ is the universal gas constant and $T$ is the temperature. Parameters $a$ and $b$ are the energy parameter and the covolume respectively, which take the following
forms:

$$
\begin{aligned}
a & =\frac{\rho_{1}^{2} a_{1}\left(1-k_{11}\right)+2 \rho_{1} \rho_{2} \sqrt{a_{1} a_{2}}\left(1-k_{12}\right)+\rho_{2}^{2} a_{2}\left(1-k_{22}\right)}{\rho^{2}} \\
b & =\frac{0.07780 R}{\rho_{1}+\rho_{2}}\left(\rho_{1} \frac{T_{\rho_{1}}}{P_{\rho_{1}}}+\rho_{2} \frac{T_{\rho_{2}}}{P_{\rho_{2}}}\right)
\end{aligned}
$$

The parameter $k_{i j}$ is the given binary interaction coefficients for the energy parameters. Here we assume $k_{12}=k_{21}$. The parameters $a_{i}, b_{i}$ are determined as

$$
\begin{aligned}
a_{i} & =0.45724 \frac{R^{2} T_{\rho_{i}}^{2}}{P_{\rho_{i}}}\left[1+m_{i}\left(1-\sqrt{T_{r_{i}}}\right)\right]^{2}, \\
b_{i} & =0.07780 \frac{R T_{\rho_{i}}}{P_{\rho_{i}}} .
\end{aligned}
$$

where $T_{\rho_{i}}, P_{\rho_{i}}$ are the critical temperature and the critical pressure corresponding to the $i$ th component, and $T_{r_{i}}=\frac{T}{T_{\rho_{i}}}$ is the reduced temperature of component $i$. The coefficients $m_{i}$ takes the form:

$$
m_{i}= \begin{cases}0.37464+1.54226 \omega_{i}-0.26992 \omega_{i}^{2}, & \omega_{i} \leq 0.49 \\ 0.379642+1.485030 \omega_{i}-0.164423 \omega_{i}^{2}+0.016666 \omega_{i}^{3}, & \omega_{i}>0.49\end{cases}
$$

where $\omega_{i}$ is the acentric factor associated with the $i$ th component.

### 2.2.2 Helmholtz free energy

Helmholtz free energy $F$ of the system at a given time is computed as

$$
F=\int_{\Omega} f
$$

where $f$ denotes the Helmholtz free energy density of the system. According to [16], based on the Peng-Robinson equation of state, the Holmholtz free energy density is
derived as

$$
\begin{aligned}
f & =f_{b}+f_{\nabla} \\
f_{b} & =f_{b}^{\text {ideal }}+f_{b}^{\text {repulsion }}+f_{b}^{\text {attraction }} \\
f_{\nabla} & =\frac{1}{2} \sum_{i, j=1}^{2} c_{i j} \nabla \rho_{1} \cdot \nabla \rho_{2}
\end{aligned}
$$

The three contributions of the bulk phase Helmholtz free energy are determined as

$$
\begin{aligned}
f_{b}^{\text {ideal }}\left(\rho_{1}, \rho_{2}\right) & =R T\left(\rho_{1}\left(\ln \rho_{1}-1\right)+\rho_{2}\left(\ln \rho_{2}-1\right)\right) \\
f_{b}^{\text {repulsion }}\left(\rho_{1}, \rho_{2}\right) & =-\rho R T \ln (1-b \rho) \\
f_{b}^{\text {attraction }}\left(\rho_{1}, \rho_{2}\right) & =\frac{a \rho}{2 \sqrt{2} b} \ln \left(\frac{1+(1-\sqrt{2}) b \rho}{1+(1+\sqrt{2}) b \rho}\right) .
\end{aligned}
$$

The function $f_{b}^{\text {ideal }}$ computes the Helmholtz free energy of a hypothetical ideal gas, whose molecules do not interact. While functions $f_{b}^{\text {attraction }}$ and $f_{b}^{\text {repulsion }}$ account for the additional energy contributions from the inter-molecular attraction and repulsion.

Base on the model in [16], the influence parameter $c_{i j}$ is formulated as follows:

$$
c_{i j}=\left(1-\beta_{i j}\right) \sqrt{c_{i} c_{j}},
$$

where $\beta_{i j}$ is given bineary interaction coefficient, and pure component influence parameters $c_{i}$ are calculated as follows

$$
c_{i}=a_{i} b_{i}^{2 / 3}\left(\alpha_{i}\left(1-T_{r_{i}}\right)+\beta_{i}\right)
$$

with coefficients $\alpha_{i}, \beta_{i}$ defined as

$$
\alpha_{i}=\frac{-10^{-16}}{1.2326+1.3757 \omega_{i}}, \quad \beta_{i}=\frac{10^{-16}}{0.9051+1.5410 \omega_{i}}
$$

### 2.3 Boundary Conditions

Here we assume homogeneous diffusive fluxes on the boundary $\partial \Omega$ :

$$
\begin{array}{lc}
J_{1} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega \times(0, T), \\
J_{2} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega \times(0, T),
\end{array}
$$

where $\boldsymbol{n}$ is the outward normal.
In the case where $M_{12}, M_{21}$ are neglected, we obtain:

$$
\begin{array}{lc}
M_{11} \boldsymbol{\nabla} \mu_{1} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega \times(0, T), \\
M_{22} \boldsymbol{\nabla} \mu_{2} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega \times(0, T) . \tag{2.6}
\end{array}
$$

Boundary conditions (2.5)-(2.6) allow us to enforce the law of mass conservation, which states that the mass of a closed system must remain constant over time. This can be proved as follows for $i=1,2$ :

$$
\begin{aligned}
\frac{\partial}{\partial t} \int_{\Omega} \rho_{i} & =\int_{\Omega} \frac{\partial \rho_{i}}{\partial t} \\
& =\int_{\Omega} \boldsymbol{\nabla} \cdot M_{i i} \boldsymbol{\nabla} \mu_{i} \\
& =\int_{\partial \Omega} M_{i i} \boldsymbol{\nabla} \mu_{i} \cdot \boldsymbol{n} \\
& =0,
\end{aligned}
$$

Let $\partial \Omega^{\mathrm{D}}, \partial \Omega^{\mathrm{N}}$ denote Dirichlet boundary and Neumann boundary respectively. These two together make up the whole boundary $\partial \Omega$. We assume a given amount of mass of the two components is coming in from the Dirichlet boundary and no mass
is passing through the Neumann boundary and the solid wall, that is

$$
\begin{array}{cc}
\rho_{1}=\rho_{1, \text { in }}, & \text { on } \partial \Omega^{\mathrm{D}} \times(0, T), \\
\rho_{2}=\rho_{2, \text { in }}, & \text { on } \partial \Omega^{\mathrm{D}} \times(0, T), \\
\nabla \rho_{1} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega^{\mathrm{N}} \times(0, T), \\
\nabla \rho_{2} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega^{\mathrm{N}} \times(0, T) . \tag{2.10}
\end{array}
$$

### 2.4 Initial Conditions

Let us define the initial conditions as following:

$$
\begin{array}{ll}
\rho_{1}=\rho_{1}^{\text {ini }}, & \text { in } \Omega \times\{0\}, \\
\rho_{2}=\rho_{2}^{\text {ini }}, & \text { in } \Omega \times\{0\} .
\end{array}
$$

### 2.5 Mathematical Model

Assembling the mass balance equations, boundary conditions and initial conditions yields our final mathematical model, which is to find $\rho_{1}, \rho_{2}, \mu_{1}, \mu_{2}$ such that

$$
\begin{align*}
\frac{\partial \rho_{1}}{\partial t}-\nabla \cdot M_{11} \nabla \mu_{1}=0, & \text { in } \Omega \times(0, T),  \tag{2.11}\\
\frac{\partial \rho_{2}}{\partial t}-\nabla \cdot M_{22} \nabla \mu_{2}=0, & \text { in } \Omega \times(0, T),  \tag{2.12}\\
\mu_{1}=\mu_{b 1}\left(\rho_{1}, \rho_{2}\right)-c_{11} \Delta \rho_{1}-c_{12} \Delta \rho_{2}, & \text { in } \Omega \times(0, T),  \tag{2.13}\\
\mu_{2}=\mu_{b 2}\left(\rho_{1}, \rho_{2}\right)-c_{21} \Delta \rho_{1}-c_{22} \Delta \rho_{2}, & \text { in } \Omega \times(0, T),  \tag{2.14}\\
M_{11} \nabla \mu_{1} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega \times(0, T),  \tag{2.15}\\
M_{22} \nabla \mu_{2} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega \times(0, T),  \tag{2.16}\\
\rho_{1}=\rho_{1, \text { in }}, & \text { on } \partial \Omega^{\mathrm{D}} \times(0, T),  \tag{2.17}\\
\rho_{2}=\rho_{2, \text { in }}, & \text { on } \partial \Omega^{\mathrm{D}} \times(0, T),  \tag{2.18}\\
\nabla \rho_{1} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega^{\mathrm{N}} \times(0, T),  \tag{2.19}\\
\nabla \rho_{2} \cdot \boldsymbol{n}=0, & \text { on } \partial \Omega^{\mathrm{N}} \times(0, T),  \tag{2.20}\\
\rho_{1}=\rho_{1}^{\text {ini }}, & \text { in } \Omega \times\{0\},  \tag{2.21}\\
\rho_{2}=\rho_{2}^{\text {ini },} & \text { in } \Omega \times\{0\} . \tag{2.22}
\end{align*}
$$

### 2.6 Non-dimensionalization

Before the start the non-dimensionalization, let us take a brief review of the major quantities and their units of our model in Table 2.1

| Quantity | Symbol | Unit |
| :--- | :--- | :--- |
| length | $x$ | m |
| time | $t$ | s |
| molar density | $\rho_{1}, \rho_{2}$ | $\mathrm{~mol} \mathrm{~m}^{-3}$ |
| influence parameters | $c_{i j}$ | $\mathrm{~J} \mathrm{~m}^{5} \mathrm{~mol}^{-2}$ |
| mobility coefficients | $M_{i j}$ | $\mathrm{~mol}^{2} \mathrm{~J}^{-1} \mathrm{~m}^{-1} \mathrm{~s}^{-1}$ |
| energy density | $f$ | $\mathrm{~J} \mathrm{~m}^{-3}$ |
| chemical potential | $\mu_{1}, \mu_{2}$ | $\mathrm{~J} \mathrm{~mol}^{-1}$ |

Table 2.1: Major quantities and their units used in the our model

Let us write the dimensional quantity by a product of a characteristic unit and a dimensionless quantity. That is, we define:

$$
\begin{aligned}
x & =x_{c} \tilde{x}, \\
t & =t_{c} \tilde{t}, \\
f\left(\rho_{1}, \rho_{2}\right) & =f\left(\rho_{c} \tilde{\rho}_{2}, \rho_{c} \tilde{\rho}_{2},\right)=f_{c} \tilde{f}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right), \\
\rho_{i}(x, t) & =\rho_{i}\left(x_{c} \tilde{x}, t_{c} \tilde{t}\right)=\rho_{c} \tilde{\rho}_{i}(\tilde{x}, \tilde{t}), \\
M_{i j} & =M_{c} \tilde{M}_{i j}, \\
c_{i j}\left(\rho_{1}, \rho_{2}\right) & =c_{c} \tilde{c}_{i j}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right), \\
\mu_{i}\left(\rho_{1}, \rho_{2}\right) & =\frac{\partial f\left(\rho_{1}, \rho_{2}\right)}{\partial \rho_{i}}=\frac{f_{c}}{\rho_{c}} \frac{\partial \tilde{f}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right)}{\partial \tilde{\rho}_{i}}=\frac{f_{c}}{\rho_{c}} \tilde{\mu}_{i}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right) .
\end{aligned}
$$

Substituting these into the PDEs (2.11)-(2.22), we obtain

$$
\begin{array}{rr}
\frac{\rho_{c}}{t_{c}} \frac{\partial \tilde{\rho}_{1}}{\partial \tilde{t}}-\frac{f_{c} M_{c}}{\rho_{c} x_{c}^{2}} \tilde{\boldsymbol{\nabla}} \cdot \tilde{M}_{11} \tilde{\boldsymbol{\nabla}} \tilde{\mu}_{1}=0, & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\frac{\rho_{c}}{t_{c}} \frac{\partial \tilde{\rho}_{2}}{\partial \tilde{t}}-\frac{f_{c} M_{c}}{\rho_{c} x_{c}^{2}} \tilde{\boldsymbol{\nabla}} \cdot \tilde{M}_{22} \tilde{\boldsymbol{\nabla}} \tilde{\mu}_{2}=0, & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\frac{f_{c}}{\rho_{c}} \tilde{\mu}_{1}=\frac{f_{c}}{\rho_{c}} \tilde{\mu}_{b 1}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right)-\frac{\rho_{c} c_{c}}{x_{c}^{2}} \tilde{c}_{11} \tilde{\Delta} \tilde{\rho}_{1}-\frac{\rho_{c} c_{c}}{x_{c}^{2}} \tilde{c}_{12} \tilde{\Delta} \tilde{\rho}_{2}, & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\frac{f_{c}}{\rho_{c}} \tilde{\mu}_{2}=\frac{f_{c}}{\rho_{c}} \tilde{\mu}_{b 2}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right)-\frac{\rho_{c} c_{c}}{x_{c}^{2}} \tilde{c}_{21} \tilde{\Delta} \tilde{\rho}_{1}-\frac{\rho_{c} c_{c}}{x_{c}^{2}} \tilde{c}_{22} \tilde{\Delta} \tilde{\rho}_{2}, & \text { in } \tilde{\Omega} \times(0, \tilde{T}) . \tag{2.26}
\end{array}
$$

Rearranging the coefficients, we have:

$$
\begin{array}{rr}
\frac{\partial \tilde{\rho}_{1}}{\partial \tilde{t}}-\frac{f_{c} M_{c} t_{c}}{\rho_{c}^{2} x_{c}^{2}} \tilde{\boldsymbol{\nabla}} \cdot \tilde{M}_{11} \tilde{\boldsymbol{\nabla}} \tilde{\mu}_{1}=0, & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\frac{\partial \tilde{\rho}_{2}}{\partial \tilde{t}}-\frac{f_{c} M_{c} t_{c}}{\rho_{c}^{2} x_{c}^{2}} \tilde{\boldsymbol{\nabla}} \cdot \tilde{M}_{22} \tilde{\boldsymbol{\nabla}} \tilde{\mu}_{2}=0, & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\tilde{\mu}_{1}=\tilde{\mu}_{b 1}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right)-\frac{\rho_{c}^{2} c_{c}}{f_{c} x_{c}^{2}}\left(\tilde{c}_{11} \tilde{\Delta} \tilde{\rho}_{1}+\tilde{c}_{12} \tilde{\Delta} \tilde{\rho}_{2}\right), & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\tilde{\mu}_{2}=\tilde{\mu}_{b 2}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right)-\frac{\rho_{c}^{2} c_{c}}{f_{c} x_{c}^{2}}\left(\tilde{c}_{21} \tilde{\Delta} \tilde{\rho}_{1}+\tilde{c}_{22} \tilde{\Delta} \tilde{\rho}_{2}\right), & \text { in } \tilde{\Omega} \times(0, \tilde{T}) .
\end{array}
$$

If we define two dimensionless numbers, $\eta, \xi$, such that

$$
\eta=\frac{f_{c} M_{c} t_{c}}{\rho_{c}^{2} x_{c}^{2}}, \quad \xi=\frac{\rho_{c}^{2} c_{c}}{f_{c} x_{c}^{2}}
$$

then the desired non-dimensionalized PDEs will become: finding $\tilde{\rho}_{1}, \tilde{\rho}_{2}, \tilde{\mu}_{1}, \tilde{\mu}_{2}$ such
that the following system of equations are satisfied.

$$
\begin{array}{rc}
\frac{\partial \tilde{\rho}_{1}}{\partial \tilde{t}}-\eta \tilde{\boldsymbol{\nabla}} \cdot \tilde{M}_{11} \tilde{\boldsymbol{\nabla}} \tilde{\mu}_{1}=0, & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\frac{\partial \tilde{\rho}_{2}}{\partial \tilde{t}}-\eta \tilde{\boldsymbol{\nabla}} \cdot \tilde{M}_{22} \tilde{\boldsymbol{\nabla}} \tilde{\mu}_{2}=0, & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\tilde{\mu}_{1}=\tilde{\mu}_{b 1}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right)-\xi\left(\tilde{c}_{11} \tilde{\Delta} \tilde{\rho}_{1}+\tilde{c}_{12} \tilde{\Delta} \tilde{\rho}_{2}\right), & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\tilde{\mu}_{2}=\tilde{\mu}_{b 2}\left(\tilde{\rho}_{1}, \tilde{\rho}_{2}\right)-\xi\left(\tilde{c}_{21} \tilde{\Delta} \tilde{\rho}_{1}+\tilde{c}_{22} \tilde{\Delta} \tilde{\rho}_{2}\right), & \text { in } \tilde{\Omega} \times(0, \tilde{T}), \\
\tilde{\nabla} \tilde{\mu}_{1} \cdot \boldsymbol{n}=0, & \text { on } \partial \tilde{\Omega} \times(0, \tilde{T}), \\
\tilde{\nabla}^{2} \tilde{\mu}_{2} \cdot \boldsymbol{n}=0, & \text { on } \partial \tilde{\Omega} \times(0, \tilde{T}), \\
\tilde{\rho}_{1}=\frac{1}{\rho_{c}} \rho_{1, \text { in }}, & \text { on } \partial \tilde{\Omega}^{\mathrm{D}} \times(0, \tilde{T}), \\
\tilde{\rho}_{2}=\frac{1}{\rho_{c}} \rho_{2, \text { in }}, & \text { on } \partial \tilde{\Omega}^{\mathrm{D}} \times(0, \tilde{T}), \\
\tilde{\boldsymbol{\nabla}} \tilde{\rho}_{1} \cdot \boldsymbol{n}=0, & \text { on } \partial \tilde{\Omega}^{\mathrm{N}} \times(0, \tilde{T}), \\
\tilde{\boldsymbol{\nabla}} \tilde{\rho}_{2} \cdot \boldsymbol{n}=0, & \text { on } \partial \tilde{\Omega}^{\mathrm{N}} \times(0, \tilde{T}), \\
\tilde{\rho}_{1}=\frac{1}{\rho_{c}} \rho_{1}^{\text {ini }}, & \text { in } \tilde{\Omega} \times\{0\}, \\
\tilde{\rho}_{2}=\frac{1}{\rho_{c}} \rho_{2}^{\text {ini }}, & \text { in } \tilde{\Omega} \times\{0\} . \tag{2.38}
\end{array}
$$

## Chapter 3

## Numerical Methods

Finding a strong solution to the previously introduced problem in Section 2.6 may be extremely challenging. Instead of solving it directly, we aim to find a weak solution to this problem in a space of piecewise discontinuous polynomials. In this chapter, we explain the semi-discrete scheme and fully discrete scheme, and derive the matrix formulation for the given problem.

### 3.1 Spatial Discretization By DG Method

The method we use for the spatial discretization is referred to as Discontinuous Galerkin (DG) method.

### 3.1.1 Notation

Before describing the DG method, let us partition the spatial domain $\Omega$ into uniform cubes with size $h$, denoted by $E_{k}, k=0, \ldots, N-1$. Similarly we denote the face between neighboring cubes by $e$. Let the union of all the cubes be $\mathcal{E}_{h}$; and let the union of all the faces be $\partial \Omega \cup \Gamma_{h}$, where $\Gamma_{h}$ represents the collection of all the interior faces. For a given face $e$, let $\boldsymbol{n}_{e}$ be a fixed unit normal vector. We denote by $E_{e}^{-}$and $E_{e}^{+}$the elements that share the face $e$, such that $\boldsymbol{n}_{e}$ points from $E_{e}^{-}$to $E_{e}^{+}$. Let us denote the jump of a discontinuous function on a face by $[\cdot]$ and the average on a face
by $\{\cdot\}$. That is, for all $e=\partial E_{e}^{-} \cap \partial E_{e}^{+}$,

$$
[u]=\left.u\right|_{E_{e}^{-}}-\left.u\right|_{E_{e}^{+}}, \quad \quad\{u\}=\frac{1}{2}\left(\left.u\right|_{E_{e}^{-}}+\left.u\right|_{E_{e}^{-}}\right) .
$$

W can extend these to the boundary faces as follows:

$$
\begin{aligned}
{[u]=\left.u\right|_{E}, } & \text { if } e \in \partial E \cap \partial \Omega, \\
\{u\}=\left.u\right|_{E}, & \text { if } e \in \partial E \cap \partial \Omega
\end{aligned}
$$

Denote the DG space by $\mathcal{D}_{k}\left(\mathcal{E}_{h}\right)$, a space of piecewise discontinuous polynomials of degree k , as follows

$$
\mathcal{D}_{k}\left(\mathcal{E}_{h}\right)=\left\{v:\left.v\right|_{E_{i}} \in \mathbb{P}_{k}\left(E_{i}\right), \forall i=1, \ldots, N\right\} .
$$

We use the notation $(\cdot, \cdot)$ for the $L^{2}$ inner-product on $\Omega$.

### 3.1.2 DG Diffusion Bilinear Form

Let us look at the sum of the integral of the generic diffusion term $\boldsymbol{\nabla} \cdot M \boldsymbol{\nabla} \mu$. Under the assumption of Neumann boundary condition, applying generalized Green's theorem yields

$$
\begin{aligned}
-\sum_{E_{k} \in \mathcal{E}_{h}} \int_{E_{k}}(\boldsymbol{\nabla} \cdot M \boldsymbol{\nabla} \mu) v= & \sum_{E_{k} \in \mathcal{E}_{h}} \int_{E_{k}} M \boldsymbol{\nabla} \mu \cdot \boldsymbol{\nabla} v-\sum_{E_{k} \in \mathcal{E}_{h}} \int_{\partial E_{k}}\left(M \nabla \mu \cdot \boldsymbol{n}_{E_{k}}\right) v \\
= & \sum_{E_{k} \in \mathcal{E}_{h}} \int_{E_{k}} M \boldsymbol{\nabla} \mu \cdot \boldsymbol{\nabla} v-\sum_{e \in \Gamma_{h}} \int_{e}\left\{M \boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e}\right\}[v] \\
& -\sum_{e \in \partial \Omega} \int_{e} M \boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e} v \\
= & \sum_{E_{k} \in \mathcal{E}_{h}} \int_{E_{k}} M \boldsymbol{\nabla} \mu \cdot \boldsymbol{\nabla} v-\sum_{e \in \Gamma_{h}} \int_{e}\left\{M \boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e}\right\}[v] .
\end{aligned}
$$

Since the exact solution of chemical potential $\mu$ is continuous, adding terms involving [ $\mu$ ] would not change the equality of the previous equation. This leads to

$$
\begin{aligned}
-\sum_{E_{k} \in \mathcal{E}_{h}} \int_{E_{k}}(\boldsymbol{\nabla} \cdot M \boldsymbol{\nabla} \mu) v=\sum_{E_{k} \in \mathcal{E}_{h}} \int_{E_{k}} M \boldsymbol{\nabla} \mu \cdot \boldsymbol{\nabla} v & -\sum_{e \in \Gamma_{h}} \int_{e}\left\{M \boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e}\right\}[v] \\
& +\epsilon \sum_{e \in \Gamma_{h}} \int_{e}\left\{M \boldsymbol{\nabla} v \cdot \boldsymbol{n}_{e}\right\}[\mu]
\end{aligned}
$$

where the parameter $\epsilon$ of the intrinsic zero term is restricted to the values $-1,0,1$. When $\epsilon=-1$, the method is referred as symmetric interior penalty Galerkin method (SIPG); when $\epsilon=1$, the method is referred as nonsymmetric interior penalty Galerkin method (NIPG); when $\epsilon=0$, the method is referred as incomplete interior penalty Galerkin method (IIPG).

We are now able to associate a diffusion bilinear form $a(M ; \mu, v)$ with the diffusion term, such that

$$
\begin{aligned}
a(M ; \mu, v):=\sum_{E_{k} \in \mathcal{E}_{h}} \int_{E_{k}} M \boldsymbol{\nabla} \mu \cdot \boldsymbol{\nabla} v & -\sum_{e \in \Gamma_{h}} \int_{e}\left\{M \boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e}\right\}[v] \\
& +\epsilon \sum_{e \in \Gamma_{h}} \int_{e}\left\{M \boldsymbol{\nabla} v \cdot \boldsymbol{n}_{e}\right\}[\mu] \\
& +\frac{\sigma}{h} \sum_{e \in \Gamma_{h}} \int_{e}\{M\}[\mu][v]
\end{aligned}
$$

where $\sigma>0$ is called penalty parameter. The last added term penalizes any large jump in $\mu$ or in $v$.

Suppose there are not only Neumann boundary conditions, but also inhomogeneous Dirichlet boundary conditions. That is, $\boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e}=0$ on $\partial \Omega \backslash \partial \Omega^{\mathrm{D}}$, and $\mu=\hat{\mu}(t)$
on $\partial \Omega^{\mathrm{D}}$, then the diffusion bilinear form need to be modified as follows:

$$
\begin{aligned}
a_{\Gamma_{D}}(M ; \mu, v):=\sum_{E_{k} \in \mathcal{E}_{h}} \int_{E_{k}} M \boldsymbol{\nabla} \mu \cdot \boldsymbol{\nabla} v & -\sum_{e \in \Gamma_{h}} \int_{e}\left\{M \boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e}\right\}[v]-\sum_{e \in \partial \Omega^{\mathrm{D}}} \int_{e} M\left(\boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e}\right) v \\
& +\epsilon \sum_{e \in \Gamma_{h}} \int_{e}\left\{M \boldsymbol{\nabla} v \cdot \boldsymbol{n}_{e}\right\}[\mu]+\epsilon \sum_{e \in \partial \Omega^{\mathrm{D}}} \int_{e} M\left(\boldsymbol{\nabla} v \cdot \boldsymbol{n}_{e}\right) \mu \\
& +\frac{\sigma}{h} \sum_{e \in \Gamma_{h}} \int_{e}\{M\}[\mu][\boldsymbol{\nabla} v]+\frac{\sigma}{h} \sum_{e \in \partial \Omega^{\mathrm{D}}} \int_{e} M \mu v .
\end{aligned}
$$

That is

$$
a_{\Gamma_{D}}(M ; \mu, v):=a(M ; \mu, v)+a_{b d r y}(M ; \mu, v),
$$

where
$a_{b d r y}(M ; \mu, v)=-\sum_{e \in \partial \Omega^{\mathrm{D}}} \int_{e} M\left(\boldsymbol{\nabla} \mu \cdot \boldsymbol{n}_{e}\right) v+\epsilon \sum_{e \in \partial \Omega^{\mathrm{D}}} \int_{e} M\left(\boldsymbol{\nabla} v \cdot \boldsymbol{n}_{e}\right) \mu+\frac{\sigma}{h} \sum_{e \in \partial \Omega^{\mathrm{D}}} \int_{e} M \mu v$.
We also need to add the following term to the right hand side

$$
d(M ; \hat{\mu}, v):=\epsilon \sum_{e \in \partial \Omega^{\mathrm{D}}} \int_{e} M\left(\boldsymbol{\nabla} v \cdot \boldsymbol{n}_{e}\right) \hat{\mu}+\frac{\sigma}{h} \sum_{e \in \partial \Omega^{\mathrm{D}}} \int_{e} M \hat{\mu} v .
$$

### 3.2 Semi-Discrete Scheme

We consider the non-dimensional problem (2.27)-(2.38) and drop the tilde notation for simplicity. By assembling all the DG forms, the problem becomes: find $\rho_{1}, \rho_{2}, \mu_{1}, \mu_{2} \in$ $\mathcal{D}_{k}\left(\mathcal{E}_{h}\right)$ such that $\forall v \in \mathcal{D}_{k}\left(\mathcal{E}_{h}\right)$

$$
\begin{gathered}
\left(\frac{\partial \rho_{1}(t)}{\partial t}, v\right)+\eta a\left(M_{11} ; \mu_{1}(t), v\right)=0 \\
\left(\frac{\partial \rho_{2}(t)}{\partial t}, v\right)+\eta a\left(M_{22} ; \mu_{2}(t), v\right)=0 \\
\left(\mu_{1}(t), v\right)-\xi a\left(c_{11} ; \rho_{1}(t), v\right)-\xi a_{b d r y}\left(c_{11} ; \rho_{1}(t), v\right) \\
-\left(\mu_{b 1}\left(\rho_{1}(t), \rho_{2}(t)\right), v\right)-\xi a\left(c_{12} ; \rho_{2}(t), v\right)-\xi a_{b d r y}\left(c_{12} ; \rho_{2}(t), v\right)=\xi d\left(c_{11} ; \frac{\rho_{1, \text { in }}}{\rho_{c}}, v\right)+\xi d\left(c_{12} ; \frac{\rho_{2, \text { in }}}{\rho_{c}}, v\right), \\
\left(\mu_{2}(t), v\right)-\xi a\left(c_{21} ; \rho_{1}(t), v\right)-\xi a_{b d r y}\left(c_{21} ; \rho_{1}(t), v\right) \\
-\left(\mu_{b 2}\left(\rho_{1}(t), \rho_{2}(t)\right), v\right)-\xi a\left(c_{22} ; \rho_{2}(t), v\right)-\xi a_{b d r y}\left(c_{22} ; \rho_{2}(t), v\right)=\xi d\left(c_{21} ; \frac{\rho_{1, \text { in }}}{\rho_{c}}, v\right)+\xi d\left(c_{22} ; \frac{\rho_{2, \text { in }}}{\rho_{c}}, v\right) .
\end{gathered}
$$

### 3.3 Fully Discrete Scheme

Let $\tau>0$ denote the time step and let $t^{n}=n \tau$ for $n \geq 0$. We approximate the time derivative by a first order finite difference:

$$
\frac{\partial \rho\left(t^{n}\right)}{\partial t}=\frac{\rho\left(t^{n}\right)-\rho\left(t^{n-1}\right)}{\tau}+\mathcal{O}(\tau)
$$

We apply backward Euler to the semi discrete scheme in previous section to obtain the fully discrete scheme. That is: find $\rho_{1}^{n}, \rho_{2}^{n}, \mu_{1}^{n}, \mu_{2}^{n} \in \mathcal{D}_{k}\left(\mathcal{E}_{h}\right)$ for $n=1, \ldots, N_{T}$ sequentially, such that $\forall v \in \mathcal{D}_{k}\left(\mathcal{E}_{h}\right)$

$$
\begin{align*}
\left(\rho_{1}^{n}, v\right)+\tau \eta a\left(M_{11} ; \mu_{1}^{n}, v\right) & =\left(\rho_{1}^{n-1}, v\right)  \tag{3.3}\\
\left(\rho_{2}^{n}, v\right)+\tau \eta a\left(M_{22} ; \mu_{2}^{n}, v\right) & =\left(\rho_{2}^{n-1}, v\right)  \tag{3.4}\\
\left(\mu_{1}^{n}, v\right)-\xi a\left(c_{11} ; \rho_{1}^{n}, v\right)-\xi a_{b d r y}\left(c_{11} ; \rho_{1}^{n}, v\right) & \\
-\left(\mu_{b 1}\left(\rho_{1}^{n}, \rho_{2}^{n}\right), v\right)-\xi a\left(c_{12} ; \rho_{2}^{n}, v\right)-\xi a_{b d r y}\left(c_{12} ; \rho_{2}^{n}, v\right) & =\xi d\left(c_{11} ; \frac{\rho_{1, \mathrm{in}}}{\rho_{c}}, v\right)+\xi d\left(c_{12} ; \frac{\rho_{2, \text { in }}}{\rho_{c}}, v\right),  \tag{3.5}\\
\left(\mu_{2}^{n}, v\right)-\xi a\left(c_{21} ; \rho_{1}^{n}, v\right)-\xi a_{b d r y}\left(c_{21} ; \rho_{1}^{n}, v\right) & \\
-\left(\mu_{b 2}\left(\rho_{1}^{n}, \rho_{2}^{n}\right), v\right)-\xi a\left(c_{22} ; \rho_{2}^{n}, v\right)-\xi a_{b d r y}\left(c_{22} ; \rho_{2}^{n}, v\right) & =\xi d\left(c_{21} ; \frac{\rho_{1, \text { in }}}{\rho_{c}}, v\right)+\xi d\left(c_{22} ; \frac{\rho_{2, \text { in }}}{\rho_{c}}, v\right),  \tag{3.6}\\
\left(\rho_{1}^{0}, v\right) & =\left(\frac{\rho_{1}^{\mathrm{ini}}}{\rho_{c}}, v\right)  \tag{3.7}\\
\left(\rho_{2}^{0}, v\right) & =\left(\frac{\rho_{2}^{\text {ini }}}{\rho_{c}}, v\right) \tag{3.8}
\end{align*}
$$

To deal with the non-linearity of the terms $\mu_{b 1}\left(\rho_{1}^{n}, \rho_{2}^{n}\right), \mu_{b 2}\left(\rho_{1}^{n}, \rho_{2}^{n}\right)$, we adopt the convex-concave splitting method, which yields unconditional stable time stepping for the Cahn-Hilliard problem. We split $\mu_{b 1}\left(\rho_{1}, \rho_{2}\right), \mu_{b 2}\left(\rho_{1}, \rho_{2}\right)$ into convex parts and concave parts. We treat the convex parts implicitly and treat the concave parts explicitly.

Recalling Section 2.2, we decompose:

$$
f_{b}=f_{b}^{\text {convex }}+f_{b}^{\text {concave }}
$$

with

$$
\begin{aligned}
f_{b}^{\text {convex }} & =f_{b}^{\text {ideal }}+f_{b}^{\text {repulsion }} \\
f_{b}^{\text {concave }} & =f_{b}^{\text {attraction }}
\end{aligned}
$$

In order to enhance the convexity, let us introduce an auxiliary function that is convex:

$$
f_{b}^{\text {auxiliary }}(\boldsymbol{\rho})=R T\left(\rho_{1} \ln \rho_{1}+\rho_{2} \ln \rho_{2}-\rho-\rho_{1} \ln \left(1-b_{1} \rho_{1}\right)-\rho_{2} \ln \left(1-b_{2} \rho_{2}\right)\right)
$$

For any positive $\lambda$, we write for $i=1,2$ :

$$
\begin{aligned}
& \mu_{b i}^{+}\left(\rho_{1}, \rho_{2}\right)=\frac{\partial f_{b}^{\text {convex }}}{\partial \rho_{i}}+\lambda \frac{\partial f_{b}^{\text {auxiliary }}}{\partial \rho_{i}} \\
& \mu_{b i}^{-}\left(\rho_{1}, \rho_{2}\right)=\frac{\partial f_{b}^{\text {concave }}}{\partial \rho_{i}}-\lambda \frac{\partial f_{b}^{\text {auxiliary }}}{\partial \rho_{i}}
\end{aligned}
$$

where

$$
\begin{aligned}
\frac{\partial f_{b}^{\text {convex }}}{\partial \rho_{i}} & =\frac{\partial\left(f_{b}^{\text {ideal }}+f_{b}^{\text {repulsion }}\right)}{\partial \rho_{i}}=R T\left(\ln \rho_{i}+\frac{b_{i} \rho}{1-b \rho}-\ln (1-b \rho)\right) \\
\frac{\partial f_{b}^{\text {auxiliary }}}{\partial \rho_{i}} & =R T\left(\ln \rho_{i}-\ln \left(1-b_{i} \rho_{i}\right)+\frac{b_{i} \rho_{i}}{1-b_{i} \rho_{i}}\right) \\
\frac{\partial f_{b}^{\text {concave }}}{\partial \rho_{i}} & =\frac{\partial f_{b}^{\text {attraction }}}{\partial \rho_{i}} \\
& =\frac{1}{2 \sqrt{2}}\left(\frac{2 \sum_{j=1}^{M} \rho_{j} \sqrt{a_{i} a_{j}}\left(1-k_{i j}\right)}{b \rho}-\frac{a b_{i}}{b^{2}}\right) \ln \left(\frac{1+(1-\sqrt{2}) b \rho}{1+(1+\sqrt{2}) b \rho}\right)-\frac{a b_{i} \rho}{b+2 b^{2} \rho-b^{3} \rho^{2}} .
\end{aligned}
$$

Here the parameters $a, b, a_{i}, b_{i}, k_{i j}$ are introduced in Section 2.2.
We now describe two approaches for evaluating the bulk chemical potentials. The fully implicit splitting method is written as

$$
\begin{aligned}
& \mu_{b 1}\left(\rho_{1}^{n}, \rho_{2}^{n}\right)=\mu_{b 1}^{+}\left(\rho_{1}^{n}, \rho_{2}^{n}\right)+\mu_{b 1}^{-}\left(\rho_{1}^{n-1}, \rho_{2}^{n-1}\right), \\
& \mu_{b 2}\left(\rho_{1}^{n}, \rho_{2}^{n}\right)=\mu_{b 2}^{+}\left(\rho_{1}^{n}, \rho_{2}^{n}\right)+\mu_{b 2}^{-}\left(\rho_{1}^{n-1}, \rho_{2}^{n-1}\right) .
\end{aligned}
$$

For the fully implicit method, the concave part is treated explicitly, whereas the convex part is treated implicitely.

The semi implicit splitting method is written as

$$
\begin{aligned}
& \mu_{b 1}\left(\rho_{1}^{n}, \rho_{2}^{n}\right)=\mu_{b 1}^{+}\left(\rho_{1}^{n}, \rho_{2}^{n-1}\right)+\mu_{b 1}^{-}\left(\rho_{1}^{n-1}, \rho_{2}^{n-1}\right), \\
& \mu_{b 2}\left(\rho_{1}^{n}, \rho_{2}^{n}\right)=\mu_{b 2}^{+}\left(\rho_{1}^{n-1}, \rho_{2}^{n}\right)+\mu_{b 2}^{-}\left(\rho_{1}^{n-1}, \rho_{2}^{n-1}\right) .
\end{aligned}
$$

The semi-implicit method treats the convex part implicitly only with respect to the $i^{\text {th }}$ component considered.

In the case of the semi-implicit splitting, the fully discrete problem reads: for $n=1, \ldots, N_{T}$, find $\rho_{1}^{n}, \rho_{2}^{n}, \mu_{1}^{n}, \mu_{2}^{n} \in \mathcal{D}_{k}\left(\mathcal{E}_{h}\right)$, such that $\forall v \in \mathcal{D}_{k}\left(\mathcal{E}_{h}\right)$ that satisfy

$$
\begin{align*}
&\left(\rho_{1}^{n}, v\right)+\tau \eta a\left(M_{11} ; \mu_{1}^{n}, v\right)=\left(\rho_{1}^{n-1}, v\right)  \tag{3.9}\\
&\left(\rho_{2}^{n}, v\right)+\tau \eta a\left(M_{22} ; \mu_{2}^{n}, v\right)=\left(\rho_{2}^{n-1}, v\right)  \tag{3.10}\\
&\left(\mu_{1}^{n}, v\right)-\xi a\left(c_{11} ; \rho_{1}^{n}, v\right)-\xi a_{b d r y}\left(c_{11} ; \rho_{1}^{n}, v\right)\left(\mu_{b 1}^{-}\left(\rho_{1}^{n-1}, \rho_{2}^{n-1}\right), v\right) \\
&-\left(\mu_{b 1}^{+}\left(\rho_{1}^{n}, \rho_{2}^{n-1}\right), v\right)-\xi a\left(c_{12} ; \rho_{2}^{n}, v\right)-\xi a_{b d r y}\left(c_{12} ; \rho_{2}^{n}, v\right)=+\xi d\left(c_{11} ; \frac{\rho_{1, \text { in }}}{\rho_{c}}, v\right)+\xi d\left(c_{12} ; \frac{\rho_{2, \text { in }}}{\rho_{c}}, v\right),  \tag{3.11}\\
&\left(\mu_{2}^{n}, v\right)-\xi a\left(c_{21} ; \rho_{1}^{n}, v\right)-\xi a_{b d r y}\left(c_{21} ; \rho_{1}^{n}, v\right) \quad\left(\mu_{b 2}^{-}\left(\rho_{1}^{n-1}, \rho_{2}^{n-1}\right), v\right) \\
&-\left(\mu_{b 2}^{+}\left(\rho_{1}^{n-1}, \rho_{2}^{n}\right), v\right)-\xi a\left(c_{22} ; \rho_{2}^{n}, v\right)-\xi a_{b d r y}\left(c_{22} ; \rho_{2}^{n}, v\right)=+\xi d\left(c_{21} ; \frac{\rho_{1, \text { in }}}{\rho_{c}}, v\right)+\xi d\left(c_{22} ; \frac{\rho_{2, \text { in }}}{\rho_{c}}, v\right),  \tag{3.12}\\
&\left(\rho_{1}^{0}, v\right)=\left(\frac{\rho_{1}^{\text {ini }}}{\rho_{c}}, v\right)  \tag{3.13}\\
&\left(\rho_{2}^{0}, v\right)=\left(\frac{\rho_{2}^{\text {ini }}}{\rho_{c}}, v\right) . \tag{3.14}
\end{align*}
$$

### 3.4 Matrix Formulation

Let $\hat{E}=[-1,1]^{3}$ be the reference element and let $\mathbb{P}_{1}(\hat{E})$ denote the space of linear polynomials. The linear polynomial space on $\mathcal{E}_{h}$ is decomposed as

$$
\mathbb{P}_{1}\left(\mathcal{E}_{h}\right):=\prod_{E_{k} \in \mathcal{E}_{h}} \mathbb{P}_{1}\left(E_{k}\right)
$$

We use a hierarchical modal orthonormal basis $\left\{\hat{\psi}_{0}, \ldots, \hat{\psi}_{3}\right\}$ on $\hat{E}$, i.e. $\mathbb{P}_{1}(\hat{E})=$ $\operatorname{span}\left\{\hat{\psi}_{0}, \ldots, \hat{\psi}_{3}\right\}$. This basis is constructed by using tensor products of one-dimensional Legendre polynomials. The basis functions $\hat{\psi}_{i}, i=0, \ldots, 3$, are orthonormal with respect to $L^{2}(\hat{E})$ inner product.

Let $F_{k}$ denote the mapping from $\hat{E}$ to $E_{k}$, for $k=0, \ldots, N-1$. Then the basis
functions $\psi_{k i}$ on $E_{k}$, for $i=0, \ldots, 3$, can be obtained as

$$
\psi_{k i}=\hat{\psi}_{i} \circ F_{k}^{-1} .
$$

The entries of the mass matrix $\boldsymbol{M}$ is written as

$$
[\boldsymbol{M}]_{4 k+i, 4 l+j}=\int_{\Omega} \psi_{k i} \psi_{l j}
$$

for $k, l=0, \ldots, N-1, i, j=0, \ldots, 3$. Due to orthonormality of the basis functions, $[\boldsymbol{M}]_{4 k+i, 4 l+j}=0$, for all $k \neq l$ or $i \neq j$; and

$$
[\boldsymbol{M}]_{4 k+i, 4 k+i}=\int_{\Omega} \psi_{k i} \psi_{k i}=\int_{E_{k}} \psi_{k i} \psi_{k i}=\frac{h^{3}}{8} \int_{\hat{E}} \hat{\psi}_{i} \hat{\psi}_{i}=\frac{h^{3}}{8} .
$$

Thus, the mass matrix is $\boldsymbol{M}=\frac{h^{3}}{8} \boldsymbol{I}$, with size $4 N \times 4 N$.

The numerical solutions $\rho_{1}^{n}, \rho_{2}^{n}, \mu_{1}^{n}, \mu_{2}^{n} \in \mathbb{P}_{1}\left(\mathcal{E}_{h}\right)$ can be written as linear combinations of the basis functions as follows

$$
\begin{array}{ll}
\rho_{1}^{n}(\boldsymbol{x})=\sum_{k=0}^{N-1} \sum_{i=0}^{3} \rho_{1 k i}^{n} \psi_{k i}(\boldsymbol{x}), & \mu_{1}^{n}(\boldsymbol{x})=\sum_{k=0}^{N-1} \sum_{i=0}^{3} \mu_{1 k i}^{n} \psi_{k i}(\boldsymbol{x}), \\
\rho_{2}^{n}(\boldsymbol{x})=\sum_{k=0}^{N-1} \sum_{i=0}^{3} \rho_{2 k i}^{n} \psi_{k i}(\boldsymbol{x}), & \mu_{2}^{n}(\boldsymbol{x})=\sum_{k=0}^{N-1} \sum_{i=0}^{3} \mu_{2 k i}^{n} \psi_{k i}(\boldsymbol{x}),
\end{array}
$$

Let us denote the vectors of the coefficients of basis functions with respect to $\rho_{1}^{n}, \rho_{2}^{n}, \mu_{1}^{n}, \mu_{2}^{n}$ by

$$
\begin{array}{ll}
{\left[\boldsymbol{X}_{\rho_{1}}^{n}\right]_{4 k+i}:=\rho_{1 k i}^{n},} & {\left[\boldsymbol{X}_{\mu_{1}}^{n}\right]_{4 k+i}:=\mu_{1 k i}^{n},} \\
{\left[\boldsymbol{X}_{\rho_{2}}^{n}\right]_{4 k+i}:=\rho_{2 k i}^{n},} & {\left[\boldsymbol{X}_{\mu_{2}}^{n}\right]_{4 k+i}:=\mu_{2 k i}^{n},}
\end{array}
$$

for $k=0, \ldots, N-1, i=0, \ldots, 3$.

Let us define the following matrices and vectors:

$$
\begin{aligned}
{[\boldsymbol{A}]_{4 k+i, 4 l+j} } & :=a\left(1 ; \psi_{k i}, \psi_{l j}\right), \\
{\left[\boldsymbol{A}_{b d r y}\right]_{4 k+i, 4 l+j} } & :=a_{b d r y}\left(1 ; \psi_{k i}, \psi_{l j}\right), \\
{\left[\boldsymbol{D}_{1}^{n}\right]_{4 k+i} } & :=d\left(1 ; \frac{\rho_{1, \text { in }}}{\rho_{c}}, \psi_{k i}\right), \\
{\left[\boldsymbol{D}_{2}^{n}\right]_{4 k+i} } & :=d\left(1 ; \frac{\rho_{2, \text { in }}}{\rho_{c}}, \psi_{k i}\right), \\
{\left[\boldsymbol{E}_{\mu_{b 1}^{ \pm}}\left(\boldsymbol{X}_{\rho_{1}}^{n}, \boldsymbol{X}_{\rho_{2}}^{m}\right)\right]_{4 k+i} } & :=\left(\mu_{b 1}^{ \pm}\left(\rho_{1}^{n}, \rho_{2}^{m}\right), \psi_{k i}\right), \\
{\left[\boldsymbol{E}_{\mu_{b 2}^{ \pm}}\left(\boldsymbol{X}_{\rho_{1}}^{n}, \boldsymbol{X}_{\rho_{2}}^{m}\right)\right]_{4 k+i} } & :=\left(\mu_{b 2}^{ \pm}\left(\rho_{1}^{n}, \rho_{2}^{m}\right), \psi_{k i}\right) .
\end{aligned}
$$

Then the fully discrete scheme in the previous section is equivalent to: find $\boldsymbol{X}_{\rho_{1}}^{n}, \boldsymbol{X}_{\rho_{2}}^{n}, \boldsymbol{X}_{\mu_{1}}^{n}, \boldsymbol{X}_{\mu_{2}}^{n}$, for $n=1, \ldots, N_{T}$, that satisfy the following system of equations:

$$
\begin{gathered}
\boldsymbol{M} \boldsymbol{X}_{\rho_{1}}^{n}+\tau \eta M_{11} \boldsymbol{A} \boldsymbol{X}_{\mu_{1}}^{n}=\boldsymbol{M} \boldsymbol{X}_{\rho_{1}}^{n-1}, \\
\boldsymbol{M} \boldsymbol{X}_{\rho_{2}}^{n}+\tau \eta M_{22} \boldsymbol{A} \boldsymbol{X}_{\mu_{2}}^{n}=\boldsymbol{M} \boldsymbol{X}_{\rho_{2}}^{n-1}, \\
\boldsymbol{M} \boldsymbol{X}_{\mu_{1}}^{n}-\boldsymbol{E}_{\mu_{b 1}^{+}}\left(\boldsymbol{X}_{\rho_{1}}^{n}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)-\xi c_{11}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \boldsymbol{X}_{\rho_{1}}^{n} \\
-\xi c_{12}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \boldsymbol{X}_{\rho_{2}}^{n}=\boldsymbol{E}_{\mu_{b 1}^{-}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\xi c_{11} \boldsymbol{D}_{1}^{n}+\xi c_{12} \boldsymbol{D}_{2}^{n}, \\
\boldsymbol{M} \boldsymbol{X}_{\mu_{2}}^{n}-\boldsymbol{E}_{\mu_{b 2}^{+}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n}\right)-\xi c_{21}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \boldsymbol{X}_{\rho_{1}}^{n} \\
-\xi c_{22}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \boldsymbol{X}_{\rho_{2}}^{n}=\boldsymbol{E}_{\mu_{b 2}^{-}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\xi c_{21} \boldsymbol{D}_{1}^{n}+\xi c_{22} \boldsymbol{D}_{2}^{n},
\end{gathered}
$$

provided with the initial terms

$$
\begin{aligned}
\boldsymbol{M} \boldsymbol{X}_{\rho_{1}}^{0} & =\frac{1}{\rho_{c}} b_{1} \\
\boldsymbol{M} \boldsymbol{X}_{\rho_{2}}^{0} & =\frac{1}{\rho_{c}} b_{2}
\end{aligned}
$$

This system of equations can be rewritten in a block system:

$$
\left[\begin{array}{cccc}
\boldsymbol{M} & 0 & \tau \eta M_{11} \boldsymbol{A} & 0 \\
0 & \boldsymbol{M} & 0 & \tau \eta M_{22} \boldsymbol{A}  \tag{3.15}\\
-\xi c_{11}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) & -\xi c_{12}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) & \boldsymbol{M} & 0 \\
-\xi c_{21}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) & -\xi c_{22}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) & 0 & \boldsymbol{M}
\end{array}\right]\left[\begin{array}{c}
\boldsymbol{X}_{\rho_{1}}^{n} \\
\boldsymbol{X}_{\rho_{2}}^{n} \\
\boldsymbol{X}_{\mu_{1}}^{n} \\
\boldsymbol{X}_{\mu_{2}}^{n}
\end{array}\right]-\left[\begin{array}{c}
0 \\
0 \\
\boldsymbol{\boldsymbol { E } _ { \mu _ { b 1 } ^ { + } } ( \boldsymbol { X } _ { \rho _ { 1 } } ^ { n } , \boldsymbol { X } _ { \rho _ { 2 } } ^ { n - 1 } )} \\
\boldsymbol{E}_{\mu_{b 2}^{+}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n}\right)
\end{array}\right] .\left[\begin{array}{c}
{\left[\begin{array}{c}
n-1
\end{array}\right.} \\
\boldsymbol{M} \boldsymbol{X}_{\rho_{1}}^{n-1} \\
\boldsymbol{E}_{\mu_{b 1}^{-}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\xi c_{11} \boldsymbol{D}_{1}^{n}+\xi c_{12} \boldsymbol{D}_{2}^{n} \\
\boldsymbol{E}_{\mu_{b 2}^{-}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\xi c_{21} \boldsymbol{D}_{1}^{n}+\xi c_{22} \boldsymbol{D}_{2}^{n}
\end{array}\right] .
$$

### 3.4.1 System Reduction

The unknowns $\boldsymbol{X}_{\mu_{1}}^{n}, \boldsymbol{X}_{\mu_{2}}^{n}$ can be solved as follows

$$
\begin{aligned}
\boldsymbol{X}_{\mu_{1}}^{n}= & \boldsymbol{M}^{-1}\left(\xi c_{11}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \boldsymbol{X}_{\rho_{1}}^{n}+\xi c_{12}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \boldsymbol{X}_{\rho_{2}}^{n}\right) \\
& +\boldsymbol{M}^{-1}\left(\boldsymbol{E}_{\mu_{b 1}^{+}}\left(\boldsymbol{X}_{\rho_{1}}^{n}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\boldsymbol{E}_{\mu_{b 1}^{-}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\xi c_{11} \boldsymbol{D}_{1}^{n}+\xi c_{12} \boldsymbol{D}_{2}^{n}\right), \\
\boldsymbol{X}_{\mu_{2}}^{n}= & \boldsymbol{M}^{-1}\left(\xi c_{21}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \boldsymbol{X}_{\rho_{1}}^{n}+\xi c_{22}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \boldsymbol{X}_{\rho_{2}}^{n}\right) \\
& +\boldsymbol{M}^{-1}\left(\boldsymbol{E}_{\mu_{b 2}^{+}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n}\right)+\boldsymbol{E}_{\mu_{b 2}^{-}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\xi c_{21} \boldsymbol{D}_{1}^{n}+\xi c_{22} \boldsymbol{D}_{2}^{n}\right) .
\end{aligned}
$$

Plugging these back to the system (3.15), we obtain the following $2 \times 2$ blocks system.

$$
\begin{array}{r}
\underbrace{\left[\begin{array}{cc}
\boldsymbol{M}+\tau \eta \xi M_{11} \boldsymbol{A} \boldsymbol{M}^{-1} c_{11}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) & \tau \eta \xi M_{11} \boldsymbol{A} \boldsymbol{M}^{-1} c_{12}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) \\
\tau \eta \xi M_{22} \boldsymbol{A} \boldsymbol{M}^{-1} c_{21}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right) & \boldsymbol{M}+\tau \eta \xi M_{22} \boldsymbol{A} \boldsymbol{M}^{-1} c_{22}\left(\boldsymbol{A}+\boldsymbol{A}_{b d r y}\right)
\end{array}\right]\left[\begin{array}{c}
\boldsymbol{X}_{\rho_{1}}^{n} \\
\boldsymbol{X}_{\rho_{2}}^{n}
\end{array}\right]}_{=: \mathcal{L} \boldsymbol{X}_{\rho}^{n}} \\
+\underbrace{\left[\begin{array}{c}
\tau \eta M_{11} \boldsymbol{A} \boldsymbol{M}^{-1} \boldsymbol{E}_{\mu_{b 1}^{+}}\left(\boldsymbol{X}_{\rho_{1}}^{n}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right) \\
\tau \eta M_{22} \boldsymbol{A} \boldsymbol{M}^{-1} \boldsymbol{E}_{\mu_{b 2}^{+}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n}\right)
\end{array}\right]}_{=: \mathcal{N} \boldsymbol{X}_{\rho}^{n}} \\
\quad-\underbrace{\left[\begin{array}{l}
\boldsymbol{M} \boldsymbol{X}_{\rho_{1}}^{n-1}-\tau \eta M_{11} \boldsymbol{A} \boldsymbol{M}^{-1}\left(\boldsymbol{E}_{\mu_{b 1}^{-}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\xi c_{11} \boldsymbol{D}_{1}^{n}+\xi c_{12} \boldsymbol{D}_{2}^{n}\right) \\
\boldsymbol{M} \boldsymbol{X}_{\rho_{2}}^{n-1}-\tau \eta M_{22} \boldsymbol{A} \boldsymbol{M}^{-1}\left(\boldsymbol{E}_{\mu_{b 2}^{-}}\left(\boldsymbol{X}_{\rho_{1}}^{n-1}, \boldsymbol{X}_{\rho_{2}}^{n-1}\right)+\xi c_{21} \boldsymbol{D}_{1}^{n}+\xi c_{22} \boldsymbol{D}_{2}^{n}\right)
\end{array}\right]}_{=: \mathcal{C}^{n}}=0 . \tag{3.16}
\end{array}
$$

The block system (3.15) of size $(4 \times 4 N) \times(4 \times 4 N)$ is reduced to system (3.16) of size $(2 \times 4 N) \times(2 \times 4 N)$.

## Chapter 4

## Numerical Results

In this chapter, we present some numerical tests regarding partially miscible twocomponent two-phase flow. The implementation for the simulator and the setup for each test are discussed in the relative sections. The numerical results indicate the robustness and the stability of our simulator, and its capability for capturing real physical phenomena.

### 4.1 Implementation

Our partially miscible two-component two phase flow simulator is implemented as an module, named M2C, in the Pore-Scale Multiphase Flow Simulator (PMFS), which is a $\mathrm{C}++$ based software developed by the group COMP-M from Rice university. The software PMFS uses Trilinos for parallel linear algebra and iterative linear solvers, and uses METIS for domain decomposition. The simulator is developed for 3-dimensional simulation. Any 2D or 1D simulation is actually achieved by imposing only one element on the rest of the dimensions.

### 4.2 Numerical Tests

In the following numerical tests, we consider a binary flow consists of methane and decane, associated with $\rho_{1}$ and $\rho_{2}$ respectively. The critical information about these two components are used as input parameters for the Peng-Robinson equation of
state, which are listed in Table 4.1.

| critial temperate [K]: | $T_{\rho_{1}}=190.56$ | $T_{\rho_{2}}=617.70$, |
| :--- | :--- | :--- |
| critial pressure [Pa]: | $P_{\rho_{1}}=4.604 \times 10^{6}$ | $P_{\rho_{1}}=2.123 \times 10^{6}$ |
| accentric factor: | $\omega_{1}=0.011$ | $\omega_{2}=0.484$ |
| binary interaction coefficient: | $k_{1,1}=k_{2,2}=0$ | $k_{1,2}=k_{1,2}=0.0409$ |
| binary interaction coefficient: | $\beta=0.5$ |  |

Table 4.1 : Critical input information used in the methane-decane system

### 4.2.1 Convexity of Helmholtz Free Energy Density

Recalling section 3.3, the Helmholtz free energy density based on the Peng-Robinson equation of state is determined as

$$
f_{b}=f_{b}^{\text {convex }}+f_{b}^{\text {concave }},
$$

where

$$
\begin{aligned}
f_{b}^{\text {convex }} & =f_{b}^{\text {ideal }}+f_{b}^{\text {repulsion }} \\
f_{b}^{\text {concave }} & =f_{b}^{\text {attraction }}
\end{aligned}
$$

In order to do a proper convex-concaving splitting for the time discretization, we need to check the convexity of each part. Figure 4.1 and Figure 4.2 show the values of convex and concave part of Helmholtz free energy density for $\rho_{1}, \rho_{2} \in[20,8000]$ $\mathrm{mol} / \mathrm{m}^{3}$ under the given numerical test setup. Figure 4.3 shows the determinant of the hessian of $f_{b}^{\text {convex }}$.


Figure 4.1 : Convex part of the Helmholtz free energy density $f_{b}^{\text {convex }}$


Figure 4.2 : Concave part of the Helmholtz free energy density $f_{b}^{\text {concave }}$


Figure 4.3 : Determinant of the hessian of $f_{b}^{\text {concave }}$

The hessian of $f_{b}^{\text {concave }}$ and its determinant are calculated as follows:

$$
\begin{aligned}
f_{b}^{\text {convex }}\left(\rho_{1}, \rho_{2}\right) & =R T\left(\rho_{1} \ln \rho_{1}+\rho_{2} \ln \rho_{2}-\rho-\rho \ln (1-b \rho)\right), \\
\frac{\partial f_{b}^{\text {convex }}}{\partial \rho_{i}} & =R T\left(\ln \rho_{i}+\frac{b_{i} \rho}{1-b \rho}-\ln (1-b \rho)\right), \\
H\left(f_{b}^{\text {convex }}\right) & =R T\left(\begin{array}{ll}
\frac{1}{\rho_{1}}+\frac{2 b_{1}}{1-b \rho}+\frac{b_{1}^{2} \rho}{(1-b \rho)^{2}} & \frac{b_{1}+b_{2}}{1-b \rho}+\frac{b_{1} b_{2} \rho}{(1-b \rho)^{2}} \\
\frac{b_{1}+b_{2}}{1-b \rho}+\frac{b_{1} b_{2} \rho}{(1-b \rho)^{2}} & \frac{1}{\rho_{2}}+\frac{2 b_{2}}{1-b \rho}+\frac{b_{2}^{2} \rho}{(1-b \rho)^{2}}
\end{array}\right) \\
\operatorname{det}\left(H\left(f_{b}^{\text {convex }}\right)\right) & =\frac{1}{(1-b \rho)^{2} \rho_{1} \rho_{2}}>0
\end{aligned}
$$

By these visual checks, we can see that $f_{b}^{\text {convex }}$ and $f_{b}^{\text {concave }}$ are indeed convex and concave functions, although the convexity of $f_{b}^{\text {convex }}$ might not be strong if inputting large $\rho_{1}, \rho_{2}$.

To fix this problem, we add and subtract a convex auxiliary function $f_{b}^{\text {auxiliary }}$, defined in section 3.3, to the convex and concave part of $f_{b}$. Figure 4.4 shows the determinant of the hessian of $f_{b}^{\text {auxiliary }}$ for $\rho_{1}, \rho_{2} \in[20,8000] \mathrm{mol} / \mathrm{m}^{3}$ under our numerical tests setup. We observe that this auxiliary function is convex even for a large $\rho_{1}$ or $\rho_{2}$.


Figure 4.4 : Determinant of the hessian of $f_{b}^{\text {auxiliary }}$

The hessian of the auxiliary function is calculated as follows

$$
\begin{aligned}
f_{b}^{\text {auxiliary }}(\boldsymbol{\rho}) & =R T\left(\rho_{1} \ln \rho_{1}+\rho_{2} \ln \rho_{2}-\rho-\rho_{1} \ln \left(1-b_{1} \rho_{1}\right)-\rho_{2} \ln \left(1-b_{2} \rho_{2}\right)\right) \\
\frac{\partial f_{b}^{\text {auxiliary }}}{\partial \rho_{i}} & =R T\left(\ln \rho_{i}-\ln \left(1-b_{i} \rho_{i}\right)+\frac{b_{i} \rho_{i}}{1-b_{i} \rho_{i}}\right) \\
H\left(f_{b}^{\text {auxiliary }}\right) & =R T\left(\begin{array}{cc}
\frac{1}{\rho_{1}}+\frac{b_{1}}{1-b_{1} \rho_{1}}+\frac{b_{1}}{\left(1-b_{1} \rho_{1}\right)^{2}} & 0 \\
0 & \frac{1}{\rho_{2}}+\frac{b_{2}}{1-b_{2} \rho_{2}}+\frac{b_{2}}{\left(1-b_{2} \rho_{2}\right)^{2}}
\end{array}\right)
\end{aligned}
$$

In the following numerical simulations of the two-component partially miscible flow, the convex and concave Holmhelz free energy density functions are modified to

$$
\begin{aligned}
& f_{b}^{+}=f_{b}^{\text {convex }}+\lambda f_{b}^{\text {auxiliary }} \\
& f_{b}^{-}=f_{b}^{\text {concave }}-\lambda f_{b}^{\text {auxiliary }}
\end{aligned}
$$

where the coefficient $\lambda$ is chosen to be one.

### 4.2.2 Droplet in Fluid

This is a 2 D test. In this test, we place a square droplet in the center of the computational domain and let the droplet evolve over time. The computational domain is the unit square $[0,1]^{2}$. The grid is chosen to be $40 \times 40$, which makes mesh size $h$ equals to 0.025 . We set the temperature to be 320 K . The characteristic length and the characteristic time are chosen to be $2 \times 10^{-8} \mathrm{~m}$ and $10^{-13} \mathrm{~s}$. The initial molar densities for methane and decane are $3513.2 \mathrm{~mol} / \mathrm{m}^{3}$ and $3814.6 \mathrm{~mol} / \mathrm{m}^{3}$ in the inner phase, $7133.9 \mathrm{~mol} / \mathrm{m}^{3}$ and $26.5 \mathrm{~mol} / \mathrm{m}^{3}$ in the outer phase. The initial set up can be seen in Figure 4.5.

methane


Figure 4.7 : Molar density profiles for methane, green, and decane, purple, at the inial and final time steps.

### 4.2.3 Stability Tests

This is a series of 1D tests. In these tests, we vary the benchmark inner phase and outer phase methane, decane molar densities, such that the total moles of these two components among the whole domain are still the same. Then we compare the final molar density profile of those cases against the benchmark.

## Test 1. Benchmark.

For the benchmark case, the grid is chosen to be 40. The temperature is set to be 320K. The characteristic length and the characteristic time are $2 \times 10^{-8} \mathrm{~m}$ and $10^{-12} \mathrm{~s}$. The initial molar densities for methane and decane are $3513.2 \mathrm{~mol} / \mathrm{m}^{3}$ and $3814.6 \mathrm{~mol} / \mathrm{m}^{3}$ in the inner phase, $7133.9 \mathrm{~mol} / \mathrm{m}^{3}$ and $26.5 \mathrm{~mol} / \mathrm{m}^{3}$ in the outer phase. We set the final time to be the 300 th time step. The initial and final molar density profiles for the benchmark case are given in Figure 4.8. The solid curve is associated with methane, while the dashed curve is associated with decane.


Figure 4.8 : Initial and final molar density profiles for the benchmark case

Test 2. $\rho_{1}$ increase by $\mathbf{1 0 0 \%}$
In this test, we increase the molar density of methane, $\rho_{1}$, in the inner phase by $100 \%$, and decrease $\rho_{1}$ accordingly in the outer phase, such that the total moles of methane among the entire domain are still the same. The result is given in Figure 4.9. The final molar density profile of this test is perfectly overlapped with the benchmark case.


$$
\mathrm{t}=0
$$


$t=300$

Figure 4.9 : Initial and final molar density profiles for Test 2

Test 3. $\rho_{2}$ average out

In this test, we increase average out the molar density of decane, $\rho_{2}$, in the entire domain. The result is given in Figure 4.10. The final molar density profile of this test is perfectly overlapped with the benchmark case.


Figure 4.10 : Initial and final molar density profiles for Test 3

## Test 4. $\rho_{1}$ increase by $5 \%, \rho_{2}$ average out

In this test, we increase the molar density of methane, $\rho_{1}$, in the inner phase by $5 \%$, and decrease $\rho_{1}$ accordingly in the outer phase so that the total moles of methane among the entire domain are still the same. Meanwhile, we average out molar density of decane, $\rho_{2}$, in the whole domain. The result is given in Figure 4.11. The final molar density profile of this test is perfectly overlapped with the benchmark case.


Figure 4.11 : Initial and final molar density profiles for Test 4

## Test 5. $\rho_{1}$ increase by $10 \%, \rho_{2}$ average out

In this test, we increase the molar density of methane, $\rho_{1}$, in the inner phase by $10 \%$, and decrease $\rho_{1}$ accordingly in the outer phase so that the total moles of methane among the entire domain are still the same. Meanwhile, we average out molar density of decane, $\rho_{2}$, in the whole domain. The result is given in Figure 4.12. The final molar density profile of this test is perfectly overlapped with the benchmark case.


Figure 4.12 : Initial and final molar density profiles for Test 5

## Test 6. $\rho_{1}$ increase by $\mathbf{2 0 \%}, \rho_{2}$ average out

In this test, we increase the molar density of methane, $\rho_{1}$, in the inner phase by $20 \%$, and decrease $\rho_{1}$ accordingly in the outer phase so that the total moles of methane among the entire domain are still the same. Meanwhile, we average out molar density of decane, $\rho_{2}$, in the whole domain. The result is given in Figure 4.13. The final molar density profile of this test is perfectly overlapped with the benchmark case.


Figure 4.13 : Initial and final molar density profiles for Test 6

Test 7. $\rho_{1}$ increase by $50 \%, \rho_{2}$ average out
In this test, we increase the molar density of methane, $\rho_{1}$, in the inner phase by $50 \%$, and decrease $\rho_{1}$ accordingly in the outer phase so that the total moles of methane among the entire domain are still the same. Meanwhile, we average out molar density of decane, $\rho_{2}$, in the whole domain. The result is given in Figure 4.14. The final molar density profile of this test is perfectly overlapped with the benchmark case.


Figure 4.14 : Initial and final molar density profiles for Test 7

Test 8. $\rho_{1}$ increase by $\mathbf{1 0 0 \%}, \rho_{2}$ average out
In this test, we increase the molar density of methane, $\rho_{1}$, in the inner phase by $100 \%$, and decrease $\rho_{1}$ accordingly in the outer phase so that the total moles of methane among the entire domain are still the same. Meanwhile, we average out molar density of decane, $\rho_{2}$, in the whole domain. The result is given in Figure 4.15. The final molar density profile of this test does not overlap with the benchmark case. It is a shift of the benchmark mass density profile.


Figure 4.15 : Initial and final molar density profiles for Test 8

## Test 9. Reversed benchmark

In this test, we switch the inner phase and outer phase molar density of methane, $\rho_{1}$, and decane, $\rho_{2}$. Figure 4.16 shows that the final molar density profile of this test is perfectly overlapped with the profile from the previous test.


Figure 4.16 : Initial and final molar density profiles for Test 9

### 4.2.4 Increasing Temperature

This is a series of 1 D tests. In each of these test, we simulate with the same twophase flow, and a different temperature. Then we compare the results with the phase diagram, which is based on the same methane-decane composition proportion.

In these tests, the grid is chosen to be 80 . The characteristic length and the characteristic time are $10^{-7} \mathrm{~m}$ and $10^{-13} \mathrm{~s}$. The initial molar densities for methane and decane are $3513.2 \mathrm{~mol} / \mathrm{m}^{3}$ and $3814.6 \mathrm{~mol} / \mathrm{m}^{3}$ in the inner phase, $7133.9 \mathrm{~mol} / \mathrm{m}^{3}$ and $26.5 \mathrm{~mol} / \mathrm{m}^{3}$ in the outer phase.

Figure 4.17 shows the equilibrium molar density profiles, obtained through the center of computational domain alone the x -axis, for the temperature equals to 320 K , $400 \mathrm{~K}, 450 \mathrm{~K}, 560 \mathrm{~K}, 470 \mathrm{~K}, 490 \mathrm{~K}$. The flow is two-phase under 470 K , and is one-phase
when temperature is above 470 K . Table 4.2 listed the computed average pressure of the inner and outer phases under the corresponding temperatures.


Figure 4.17 : The molar density profiles for the various temperature setup

| Temperature $[\mathrm{K}]$ | Pressure [bar] | at Equilibrium State |
| :---: | :---: | :---: |
| 320 | 156 | two-phase |
| 400 | 219 | two-phase |
| 450 | 255 | two-phase |
| 460 | 262 | two-phase |
| 470 | 275 | one-phase |
| 490 | 309 | one-phase |
| 510 | 343 | one-phase |

Table 4.2 : The computed pressure and the corresponding temperature

With the help of Dr. Walter Chapman, we obtained the phase diagram for the same methane-decane composition proportion, as given in Figure 4.18. After plotting our results against the phase diagram, we observed that these results agree with the phase diagram, indicating the capability of our simulator of predicting the real physical phenomena.


Figure 4.18 : Phase diagram of $73.5 \%$ methane and $0.265 \%$ decane system

## Chapter 5

## Conclusion

In this thesis, we established an effective simulator for two-component two-phase flow with partial miscibility at the pore scale. The mathematical model consists of two generalized Cahn Hilliard equations, where the chemical potential terms are derived from the realistic Peng-Robinson equation of state. For the nermical scheme, the interior penalty discontinuous Galerkin method is adopted for the spatial discretization, and the backward Euler method in combined with the convex-concave splitting method are used for the temporal discretization. The numerical results indicates the stability and robustness of our simulator, and proves its capability of capturing the real physical phenomena. The current model has only diffusion terms in it, which hugely diminishes the affects of avdection. For the future work, we would add avdection terms by coupling this model with two momentum balance governing equations, for instance Navier-Stokes equations.

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