The Pennsylvania State University

The Graduate School

Department of Mathematics

NUMERICAL METHODS FOR MULTIPHYSICS, MULTIPHASE,
AND MULTICOMPONENT MODELS FOR FUEL CELLS

A Dissertation in

Mathematics

by

Guangri Xue

© 2008 Guangri Xue

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2008
The thesis of Guangri Xue was reviewed and approved* by the following:

Jinchao Xu  
Distinguished Professor of Mathematics  
Thesis Adviser  
Chair of Committee

Ludmil T. Zikatanov  
Associate Professor of Mathematics

Chun Liu  
Professor of Mathematics  
Director of Graduate Studies in Department of Mathematics

Alberto Bressan  
Eberly Chair Professor of Mathematics

Chao-Yang Wang  
Distinguished Professor of Mechanical Engineering  
Professor of Materials Science and Engineering

*Signatures are on file in the Graduate School.
Abstract

In this dissertation, we design and analyze efficient numerical methods for obtaining accurate solutions to model problems arising in fuel cells. A basic fuel cell model consists of five principles of conservation, namely, mass, momentum, species, charges (electrons and ions), and thermal energy. Overall, transport equations couple with electrochemical processes through source terms to describe reaction kinetics and electro-osmotic drag in the polymer electrolyte.

To model multiphase species transport in the porous media and the gas channel of fuel cells, we consider a multiphase mixture model framework. The diffusivity of the two-phase mixture water conservation equation in this model is nonlinear, discontinuous, and degenerate. To handle this difficulty, we developed efficient and fast nonlinear iterative solvers based on the Kirchhoff transformation and nonlinear Dirichlet-Neumann domain decomposition methods.

To model the coupling between the multiphase flow in the porous media and the viscous flow in the gas channel of fuel cells, we consider the Darcy-Stokes-Brinkman model, which treats both the Darcy equation and the Stokes equation in a single form of partial differential equation (PDE) but with strongly discontinuous viscosity and permeability coefficients. For this model, we develop robust finite element methods that are uniformly stable with respect to the highly discontinuous coefficients and their jumps.

Finally, we develop new numerical methods for the full steady-state 3D multiphysics simulation of liquid-feed direct methanol fuel cells (DMFC), consisting of five
fundamental conservation equations: mass, momentum, species, charges, and thermal energy. Fast convergence of nonlinear iteration is achieved in our method.
Table of Contents

List of Tables ................................................................. viii

List of Figures ................................................................. ix

Acknowledgments .............................................................. xii

Chapter 1. INTRODUCTION .................................................. 1
  1.1 Background ............................................................. 1
  1.2 Organization of the present work .................................... 4

Chapter 2. NUMERICAL SIMULATIONS OF THE MULTIPHASE AND MULTICOMPONENT TRANSPORT .............................................. 5
  2.1 Introduction ............................................................. 5
  2.2 Model description ...................................................... 6
    2.2.1 Multiphase approach ............................................ 6
    2.2.2 Constitutive relationships ...................................... 9
    2.2.3 Multiphase-mixture model .................................... 11
  2.3 Numerical techniques on the two-phase mixture transport in the porous cathode backing layer (CBL) of the Polymer Electrolyte Fuel Cell (PEFC) .................................................. 18
    2.3.1 Method based on Kirchhoff transformation .................... 24
2.4 Numerical techniques on the two-phase mixture transport in the cathode of the PEFC .................................................. 29

2.4.1 Method based on Kirchhoff transformation ......................... 34

2.4.2 Nonlinear Dirichlet-Neumann domain decomposition method 45

Chapter 3. THE COUPLING BETWEEN POROUS MEDIA FLOW AND VISCOUS FLOW IN GAS CHANNEL .......................... 58

3.1 Introduction ........................................................................ 58

3.2 Darcy-Stokes-Brinkman equations ........................................ 60

3.3 Construction of uniformly stable finite element methods ........... 62

3.3.1 Analysis of stable Stokes elements for Darcy-Stokes-Brinkman models ............................................................. 68

3.3.2 Analysis of $H(\text{div})$-conforming type elements for Darcy-Stokes-Brinkman models ................................................... 74

3.3.3 Stabilized formulation and families of stable Stokes elements . 89

3.4 New discrete de Rham complexes with extra smoothness .......... 92

3.4.1 Preliminaries .................................................................... 93

3.4.2 3D discrete de Rham complexes with extra smoothness ...... 96

3.4.3 2D discrete de Rham complexes with extra smoothness ....... 108

3.4.4 Applications to the singularly perturbed high-order equations 113

Chapter 4. MULTIPHYSICS DIRECT METHANOL FUEL CELL SIMULATIONS 119

4.1 Introduction ......................................................................... 119

4.2 Model description .................................................................. 121
4.3 Computational domain and boundary conditions .......................... 136
4.4 Numerical simulation techniques ........................................... 142
  4.4.1 Investigation of water source terms ................................. 142
  4.4.2 Sequence of unknowns in the nonlinear iterative procedure .... 144
  4.4.3 Linearization method .................................................. 146
  4.4.4 Coupled finite element and upwind finite volume discretizations 149
4.5 Numerical results ............................................................ 155

Chapter 5. CONCLUSIONS AND FUTURE WORK .............................. 165

References ................................................................. 167
List of Tables

2.1 Physical properties. .................................................. 23
2.2 Convergence history on a 10 × 10 mesh ......................... 30
2.3 Convergence history on a 50 × 10 mesh ......................... 30
2.4 Convergence history on a 100 × 10 mesh ...................... 31
2.5 Convergence history on an unstructured mesh ................. 31
2.6 Mesh dependence of the nonlinear alternating Dirichlet-Neumann method 56
3.1 Six modified $H(\text{div})$-conforming elements ................. 118
4.1 Transport properties .................................................. 161
4.2 Electrochemical properties ......................................... 162
4.3 Material properties ................................................... 162
4.4 Computational subdomains of the DMFC for each variable ... 163
4.5 Number of mesh intervals at each subdomain of the 3D DMFC . 163
List of Figures

1.1 A schematic diagram of a unit fuel cell. ...................................... 1

2.1 Computational domain of the Cathode Backing Layer (CBL). ............ 22

2.2 Two-phase mixture diffusivity $\Gamma(C)$. ...................................... 24

2.3 Concentration on a $10 \times 10$ mesh. ........................................ 28

2.4 Pressure on a $10 \times 10$ mesh. ............................................. 28

2.5 Concentration on a $50 \times 10$ mesh. ........................................ 28

2.6 Pressure on a $50 \times 10$ mesh. ............................................. 28

2.7 Concentration on a $100 \times 10$ mesh. ...................................... 28

2.8 Pressure on a $100 \times 10$ mesh. ........................................... 28

2.9 Concentration on an unstructured mesh. .................................... 29

2.10 Pressure on an unstructured mesh. .......................................... 29

2.11 Computational domain of the CBL and CGC. ................................. 32

2.12 Convergence histories of the water equation (left) and the momentum equation (right). ............................................. 41

2.13 Horizontal two-phase mixture velocity in the case of $C_{in} = 12 mol/m^3, u_{in} = 1 m/s, I_1 = 1.2 A cm^{-2}$, and $I_2 = 1.6 A cm^{-2}$. ............................................. 42

2.14 Water concentration in the case of $C_{in} = 12 mol/m^3, u_{in} = 1 m/s, I_1 = 1.2 A cm^{-2}$, and $I_2 = 1.6 A cm^{-2}$. ............................................. 43

2.15 Water vapor concentration in the case of $C_{in} = 12 mol/m^3, u_{in} = 1 m/s, I_1 = 1.2 A cm^{-2}$, and $I_2 = 1.6 A cm^{-2}$. ............................................. 44
2.16 Liquid water saturation in the case of $C_{in} = 12mol/m^3$, $u_{in} = 1m/s$, $I_1 = 1.2Acm^{-2}$, and $I_2 = 1.6Acm^{-2}$. ...................................................... 45

2.17 New variable $W$ in the case of $C_{in} = 12mol/m^3$, $u_{in} = 1m/s$, $I_1 = 1.2Acm^{-2}$, and $I_2 = 1.6Acm^{-2}$. ...................................................... 46

2.18 Water concentration (top) and new variable $W$ (bottom) in the case of $C_{in} = 12mol/m^3$, $u_{in} = 1m/s$, $I_1 = 1.0Acm^{-2}$, and $I_2 = 1.4Acm^{-2}$. . 47

2.19 Convergence history of FEM with Kirchhoff transformation and alternating Dirichlet-Neumann iteration. ....................... 52

2.20 The inner iteration number of the alternating Dirichlet-Neumann (DN) method at each outer iteration. ................................. 53

2.21 Horizontal two-phase mixture velocity when $C_{in} = 14mol/m^3$, $u_{in} = 1m/s$, $I_1 = 1.2Acm^{-2}$, and $I_2 = 1.6Acm^{-2}$ ....................... 54

2.22 Concentrations of the two-phase mixture water (top) and water vapor (bottom) when $C_{in} = 14mol/m^3$, $u_{in} = 1m/s$, $I_1 = 1.2Acm^{-2}$, and $I_2 = 1.6Acm^{-2}$. ...................................................... 55

2.23 Liquid water saturation when $C_{in} = 14mol/m^3$, $u_{in} = 1m/s$, $I_1 = 1.2Acm^{-2}$, and $I_2 = 1.6Acm^{-2}$. ...................................................... 56

2.24 Concentrations of the two-phase mixture water (top) and water vapor (bottom) when $C_{in} = 12mol/m^3$, $u_{in} = 0.8m/s$, $I_1 = 1.2A/cm^2$, and $I_2 = 1.6A/cm^2$. ...................................................... 56

2.25 Concentrations of the two-phase mixture water (top) and water vapor (bottom) when $C_{in} = 12mol/m^3$, $u_{in} = 1m/s$, $I_1 = 1.2Acm^{-2}$, and $I_2 = 1.6Acm^{-2}$. ...................................................... 57
3.1 Domain. ......................................................... 61
3.2 Degrees of freedom for the first 2D element. ................. 81
3.3 Degrees of freedom for the second 2D element. .............. 81
3.4 Degrees of freedom for the first 3D element. ................. 81
3.5 Degrees of freedom for the second 3D element. .............. 81
3.6 Degrees of freedom for the third 3D element. ............... 81
3.7 Degrees of freedom for the fourth 3D element. .............. 81

4.1 3D computational domain (bottom) and its cross-sectional domain in the $xz$-plane (top). ......................................................... 137
4.2 Numerical mesh used for 3D simulations. ...................... 156
4.3 Convergence history of the steady-state simulation of the DMFC. ... 157
4.4 Methanol $Y_{l}^{MeOH}$ in the $xz$-plane: (left) near the inlet, (middle) near the middle of the cell length, (right) near the outlet, in the anode. ... 158
4.5 Oxygen $Y_{g}^{O_2}$ in the $xz$-plane: (left) near the inlet, (middle) near the middle of the cell length, (right) near the outlet, in the cathode. ... 159
4.6 Water $Y_{l}^{H_2O}$ in the $xz$-plane: (left) near the inlet, (right) near the middle of the cell length, (bottom) near the outlet, in both the anode and cathode. 160
4.7 (left) Methanol $Y_{l}^{MeOH}$ in the anode; (middle) Oxygen $Y_{g}^{O_2}$ in the cathode; (right) Water $Y_{l}^{H_2O}$ in both the anode and cathode, in the $xy$-plane through the cell center. .......................... 160
4.8 Temperature $T$ (left), Proton potential $\Phi_e$ (middle), and Electron potential $\Phi_s$ (right) in the $xy$-plane through the cell center. .................... 164
Acknowledgments

First I am most grateful and indebted to my advisor, Prof. Jinchao Xu, for the tremendous guidance and unfailing support, patience, and encouragement he has shown me during my time here at Penn State. He provided me wonderful research opportunities that benefited me throughout my research program. My great thanks to Prof. Ludmil Zikatanov, for his invaluable supervision and the inspiration he provided for my thesis and research work over the years. I wish to especially thank my collaborator, Prof. Pengtao Sun, for his great contribution to my thesis. In particular, he brought concerted effort to the computational work in Chapter 4 of this thesis. With Prof. Xiaoping Xie, I enjoyed many enlightening discussions and the benefits of a fruitful research collaboration.

I am particularly grateful to Dr. Robert Falgout of the Center for Applied Scientific Computing at Lawrence Livermore National Laboratory (LLNL). He was my supervisor and mentor during my summer internship in 2005 and 2007 at LLNL, and as such he ensured that I participated fully in many projects that furthered my education. I am thankful to Prof. Chao-Yang Wang and his co-workers for helping me gain insight into fuel cell modeling. I also thank my other committee members, Prof. Chun Liu and Prof. Alberto Bressan, for their great kindness and many suggestions in regard to finetuning this study.

Without my family’s support and encouragement, I could not have completed this degree. I thank my parents for their constant love and support. Finally, I must thank my wife Ji Xuan for her love, support, and encouragement: She is all of my reasons.
1.1 Background

The fuel cell is an electrochemical device that converts chemical energy from fuels into electrical energy. Because they provide a high level of energy efficiency and a low level of pollution and noise, fuel cells may become the energy-conversion devices for mobile, stationary, and portable power for the 21st century.

Fig. 1.1. A schematic diagram of a unit fuel cell.

As shown in the schematic diagram in Fig. 1.1, a fuel cell typically has nine components: anode bipolar plate (ABP or current collector), anode gas channel (AGC), anode backing layer (ABL), anode catalyst layer (ACL), proton exchange membrane
(PEM), cathode catalyst layer (CCL), cathode backing layer (CBL), cathode gas channel (CGC), and cathode bipolar plate (CBP, or current collector).

Fuel is fed from the anode gas channel, diffuses through the two porous medias (ABL and ACL), and reaches the reaction site of the anode catalyst layer. In the polymer electrolyte fuel cell (PEFC), the fuel is hydrogen with the following chemical reaction:

\[
H_2 = 2H^+ + 2e^-. \tag{1.1}
\]

As a byproduct, the proton is transported through the membrane mainly by the diffusion process and the electro-osmotic mechanism in which each water molecular carries four protons. The electrons conduct through the ACL, ABL, and ABP, and form an outer circuit toward the cathode side.

At the same time, at the cathode side, oxygen from air is injected into the gas channel. Similarly, oxygen arrives at the cathode reaction site. With electrons and protons from the anode side, the chemical reaction is given by:

\[
\frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O. \tag{1.2}
\]

As a byproduct of the cathode side, water is removed through the CCL and CBL, and carried away with the flow in the gas channel.

The cell reaction, overall, is

\[
H_2 + \frac{1}{2}O_2 = H_2O. \tag{1.3}
\]
Multi-physicochemical phenomena takes place in a fuel cell, including the transport of species and charges, multiple electrochemical reactions, and gas-liquid two-phase flow in both the anode and cathode. All these processes are essentially coupled. This means that it is necessary to search for optimal cell design and operating conditions. A good understanding of these coupled multi-physicochemical phenomena is thus essential and is most likely to be achieved through a combination of mathematical model equations and detailed physicochemical and numerical experimental approaches.

In comprehensive fuel cell models, there are five fundamental principles of conservation, namely, mass, momentum, species, charges (electrons and ions), and thermal energy. In addition, these transport equations couple with electrochemical processes through source terms to describe reaction kinetics and electro-osmotic drag in the polymer electrolyte.

In recent years, studies have proposed a number of mathematical models to describe the processes in fuel cells. Reviews of most of these models can be found in [93, 103]. The liquid-water flow was shown to be important in describing the overall transport in fuel cells [27, 28, 9, 34, 22, 41, 65]. The works of Wang et al. [102, 73, 74, 100, 52] are primary examples of models that comprehensively describe two-phase flow. Their models incorporated liquid effects rigorously using the multiphase-mixture model framework of Wang, Cheng et al. in [95, 96, 91, 94, 92, 23].

The purpose of the present work is to develop efficient numerical methods for obtaining accurate solutions to the equations arising from the multiphase, multicomponent, multidomain, and multiphysics models in fuel cells.
1.2 Organization of the present work

Among all conservation equations for describing the physical phenomena happening in fuel cells, this thesis begins with species transport equations in Chapter 2. Water species may be present in coexistence with both the single phase and two phase in the porous media part of the polymer electrolyte fuel cell (PEFC). This induces a nonlinear, discontinuous, and degenerate diffusivity in the water equation. Further, this diffusivity slows down the convergence of the steady-state simulation. We design numerical methods based on the Kirchhoff transformation and the nonlinear alternating Dirichlet-Neumann domain decomposition method to achieve fast convergence towards the solution.

Next, in Chapter 3, we consider the momentum and continuity equations. Darcy-Stokes-Brinkma equations model the coupling between the porous media flow and the single phase viscous flow in a single form of equations with a strongly discontinuous permeability and viscosity. We adopt the finite element framework and design three uniformly stable methods with respect to those strong discontinuities.

In Chapter 4, we develop numerical methods in the full 3D steady-state direct methanol fuel cell (DMFC) simulation. We demonstrate fast convergence towards the solution, based on proper linearization and discretization methods for each equation, coupling and decoupling strategies of solution variables, optimal sequence of decoupling procedure, and modification of water source terms.
2.1 Introduction

Water management is one of central issues in regard to the polymer electrolyte fuel cell (PEFC) and the direct methanol fuel cell (DMFC). Too much water will condense, filling the pores of electrodes with liquid water and hence block the reactant transport to the reaction site in the catalyst layer of the fuel cell. Too little water will limit the proton conductivity in the membrane, thus causing ohmic voltage loss to increase.

In this chapter, we focus on the transport of multiphase species in fuel cells. We consider the two-phase mixture model of porous media flow and transport as developed by Wang, Cheng et al. [95, 96, 91, 94, 92, 23]. Compared to the standard model, one of greatest advantages of this mixture model is that it is not necessary to explicitly check the free interface between the gas-phase region and the two-phase region that may appear in porous media parts of the PEFC. On the other hand, we do need to address the difficulty of treating the discontinuous, degenerate, and nonlinear diffusion-coefficient in the water equation. Because of this "bad" diffusivity, nonlinear iterations of the steady-state simulation converge very slowly based on standard finite element (or finite volume) discretizations and standard linearization techniques. To achieve fast convergence and accurate approximation to the solutions, we develop new methods based
on the Kirchhoff transformation and nonlinear alternating Dirichlet-Neumann domain decomposition methods.

2.2 Model description

In this section, we summarize the traditional multiphase flow and transport model based on the multiphase approach. After that, we derive the multiphase-mixture model [96] from the traditional model.

2.2.1 Multiphase approach

Traditionally multiphase flow and transport in the porous media is modeled using the multiphase approach [10, 1]. In this approach, different phases are considered as distinct fluids with individual transport and thermodynamic properties. The individual phase/energy transport is then modeled by standard conservation equations with additional source terms arising from interfacial mass/heat transfer. The governing equations for this multiphase approach are as follows:

1. Conservation of mass in phase $k$:

$$
\epsilon \frac{\partial (\rho_k s_k)}{\partial t} + \nabla \cdot (\rho_k u_k) = \bar{m}_k. \quad (2.1)
$$

Here, $\epsilon$ is the porosity of porous media; $\rho_k$ is the phase density; $s_k$ is the phase saturation denoting the volumetric fraction of the void space occupied by phase $k$; and $u_k$ is the superficial velocity (based on the total cross-sectional area of multiple
fluids and porous medium). By definition,

\[ \sum_k s_k = 1. \tag{2.2} \]

\( \bar{m}_k \) represents the interfacial mass transfer rate from all other phases to phase \( k \).

With no external mass source or sink, it follows that

\[ \sum_k \bar{m}_k = 0. \tag{2.3} \]

2. Conservation of momentum in phase \( k \):

\[ \mathbf{u}_k = -K_k \frac{k_{rk}}{\mu_k} (\nabla p_k - \rho_k g), \tag{2.4} \]

where \( K \) is the absolute permeability tensor of porous media; \( k_{rk} \) is the relative permeability of phase \( k \); and \( \mu_k \) is the dynamic viscosity for phase \( k \). \( g \) is the gravitational constant vector that accounts for the gravitational force. This generalized Darcy’s law is valid if inertia as well as viscous effect can be neglected.

3. Conservation of mass for species \( \alpha \) in phase \( k \):

\[ \frac{\partial}{\partial t} (\rho_k s_k \rho_k Y_k^\alpha) + \nabla \cdot (\rho_k u_k \rho_k Y_k^\alpha) = -\nabla \cdot \mathbf{j}_k^\alpha + \bar{J}_k^\alpha, \tag{2.5} \]

where \( \rho_k \) is the mass concentration of species \( \alpha \) in phase \( k \). By definition,

\[ \sum_\alpha Y_k^\alpha = 1. \tag{2.6} \]
\( j^\alpha_k \) is an average flux of species \( \alpha \) in phase \( k \) based on the molecular diffusion and/or hydrodynamic dispersion. It is usually in the Fickian form:

\[
j^\alpha_k = -\epsilon \rho_k s_k D^\alpha_k \nabla Y^\alpha_k ,
\]

(2.7)

where \( D^\alpha_k \) is a macroscopic second-order tensor representing both diffusive and dispersive effects. The term \( \bar{J}^\alpha_k \) denotes the interphase mass transfer rate of species \( \alpha \) in phase \( k \) caused by chemical reaction and phase change at the interfaces between phase \( k \) and all other phases. It is assumed that there is no external generation of species due to chemical reactions. Thus it follows that

\[
\sum_k \bar{J}^\alpha_k = 0.
\]

(2.8)

4. Conservation of energy in phase \( k \):

\[
\frac{\partial}{\partial t} (\epsilon \rho_k s_k h_k) + \nabla \cdot (\rho_k u_k h_k) = \nabla \cdot (\epsilon s_k k_k \nabla T) + \bar{q}_k .
\]

(2.9)

For the solid matrix, which does not move, the energy equation reads as follows:

\[
\frac{\partial}{\partial t} ((1 - \epsilon) \rho_s h_s) = \nabla \cdot ((1 - \epsilon) s_k k_s \nabla T) + \bar{q}_s ,
\]

(2.10)

by replacing \( \epsilon \) by \( 1 - \epsilon \), \( u_k = 0 \) and \( s_k = 1 \) in the above equation (2.9).

Local thermal equilibrium among phases has been assumed, i.e., \( T_k = T \). \( k_k \) is the effective thermal conductivity of phase \( k \), and \( \bar{q}_k \) is the interphase heat transfer.
rate associated with phase $k$. Let $q$ denote an external volumetric heat source or sink. Then,

\[
\left( \sum_k \bar{\dot{q}}_k \right) + \bar{\dot{q}}_s = q.
\]

(2.11)

The phase enthalpy $h_k$ is related to the common temperature $T$ via

\[
h_k = \int_0^T c_k dt + h^0_k,
\]

(2.12)

where $c_k$ and $h^0_k$ represent the effective specific heat and the reference enthalpy respectively of phase $k$.

The above basic conservation laws provide a full system of governing equations for velocity $u_k$, pressures $p_k$, mass concentrations $Y^\alpha_k$, and common temperature $T$.

### 2.2.2 Constitutive relationships

To close the system, we need an additional set of equations. The constitutive equations specify how the phases interact with each other and with the surrounding porous medium. The state equations specify the thermodynamic state of the phases as a function of state variables. These conditions are usually determined by experiments.

The capillary pressure $p_{cik}$ between phase $i$ and phase $k$ is defined by

\[
p_{cik} = p_i - p_k.
\]

(2.13)
The two-phase capillary pressure between the gas phase and the liquid phase can be expressed by

\[ p_{cgl} = \sigma \cos(\theta) \left( \frac{\epsilon}{k} \right)^{1/2} J(s), \]  

(2.14)

where \( \sigma \) is the surface tension, \( \theta \) is the contact angle between the gas phase and the liquid phase, and the Leverett function \( J(s) \) given by [50, 73]:

\[ J(s, \theta) = \begin{cases} 
1.417(1 - s) - 2.120(1 - s)^2 + 1.263(1 - s)^3, & \theta < \pi/2, \\
1.417s - 2.120s^2 + 1.263s^3, & \theta > \pi/2.
\]  

(2.15)

For the general multiphase case, the capillary pressure between phases depends on the porosity \( \epsilon \), the surface tension \( \sigma_{kj} \) between phase \( k \) and phase \( j \), and the phase saturations \( s_k \) [72]:

\[ p_{ckj} = f(\epsilon, \sigma_{kj}, s_1, s_2, \ldots, s_n). \]  

(2.16)

Here, \( n \) is the number of different phases.

The relative permeability is assumed to be a function of saturation \( s \). For the two-phase flow, we use

\[ k_{rl} = s^3, \quad k_{rg} = (1 - s)^3. \]  

(2.17)

In the next subsection, we derive the multiphase-mixture model from the traditional multiphase model that is based on the multiphase approach in Section 2.2.1.
2.2.3 Multiphase-mixture model

An alternative approach was developed to model multiphase flow and multispecies transport in porous media. This is referred to as the multiphase-mixture model [96]. A key idea in the multiphase-mixture model is that the system is viewed as being a multiphase mixture. Then the multiphase flow is described by a mass average mixture velocity and phase diffusive flux relative to other phases. This diffusive flux represents the difference between a mixture velocity and an individual phase velocity. A new set of conservation equations based on the multiphase mixture was derived from the traditional multiphase-approach models. In addition, explicit relationships describing the relative motions between the multiphase mixture and an individual phase can be obtained and used to recover the individual phase velocities, interfacial mass transfer rates, etc.

Mixture Variables

The multiphase-mixture model is based on mixture variables. A mixture density - \( \rho \), mixture velocity - \( \mathbf{u} \), mixture mass concentration of species \( \alpha \) - \( Y_\alpha \), and mixture enthalpy - \( h \) are defined by

\[
\rho = \sum_k \rho_k s_k, \tag{2.18}
\]

\[
\rho \mathbf{u} = \sum_k \rho_k \mathbf{u}_k, \tag{2.19}
\]

\[
\rho Y_\alpha = \sum_k \rho_k s_k Y_\alpha, \tag{2.20}
\]

\[
\rho h = \sum_k \rho_k s_k h_k. \tag{2.21}
\]
By definition, mixture mass fractions of species satisfy

\[ \sum_{\alpha} Y^{\alpha} = 1. \quad (2.22) \]

The mixture kinematic viscosity is given by

\[ \nu = \left( \sum_{k} \frac{k_{r k}}{\nu_k} \right)^{-1}, \quad (2.23) \]

where \( \nu_k = \mu_k / \rho_k \) is the kinematic viscosity of phase k. The mobility of each phase is defined by

\[ \lambda_k = \frac{k_{r k}}{\nu_k} \nu, \quad (2.24) \]

thus it follows that

\[ \sum_{k} \lambda_k = 1. \quad (2.25) \]

The definition of mixture pressure is given by

\[ \nabla p = \sum_{i} \lambda_i \nabla p_i. \quad (2.26) \]

This definition of mixture pressure is not straightforward. However, from the derivation of the mixture momentum equation, we shall see in a moment that it is appropriate to define the mixture pressure in this way in order to obtain a similar type of momentum equation as the individual momentum equation (2.4) in the multiphase approach.
Model Equations

1. Mass conservation of the multiphase mixture.

By adding the phase conservation equations (2.1) for all phases and using the definition of mixture density (2.18) and mixture velocity (2.19), we get

$$
\epsilon \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0.
$$

(2.27)

The right hand side is zero using the fact that (2.3) holds. Since the mixture density $\rho$ is a function of saturation $s$, this multiphase-mixture flow is viewed as compressible.

2. Momentum conservation of the multiphase mixture.

From the conservation of momentum in phase $k$ (2.28) and the definition of mobility (2.24), we get

$$
\rho_k \mathbf{u}_k = -K \frac{k_{rk}}{\nu_k} (\nabla p_k - \rho_k \mathbf{g}) = -\frac{K}{\nu} (\lambda_k \nabla p_k - \lambda_k \rho_k \mathbf{g}).
$$

(2.28)

By adding these equations for all phases and using the definition of mixture velocity (2.19) and mixture pressure (2.26), we obtain

$$
\rho \mathbf{u} = -\frac{K}{\nu} \left( \nabla p - \sum_k (\lambda_k \rho_k) \mathbf{g} \right).
$$

(2.29)
Introduce a mixture density correction factor $\gamma_\rho$,

$$
\gamma_\rho = \left( \sum_k \lambda_k \rho_k \right) / \rho.
$$

(2.30)

Then, we get the momentum conservation of the multiphase mixture as follows:

$$
\rho \mathbf{u} = -\frac{K}{\nu} \left( \nabla p - \gamma_\rho \rho \mathbf{g} \right).
$$

(2.31)

Since the density correction factor depends only on saturation $s$, it can be regarded as a property of the multiphase mixture. This physically means that the effective mixture density $\rho \gamma_\rho$ for the gravitational force, contains certain dynamic properties of phases, since $\gamma_\rho$ depends on $\lambda_k$ and hence on $\nu_k$, due to the relative motion between phases. In the case of single-phase multicomponent mixtures, $\gamma_\rho = 1$, the body force for the multiphase mixture is presented by the mixture density.

3. Mass conservation of species $\alpha$ in the multiphase mixture.

The diffusive mass flux of phase $k$ relative to the multiphase mixture is defined as

$$
\mathbf{j}_k = \rho_k \mathbf{u}_k - \lambda_k \rho \mathbf{u}.
$$

(2.32)

From the definition of mixture velocity (2.19) and mobility (2.24), it follows that

$$
\sum_k \mathbf{j}_k = 0.
$$

(2.33)
Substitute the momentum equation in phase $k$ (2.28) and the multiphase mixture one (2.31) into (2.32), and we get

$$
\mathbf{j}_k = -\frac{K\lambda_k}{\nu}(\nabla p_k - \rho_k \mathbf{g}) + \frac{K\lambda_k}{\nu} \sum_i (\lambda_i \nabla p_i - \lambda_i \rho_i \mathbf{g})
$$

$$
= \frac{K\lambda_k}{\nu} \sum_i (\lambda_i \nabla p_{ci(k)}) + \frac{K\lambda_k}{\nu} \sum_i (\lambda_i (\rho_k - \rho_i) \mathbf{g}).
$$

(2.34)

Further, by adding the species conservation equations (2.5) for all phases, we obtain

$$
\epsilon \frac{\partial}{\partial t} (\rho Y^\alpha) + \nabla \cdot \left( \sum_k \rho_k \mathbf{u}_k Y^\alpha_k \right) = -\nabla \cdot \left( \sum_k \mathbf{j}_k^\alpha \right).
$$

(2.35)

By the definition of the diffusive mass flux of phase $k$ relative to the multiphase mixture (2.32) and the Fickian diffusive flux for species $\alpha$ in phase $k$ (2.7), we have

$$
\epsilon \frac{\partial}{\partial t} (\rho Y^\alpha) + \nabla \cdot \left( \sum_k \lambda_k \rho_k \mathbf{u}_k Y^\alpha_k \right) = -\nabla \cdot \left( \sum_k \mathbf{j}_k^\alpha \right) + \nabla \cdot \left( \sum_k \epsilon \rho_k s_k D^\alpha_k \nabla Y^\alpha_k \right).
$$

(2.36)

Define the advection correction factor and the effective diffusion coefficient for the multiphase mixture as

$$
\gamma_\alpha = \left( \rho \sum_k \lambda_k Y^\alpha_k \right) / (\rho Y^\alpha),
$$

(2.37)

$$
\rho D^\alpha = \sum_k \rho_k s_k D^\alpha_k.
$$

(2.38)
Then, the species conversation equation for the multiphase mixture is in the form

$$
\epsilon \frac{\partial}{\partial t} (\rho Y^\alpha) + \nabla \cdot (\gamma \alpha \rho \mathbf{u} Y^\alpha) = -\nabla \cdot \left( \sum_k j_k Y_k^\alpha \right) + \nabla \cdot \left( \sum_k \epsilon \rho_k s_k D^\alpha_k \nabla Y_k^\alpha \right). \tag{2.39}
$$

In this multiphase-mixture framework, the advection correction factor $\gamma \alpha$ indicates that the species is advected by modified velocity $\gamma \alpha \mathbf{u}$ rather than by the mixture velocity $\mathbf{u}$. The first term on the right hand side represents the diffusive flux of species $\alpha$ across phases. The last term on the right hand side represents the Fickian diffusion fluxes within various phases.

In the multiphase zone, the phase mass concentration $Y_k^\alpha$ is usually given by phase equilibrium diagrams under the assumption of a local chemical equilibrium. Thus the mixture mass concentration $Y^\alpha$ is essentially a function of phase saturation $s_k$.

4. Energy Conservation for the Multiphase Mixture

Adding up the energy equations for all phases (2.9) and for the solid matrix (2.10), and applying the relation (2.11), we obtain

$$
\frac{\partial}{\partial t} \left( \sum_k (1 - \epsilon) \rho_s h_s + \epsilon \rho h \right) + \nabla \cdot \left( \sum_k \rho_k \mathbf{u}_k h_k \right) = \nabla \cdot \left( \epsilon \sum_k (s_k k_k) + (1 - \epsilon) k_s \right) \nabla T \right) + q. \tag{2.40}
$$
Define the effective thermal conductivity $k_{eff}$ of the composite system consisting
of the solid matrix and the multiphase mixture as follows:

$$k_{eff} = \epsilon \sum_k (s_k k_k) + (1 - \epsilon) k_s. \quad (2.41)$$

Similar to (2.37), define the advection correction factor for energy as

$$\gamma_h = \left( \rho \sum_k \lambda_k h_k \right) / (\rho h). \quad (2.42)$$

Following the similar derivation of the conservation equation for multiphase mixture species $\alpha$, we obtain

$$\frac{\partial}{\partial t} \left( \sum_k (1 - \epsilon) \rho_s h_s + \epsilon \rho h \right) + \nabla \cdot \left( \gamma_h \rho u h \right)$$

$$= -\nabla \cdot \left( \sum_k j_k h_k \right) + \nabla \cdot \left( k_{eff} \nabla T \right) + q. \quad (2.43)$$

The first term on the right hand side of this equation represents energy flux due
to relative phase motions.

Next, we apply the modeling equations in this section to solve the water transport
equations in the porous media part of fuel cells.
2.3 Numerical techniques on the two-phase mixture transport in the porous cathode backing layer (CBL) of the Polymer Electrolyte Fuel Cell (PEFC)

In this section, we focus on the two-phase mixture water transport equation in the porous cathode backing layer (CBL) of the PEFC. We further derive the two-phase mixture water transport equation from (2.39) and design numerical methods to solve the transport equation.

The two-phase mixture species conservation of equation (2.39) is written as

\[
\epsilon \frac{\partial}{\partial t} (\rho Y^\alpha) + \nabla \cdot (\gamma^\alpha \rho u Y^\alpha) = -\nabla \cdot \left( (Y_l^\alpha - Y_g^\alpha) j_l \right) + \nabla \cdot \left( \epsilon \rho_l s D_l^\alpha \nabla Y_l^\alpha + \epsilon (1 - s) \rho_g D_g^\alpha \nabla Y_g^\alpha \right). 
\]  

(2.44)

It is assumed that the gases (oxygen, hydrogen, nitrogen) other than water vapor are insoluble in the liquid phase. Thus \( Y_l^\alpha = 0 \) (\( \alpha = H_2, O_2, N_2 \)) and \( Y_l^{H_2O} = 1 \). Then the equation (2.44) is further simplified as

\[
\epsilon \frac{\partial}{\partial t} (\rho Y^\alpha) + \nabla \cdot (\gamma^\alpha \rho u Y^\alpha) = -\nabla \cdot \left( (Y_l^\alpha - Y_g^\alpha) j_l \right) + \nabla \cdot \left( \epsilon \rho_g (1 - s) D_g^\alpha \nabla Y_g^\alpha \right). 
\]  

(2.45)

In particular, we consider solution variables in terms of molar concentration. Let \( C \) denote the molar concentration. The relationships between mass concentrations and
molar concentrations are

\[
\rho Y^\alpha = C^\alpha M^\alpha, \quad (2.46)
\]

\[
\rho_k Y_k^\alpha = C_k^\alpha M^\alpha, \quad (2.47)
\]

where \(M^\alpha\) is the molecular weight of species \(\alpha\). Using these relationships, we can rewrite the species conservation equation (2.39) in terms of molar concentration, assuming that the phase densities \(\rho_l\) and \(\rho_g\) are constants:

\[
\epsilon \frac{\partial}{\partial t} C^\alpha + \nabla \cdot (\gamma_\alpha u C^\alpha) = -\nabla \cdot \left( \left( \frac{Y^\alpha}{M^\alpha} - \frac{Y^\alpha}{M^\alpha} \right) j_l \right) + \nabla \cdot \left( (\epsilon(1-s)D^\alpha_g) \nabla C^\alpha_g \right). \quad (2.48)
\]

From (2.14) and (2.34), ignoring gravitational effect, we get

\[
j_l = \frac{K\lambda_l\lambda_g}{\nu} \nabla p_{cgl} = \frac{K\lambda_l\lambda_g}{\nu} \nabla \left( \sigma \cos(\theta) \left( \frac{\epsilon}{K} \right)^{1/2} J(s) \right) = \frac{\sigma \cos(\theta)(\epsilon K)^{1/2} \lambda_l\lambda_g}{\nu} \nabla J(s).
\]

(2.49)

Under the molar concentration framework, we have similar relationships between the mixture molar concentration and individual phase molar concentrations. From (2.46), (2.47), and the mixture mass concentrations (2.18) and (2.20), we have

\[
C^\alpha = (1-s)C^\alpha_g + sC^\alpha_l. \quad (2.50)
\]
Assume that the water vapor is always saturated, i.e., \( C_{g}^{H_2O} = C_{g,sat}^{H_2O} \) in the two-phase zone. Then the water molar concentration reads:

\[
C_{H_2O} = \begin{cases} 
  C_{g}^{H_2O} & s = 0 \ i.e. \ C \leq C_{g,sat}^{H_2O}, \\
  (1-s)C_{g,sat}^{H_2O} + sC_1^{H_2O} & s > 0 \ i.e. \ C > C_{g,sat}^{H_2O}.
\end{cases}
\] (2.51)

Under this relation, \( \nabla J(s) \) in (2.49) can be written as:

\[
\nabla J(s) = \frac{J'(s)}{C_l^{H_2O} - C_{g,sat}^{H_2O}} \nabla C_{H_2O}.
\] (2.52)

The liquid diffusive flux (2.49) relative to the two-phase mixture can be further written as

\[
j_l = \frac{\sigma \cos(\theta)(\epsilon K)^{1/2} \lambda_l \lambda_g}{\nu(C_l^{H_2O} - C_{g,sat}^{H_2O})} J'(s) \nabla C_{H_2O}.
\] (2.53)

Thus we define two-phase mixture water diffusivity as follows:

\[
\Gamma_{H_2O} = \begin{cases} 
  D_{g,eff}^{H_2O} & s = 0, \\
  -\left( \frac{Y_{l}^{H_2O} - Y_{g}^{H_2O}}{M_{H_2O}^{l} - M_{H_2O}^{g}} \right) \sigma \cos(\theta)(\epsilon K)^{1/2} \lambda_l \lambda_g \frac{J'(s)}{\nu(C_l^{H_2O} - C_{g,sat}^{H_2O})} & s > 0.
\end{cases}
\] (2.54)

According to the above derivation, \( D_{g,eff}^{H_2O} = \epsilon D_{g}^{H_2O} \). In practice, considering the tortuosity factor of electrodes, we use the effective diffusivity via the Bruggeman correlation [58] as follows:

\[
D_{g,eff}^{H_2O} = 1.5 \epsilon D_{g}^{H_2O}.
\] (2.55)
Finally, we can write the water conservation equation in the convection-diffusion form:

$$
\epsilon \frac{\partial}{\partial t} C_{H_2O} + \nabla \cdot \left( \gamma_{H_2O} u C_{H_2O} \right) = \nabla \cdot \left( \Gamma_{H_2O} \nabla C_{H_2O} \right).
$$

(2.56)

In the rest of Chapter 2, we consider the steady-state two-phase water equation. For convenience, we drop the super- or sub-script $H_2O$ in the equation.

We consider the following coupled model equations that consist of the two-phase steady-state mixture water transport equation (2.56), the mixture momentum equation (2.31), and the continuity equation (2.27).

**Governing Equations**

\[
\begin{align*}
-\nabla \cdot (\Gamma \nabla C) + \nabla \cdot (\gamma u C) &= 0 \\
\nabla \cdot (\rho u) &= 0 \\
\rho u &= -\frac{K}{\nu} \nabla p
\end{align*}
\]

(2.57)

In the above equations, by plugging the third equation into the first and second, we get the governing equations in terms of the molar concentration $C$ and the pressure $p$ as follows:

\[
\begin{align*}
-\nabla \cdot (\Gamma \nabla C) + \nabla \cdot (-\gamma \frac{K}{\mu} \nabla p C) &= 0 \\
\nabla \cdot (-\frac{K}{\nu} \nabla p) &= 0
\end{align*}
\]

(2.58)

Fig. 2.1 demonstrates the computational domain. The computational domain is the two-dimensional cathode backing layer (CBL) of the PEFC. The horizontal $x$-axis and
vertical $y$-axis represent the along-channel direction and through-plane direction of the fuel cell respectively.

**Fig. 2.1.** Computational domain of the Cathode Backing Layer (CBL).

**Boundary Conditions**

- At the bottom boundary ($\partial\Omega)_1$, 

  $$C = c_1 + (c_2 - c_1) \frac{x}{l_{PEFC}}, \quad p = p_1 + (p_2 - p_1) \frac{x}{l_{PEFC}},$$

  $c_1$, $c_2$, $p_1$, and $p_2$ are constants. Denote $l_{PEFC}$ by the length of the CBL.

- At the left and right boundaries ($\partial\Omega)_2$ and ($\partial\Omega)_3$, 

  $$\nabla C \cdot \mathbf{n} = 0, \quad \nabla p \cdot \mathbf{n} = 0,$$
where \( \mathbf{n} \) is the unit vector with the outward normal direction to the boundary.

- At the top boundary \( (\partial\Omega)_4 \),

\[
\left( -\Gamma \nabla C - \frac{K}{\mu} \nabla pC \right) \cdot \mathbf{n} = -\frac{I(x)}{2F}, \quad \nabla p \cdot \mathbf{n} = 0,
\]

where \( F \) is the Faraday constant. \( I(x) \) is given by

\[
I(x) = I_1 + (I_2 - I_1) \frac{x}{\delta_{CBL}},
\]

(2.59)

here \( I_1 \) and \( I_2 \) are constant current densities, and \( \delta_{CBL} \) denotes the thickness of CBL.

In Table 2.1, we give the physical quantities used in our numerical simulations.

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water molecular weight</td>
<td>( M )</td>
<td>0.018 kg/mol</td>
</tr>
<tr>
<td>Saturated vapor molar concentration</td>
<td>( C_{g,\text{sat}} )</td>
<td>16 mol/m(^3)</td>
</tr>
<tr>
<td>Water vapor density</td>
<td>( \rho_g )</td>
<td>0.882 kg/m(^3)</td>
</tr>
<tr>
<td>Liquid water density</td>
<td>( \rho_l )</td>
<td>971.8 kg/m(^3)</td>
</tr>
<tr>
<td>Surface tension</td>
<td>( \sigma )</td>
<td>0.0625 kg/s(^2)</td>
</tr>
<tr>
<td>Contact angle</td>
<td>( \theta )</td>
<td>( \frac{2}{3}\pi )</td>
</tr>
<tr>
<td>Porosity of CBL</td>
<td>( \epsilon )</td>
<td>0.7</td>
</tr>
<tr>
<td>Permeability of CBL</td>
<td>( K )</td>
<td>( 1.0 \times 10^{-12} ) m(^2)</td>
</tr>
<tr>
<td>Kinematic liquid water viscosity</td>
<td>( \nu_l )</td>
<td>( 3.533 \times 10^{-7} ) m(^2)/s</td>
</tr>
<tr>
<td>Kinematic vapor viscosity</td>
<td>( \nu_g )</td>
<td>( 3.59 \times 10^{-5} ) m(^2)/s</td>
</tr>
<tr>
<td>Faraday constant</td>
<td>( F )</td>
<td>96487 A·s/mol</td>
</tr>
<tr>
<td>Water vapor diffusivity</td>
<td>( D_{gas} )</td>
<td>( 2.6 \times 10^{-5} ) m(^2)/s</td>
</tr>
</tbody>
</table>
We plot the function $\Gamma(C)$ in Fig. 2.2. The diffusion coefficient $\Gamma$ is nonlinear, discontinuous with large jumps, and degenerate at two points: $C = C_{g, sat}$ and $C = C_l$. Because of this, standard linearization techniques hardly make the nonlinear iterative procedures converge. In the following section, we will consider special linearization techniques to overcome this difficulty.

2.3.1 Method based on Kirchhoff transformation

Introduce the Kirchhoff transformation,

$$W(x) = \int_0^{C(x)} \Gamma(r) dr.$$  \hspace{1cm} (2.60)

Then taking the gradient to both sides of (2.60), we obtain

$$\nabla W = \Gamma(C) \nabla C, \quad \text{for } a.e. \ x.$$  \hspace{1cm} (2.61)
Thus, the governing equation (2.58) is reduced to the following:

\[
\begin{align*}
-\Delta W + \nabla \cdot ( -\gamma \frac{K}{\mu} \nabla pC ) &= 0 \\
-\nabla \cdot ( \frac{K}{\nu} \nabla p ) &= 0
\end{align*}
\] (2.62)

Given the linear diffusion in this equation, the new variable is "smoother" than the original variable. The discontinuity is "hidden" inside the Kirchhoff transformation (2.60). It is possible to obtain better numerical performance under this new formulation.

The boundary conditions corresponding to the new variable $W$ are as follows:

- At the bottom boundary $(\partial\Omega)_1$:
  \[ W(x) = \int_0^{C(x)} \Gamma(r) dr. \]

- At the left and right boundaries $(\partial\Omega)_2$ and $(\partial\Omega)_3$:
  \[ \nabla W \cdot \mathbf{n} = 0. \]

- At the top boundary $(\partial\Omega)_4$:
  \[ \left( -\nabla W - \gamma \frac{K}{\mu} \nabla pC \right) \cdot \mathbf{n} = -\frac{I(x)}{2F}. \]
We introduce the following Sobolev spaces as:

\[ Q_D := \left\{ W \in H^1(\Omega) : W(x) = \int_0^{C(x)} \Gamma(r)dr, \text{ on } (\partial \Omega)_1 \right\}, \]

\[ Q_0 := \left\{ W \in H^1(\Omega) : W = 0, \text{ on } (\partial \Omega)_1 \right\}, \]

\[ P_D := \left\{ p \in H^1(\Omega) : p = p_1 + (p_2 - p_1) \frac{x}{l_{PFC}}, \text{ on } (\partial \Omega)_1 \right\}, \]

\[ P_0 := \left\{ p \in H^1(\Omega) : p = 0, \text{ on } (\partial \Omega)_1 \right\}. \]

Then the variational formulation of (2.62) is: for all \( \tilde{W} \in Q_0 \) and \( \tilde{p} \in P_0 \), find \( W \in Q_D \) and \( p \in P_D \), such that

\[
\begin{align*}
\langle \nabla W + \gamma \frac{K}{\mu} \nabla p C, \nabla \tilde{W} \rangle &= \int_{(\partial \Omega)_4} \frac{I(x) I(x)}{2F} \tilde{W} dx, \\
(\frac{K}{\nu} \nabla p, \nabla \tilde{p}) &= 0.
\end{align*}
\]

(2.63)

Given the \( n \)-th iterative solution \((C^n, p^n)\), find \((W^{n+1}, p^{n+1})\), for all \( \tilde{W} \) and \( \tilde{p} \),

\[
\begin{align*}
\langle \nabla W^{n+1}, \nabla \tilde{W} \rangle &= -(\gamma(C^n) \frac{K}{\mu(C^n)} \nabla p^n C^n, \nabla \tilde{W}) + \int_{(\partial \Omega)_4} \frac{I(x)}{2F} \tilde{W} dx, \\
\langle \frac{K}{\nu(C^n)} \nabla p^{n+1}, \nabla \tilde{p} \rangle &= 0.
\end{align*}
\]

(2.64)

We use the continuous piecewise linear finite element method to discretize this weak formulation for both variables.

**Efficient computation of the inverse Kirchhoff transformation.** In the above iterative procedure, for given \( W \), it is necessary to find the corresponding \( C \); therefore,
consider how to effectively take the inverse of the Kirchhoff transformation. Let
\( \alpha_0 = \int_{c_0}^{C_{g,\text{sat}}} \Gamma(s) \, ds \), then \( \alpha_0 = D_{g,\text{eff}}(C_{g,\text{sat}} - c_0) \), which is a constant.

**Algorithm 3.1:**

**Case 1** If \( W \leq \alpha_0 \), \( W = D_{g,\text{eff}} C \), then \( C = \frac{W}{D_{g,\text{eff}}} \).

**Case 2** If \( W > \alpha_0 \), i.e., \( C > C_{g,\text{sat}} \)

\[
W = \alpha_0 + \int_{C_{g,\text{sat}}}^{C} \Gamma(s) \, ds.
\]

Let \( F(x) = \int_{C_{g,\text{sat}}}^{x} \Gamma(s) \, ds + \alpha_0 - W \). Taking the inverse Kirchhoff transformation is equivalent to finding the root of this equation for a given \( W \). Since the function \( F(x) \) is monotonically increasing function, we use Newton’s method to solve the equation efficiently. Let \( x_{n+1} = x_n - \frac{F(x_n)}{F'(x_n)} \). We know \( F'(x) = \Gamma(x) \), therefore \( x_{n+1} = x_n - \frac{F(x_n)}{\Gamma(x_n)} \). To evaluate \( F(x_n) \), we can use symbolic software (matlab or mathematica) to find the antiderivative of \( \Gamma \) and then directly evaluate the function value of it.

**Numerical results.** In our numerical simulations, we use the following geometric parameters and operating conditions: \( \delta_{CBL} = 3 \times 10^{-4} \, \text{m} \), \( l_{\text{PEFC}} = 0.07 \, \text{m} \), \( c_1 = 13.5 \, \text{mol/m}^3 \), \( c_2 = 15.9 \, \text{mol/m}^3 \), \( p_1 = 101325 \, \text{Pa} \), \( p_2 = 101000 \, \text{Pa} \), \( I_1 = 1 \, \text{Acm}^{-2} \), and \( I_2 = 2 \, \text{Acm}^{-2} \). The stopping criteria of the iterative algorithm (2.64) is that the \( l_2 \) norm of the relative residual for both the concentration equation and the pressure equation is less than \( 10^{-8} \); then in three iterations the relative residual drops to the tolerance for four different meshes. Tables 2.2–2.5 demonstrate the convergence histories. For the concentration and pressure profiles, see Figs. 2.3–2.10.
Fig. 2.3. Concentration on a 10×10 mesh.

Fig. 2.4. Pressure on a 10 × 10 mesh.

Fig. 2.5. Concentration on a 50×10 mesh.

Fig. 2.6. Pressure on a 50 × 10 mesh.

Fig. 2.7. Concentration on a 100 × 10 mesh.

Fig. 2.8. Pressure on a 100 × 10 mesh.
Next, we extend our computational domain into the two sub-domains containing both the cathode backing layer (CBL) and the cathode gas channel (CGC).

2.4 Numerical techniques on the two-phase mixture transport in the cathode of the PEFC

The work presented in this section is based on the collaborative work in [85, 84].

In the following discussion, we consider model equations in the domain containing both the porous CBL and the CGC.

Mixture water concentration equation. We have the following mixture water conservation equation in the CBL and CGC:

\[
\begin{align*}
-\nabla \cdot (\Gamma(C) \nabla C) + \nabla \cdot (\gamma u C) &= 0, \quad \text{in CBL,} \\
-\nabla \cdot (D_g \nabla C) + \nabla \cdot (u C) &= 0, \quad \text{in CGC.}
\end{align*}
\] (2.65)

In addition, at the CBL and CGC interface, the concentration and the normal component of total (including convection and diffusive) flux are continuous. The first equation of

Fig. 2.9. Concentration on an unstructured mesh.

Fig. 2.10. Pressure on an unstructured mesh.
Table 2.2. Convergence history on a $10 \times 10$ mesh

<table>
<thead>
<tr>
<th>Iteration No.</th>
<th>Water</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.2075e-003</td>
<td>3.2075e-003</td>
</tr>
<tr>
<td>2</td>
<td>1.9476e-008</td>
<td>1.2983e-002</td>
</tr>
<tr>
<td>3</td>
<td>6.4627e-015</td>
<td>4.8190e-009</td>
</tr>
</tbody>
</table>

Table 2.3. Convergence history on a $50 \times 10$ mesh

<table>
<thead>
<tr>
<th>Iteration No.</th>
<th>Water</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.2075e-003</td>
<td>3.2075e-003</td>
</tr>
<tr>
<td>2</td>
<td>7.5136e-008</td>
<td>1.4844e-002</td>
</tr>
<tr>
<td>3</td>
<td>1.1777e-014</td>
<td>1.3553e-009</td>
</tr>
</tbody>
</table>

(2.65) is the same as the first one of (2.57). In the CGC, the second equation is a single gas phase water conservation equation without advection correction factor $\gamma$ (or with $\gamma = 1$), where $D_g$ is the water vapor diffusivity.

**Momentum equation and continuity equations.** Introduce the following extended steady-state Navier-Stokes equations:

\[
\begin{align*}
-\nabla \cdot (\mu \nabla \mathbf{u}) + \frac{1}{\varepsilon^2} \nabla \cdot (\rho \mathbf{uu}) + \nabla p + \frac{\mu}{K} \mathbf{u} & = 0, \\
\nabla \cdot (\rho \mathbf{u}) & = 0.
\end{align*}
\]

(2.66)

The interfacial boundary conditions between CBL and CGC are the continuity of the velocity and the normal component of the stress tensor. We add a further Darcy’s drag term $\frac{\mu}{K} \mathbf{u}$, exerted from the porous CBL. Permeability $K$ is position-dependent and is
Table 2.4. Convergence history on a 100 \times 10 mesh

<table>
<thead>
<tr>
<th>Iteration No.</th>
<th>Water</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.2075e-003</td>
<td>3.2075e-003</td>
</tr>
<tr>
<td>2</td>
<td>1.2337e-007</td>
<td>1.3234e-002</td>
</tr>
<tr>
<td>3</td>
<td>1.2925e-014</td>
<td>5.2707e-010</td>
</tr>
</tbody>
</table>

Table 2.5. Convergence history on an unstructured mesh

<table>
<thead>
<tr>
<th>Iteration No.</th>
<th>Water</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.2075e-003</td>
<td>3.2075e-003</td>
</tr>
<tr>
<td>2</td>
<td>2.2779e-008</td>
<td>1.2407e-002</td>
</tr>
<tr>
<td>3</td>
<td>8.6170e-015</td>
<td>5.4213e-009</td>
</tr>
</tbody>
</table>

defined as

\[
K = \begin{cases} 
+\infty & \text{in CGC}, \\
10^{-12} & \text{in CBL}.
\end{cases}
\]  

(2.67)

When \( K = \infty \) in the CGC, (2.66) is reduced to the steady-state Navier-Stokes equations, which model the single-phase viscous flow in the CGC. On the other hand, when \( K \) is a small number \( 10^{-12} \), the terms \( \frac{\mu}{K} u \) and \( \nabla p \) are dominant, and thus (2.66) is close to the momentum conservation equation in (2.57) in the porous CBL.

By adding this Darcy’s drag term, we have the same type of momentum equation (2.66), which is valid in both the CBL and CGC, with the highly discontinuous coefficient \( K \). The advantage of the modified steady-state Navier-Stokes equations is that we solve the two-domain problem in a single-domain approach in which the interface boundary conditions are automatically carried on by the weak formulation, instead of the two-domain approach in which Darcy’s law and Stokes equations are coupled with three
interface conditions: continuity of the normal flux, continuity of the normal component of the stress, and the Beavers-Joseph-Saffman condition [11, 81]. A single-domain approach is easier to implement in practice, especially in the simulation of 3D complete fuel cell models, which will be discussed in Chapter 4.

![Diagram](image)

**Fig. 2.11.** Computational domain of the CBL and CGC.

**Computational domain and boundary conditions.** Our computational domain consists of the porous CBL and the CGC, as schematically shown in Fig. 2.11. The horizontal $x$-axis represents the along-channel direction; and the vertical $y$-axis represents the through-plane direction. The width, along the through-plane direction, of the CBL and the CGC are $\delta_{CBL} = 3 \times 10^{-4} \text{m}$ and $\delta_{CGC} = 10^{-3} \text{m}$ respectively. In comparison with the length in the along-channel direction $l_{PEFC} = 2.5 \times 10^{-2} \text{m}$, the aspect ratio is up to $25 : 1$. 
• At the inlet of CGC ($\partial \Omega)_1$:

\[
\begin{align*}
\mathbf{u} &= \mathbf{u}_0 := \left( u_{in}, \frac{4y(\delta_{CH} - y)}{\delta_{CH}^2}, 0 \right)^T, \\
C &= C_{in}.
\end{align*}
\]  

(2.68)  

(2.69)

$C_{in}$ and $u_{in}$ are to be given constants.

• At the left and right side walls ($\partial \Omega)_2,$ ($\partial \Omega)_4,$ and the bottom wall ($\partial \Omega)_5$:

\[
\begin{align*}
\mathbf{u} &= 0, \\
\nabla C \cdot \mathbf{n} &= 0.
\end{align*}
\]

(2.70)  

(2.71)

• At the outlet of CGC ($\partial \Omega)_3$:

\[
\begin{align*}
(-\mu \nabla \mathbf{u} + p \mathbf{I}) \cdot \mathbf{n} &= 0, \\
\nabla C \cdot \mathbf{n} &= 0.
\end{align*}
\]

(2.72)  

(2.73)

• At the top wall ($\partial \Omega)_6$:

\[
\begin{align*}
\mathbf{u} &= 0, \\
(-\Gamma(C) \nabla C + \gamma \mathbf{u} C) \cdot \mathbf{n} &= -\frac{I(x)}{2F},
\end{align*}
\]

(2.74)  

(2.75)

where $I(x)$ is given by (2.59) in Section 2.3.

We use the same physical and chemical properties as in Table 2.1 in this section.
In sections 2.4.1 and 2.4.2, we discuss how to efficiently solve the coupled governing equations (2.65) and (2.66), with the above boundary conditions.

### 2.4.1 Method based on Kirchhoff transformation

**Kirchhoff transformation.** Introduce a new variable $W$ by the Kirchhoff transformation in the two sub-domains (CBL and CGC) individually.

$$
W(C) = \int_0^C \Gamma(r) dr, \quad \text{in CBL,} \tag{2.76}
$$

$$
W(C) = \int_0^C D_{g,eff} dr = D_{g,eff} C, \quad \text{in CGC.} \tag{2.77}
$$

By differentiating both sides of (2.76) and (2.77), we get

$$
\nabla W = \Gamma(C) \nabla C \quad \text{in CBL,} \tag{2.78}
$$

$$
\nabla W = D_{g,eff} \nabla C \quad \text{in CGC.} \tag{2.79}
$$

In terms of the original variable, we know that the normal component of flux is continuous at the CBL/CGC interface:

$$
(\nabla W + \gamma u C) \cdot \mathbf{n} = \left( -\Gamma C \nabla C + \gamma u C \right) \cdot \mathbf{n}. \tag{2.80}
$$

Here, $\mathbf{n}$ is the normal unit vector at the interface toward the CBL. From (2.77)–(2.79), we get the above interface condition in terms of the new variable:

$$
(-\nabla W + \gamma u C) \cdot \mathbf{n} = \left( -\epsilon^{-1.5} \nabla W + D_{g,eff}^{-1} u W \right) \cdot \mathbf{n}. \tag{2.81}
$$
In this section we are looking at a dry CGC case. This means that the single-phase region traverses the CBL/CGC interface and fills in the entire CGC. Thus $\Gamma(C)$ equals the constant gas diffusivity $D_{g,eff}$ at the interface. Therefore, the new variable $W$ is continuous across the interface.

Now we reformulate the concentration equation (2.65) and corresponding boundary conditions in terms of the new variable $W$ as follows:

\[
\begin{align*}
-\Delta W &= -\nabla \cdot (\gamma u C) \quad \text{in CBL,} \quad (a) \\
-\epsilon^{-1.5} \Delta W + \nabla \cdot \left( D_{g,eff}^{-1} u W \right) &= 0 \quad \text{in CGC,} \quad (b) \\
W &= \int_0^{C_{in}} D_{g,eff} dr \quad \text{on } (\partial \Omega)_1, \quad (c) \\
(-\nabla W + \gamma u C) \cdot n &= -\frac{I}{2F} \quad \text{on } (\partial \Omega)_6, \quad (d) \\
\nabla W \cdot n &= 0 \quad \text{elsewhere on } \partial \Omega, \quad (e)
\end{align*}
\]

(2.82)

together with two interface boundary conditions: the continuity of normal flux (2.81) and the continuity of $W$.

Notice that the original nonlinear discontinuous degenerate diffusion term simply becomes a Laplacian term. This significantly reduces the nonlinearity and makes fast convergence feasible. The only nonlinearity appears in the right hand side of (2.82a), the convective term $\nabla \cdot (\gamma u C)$, where $C$ is an implicit function of $W$ in terms of the inverse Kirchhoff transformation.

Also, notice that the convection term in the CBL differs from that in CGC. In fact, the Kirchhoff transformation (2.77) is linear in the CGC. So we can explicitly write $C$ as function of $W$. However, the Kirchhoff transformation (2.76) in CBL is nonlinear,
and there is no explicit formula to write $C$ as a function of $W$. Thanks to the relatively small convective term in comparison with the diffusion in the CBL, we can keep the convective term in the CBL in the right hand side of the equation and treat it as a "source" term.

**Linearizations and discretizations.** In terms of the weak nonlinearity in the new formulated equation (2.82), we employ Picard’s linearization method as follows:

Given $(u^n, C^n)$, we define $(W^{n+1}, C^{n+1})$ as the solution of the following equation $(n = 0, 1, 2, \cdots)$:

\[
\begin{cases}
-\Delta W^{n+1} = -\nabla \cdot (\gamma u^n C^n) \quad \text{in CBL}, \\
-\epsilon^{-1.5} \Delta W^{n+1} + \nabla \cdot \left( D_{g, eff}^{-1} u^n W^{n+1} \right) = 0 \quad \text{in CGC}.
\end{cases}
\] (2.83)

Here, we obtain $C^n$ from $W^n$ by the inverse Kirchhoff transformation in Algorithm 3.1.

We also use the Picard method to linearize the momentum equation (2.66). Given $(u^n, C^{n+1})$, find $(u^{n+1}, p^{n+1})$ by solving the following linearized equation, $(n = 0, 1, 2, \cdots)$:

\[
\begin{cases}
-\nabla \cdot (\mu^{n+1} \nabla u^{n+1}) + \frac{\rho^{n+1}}{\varepsilon^2} u^n \cdot \nabla u^{n+1} + \nabla p^{n+1} + \frac{\mu^{n+1}}{\lambda} u^{n+1} = 0, \\
\nabla \cdot u^{n+1} = -\frac{\nabla \rho^{n+1}}{\rho^{n+1}} \cdot u^n.
\end{cases}
\] (2.84)

Then update

\[
u^{n+1} \leftarrow (1 - \omega) u^n + \omega u^{n+1},
\] (2.85)

with a relaxation parameter $\omega$. 

Weak formulation. We first introduce the following Sobolev spaces.

\[ Q_D := \left\{ W \in H^1(\Omega) : W = \int_0^{C_{\text{in}}} \Gamma(r) dr, \text{ on } (\partial \Omega)_1 \right\}, \]
\[ Q_0 := \left\{ W \in H^1(\Omega) : W = 0, \text{ on } (\partial \Omega)_1 \right\}, \]
\[ V_D := \left\{ V \in H^1(\Omega) : v = u_0 \text{ on } (\partial \Omega)_1; v = 0, \text{ on } (\partial \Omega)_2, (\partial \Omega)_4, (\partial \Omega)_5, \text{ and } (\partial \Omega)_6 \right\}, \]
\[ V_0 := \left\{ V \in H^1(\Omega) : v = 0, \text{ on } (\partial \Omega)_1, (\partial \Omega)_2, (\partial \Omega)_4, (\partial \Omega)_5, \text{ and } (\partial \Omega)_6 \right\}. \]

At each nonlinear step, we solve the following two decoupled linearized problems.

The first one: find \( W^{n+1} \in Q_D \), for all \( \tilde{W} \in Q_0 \), such that

\[
\begin{align*}
(\nabla W^{n+1}, \nabla \tilde{W})_{CBL} + \epsilon^{-1.5} (\nabla W^{n+1}, \nabla \tilde{W})_{CGC} \\
- \left( D^{-1}_g \cdot u^n W^{n+1}, \nabla \tilde{W} \right)_{CGC} + \int_{(\partial \Omega)_3} D^{-1}_g \cdot u^n \cdot W^{n+1} \tilde{W} ds \\
= (\gamma u^n C^n, \nabla \tilde{W})_{CBL} + \int_{(\partial \Omega)_6} I_{2F} \tilde{W} ds.
\end{align*}
\]  

(2.86)

The notations \((\cdot, \cdot)_{CGC}\) and \((\cdot, \cdot)_{CBL}\) imply that the \(L^2\)-inner product in the cathode gas channel (CGC) and the cathode backing layer (CBL) respectively.

The second one: find \( u \in V_D \) and \( p \in L^2(\Omega) \), for all \( v \in V_0 \) and \( q \in L^2(\Omega) \), such that

\[
\begin{align*}
\left\{ 
\begin{array}{l}
(\mu^{n+1} \nabla u^{n+1}, \nabla v) + \left( \frac{p^{n+1}}{\varepsilon^2} u^n \cdot \nabla u^{n+1}, v \right) - (p^{n+1}, \nabla \cdot v) + \left( \frac{\mu^{n+1}}{\kappa} u^{n+1}, v \right) = 0, \\
- (\nabla \cdot u^{n+1}, q) = \left( \frac{\nabla p^{n+1}}{\rho^{n+1}}, u^n, q \right).
\end{array}
\right.
\end{align*}
\]  

(2.87)
Finite element discretization. We use the finite element method to discretize the weak formulations (2.86) and (2.87). For the water concentration equation (2.86), we employ the continuous piecewise linear finite element method: for all $\tilde{W} \in \tilde{W}_h \subset Q_0$, find $W_h \in W_h \subset Q_D$, such that

\[
\begin{align*}
(\nabla W_{n+1}^h, \nabla \tilde{W})_{CBL} &+ \epsilon^{-1.5} (\nabla W_{n+1}^h, \nabla \tilde{W})_{CGC} \\
- (D^{-1}_{g,eff} u_{n}^W W_{n+1}^h, \nabla \tilde{W})_{CGC} &+ \int_{(\partial \Omega)_3} D^{-1}_{g,eff} u_{n}^\cdot \n W_{n+1}^h \tilde{W} ds \\
= & (\gamma u_{n}^C, \nabla \tilde{W})_{CBL} + \int_{(\partial \Omega)_6} \frac{I}{2F} \tilde{W} ds.
\end{align*}
\] (2.88)

For the flow equation, we use the $P2-P1$ Taylor-Hood finite element method, which satisfies the Babuska-Brezzi (BB) inf-sup discrete stability condition. For all $v \in \tilde{V}_h \subset V_0$ and $q \in L_h \in L^2$, find $u_{n+1}^h \in V_h \subset V_D$ and $p_{n+1}^h \in L_h \subset L^2$, $(n = 0, 1, 2, \cdots)$, such that

\[
\begin{align*}
&\left\{ \begin{array}{l}
(\mu(C_{n+1}^h) \nabla u_{n+1}^h, \nabla v) + \left( \frac{\rho(C_{n+1}^h)}{\varepsilon^2} u_{n}^\cdot \nabla u_{n+1}^h, v \right) \\
-(p_{n+1}^h, \nabla \cdot v) + \left( \frac{\mu(C_{n+1}^h)}{K} u_{n+1}^h, v \right) \\
+ \left( \mathcal{L}(u_{n+1}^h, p_{n+1}^h; C_{n+1}^h, u_{n}^h), \tau(h) \mathcal{L}(v, q; C_{n+1}^h, u_{n}^h) \right) = 0, \\
-(\nabla \cdot u_{n+1}^h, q) = \left( \frac{\nabla \rho(C_{n+1}^h)}{\rho(C_{n+1}^h)} \cdot u_{n}^h, q \right),
\end{array} \right.
\end{align*}
\] (2.89)

where the last term on the left hand side of the first equation in (2.89) is a stabilizing term derived from Galerkin/least-squares scheme in terms of $\mathcal{L}$, a linear momentum operator defined as $\mathcal{L}(u, p; C_{n+1}^h, u_{n}^h) = -\nabla \cdot \left( \mu(C_{n+1}^h) \nabla u \right) + \frac{\rho(C_{n+1}^h)}{\varepsilon^2} u_{n}^\cdot \nabla u + \nabla p + \frac{\mu(C_{n+1}^h)}{K} u$.

For the choices of the two stabilization parameters, see [39, 88].
Finally, we state the nonlinear iterative procedure of solving the coupled problem (2.65) and (2.66) as follows:

**Algorithm 3.2.** For $n = 0, 1, 2, \cdots$, and given initial guesses $C^n_h$ and $u^n_h$:

1. Given $C^n_h$, solve the equation (2.88) for $W^{n+1}_h$.

2. Given $W^{n+1}_h$, calculate $C^{n+1}_h$ in terms of the inverse Kirchhoff transformation (Algorithm 3.1).

3. Given $C^{n+1}_h$ and $u^n_h$, solve the momentum equation (2.89) for $(u^{n+1}_h, p^{n+1}_h)$ and update $u^{n+1}_h \leftarrow (1 - \omega)u^n_h + \omega u^{n+1}_h$ with a relaxation parameter $\omega$.

4. Determine if both of the following two stopping criteria hold:

$$\frac{\|W^{n+1}_h - W^n_h\|_{L^2(\Omega)}}{\|W^n_h\|_{L^2(\Omega)}} < \text{tolerance},$$

and

$$\frac{\|u^{n+1}_h - u^n_h\|_{L^2(\Omega)} + \|p^{n+1}_h - p^n_h\|_{L^2(\Omega)}}{\|u^n_h\|_{L^2(\Omega)} + \|p^n_h\|_{L^2(\Omega)}} < \text{tolerance},$$

which are the relative errors in the two successive iteration steps. If yes, then stop. Otherwise, $n \leftarrow n + 1$ and go back to the first step.

**Numerical results.** The numerical method developed in this section is for the dry gas channel case, in which the water concentration both in the CGC and at the CGC/CBL interface is lower than the saturation value $C_{g, \text{sat}}$. There are three important operating parameters to determine the gas/liquid phase characteristics of the cathode side of the
fuel cell in our model. Those are the transfer current density $I$, inlet velocity $u_{\text{in}}$, and the inlet water concentration $C_{\text{in}}$. Incorporated as a boundary flux term, the transfer current density is directly proportional to the generated water concentration by Faraday’s Law. Thus, the higher amount of transfer current density is generated, and the higher amount of water is specified as the boundary flux condition (2.75). In the CGC, the water is transported by the flow field. So, higher inlet velocity $u_{\text{in}}$ will render the water removal faster, and a lower inlet concentration $C_{\text{in}}$ will make the CGC dryer.

As for the triangulation of the domain, we first divide the domain into 20 intervals along the $x$-direction, 10 intervals along the $y$-direction of the CGC, and 10 intervals along the $y$-direction of the CBL. Thus we get 400 rectangles in the domain. In each rectangle, by connecting the positive slope diagonals, we get 800 triangles.

In Algorithm 3.2, we give initial guesses for the velocity and concentration as follows:

$$
(u^0_h)_x = \begin{cases} 
  u_{\text{in}} \frac{4y(\delta CH - y)}{\delta CH^2}, & 0 \leq y \leq \delta CH, \\
  0, & \text{others},
\end{cases} 
$$

$$
(u^0_h)_y = 0, 
$$

$$
C^0_h = C_{\text{in}}. 
$$

The tolerance of the stopping criteria in Algorithm 3.2, is $10^{-10}$.

**Case 1:** $C_{\text{in}} = 12 \text{mol/m}^3, u_{\text{in}} = 1 \text{m/s, } I_1 = 1.2 \text{Acm}^{-2}, \text{ and } I_2 = 1.6 \text{Acm}^{-2}$

In this case, the average current density is $1.4 \text{Acm}^{-2}$. Fig. 2.12 demonstrates the convergence history of both of the water equation and the momentum equation. The relative consecutive errors, (2.90) and (2.91), in Algorithm 3.2 drop to $10^{-10}$ by 12 and 16 iterations for the water equation and the momentum equation respectively. Since the
velocity field studied in the present work is relatively simple and the initial guess is quite close to the true solution, we could get the nonlinear iteration converges 16 steps with a simple Picard iteration. For more complicated situations such that the computational domain contains a fuel cell with a serpentine multiple channel [46, 36, 51], we need Newton’s method with globalization techniques [75] to make the convergence faster. Our main result in this work is the fast convergence of water equation, which has the strongly discontinuous nonlinear diffusivity (2.54) arising from the single-phase transport and the two-phase capillary-diffusion transport phenomena in the porous media.

We next discuss the numerical results of the solutions of Algorithm 3.2, shown in Figs. 2.13 – 2.17. In these figures, we draw a solid blue line to denote the CBL/CGC interface.

As shown in Fig. 2.13, there is a big difference in the magnitude of the velocity between the porous CBL and CGC. In fact, the diffusion is dominant in the porous CBL.
Fig. 2.13. Horizontal two-phase mixture velocity in the case of $C_{\text{in}} = 12 \text{mol/m}^3$, $u_{\text{in}} = 1 \text{m/s}$, $I_1 = 1.2 \text{Acm}^{-2}$, and $I_2 = 1.6 \text{Acm}^{-2}$.

The flow field in the CGC is fully developed in view of the large aspect ratio (equal to 25).

As air that contains both water vapor and oxygen is injected into the CGC inlet by the flow field, oxygen is transported through the CGC by convection and diffusion, and toward the CBL mainly by diffusion. Then oxygen reaches the reaction site of the catalyst layer. As a by-product of the chemical reaction, water is generated and is incorporated as a boundary flux term in our model. More water will appear at the top wall (CCL/CBL interface) near the channel outlet as the current density becomes bigger along the channel direction. Thus Fig. 2.14 shows more water condensing into the liquid phase at the top wall near the channel outlet than inlet. From Fig. 2.14, we can see that the evaporation front stays entirely in the CBL; it does not reach the CBL/CGC interface. This indicates that it is a dry gas channel case.

Fig 2.15 demonstrates the water vapor concentration distribution in the CBL and CGC. As the air is carried down the channel by the flow field, water vapor is continuously
added from the CBL, leading to an increased water vapor concentration profile. A two-phase zone in the CBL is shown in Fig. 2.15 where the molar concentration is the saturated value 16. Also we can see that the two-phase zone appears within the CBL.

Fig 2.16 displays the liquid water saturation distribution. Liquid water is seen in the upper-right corner of the CBL and coexists with the saturated water vapor. The largest liquid amount computed is around 7.3%.

Finally, Fig. 2.17 shows the distribution of the new variable $W$. As expected, the new variable is smooth in the domain. However, due to the strongly discontinuous diffusivity $\Gamma(C)$, the molar concentration variable $C$, computed from the inverse Kirchhoff transformation, has a huge gradient at the single- and two-phase zone interface as shown in Fig. 2.14.

**Case 2:** $C_{in} = 12 \text{mol/m}^3$, $u_{in} = 1 \text{m/s}$, $I_1 = 1.0 \text{Acm}^{-2}$, and $I_2 = 1.4 \text{Acm}^{-2}$

In this case, we reduce the average current density to 1.2 Acm$^{-2}$. Fig. 2.18 displays the distribution of water concentration $C$ and the new variable $W$. As expected, less amount of liquid water appears in the CBL than in Case 1. The maximum liquid
water saturation predicted is about 6.1%. The iteration converges in 12 and 16 steps for the water equation and flow equation under the stopping criteria.

**Conclusions.** The main difficulty in the simulation of the steady-state two-phase mixture flow and transport in the cathode of the polymer electrolyte fuel cell is oscillating nonlinear iterations caused by the discontinuous degenerate nonlinear diffusion-coefficient. To overcome this difficulty, we introduce the Kirchhoff transformation and reformulate the water conservation equation in terms of the new variable. The ”bad” nonlinearity is hidden inside this transformation. Meanwhile, we develop an efficient algorithm to compute the inverse transformation needed to obtain the original variable in terms of the new variable. Our method demonstrates fast convergence toward solutions.

Procedures developed in this section are valid only for the dry CGC case, where the new variable $W$ after the Kirchhoff transformation are continuous across the CBL/CGC interface. In the next section, we will discuss the wetted CGC case: specifically, after the Kirchhoff transformation, the new variable $W$ is discontinuous across the interface.
2.4.2 Nonlinear Dirichlet-Neumann domain decomposition method

We denote the Kirchhoff transformations (2.76) and (2.77) in the previous section by $\kappa_1$ and $\kappa_2$ as,

$$W_1(C) = \kappa_1(C) := \int_C \Gamma(r)dr, \text{ in CBL,}$$

$$W_2(C) = \kappa_2(C) := \int_C D_{g,eff} dr = D_{g,eff} C, \text{ in CGC.}$$

Let $\Sigma$ denote the interface between the CBL and CGC. Then the interface boundary conditions are the continuity of the concentration and the normal flux, on $\Sigma$, i.e.,

$$\kappa_1^{-1}(W_1) = \kappa_2^{-1}(W_2),$$

$$(-\nabla W_1 + \gamma u C_1) \cdot n_1 = -\left(-\epsilon^{-1.5} \nabla W_2 + D_{g,eff}^{-1} u W_2\right) \cdot n_2.$$  

Here, $W_1$ and $C_1$ denote variables in the domain CBL; $W_2$ and $C_2$ denote variables in the domain CGC; $n_1$ and $n_2$ denote the unit normal vectors at the CBL/CGC interface toward CBL and CGC respectively.
In the previous section, we discussed the dry CGC case, in which the variables $C$ and $W$ are all continuous across the interface. In practical applications, it is possible that the liquid water may appear at the interface. This means $\Gamma$ is no longer equal to $D_{g,eff}$ at the interface. As a consequence, the continuity of concentration $C$ at the interface (2.95) implies the discontinuity of $W$ across the interface.

The reformulation of the equation (2.65) in terms of the new variable with the interface boundary conditions (2.95) and (2.96) reads as follows:

$$
\begin{align*}
-\Delta W_1 &= -\nabla \cdot (\gamma u C_1) \quad \text{in CBL}, \\
-\epsilon^{-1.5} \Delta W_2 + \nabla \cdot \left( D_{g,eff}^{-1} u W_2 \right) &= 0 \quad \text{in CGC}, \\
W_2 &= \int_0^{C_{in}} D_{g,eff} dr \quad \text{on } (\partial \Omega)_1, \\
(-\nabla W_1 + \gamma u C_1) \cdot n &= -\frac{I^2}{2F} \quad \text{on } (\partial \Omega)_6, \\
\nabla W_1 \cdot n &= \nabla W_2 \cdot n = 0 \quad \text{elsewhere on } \partial \Omega, \\
\kappa_1^{-1}(W_1) &= \kappa_2^{-1}(W_2) \quad \text{on } \Sigma, \\
(-\nabla W_1 + \gamma u C) \cdot n_1 &= -\left( -\epsilon^{-1.5} \nabla W_2 + D_{g,eff}^{-1} u W_2 \right) \cdot n_2 \quad \text{on } \Sigma.
\end{align*}
$$

(2.97)
Fig. 2.18. Water concentration (top) and new variable $W$ (bottom) in the case of $C_{in} = 12\text{mol/m}^3$, $u_{in} = 1\text{m/s}$, $I_1 = 1.0\text{Acm}^{-2}$, and $I_2 = 1.4\text{Acm}^{-2}$.

**Nonlinear alternating Dirichlet-Neumann iteration.** Considering the possible discontinuity of $W$ at the interface $\Sigma$, we reformulate (2.97) into two subproblems as follows:

- Problem P1: Dirichlet interface boundary value subproblem.

In subdomain $\Omega_1$ (CBL), for given $W_2$ at the interface $\Sigma$, we have the following well-posed elliptic boundary value problem in terms of the Kirchhoff transformation $\kappa_1$ in (2.93) and $\kappa_2$ in (2.94):

$$
\begin{align*}
(P1) \quad \begin{cases}
-\Delta W_1 &= -\nabla \cdot (\gamma u C_1) \quad \text{in } \Omega_1, \\
W_1 &= \kappa_1 \left( \kappa_2^{-1}(W_2) \right) \quad \text{on } \Sigma, \\
(-\nabla W_1 + \gamma u C_1) \cdot n &= -\frac{I}{2F} \quad \text{on } (\partial \Omega)_6, \\
\nabla W_1 \cdot n &= 0 \quad \text{on } (\partial \Omega)_2, (\partial \Omega)_4.
\end{cases}
\end{align*}
$$

(2.98)
• Problem P2: Neumann interface boundary value subproblem.

In subdomain $\Omega_2$ (CGC), given $W_1$ at the interface $\Sigma$, we have another well-posed elliptic boundary value problem:

\[
\begin{cases}
-\epsilon^{-1.5} \Delta W_2 + \nabla \cdot \left( D_{g,eff}^{-1} u W_2 \right) = 0 \quad \text{in } \Omega_2, \\
\left( -\epsilon^{-1.5} \nabla W_2 + D_{g,eff}^{-1} u W_2 \right) \cdot n_2 = 0 \quad \text{on } \Sigma, \\
W_2 = \int_0^{C_{in}} D_{g,eff} dr \quad \text{on } (\partial \Omega)_1, \\
\nabla W_2 \cdot n = 0 \quad \text{on } (\partial \Omega)_3, (\partial \Omega)_5.
\end{cases}
\]

(P2) \hspace{1cm} (2.99)

To formulate the above Dirichlet-Neumann alternating iteration in terms of weak formulations, we first introduce the following Sobolev spaces: $V_1 := H^1(\Omega_1)$, $V_1^0 := \{ v_1 \in V_1 | v_1|_{\Sigma} = 0 \}$, $V_2 := \{ v_2 \in H^1(\Omega_2) | v_2|_{(\partial \Omega)_1} = \int_0^{C_{in}} D_{g,eff} dr \}$, $V_2^0 := \{ v_2 \in H^1(\Omega_2) | v_2|_{(\partial \Omega)_1} = 0 \}$, and $\Lambda := L^2(\Sigma)$. Then the Dirichlet-Neumann iteration scheme for (2.97) is as follows: given $\lambda_2^0 \in \Lambda$, for $k = 0, 1, 2, \cdots$, solve the following weak formulation for $W_1^{k+1} \in V_1$:

\[
\begin{cases}
(\nabla W_1^{k+1}, \nabla v_1) = (\gamma u C_1^{k}, \nabla v_1) + \int_{(\partial \Omega)_6} \frac{L}{2T} v_1 ds, \quad \forall v_1 \in V_1^0, \\
W_1^{k+1} = \kappa_1 \left( \kappa_2^{-1}(\lambda_2^k) \right), \quad \text{on } \Sigma.
\end{cases}
\]

\hspace{1cm} (2.100)
Based on the above equation, solve the following weak formulation for \(W_2^{k+1} \in V_2\):

\[
\begin{align*}
\epsilon^{-1.5}(\nabla W_2^{k+1}, \nabla v_2) - \left(D^{-1}_{g,eff} u W_2^{k+1}, \nabla v_2\right) \\
+ \int_{(\partial \Omega)_3} D^{-1}_{g,eff} u \cdot n_2 W_2^{k+1} v_2 ds
\end{align*}
\]

\[
= - \int_\Sigma \left(\nabla W_1^{k+1} - \gamma u \kappa^{-1}_1 (W_1^{k+1})\right) \cdot n_1 v_2 ds, \quad \forall v_2 \in V_2^0.
\]  

(2.101)

We now give the nonlinear alternating Dirichlet-Neumann iteration scheme as follows:

**Algorithm 3.3.** For \(k = 0, 1, 2, \cdots\), and given initial guess \(C_1^0\), let \(\lambda_2^0 = W_1(C_1^0)|_{\Sigma}\).

1. With given \(\lambda_2^k\) and \(C_1^k\), solve (2.100) for \(W_1^{k+1}\).

2. With given \(W_1^{k+1}\), solve (2.101) for \(W_2^{k+1}\).

3. Update \(\lambda_2^{k+1}\) from \(W_2^{k+1}\) and \(\lambda_2^k\) with some damping parameter \(\theta\).

\[
\lambda_2^{k+1} := \theta W_2^{k+1} + (1 - \theta) \lambda_2^k.
\]  

(2.102)

4. Determine if the following stopping criteria hold:

\[
\|\lambda_2^{k+1} - \lambda_2^k\|_{L^2(\Sigma)} / \|\lambda_2^k\|_{L^2(\Sigma)} < \text{tolerance},
\]

\[
|W_1^{k+1} - W_1^k|_{L^2(\Omega_1)} / |W_1^k|_{L^2(\Omega_1)} < \text{tolerance}.
\]  

(2.103)

If yes, then stop. Otherwise, compute \(C_1^{k+1}\) from \(W_1^{k+1}\) in terms of the inverse Kirchhoff transformation (Algorithm 3.1), and then go back to step 1 and \(k \leftarrow k+1\).
In the above algorithm, we need the second stopping criterion in (2.103) since the sub-
problem \((P1)\) itself is nonlinear. The convergence of the above alternating Dirichlet-
Neumann iteration method for the nonlinear diffusion equation (without convection
term), in the continuous level, is proved in [12]. For the general convection diffusion
equation, the question of the convergence is still open. Numerical examples later in this
section shows that the method converges. Also, we will investigate how the convergence
of the method depends on the mesh size.

**Linearizations and discretizations.** For the momentum and continuity equations,
we use the same linearization (2.87) and discretization (2.89) methods as in Section
2.4.1. After we get the velocity field \(u_h^{n+1}\), we use the continuous piecewise linear finite
element method to solve the problem (2.100). Given \(\lambda_{2,h}^0 \in \Lambda\), for \(k = 0, 1, 2, \cdots\), find
\(W_{1,h}^{k+1} \in V_{1,h} \subset V_1\), for all \(v_1 \in V_{1,h}^0 \subset V_1^0\), such that

\[
\begin{cases}
(\nabla W_{1,h}^{k+1}, \nabla v_1) = (\gamma u_h^{n+1} C_{1,h}^k, \nabla v_1) + \int_{\partial \Omega_0} I v_1^s, \\
W_{1,h}^{k+1} = \kappa_1 \left( \kappa_{-1} \lambda_{2,h}^k \right), \text{ on } \Sigma.
\end{cases}
\]  
(2.104)

Based on that, find \(W_{2,h}^{k+1} \in V_{2,h} \subset V_2\), for all \(v_2 \in V_{2,h}^0 \subset V_2^0\), such that

\[
\begin{align*}
\epsilon^{-1.5} (\nabla W_{2,h}^{k+1}, \nabla v_2) & - \left( D_{g,eff}^{-1} u_h^{n+1} W_{2,h}^{k+1}, \nabla v_2 \right) \\
+ \int_{\partial \Omega_3} D_{g,eff}^{-1} u_h^{n+1} \cdot n_2 W_{2,h}^{k+1} v_2 ds \\
= - \int_{\Sigma} \left( \nabla W_{1,h}^{k+1} - \gamma u_h^{n+1} \kappa_1 (W_{1,h}^{k+1}) \right) \cdot n_1 v_2 ds.
\end{align*}
\]  
(2.105)
Then, with some damping parameter $\theta \in (0, 1]$, update $\lambda_{2,h}^{k+1}$ as follows:

$$\lambda_{2,h}^{k+1} := \theta W_{2,h}^{k+1} + (1 - \theta)\lambda_{2,h}^k.$$  

Finally, we state the numerical algorithm to solve the coupled flow equation (2.66) and the concentration equation (2.65) as follows:

**Algorithm 3.4** For $n = 0, 1, 2, \cdots$, and given initial guesses $u_h^0, C_h^0$, let $\lambda_h^0 = W_1(C_h^0|_\Sigma)$.

1. Given $u_h^n$ and $C_h^n$, solve (2.89) for $(u_h^{n+1}, p_h^{n+1})$.

2. With given $\lambda_h^0 = \lambda_h^n$ and $C_h^0 = C_h^n|_{\Omega_1}$, solve the discrete version of Algorithm 3.3 for $W_h^{n+1} = (W_{1,h}^{k+1}, W_{2,h}^{k+1})$.

3. Determine if the following stopping criteria hold:

$$\frac{\|u_h^{n+1} - u_h^n\|_{L^2(\Omega)} + \|p_h^{n+1} - p_h^n\|_{L^2(\Omega)}}{\|u_h^{n+1}\|_{L^2(\Omega)} + \|p_h^{n+1}\|_{L^2(\Omega)}} < \text{tolerance},$$

$$\frac{\|W_{1,h}^{k+1} - W_{1,h}^k\|_{L^2(\Omega_1)} + \|p_h^{n+1}\|_{L^2(\Omega)}}{\|W_{1,h}^{k+1}\|_{L^2(\Omega_1)}} < \text{tolerance},$$

$$\frac{\|W_{2,h}^{k+1} - W_{2,h}^k\|_{L^2(\Omega_2)} + \|p_h^{n+1}\|_{L^2(\Omega_2)}}{\|W_{2,h}^{k+1}\|_{L^2(\Omega_2)}} < \text{tolerance},$$

which is the relative error between the two consecutive iteration steps. If yes, then stop. Otherwise, calculate $C_h^{n+1}$ from $W_h^{n+1}$ in terms of the inverse Kirchhoff transformation (Algorithm 3.1), and then go back to the step 1 and $n \leftarrow n + 1$.

**Numerical results.** The numerical methods developed in this section are for both dry and wetted gas channel cases, in which the two-phase zone may or may not reach
the CBL/CGC interface. As discussed in the previous section, we can adjust the three operating parameters (inlet concentration \(C_{\text{in}}\), inlet velocity \(u_{\text{in}}\), and current densities \(I_1\) and \(I_2\)) to produce both cases. In our numerical examples, the first two are for wetted gas channel cases, and the third is a dry gas channel case. We use the same triangulation and initial guess (2.92) as in Section 2.4.1. The stopping criteria (2.103) and (2.107) in Algorithm 3.3 and 3.4 are \(10^{-8}\) and \(10^{-10}\) respectively.

**Case 1:** \(C_{\text{in}} = 14 \text{mol/m}^3\), \(u_{\text{in}} = 1 \text{m/s}\), \(I_1 = 1.2 Acm^{-2}\), and \(I_2 = 1.6 Acm^{-2}\)

![Convergence history of FEM with Kirchhoff transformation and alternating Dirichlet-Neumann iteration.](image)

Compared to Case 1 in Section 2.4.1, we increase the inlet water concentration from \(12 \text{mol/m}^3\) to \(14 \text{mol/m}^3\). Fig. 2.19 demonstrates the convergence history of Algorithm 3.4. The relative error in (2.107) drops to \(10^{-10}\) by 17 iterations for the flow equation, and 14 iterations for both water equations in the CBL and the CGC. Fig. 2.20
Fig. 2.20. The inner iteration number of the alternating Dirichlet-Neumann (DN) method at each outer iteration.

demonstrates the alternating Dirichlet-Neumann iteration number during the iterative procedure of Algorithm 3.4. At the beginning of the iteration, the iteration number reaches its maximum, and then decreases to one when the iterative solution is close enough to the true solution.

Similar elucidations hold for the numerical solutions displayed in Fig. 2.21 – 2.23 as in Section 2.4.1. In particular, Fig. 2.22 displays the two-phase water concentration and water vapor distribution. Clearly, the two-phase zone reaches the CBL/CGC interface. Thus, a wetted gas channel is produced. Fig. 2.23 shows the water saturation distribution. In this case, the maximum water saturation is about 7.5%.

**Case 2:** \( C_{in} = 12 \text{mol/m}^3, \ u_{in} = 0.8 \text{m/s}, \ I_1 = 1.2 \text{A/cm}^2, \text{ and } I_2 = 1.6 \text{A/cm}^2 \)

In this case, we decrease the inlet velocity from 1m/s to 0.8m/s, and retain the same current densities and inlet velocity as in Case 1 of Section 2.4.1. Fig. 2.24 demonstrates the concentration of the two-phase mixture water and vapor. As expected, water condenses into the liquid phase and the evaporation front reaches part of the
Fig. 2.21. Horizontal two-phase mixture velocity when $C_{in} = 14\text{mol/m}^3$, $u_{in} = 1\text{m/s}$, $I_1 = 1.2\text{Acm}^{-2}$, and $I_2 = 1.6\text{Acm}^{-2}$.

CBL/CGC interface. The maximum liquid saturation is about 7.48%. Algorithm 3.4 converges within 17 iterations. At the same time, Algorithm 3.3 converges up to 8 iterations.

**Case 3:** $C_{in} = 12\text{mol/m}^3$, $u_{in} = 1\text{m/s}$, $I_1 = 1.2\text{Acm}^{-2}$, and $I_2 = 1.6\text{Acm}^{-2}$

We repeat Case 1 in Section 2.4.1, where we get the dry gas channel. In this case, we obtain the numerical solutions within 23 iteration steps in Algorithm 3.4, and up to 9 iterations in the alternating Dirichlet-Neuman iteration of Algorithm 3.3. Fig. 2.25 demonstrates the concentrations of the two-phase mixture water and water vapor. As can be seen, the two-phase zone forms in the upper-right part of the CBL and does not reach the CBL/CGC interface. Thus it is a dry gas channel case, and the maximum liquid water saturation is around 7.32% at the upper-right corner of the CBL.

**Mesh dependence of the nonlinear alternating Dirichlet-Neumann algorithm.**

To investigate the mesh dependence of the nonlinear alternating Dirichlet-Neumann Algorithm 3.3, we fix the flow field as (2.92). In such a case, our iterative algorithm to compute the solution is essentially the Dirichlet-Neumann Algorithm 3.3, since the
Fig. 2.22. Concentrations of the two-phase mixture water (top) and water vapor (bottom) when \( C_{\text{in}} = 14\text{mol/m}^3 \), \( u_{\text{in}} = 1\text{m/s} \), \( I_1 = 1.2Acm^{-2} \), and \( I_2 = 1.6Acm^{-2} \).

Flow field is given. We perform our numerical study on Case 1 of this section. Starting from an initial \( 10 \times 10 \) (ten intervals along the \( x \)-axis and ten intervals along the \( y \)-axis) mesh, we fully refine the mesh to get \( 20 \times 20 \), \( 40 \times 40 \), and \( 80 \times 80 \) meshes. Table 2.6 indicates the convergence behavior under these four meshes. As the mesh gets refined, the iteration number of Algorithm 3.3 increases a little bit in our test problem.

**Concluding remarks.** Following the previous section, we discussed the wetted gas channel case in which the new variable after the Kirchhoff transformation is discontinuous across the CBL/CGC interface. To handle this discontinuity, we introduce the nonlinear alternating Dirichlet-Neumann domain decomposition method. This method also works for the dry gas channel case in which the new variable is continuous. Numerical results demonstrate the robustness of the method.
Fig. 2.23. Liquid water saturation when $C_{\text{in}} = 14 \text{mol/m}^3$, $u_{\text{in}} = 1 \text{m/s}$, $I_1 = 1.2 \text{A/cm}^{-2}$, and $I_2 = 1.6 \text{A/cm}^{-2}$.

Fig. 2.24. Concentrations of the two-phase mixture water (top) and water vapor (bottom) when $C_{\text{in}} = 12 \text{mol/m}^3$, $u_{\text{in}} = 0.8 \text{m/s}$, $I_1 = 1.2 \text{A/cm}^2$, and $I_2 = 1.6 \text{A/cm}^2$.

Table 2.6. Mesh dependence of the nonlinear alternating Dirichlet-Neumann method

<table>
<thead>
<tr>
<th>Mesh</th>
<th>$10 \times 10$</th>
<th>$20 \times 20$</th>
<th>$40 \times 40$</th>
<th>$80 \times 80$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iteration No.</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>
Fig. 2.25. Concentrations of the two-phase mixture water (top) and water vapor (bottom) when $C_{in} = 12\text{mol/m}^3$, $u_{in} = 1\text{m/s}$, $I_1 = 1.2\text{Acm}^{-2}$, and $I_2 = 1.6\text{Acm}^{-2}$. 
Chapter 3

THE COUPLING BETWEEN POROUS MEDIA FLOW AND VISCOUS FLOW IN GAS CHANNEL

3.1 Introduction

In fuel cells, we use a single set of Navier-Stokes/Brinkman equations with Darcy’s drag [19, 20] as a source term exerted from a porous media to model the coupling between multiphase flow in the porous media and single phase viscous flow in the gas channel:

\[-\nabla \cdot (\mu \nabla \mathbf{u}) + \frac{1}{\epsilon^2} \nabla \cdot (\rho \mathbf{u} \mathbf{u}) + \nabla p + \frac{\mu}{K} \mathbf{u} = 0.\] (3.1)

Here, \(\epsilon\) is the porosity; \(\mu\) is the dynamic viscosity; and \(\rho\) is the density. As the permeability \(K\) approaches infinity, the equation reduces to steady-state Navier-Stokes equations. On the other hand, for \(K\) small (approaching 0), \(\nabla p\) and \(\frac{\mu}{K} \mathbf{u}\) dominate, compared to other terms in (3.1). In this case, the equation is close to Darcy’s law.

This is a short description of the single-domain approach that models multidomain problems using a single set of equations with highly discontinuous coefficients. In the computational fuel cell dynamics (CFCD) community, the single-domain approach is widely used [109, 90, 102, 33, 108, 107, 28, 27, 89, 48, 111, 55, 43, 56, 57, 42, 98, 99, 74], because it is reliable and simple to implement, especially for the full fuel cell simulation containing nine different subdomains (see Fig. 1.1) as discussed in Chapter 1.
Since all the species and the thermal energy in fuel cells are advected by the flow field, it is important to get accurate and stable approximations to the flow fields with respect to the highly discontinuous coefficients and their jumps, throughout the multiphysics simulations.

This chapter is devoted to exploring the linear case of the equation (3.1) by neglecting the nonlinear convective term $\frac{1}{\varepsilon^2} \nabla \cdot (\rho \mathbf{u} \mathbf{u})$. This simplified model is governed by the Darcy-Stokes-Brinkman equation:

$$-\nabla \cdot (\mu \nabla \mathbf{u}) + \nabla p + \frac{\mu}{K} \mathbf{u} = 0. \quad (3.2)$$

We present three methods to construct uniformly stable finite element approximations for this equation. In the first method we consider the existing Stokes elements. Our analysis shows that any stable Stokes element is also uniformly stable with respect to the jump coefficients of the Darcy-Stokes-Brinkman equation, and this happens if and only if the discretely divergence-free velocity is also divergence-free almost everywhere. The second method focuses on the construction of uniformly stable elements from some well-known $H(\text{div})$-conforming elements. We also design and analyze these types of elements in a unified way. Another method that we consider is based on modifying the weak formulation of the Darcy-Stokes-Brinkman equations with a stabilization term. We show that many of the well-known stable Stokes elements are uniformly stable with respect to the coefficients and their jumps under this new formulation.

Among these three methods, we found that the modified $H(\text{div})$-conforming elements form a discrete de Rham complex with extra smoothness. Furthermore, we show
that this sequence is exact, resulting in natural commutative relationships with the continuous de Rham complex. We present such complex because it is useful in the design of efficient iterative solvers for the Darcy-Stokes-Brinkman models, and their analyses.

In the next section, we begin by reviewing some of the properties of Darcy-Stokes-Brinkman models.

3.2 Darcy-Stokes-Brinkman equations

The following PDE system on a bounded, connected, and polygonal domain, \( \Omega \subset \mathbb{R}^d (d = 2, 3) \), is a formal way to write the Darcy-Stokes-Brinkman model [20, 19, 37, 2]: (Fig. 3.1 is an example of the domain).

\[
- \nabla \cdot (\mu(x) \nabla u) + \alpha(x) u + \nabla p = f \quad \text{in} \quad \Omega, \\
\nabla \cdot u = g \quad \text{in} \quad \Omega, \\
u = 0 \quad \text{on} \quad \partial \Omega, \\
\text{(3.3)}
\]

where the unknowns are the velocity \( u \) and the pressure \( p \). The viscosity coefficient \( \mu(x) \) and the coefficient \( \alpha(x) \) are assumed to be piecewise constants:

\[
\mu(x) = \mu_i > 0, \quad \alpha(x) = \alpha_i \geq 0, \quad x \in \Omega_i. \\
(3.4)
\]

The zeroth-order term coefficient \( \alpha \) is a function of the permeability \( K \) and viscosity \( \mu \), which has the form:

\[
\alpha = \frac{\mu}{K}. \\
(3.5)
\]
The sub-domains \( \{ \Omega_i \}_{i=1}^m \) are assumed to be bounded connected polygonal domains such that \( \Omega_i \cap \Omega_j = \emptyset \) for \( i \neq j \) and \( \overline{\Omega} = \bigcup_{i=1}^m \overline{\Omega_i} \). By \( \Gamma_{ij} \), we denote the interface between two adjacent sub-domains \( \Omega_i \) and \( \Omega_j \), namely, \( \Gamma_{ij} = \overline{\Omega_i} \cap \overline{\Omega_j} \). Other notation that we use are \( \sigma(u,p) = \mu(x)\nabla u - pI \), which is a stress tensor; \( \mathbf{n} \), which is the unit normal vector to \( \Gamma_{ij} \); \( [u]|_{\Gamma_{ij}} = u|_{\partial \Omega_i \cap \Gamma_{ij}} - u|_{\partial \Omega_j \cap \Gamma_{ij}} \); \( [\sigma(u,p)n]|_{\Gamma_{ij}} = \sigma(u,p)n|_{\partial \Omega_i \cap \Gamma_{ij}} - \sigma(u,p)n|_{\partial \Omega_j \cap \Gamma_{ij}} \). For the interface boundary conditions, we have \( [\sigma(u,p)n]|_{\Gamma_{ij}} = 0 \), and \( [u]|_{\Gamma_{ij}} = 0 \). In addition, the source term \( g \) is assumed to satisfy the condition:

\[
\int_{\Omega} gd\mathbf{x} = 0, \tag{3.6}
\]

which guarantees the existence and uniqueness of the solution to (3.3).

---

**Porous medium region**

(Small viscosity)

(Large zero order term)

\( \Omega_1 \)

---

**Fluid region**

(Large viscosity)

(Small zero order term)

\( \Omega_2 \)

---

Fig. 3.1. Domain.

When \( \alpha_i \) is big and \( \mu_i \) is small in some sub-domains, the equation is close to the Darcy equation; in some sub-domains where \( \mu_i \) is big and \( \alpha_i \) is small together with
\( g = 0 \), the equation is close to the Stokes equation. This Darcy-Stokes equation is called the Brinkman equation [69]. It models porous media flow coupled with open fluid flow in a single form of PDE. Compared to other types of multi-domain Darcy-Stokes models that couple through three interface conditions [11, 81, 40, 26, 25, 47, 80, 79, 21], in such models, the internal interface conditions are derived in a straightforward fashion—the velocity and normal component of stress tensor are continuous.

### 3.3 Construction of uniformly stable finite element methods

The work presented in this section is based on the collaborative work in [104].

The goal of this section is to study finite element methods that approximate the solutions uniformly with respect to the highly discontinuous coefficients, \( \mu(x) \) and \( \alpha(x) \), and their jumps. We present three methods.

In the first method, we show that any stable Stokes element (such that it satisfies \((H1)\) in Section 3.3.1) leads to the uniformly stable approximation for the Darcy-Stokes-Brinkman problem if and only if the assumption \((H2)\) (in Section 3.3.1) holds. Roughly speaking, this assumption says that a discretely divergence-free velocity implies the almost everywhere divergence-free one. The element satisfying \((H2)\) is also stable for the limiting case, Darcy’s law, of the equation.

On the other hand, in the second method, we consider the construction of uniformly stable elements based on some well-known \(H(\text{div})\)-conforming elements. Under reasonable assumptions, we find that \(H(\text{div})\) stable elements are also uniformly stable for the Darcy-Stokes-Brinkman problem. In addition, we still need to add something to
the $H(\text{div})$ finite element space to approximate $H^1$ space. Based on the analysis, we construct some new uniformly stable elements for the Darcy-Stokes-Brinkman equations.

Finally, we consider a modified, but equivalent system of PDEs by adding a proper stabilization term. Brezzi, Fortin, and Marini [17] presented a stabilization technique that allows the use of continuous finite element spaces. Their technique involves a modification of the usual mixed form of elliptic equations. We employ this technique to modify our Darcy-Stokes-Brinkman models, and show that all of the stable Stokes elements are also uniformly stable with respect to the coefficients $\alpha$, $\mu$, and their jumps. We point here that there are other stabilization approaches (see e.g., Franca and Hughes [30], Burman and Hansbo [21], and the references therein).

**Notation**

In this dissertation, $H^k(\Omega)$ denotes the Sobolev space of scalar functions on $\Omega$, whose derivatives up to order $k$ are square integrable, with the norm $\| \cdot \|_k$; $| \cdot |_k$ denoting the semi-norm derived from the partial derivatives of order equal to $k$. Furthermore, $\| \cdot \|_{k,T}$ and $| \cdot |_{k,T}$ denote respectively the norm $\| \cdot \|_k$ and the semi-norm $| \cdot |_k$ restricted to the domain $T$. The notation $L^2_0(\Omega)$ denotes the space of $L^2(\Omega)$ with the mean value of zero. The space $H^k_0(\Omega)$ denotes the closure in $H^k(\Omega)$ (w.r.t. $\| \cdot \|_k$) of the set of the infinitely differentiable functions with compact support in $\Omega$. The corresponding function spaces for vector valued functions are denoted by $H^k(\Omega)^d$ and $H^k_0(\Omega)^d$. We also need the space $H(\text{div}) := H(\text{div}, \Omega) := \{ v \in L^2(\Omega) | \text{div} v \in L^2(\Omega) \}$ and $H_0(\text{div}) := \{ v \in H(\text{div}) | v \cdot n = 0, \text{ on } \partial \Omega \}$. Here, $n$ is the outward unit normal vector on $\partial \Omega$. 
Let $\mathcal{T}_h$ be a shape-regular simplicial triangulation of the domain $\Omega$, where the edges or faces lie on the interfaces. In the simplicial triangulation, the mesh parameter $h$ of $\mathcal{T}_h$ is given by $h = \max_{T \in \mathcal{T}_h} \{\text{diameter of } T\}$, where $T$ denotes a $d$-dimensional simplex. For a 2D mesh, let $\mathcal{E}(T)$ denote the set of all edges in $T$; for a 3D mesh, let $\mathcal{F}(T)$ denote the set of all faces in $T$. We also need $P^d_k(\Omega)$, the space of polynomial of $d$-variables of degree $\leq k$ on $\Omega$. In the special case of $d = 1$, we will omit the superscript $d$.

Following Xu [105], we use $X \lesssim (\gtrsim) Y$ to denote that there exists a constant $C$ independent of the mesh size $h$, the viscosity coefficient $\mu$, and the zero-order term coefficient $\alpha$, such that $X \leq (\geq) CY$.

**Continuous Problem**

We define the velocity space $V$ and pressure spaces $W$ as

$$V := H^1_0(\Omega)^d \quad \text{and} \quad W := L^2_0(\Omega),$$

with $V'$ and $W'$ as the dual spaces of $V$ and $W$ respectively. The variational formulation reads as follows: given $f \in V'$ and $g \in W'$, find $\{u, p\} \in V \times W$ such that

$$\begin{aligned}
\begin{cases}
  a(u, v) - (p, \text{div}v) &= < f, v > \quad \forall v \in V, \\
  (\text{div}u, q) &= < g, q > \quad \forall q \in W.
\end{cases}
\end{aligned}$$

Here $a(u, v) = (\mu(x)\nabla u, \nabla v) + (\alpha(x)u, v)$, and $(\cdot, \cdot)$ denotes the $L^2$ inner product.
In the limiting case of \( \mu(x) \equiv 0 \), the problem (3.7) reduces to a mixed form of elliptic equation. Then, the space \( H_0^1(\Omega)^d \) is no longer a proper function space for \( u \), and it is replaced by \( H_0(\text{div}) \). We thus introduce the following parameter-dependent norms:

\[
\|u\|^2 := a(u, u) + M(\text{div}u, \text{div}u), \quad u \in V, \tag{3.8}
\]

and

\[
\|p\|^2 = M^{-1}\|p\|^2_0. \tag{3.9}
\]

Here

\[ M = \max(\mu, \alpha, 1). \tag{3.10} \]

Then the norms in \( V' \) and \( W' \) are defined by

\[
\|f\|_{V'} := \sup_{v \in V} \frac{\langle f, v \rangle}{\|v\|} \quad \text{and} \quad \|g\|_{W'} := \sup_{q \in W} \frac{\langle g, q \rangle}{\|q\|}. \tag{3.11}
\]

We now show that the uniform stability conditions are straightforward. By definition and the Cauchy-Schwarz inequality, we clearly have

\[
a(u, v) \leq \|u\|\|v\|, \quad \forall u, v \in V, \tag{3.12}
\]

\[
a(v, v) = \|v\|^2, \quad \forall v \in Z, \tag{3.13}
\]

where

\[
Z = \{v \in V : \text{div}v = 0\}. \tag{3.14}
\]
Note that since \( \|\text{div} \mathbf{v}\| \leq M^{-1/2} \|\mathbf{v}\| \), the continuity condition follows immediately.

\[
(\text{div} \mathbf{v}, q) \leq \|\mathbf{v}\| \|q\|. \tag{3.15}
\]

Next, it is well-known that the following inf-sup condition holds [31],

\[
\sup_{\mathbf{v} \in V} \frac{(\text{div} \mathbf{v}, q)}{\|\mathbf{v}\|_1} \gtrsim \|q\|_0. \tag{3.16}
\]

Since \( \|\mathbf{v}\| \lesssim M^{1/2} \|\mathbf{v}\|_1 \), we have the uniform inf-sup condition,

\[
\sup_{\mathbf{v} \in V} \frac{(\text{div} \mathbf{v}, q)}{\|\mathbf{v}\|} \gtrsim \|q\|. \tag{3.17}
\]

Following Brezzi [13, 16], we conclude that the problem (3.7) has a unique solution and the following estimate holds uniformly with respect to \( \mu \) and \( \alpha \):

\[
\|\mathbf{u}\| + \|p\| \lesssim \|f\|_{V'} + \|g\|_{W'}. \tag{3.18}
\]

**Remark 2.1.** Let us now take a closer look at the norms defined in (3.11) when \( f, g \in L^2 \). Obviously, we always have \( \|g\|_{W'} = M\|g\|_0 \). For \( \|f\|_{V'} \), if \( \alpha \geq \alpha_0 > 0 \), we can easily see that \( \|f\|_{V'} \leq \alpha_0^{-1/2} \|f\|_0 \), since \( \|\mathbf{v}\|_0 \leq \alpha_0^{-1/2} \|\mathbf{v}\| \). If \( \alpha \equiv 0 \), Olshanskii and Reusken [71] proved that \( (\mu \mathbf{v}, v) \lesssim (\mu \nabla \mathbf{v}, \nabla v) \) if \( k = 2 \) and one of the following assumptions is satisfied: \( \text{meas}(\partial \Omega_i \cap \partial \Omega) > 0 \) for \( i = 1, 2 \), or \( \text{meas}(\partial \Omega_1 \cap \partial \Omega) > 0 \) and \( \mu_2 \lesssim \mu_1 \).

As a result, \( \|f\|_{V'} \lesssim \|\mu^{-1/2} f\|_0 \). For the general case of \( k \) sub-domains, similar results also hold if one of the following assumptions is satisfied: \( \text{meas}(\partial \Omega_i \cap \partial \Omega) > 0 \) for \( i = 1, 2 \), or \( \text{meas}(\partial \Omega_1 \cap \partial \Omega) > 0 \) and \( \mu_2 \lesssim \mu_1 \).
1, 2, · · · , k, or \( \text{meas}(\partial \Omega_i \cap \partial \Omega) > 0 \) for \( i \in S_1 \) and \( \mu_j \lesssim \mu_{j_n} \) for \( j_n \in N_j \) and \( j \in S_2 \).

Here, \( N_j \) denotes the set of sub-domain indices, of the neighbors of \( j \), sharing the same \( d - 1 \) dimensional simplex. The sets \( S_1, S_2 \subseteq \{1, 2, \cdots, n\} \), \( S_1 \cup S_2 = \{1, 2, \cdots, n\} \), and \( S_1 \cap S_2 = \emptyset \).

**Discrete Problem**

For the finite element discretization of the problem of (3.7), let \( V_h \subset \) or \( \not\subset V \) and \( W_h \subset W \) denote velocity and pressure finite element spaces respectively. The discrete weak formulation reads as follows. Find \( \{u_h, p_h\} \in V_h \times W_h \) such that

\[
\begin{align*}
& a_h(u_h, v_h) - (p_h, \nabla v_h) = \langle f, v_h \rangle \quad \forall v_h \in V_h, \\
& (\nabla u_h, q_h) = \langle g, q_h \rangle \quad \forall q_h \in W_h.
\end{align*}
\]

(3.19)

Let \((\cdot, \cdot)_T\) denote the \( L^2 \) inner product on \( T \), and define \( a_h(u_h, v_h) \) by

\[
a_h(u_h, v_h) = \sum_{T \in T_h} ((\mu(x) \nabla u_h, \nabla v_h)_T + (\alpha(x) u_h, v_h)_T).
\]

(3.20)

**Remark 2.2.** If the space \( V_h \not\subset H(\text{div}) \), throughout this section, we view \( \text{div} v_h \) as \( \text{div}_h v_h \), \( v_h \in V_h \). The operator \( \text{div}_h \) denotes the piecewise divergence operator, i.e., the divergence is taken element by element: \( (\text{div}_h v_h)|_T := \text{div} (v_h|_T) \).

Similar to the continuous problem, the discrete norm in \( V_h \) is defined as follows:

\[
\|v_h\|^2_h := a_h(v_h, v_h) + M(\nabla v_h, \nabla v_h), \quad \forall v_h \in V_h.
\]

(3.21)
The discrete norm on the pressure space is the same as the continuous one, since \( W_h \subset W \).

Denote the discretely divergence-free space \( Z_h \) as

\[
Z_h := \{ v_h \in V_h : (\text{div} v_h, q_h) = 0, \; \forall q_h \in W_h \}.
\]

(3.22)

### 3.3.1 Analysis of stable Stokes elements for Darcy-Stokes-Brinkman models

In the following, we will show the critical conditions that lead to uniformly stable finite element methods for the problem (3.3). First of all, one can expect that the elements are stable in the standard \( H^1 \) (or discrete \( H^1 \)) norm for the velocity, and \( L^2_0 \) norm for the pressure. Thus, the first assumption is the following inf-sup condition holds:

\[
(\text{H1}) \quad \sup_{v_h \in V_h} \frac{(\text{div} v_h, q_h)}{\| v_h \|_{1,h}} \gtrsim \| q_h \|_0 \quad \forall q_h \in W_h.
\]

Here, discrete \( H^1 \) norm \( \| \cdot \|_{1,h} \) is defined by

\[
\| v_h \|_{1,h}^2 := \sum_{T \in T_h} \| v_h \|_{1,T}^2, \quad \forall v_h \in V_h.
\]

When \( V_h \subset H^1_0(\Omega)^d \), the discrete norm is the same as the \( H^1 \) norm.

Our second assumption is

\[
(\text{H2}) \quad Z_h = \{ v_h \in V_h, \; \text{div} v_h = 0 \}.
\]

This assumption means that the discretely divergence-free velocity implies almost everywhere divergence-free one. If the pressure space contains the divergences of the elements of the velocity space, then the assumption (H2) follows immediately from (H2').
state this stronger assumption as

\[(H2') \quad \text{div} V_h \subseteq W_h.\]

Under the assumptions \((H1)\) and \((H2)\), we easily have uniform stability results:

\[
a_h(v_h, v_h) \geq \|v_h\|_h^2, \quad \forall v_h \in Z_h, \quad (3.23)
\]

\[
\sup_{v_h \in V_h} \frac{(\text{div} v_h, q_h)}{\|v_h\|_h} \geq \|q_h\|, \quad \forall q_h \in W_h, \quad (3.24)
\]

\[
a_h(u_h, v_h) \lesssim \|u_h\|_h \|v_h\|_h, \quad \forall u_h, v_h \in V_h, \quad (3.25)
\]

\[
(\text{div} v_h, q_h) \lesssim \|v_h\|_h \|q_h\|, \quad \forall v_h \in V_h, \quad \forall q_h \in W_h. \quad (3.26)
\]

**Theorem 3.3.1.** Any stable Stokes element (i.e., satisfying the inf-sup condition \((H1)\)) is also uniformly stable for the model problem \((3.3)\), if and only if the assumption \((H2)\) holds.

**Proof.** It is easy to see that the assumption \((H2)\) is sufficient. For the necessity of the assumption \((H2)\), we consider

\[
\sup_{u_h \in Z_h} \frac{a_h(u_h, v_h)}{\|u_h\|_h} \geq \|v_h\|_h, \quad \forall v_h \in Z_h. \quad (3.27)
\]

When \(\alpha(x)\) and \(\mu(x)\) both approach zero, in order to have the uniform inf-sup condition \((3.27)\), we must have \(\text{div} v_h = 0, \forall v_h \in Z_h\). Otherwise the left hand side of \((3.27)\) approaches zero and the right hand side of \((3.27)\) approaches \(\|\text{div} v_h\|_0\), a positive constant. This gives a contradiction. \(\square\)
For nonconforming finite element methods, multiplying the first equation (3.3) by \( v_h \in V_h \) and integrating by parts, leads to

\[
a_h(u, v_h) - \langle \text{div} v_h, p \rangle = \langle f, v_h \rangle + E_h(u, p, v_h),
\]

(3.28)

where the consistency error term is defined by

\[
E_h(u, p, v_h) = \sum_{T \in T_h} \int_{\partial T} (\mu(x) \nabla u - p I) \cdot n \cdot v_h ds = \sum_{T \in T_h} \int_{\partial T} \sigma(u, p) n \cdot v_h ds.
\]

(3.29)

We are now in a position to state the following quasi-optimal approximation property. For completeness, we give proof by following arguments similar to those presented in [13, 16, 31, 24].

**Theorem 3.3.2.** Assume that (H1) and (H2) are satisfied, and let

\[
Z_h(g) := \{ v_h \in V_h \mid \langle \text{div} v_h, q_h \rangle = \langle g, q_h \rangle, \quad \forall q_h \in W_h \}.
\]

(3.30)

Then the problem (3.19) has a unique solution \( \{ u_h, p_h \} \in V_h \times W_h \), such that

\[
\| u - u_h \|_h \lesssim \inf_{w_h \in Z_h(g)} \| u - w_h \|_h + \sup_{v_h \in Z_h} \frac{|E_h(u, p, v_h)|}{\| v_h \|_h},
\]

(3.31)

\[
\| u - u_h \|_h \lesssim \inf_{v_h \in V_h} \| u - v_h \|_h + \sup_{v_h \in Z_h} \frac{|E_h(u, p, v_h)|}{\| v_h \|_h},
\]

(3.32)

\[
\| p - p_h \| \lesssim \inf_{q_h \in W_h} \| p - q_h \| + \inf_{v_h \in V_h} \| u - v_h \|_h
\]

\[+ \sup_{v_h \in V_h} \frac{|E_h(u, p, v_h)|}{\| v_h \|_h}.\]

(3.33)
Proof. Applying Lemma I.4.1 in [31], the inf-sup condition (3.24) implies $Z_h(g)$ is not empty. Choose $u_h^0 \in Z_h(g)$. From (3.23) and (3.25), there exists a unique solution $s_h \in Z_h$, such that

$$a_h(s_h, v_h) = (f, v_h) - a_h(u_h^0, v_h), \forall v_h \in Z_h.$$ 

Let $u_h = s_h + u_h^0$. Furthermore, from Corollary I.4.1 in [31], it follows that there exists a unique $p_h$ in $W_h$ such that the pair $\{u_h, p_h\}$ is the only solution to Problem (3.19).

Clearly, for all $w_h \in Z_h(g)$, we have $u_h - w_h \in Z_h$. By assumption (H2), $\text{div}(u_h - w_h) = 0$. Thus, the following identity holds:

$$a_h(u_h - w_h, u_h - w_h) = a_h(u - w_h, u_h - w_h) + E_h(u, u_h - w_h).$$

From the coercivity condition (3.23) and continuity condition (3.25), we then get

$$\|u_h - w_h\| \lesssim \|u - w_h\| + \frac{|E_h(u, p, u_h - w_h)|}{\|u_h - w_h\|}.$$  \hspace{1cm} (3.34)

Taking the infimum of $w_h$ and using the triangle inequality, we obtain (3.31).

On the other hand, for all $v_h \in V_h$, by Lemma I.4.1 in [31], inf-sup condition (3.24) implies: there exists a unique $r_h \in Z_h^\perp$ such that $(\text{div} r_h, q_h) = (\text{div}(u - v_h), q_h)$, $\forall q_h \in W_h$, and $\|r_h\| \lesssim \|u - v_h\|$. Let $w_h = v_h + r_h$, then $w_h \in Z_h(g)$. Furthermore

$$\|u - w_h\| \leq \|u - v_h\| + \|r_h\| \lesssim \|u - v_h\|.$$  \hspace{1cm} (3.35)
(3.34), (3.35), and the triangle inequality imply (3.32).

It remains to estimate \( \|p - p_h\|_0 \). From (3.28) and (3.19), we derive that

\[
a_h(u - u_h, v_h) - (\text{div} v_h, p - p_h) = E_h(u, p, v_h), \quad \forall v_h \in V_h.
\]

Further, we get

\[
(\text{div} v_h, p_h - q_h) = a_h(u - u_h, v_h) - E_h(u, p, v_h) + (\text{div} v_h, p - q_h).
\]

By inf-sup condition (3.24),

\[
\|p_h - q_h\| \lesssim \sup_{v_h \in V_h} \frac{(\text{div} v_h, p_h - q_h)}{\|v_h\|_h}.
\]

From (3.37), continuity conditions (3.25) and (3.26), we obtain

\[
\|p_h - q_h\| \lesssim \|u - u_h\|_h + \|p - q_h\| + \frac{E_h(u, p, v_h)}{\|v_h\|_h}.
\]

Thus (3.33) follows immediately by using the triangle inequality.

**Remark 2.3.** Under the stronger assumption \((H2')\) (instead of \((H2)\)), from (3.7) and (3.19), we have that \(Q_h \text{div} u = \text{div} u_h\). Here \(Q_h : W \to W_h\) is \(L^2\)-orthogonal projection. It then follows that

\[
\|\text{div} u - \text{div} u_h\|_0 = \|(I - Q_h)\text{div} u\|_0.
\]
Example 2.1: $P^d_k - P_{k-1}$ type elements

In all these methods, we approximate the velocity by continuous piecewise polynomials or degree $\leq k$ and the pressure by the discontinuous piecewise polynomials of degree $\leq k - 1$. The resulting discretizations are all conforming in the sense that $V_h \subset V$ and $W_h \subset W$.

1. Scott and Vogelius [82] proposed a 2D family of $P^2_k - P_{k-1}$ type triangular elements for any $k \geq 4$ on a singular vertex free mesh. An internal vertex in 2D is said to be singular if edges meeting at the point fall into two straight lines.

2. Arnold and Qin [6] proposed a 2D finite element of $P^2_2 - P_1$ type on macro square meshes where each big square is subdivided into four triangles by connecting the square’s vertices to the point midway between the center of the square and its bottom edge.

3. Qin [76] proposed 2D finite elements of $P^2_k - P_{k-1}$ type, for $k = 2$ and $k = 3$, on macro triangular meshes where each big triangle is subdivided into three triangles by connecting the barycenter with three vertices.

4. Zhang [110] proposed the 3D finite elements of $P^3_k - P_{k-1}$ type, for $k \geq 3$, on macro tetrahedron meshes where each big tetrahedron is subdivided into four sub-tetrahedra by connecting the barycenter with four vertices.

For all these finite element spaces, the assumption ($H2'$) is trivially satisfied by the definition of $V_h$ and $W_h$. The inf-sup condition (assumption ($H1$)) is proved in [82],
\[ \sup_{v \in V_h} \frac{\langle \text{div} v, q \rangle}{\|v\|_1} \gtrsim \|q\|_0 \quad \forall q \in W_h. \]  

(3.40)

Thus, by Theorem 3.3.2, the quasi-optimal approximation results, (3.31), (3.32), and
(3.33) hold without the consistency error term (since these finite element methods are
conforming).

### 3.3.2 Analysis of \( H(\text{div}) \)-conforming type elements for Darcy-Stokes-Brinkman models

Another method is to construct uniformly stable elements for the Darcy-Stokes-
Brinkman equations on the basis of \( H(\text{div}) \)-conforming elements. We first consider the
following mixed formulation of a scalar elliptic problem, which can be viewed as the
limiting case of the problem (3.19): Find \( u_h \in V_h^0 \) and \( p_h \in W_h^0 \), such that

\[
\begin{aligned}
(u_h, v_h) - (p_h, \text{div} v_h) &= \langle f, v_h \rangle \quad \forall v_h \in V_h^0, \\
(\text{div} u_h, q_h) &= \langle g, q_h \rangle \quad \forall q_h \in W_h^0.
\end{aligned}
\]

(3.41)

Here, \( V_h^0 \subset V^0 \) and \( W_h^0 \subset L^2_0 \) are finite element spaces, and \( V^0 := H_0(\text{div}) \), with the
norm \( \|v\|_{H(\text{div})}^2 := (\text{div} v, \text{div} v) + (v, v), \ v \in V^0. \)
The stability conditions for this problem are

\[(v_h, v_h) \geq \|v_h\|^2_{0, h}, \quad \forall v_h \in Z_h^0, \quad (3.42)\]

\[\sup_{v_h \in V_h} \frac{(\text{div} v_h, q_h)}{\|v_h\|_{H(\text{div})}} \geq q_h \|_{0, h}, \quad \forall q_h \in W_h, \quad (3.43)\]

\[a_h(u_h, v_h) \lesssim \|u_h\|_{H(\text{div})} \|v_h\|_{H(\text{div})}, \quad u_h, v_h \in V_h^0, \quad (3.44)\]

\[(\text{div} v_h, q_h) \lesssim \|v_h\|_{H(\text{div})} q_h \|_{0, h}, \quad \forall v_h \in V_h^0, \forall q_h \in W_h^0. \quad (3.45)\]

In the lemma below, we show that any stable Stokes element satisfying (H1) and (H2) is also stable for the reduced problem (3.41).

**Lemma 3.3.3.** Suppose that a pair of finite element spaces \( \{V_h, W_h\} \) satisfy the assumption (H1) and (H2). Then the stability conditions (3.42)-(3.45) hold for \( \{V_h, W_h\} \).

**Proof.** The condition (3.42) is trivial by the assumption (H2). Under the assumption (H1), using the fact that \( \|v_h\|_{H(\text{div})} \lesssim \|v_h\|_{1, h}, \forall v_h \in V_h, \) we have (3.43) as following:

\[\sup_{v_h \in V_h} \frac{(\text{div} v_h, q_h)}{\|v_h\|_{H(\text{div})}} \geq \sup_{v_h \in V_h} \frac{(\text{div} v_h, q_h)}{\|v_h\|_{1, h}} \geq \|q_h\|_0, \quad \forall q_h \in W_h. \]

From the Cauchy-Schwarz inequality, the conditions (3.44) and (3.45) follow immediately.

As a consequence, we have the following theorem.

**Theorem 3.3.4.** Suppose that a pair of finite element spaces \( \{V_h, W_h\} \) satisfy the assumption (H1) and (H2). Then the problem (3.41) admits a unique solution \( \{u_h, p_h\} \in \)
\( V_h \times W_h \), such that

\[
\| u - u_h \|_{H(\text{div})} \lesssim \inf_{v_h \in V_h} \| u - v_h \|_{H(\text{div})}, \\
\| p - p_h \|_0 \lesssim \inf_{q_h \in W_h} \| p - q_h \|_0 + \inf_{v_h \in V_h} \| u - v_h \|_{H(\text{div})}.
\] (3.46) (3.47)

In addition, if the assumption \((H2^{'})\) holds, then

\[
\| \text{div}(u - u_h) \|_0 = \|(I - Q_h)\text{div}u\|_0.
\] (3.48)

Now, we begin from \( H(\text{div})\)-conforming stable elements to construct modified \( H(\text{div}) \) elements to approximate functions in the velocity finite element space \( V_h \). For common choices of \( V_0^h \) and \( W_0^h \), the stability conditions (3.42) and (3.43) amount to

(S1) \[
\begin{align*}
\text{There exists } \Pi_h : H_0(\text{div}) &\to V_0^h \text{ such that } \forall v \in V^0, \\
\text{div}\Pi_h v &= Q_h \text{div} v \text{ and } \| \Pi_h v \|_{H(\text{div})} \lesssim \| v \|_{H(\text{div})},
\end{align*}
\]

and

(S2) \[ \text{div}V_0^h = W_0^h. \]

In fact it is easy to see that, under the assumption (S1), the condition

\[
\text{div}V_0^h \subseteq W_0^h,
\] (3.49)

implies the assumption (S2).
To show the existence of $\Pi_h$ in (S1), we give the definition of a canonical interpolation operator as follows:

**Definition 3.3.5** (Canonical interpolation operator). Let $N_i$ be the $i$-th functional that defines the $i$-th degree of freedom in a finite element space $V_h$. The canonical interpolation operator $\Pi_h : V \rightarrow V_h$ is defined by satisfying the following conditions for all $i$ (the index for the degrees of freedom):

$$N_i (v - \Pi_h v) = 0. \quad (3.50)$$

**Remark 2.4.** The canonical interpolation operator is well-defined because of the unisolvence in finite element methods.

Then, the Raviart-Thomas or BDM families of elements satisfy (S1) and (S2) with the canonical interpolation operator $\Pi_h$ in Definition 3.3.5.

In addition, such $\Pi_h$ is also $H^1$ bounded, namely,

$$\|\Pi_h v\|_{1,h} \lesssim \|v\|_{1,h}, \quad \forall v \in V^0. \quad (3.51)$$

In fact, providing such a condition is crucial for the uniform stability conditions of the problem (3.19) to hold.

**Lemma 3.3.6.** Suppose that the boundedness condition (3.51) and the $H(\text{div})$ stability conditions (S1) and (S2) hold. Then the assumptions (H1) and (H2) hold for $V^0_h$ and $W^0_h$.

**Proof.** By Fortin’s Lemma, (S1), (S2), and (3.51) imply the assumption (H1). The assumption (H2) is a direct consequence of (S2). \qed
However, in general, the spaces $V_h^0$ and $W_h^0$ do not usually work for the original problem (3.19). These spaces lead to a nonconforming approximation. In order to have consistent discretizations, at least we need to impose a weak continuity of the tangential component of the velocity. $V_h^0$ has no continuity of the tangential component of the velocity at all. Now our task is to construct new element spaces $V_h$ and $W_h$ to approximate the original problem while preserving the structure of $V_h^0$ and $W_h^0$, namely, by satisfying the condition ($S1$) and ($S2$).

A natural choice for pressure space is $W_h = W_h^0$. This implies that, in order that ($S2$) holds for $V_h$ and $W_h$, our new space may take the form:

$$V_h = V_h^0 + \text{curl} S.$$  

(3.52)

Recall that the \text{curl} operator on a scalar function $q$ in 2D is defined by

$$\text{curl} q = \left( \begin{array}{c} -\frac{\partial q}{\partial x_2} \\ \frac{\partial q}{\partial x_1} \end{array} \right),$$

and on a vector function $\mathbf{q}$ in 3D is defined by

$$\text{curl} \mathbf{q} = \left( \begin{array}{c} \frac{\partial q_3}{\partial x_2} - \frac{\partial q_2}{\partial x_3} \\ \frac{\partial q_1}{\partial x_3} - \frac{\partial q_3}{\partial x_1} \\ \frac{\partial q_2}{\partial x_1} - \frac{\partial q_1}{\partial x_2} \end{array} \right),$$

where $\mathbf{q} = \left( \begin{array}{c} q_1 \\ q_2 \\ q_3 \end{array} \right)$. 
Now we look at the degrees of freedom. Let $\Pi_h : V \to V_h$ be the canonical interpolation operator given in Definition 3.3.5. We first note the identity,

$$
\int_T (\text{div}\Pi_h \mathbf{v} - Q_h \text{div}\mathbf{v})q_h \, dx = \int_T \text{div}(\Pi_h \mathbf{v} - \mathbf{v})q_h
$$

$$
= -\int_T (\Pi_h \mathbf{v} - \mathbf{v})\nabla q_h \, dx + \int_{\partial T} (\Pi_h \mathbf{v} - \mathbf{v}) \cdot \mathbf{n} q_h \, ds.
$$

In order to have the commutativity property in (S1), we can take degrees of freedom used in the Raviart-Thomas [78, 66] or Brezzi-Douglas-Marini elements [15, 14]. Further, we need additional degrees of freedom to have a weak continuity of the velocity approximation.

**Examples:**

Define the velocity finite element space on an element $T$:

$$
V_T := V^0_T + \text{curl}(bY). \quad (3.53)
$$

Here $b$ is the bubble function, namely $b = \Pi_{i=1}^{d+1} \lambda_i$; and $\lambda_i$, $i = 1, \cdots, d + 1$, is the barycentric coordinate of $T$. For the space $Y$, choose the following polynomial space:

$$
Y = \begin{cases}
Y_1 := P_1(T) & 2D, \\
Y_2 := P_1^3(T) & 3D, \\
Y_3 := \frac{P_1^3(T)}{\text{span}\{(\lambda_i - \frac{1}{3})\nabla \lambda_i\}_{i=1}^4} & 3D.
\end{cases} \quad (3.54)
$$
By construction, it is easy to see that \( \forall q \in \text{curl}(bY) \) satisfies

\[
\text{div} q = 0 \quad \text{and} \quad q \cdot n|_{\partial T} = 0.
\]

(3.55)

For the space \( V^0_T \), we choose the following well-known \( H(\text{div}) \)-conforming finite element spaces:

\[
V^0_T = \begin{cases}
RT_1(T) := P^2_1(T) + \tilde{P}_1(T)x & \text{2D}, \\
BDM_1(T) := P^2_1(T) & \text{2D}, \\
RT_1(T) := P^3_1(T) + \tilde{P}_1(T)x & \text{3D}, \\
BDM_1(T) := P^3_1(T) & \text{3D},
\end{cases}
\]

(3.56)

where \( \tilde{P}_1(T) := P_1(T)/P_0(T) \) (i.e., the homogeneous polynomial space of degree 1). \( RT_1(T) \) denotes both the first-order 2D Raviart-Thomas [78] and 3D Nedelec [66] finite element spaces. \( BDM_1(T) \) denotes both the first-order 2D Brezzi-Douglas-Marini [15] and 3D Brezzi-Douglas-Duran-Fortin [14] finite element spaces.

Among these six elements, the second 2D element and the second 3D element have also been proposed by Mardal-Taï-Winther [54] and Taï-Winther [87] for the problem (3.3) with \( \mu(x) \equiv \epsilon^2 \) and \( \alpha(x) \equiv 1. \)
Fig. 3.2. Degrees of freedom for the first 2D element.

Fig. 3.3. Degrees of freedom for the second 2D element.

Fig. 3.4. Degrees of freedom for the first 3D element.

Fig. 3.5. Degrees of freedom for the second 3D element.

Fig. 3.6. Degrees of freedom for the third 3D element.

Fig. 3.7. Degrees of freedom for the fourth 3D element.
Unisolvence of the new elements

Denote the dimension of a polynomial space by \( \dim(\cdot) \). It is easy to see that the following relationship holds:

\[
\dim(V_0^T + \text{curl}(bY)) = \dim(V_0^T) + \dim(\text{curl}(bY)) = \dim(V_0^T) + \dim(Y).
\]

This relationship implies that the dimension of polynomial space \( V_T \) is the same as the number of degrees of freedom for each element. In the lemma below, \( r = (x, y)^T \), and \( b_f \) is the cubic bubble function associated with face \( f \).

**Lemma 3.3.7** ([87]). If \( v \in P_1^2(f) \) is of the form \( v = \sum_{i=1}^{3} c_i (\lambda_i - \frac{1}{3}) \nabla \lambda_i \), and satisfies

\[
\int_f b_f v \cdot r dx = 0,
\]

then \( c_1 + c_2 + c_3 = 0 \).

Next, we give a proof of unisolvence for all of the six elements.

**Lemma 3.3.8.** For all six elements defined in Table 3.1, any \( v \in V_T \) is uniquely determined by the corresponding degrees of freedom.

**Proof.** Assume that all the degrees of freedom are zeros. Let \( v = v^0 + \text{curl}(bq) \); here \( v^0 \in V_0^T \) and \( q \in Y \) (In 2D, \( q \) is scalar). In 3D, \( \text{curl}(bq) \cdot n = \text{curl}_f(bq)_f = 0 \); here \( (bq)_f \) is the tangential component of \( bq \) on \( f \). In 2D, \( \text{curl}(bq) \cdot n = \frac{\partial(bq)}{\partial t} = 0 \). Then, \( v \cdot n = v^0 \cdot n \in P_1(\partial T) \). Furthermore,

\[
\begin{align*}
\int_e v^0 \cdot n r ds &= 0, \quad \forall r \in P_1(e) \quad \forall e \in \mathcal{E}(T) \quad \text{in 2D}, \\
\int_f v^0 \cdot n w ds &= 0, \quad \forall w \in P_1(f) \quad \forall f \in \mathcal{F}(T) \quad \text{in 3D}.
\end{align*}
\]
Also, by Stoke’s theorem,

\[ \int_T \text{curl}(bq) \cdot \mathbf{r} \, dx = 0, \quad \forall \mathbf{r} \in P^d_0(T), \quad d = 2, 3. \]

Hence

\[ \int_T \mathbf{v}^0 \cdot \mathbf{r} \, dx = \int_T \mathbf{v} \cdot \mathbf{r} \, dx = 0, \quad \forall \mathbf{r} \in P^d_0(T). \quad (3.58) \]

It is well-known that 2D Raviart-Thomas [78], 3D Nedelec [66], 2D Brezzi-Douglas-Marini [15], and 3D Brezzi-Douglas-Duran-Fortin [14] elements are all unisolvent. Therefore, \( \mathbf{v}^0 = 0 \).

In what follows, we shall show \( q = 0 \). For the 2D elements, \( \forall q \in P_1(e) \),

\[ 0 = \int_e \mathbf{v} \cdot \mathbf{t} \, ds = \int_e \text{curl}(bq) \cdot \mathbf{t} \, ds = \int_e \nabla (bq) \cdot \mathbf{n} \, ds = \int_e \frac{\partial b}{\partial \mathbf{n}} q \, ds. \]

Since \( \frac{\partial b}{\partial \mathbf{n}} \) remains the same sign on the edge \( e \), \( q \) has a zero-value point in the interior of each edge \( e \). Thus, \( q = 0 \). For the 3D elements, on the face \( f \), it is easy to calculate that

\[ \mathbf{v} \times \mathbf{n} = \text{curl}(bq) \times \mathbf{n} = \frac{\partial b}{\partial \mathbf{n}} (\mathbf{n} \times q) \times \mathbf{n}. \]

Here, \( \frac{\partial b}{\partial \mathbf{n}} \) is proportional to \( b_f \) on the face \( f \). Then, we get

\[ \int_f b_f (\mathbf{n} \times q) \times \mathbf{n} \cdot \mathbf{r} \, ds = 0, \quad \forall \mathbf{r} \in RT_0(f) \text{ or } P^2_0(f), \quad \forall f \in \mathcal{F}(T). \quad (3.59) \]
The remaining part of the proof follows from an argument of Tai and Winther ([87], Lemma 3). Note that \( r \in P_0^2(f) \subset RT_0(f) \), then it is easy to get

\[
q_t(x_f^b) = 0, \quad f \in F(T).
\]  

(3.60)

Here, \( q_t := (n \times q) \times n \) is the tangential component of \( q \); and \( x_f^b \) is the barycenter of the face \( f \).

The functions in \( P_1^3(T) \), satisfying (3.60), are in the the span of the four functions:

\[
q = \sum_{i=1}^{4} c_i (\lambda_i - \frac{1}{3}) \nabla \lambda_i.
\]  

(3.61)

Then, the tangential component of \( q \) on the face \( f_1 \) has the form

\[
q_t = \sum_{i=2}^{4} c_i (\lambda_i - \frac{1}{3}) \nabla \lambda_i.
\]  

(3.62)

For the first and second 3D elements, as a consequence of Lemma 3.3.7, we get that \( c_2 + c_3 + c_4 = 0 \). By considering all the four faces, we get \( c_1 + c_3 + c_4 = 0, c_1 + c_2 + c_4 = 0 \) and \( c_1 + c_2 + c_3 = 0 \). This implies that \( c_i = 0, i = 1, 2, 3, 4 \). For the third and fourth type of elements, by the construction of the space \( Y_3 \), it follows immediately that \( c_i = 0, i = 1, 2, 3, 4 \). Therefore, \( q = 0 \).

\[\square\]

**Verification of assumptions**

Corresponding to six finite elements listed in Table 3.1, let \( V_h^{(i)}, i = 1, 2, \cdots , 6, \) be the finite dimensional velocity spaces with all degrees of freedom of \( v \in V_h^{(i)} \) being
zero on $\partial \Omega$. It is easy to see $V_h^{(i)} \subset H(\text{div}, \Omega)$, but $\not\subset H^1_0(\Omega)$. These choices of spaces lead to nonconforming finite element methods of the problem (3.19).

For the pressure, let the finite dimensional space $W_h^{(i)}$, $i = 1, 2, \cdots, 6$, be as follows:

$$
\begin{align*}
W_h^{(1)} &:= \{ q \in W : q|_T \in P_1(T) \}, \\
W_h^{(2)} &:= \{ q \in W : q|_T \in P_0(T) \}, \\
W_h^{(3)} &:= \{ q \in W : q|_T \in P_1(T) \}, \\
W_h^{(4)} &:= \{ q \in W : q|_T \in P_0(T) \}, \\
W_h^{(5)} &:= \{ q \in W : q|_T \in P_1(T) \}, \\
W_h^{(6)} &:= \{ q \in W : q|_T \in P_0(T) \}.
\end{align*}
$$

Taking $V_h = V_h^{(i)}$ and $W_h = W_h^{(i)}$, the assumption (S2) is trivially satisfied by construction.

For each finite element space $V_h$, introduce the canonical interpolation operator $\Pi_h : V \to V_h$, which is given in Definition 3.3.5. For all $q \in W_h^{(i)}$ and all $v \in V$,

$$
\int_T \text{div} \Pi_h v q dx = - \int_T \Pi_h v \cdot \nabla q dx + \int_{\partial T} \Pi_h v \cdot n q ds,
$$

$$
= - \int_T v \cdot \nabla q dx + \int_{\partial T} v \cdot n q ds = \int_T \text{div} v q dx = \int_T Q_h \text{div} v q dx.
$$

Thus, by the assumption (S2), we get the commutativity property

$$
\text{div} \Pi_h v = Q_h \text{div} v.
$$
Further, as the operator $\Pi_h$ preserves linear polynomials locally, we have the interpolation error estimate

$$\|v - \Pi_h v\|_{j,h} \lesssim h^{k+1-j}|v|_{k+1,h}, \quad 0 \leq j \leq k \leq 1. \quad (3.65)$$

and the boundedness

$$\|\Pi_h v\|_{1,h} \lesssim \|v\|_{1,h}. \quad (3.66)$$

One difference to the standard scaling argument by adopting the Piola transformation is that these elements are not invariant under the Piola transformation. Consequently, a different argument is required to prove the interpolation error estimate. The analysis can be done by scaling to a similar element of unit diameter using translation, rotation, and dilation; further using the compactness argument \cite{8, 7}. Thus, the assumption (S1) and (3.51) hold.

Now we derive consistency error estimates for all six elements.

We consider the detailed discussion of the 3D case (2D case is similar and easier). By the interface condition $[\sigma(u, p)n]_{\Gamma_{ij}} = 0$, we can rewrite the consistency error (3.29) as:

$$E_h(u, p, v_h) = \sum_{f \in F(T)} \int_f \sigma(u, p) \cdot [v_h] ds.$$ 

On the face $f$, decompose the vector $\sigma(u, p)n$ and $v$, along the normal direction $n$ and along the tangential direction to the face $f$, i.e., $\sigma(u, p)n = (\sigma(u, p)n \cdot n)n + n \times (\sigma(u, p)n \times$
Let $T_f^-$ and $T_f^+$ denote the two tetrahedrons sharing the same face $f$. Denote $w^+ := w|_{T_f^+ \cap f}$, $w^- := w|_{T_f^- \cap f}$; here, $w$ can be both a scalar and vector. In addition, denote $\sigma^+(u, p) := \sigma(u^+, p^+)$ and $\sigma^-(u, p) := \sigma(u^-, p^-)$. For all four 3D elements in Section 3.3.2, the following uniform consistency error estimate holds.

**Lemma 3.3.9.** For $u \in H^1_0$, $\forall v_h \in V^{(i)}_h$, $i = 3, 4, 5, 6$,

$$|E_h(u, p, v_h)| \lesssim h|\mu^{1/2}\nabla u|_{1,h} \|v_h\|_h.$$

(3.68)

**Proof.** By the continuity of the normal component of the stress, we have $\sigma(u, p)n = \sigma^+(u, p)n = \sigma^-(u, p)n$, on the face $f$. We first estimate $\left| \int_f \left( \sigma^+(u, p)n \times n \right) \cdot [v_h \times n] ds \right|$.

Since $(p^+ I)n \times n = 0$, by the definition of $\sigma^+(u, p)$, we have

$$\left| \int_f \left( \sigma^+(u, p)n \times n \right) \cdot [v_h \times n] ds \right| = \left| \int_f (\mu^+ \nabla u^+ n \times n) \cdot [v_h \times n] ds \right|. \quad (3.69)$$
By the construction of degrees of freedom, the Cauchy-Schwarz inequality, the standard scaling argument, and the Bramble-Hilbert Lemma, we get

\[
\left| \int_{f} (\mu^{+} \nabla u^{+} \cdot n) \times [v_{h} \times n] \, ds \right| = \left| \mu^{+} \int_{f} (\nabla u^{+} \cdot n - \lambda) [v_{h} \times n - \mu] \, ds \right|
\]

\[
\leq \mu^{+} \inf_{\lambda \in \mathbb{R}^{2}} \| \nabla u^{+} \cdot n - \lambda \|_{0,f} \inf_{\mu \in \mathbb{R}^{2}} \| [v_{h} \times n - \mu] \|_{0,f}
\]

\[
\lesssim \mu^{+} h |u|_{2,T_{f}^{+}} |v_{h}|_{1,T_{f}^{+}}. \quad (3.70)
\]

Thus combining above two estimates (3.69) and (3.70), we have

\[
\left| \int_{f} (\sigma^{+}(u,p) \cdot n) \times [v_{h} \times n] \, ds \right| \lesssim \mu^{+} h |u|_{2,T_{f}^{+}} |v_{h}|_{1,T_{f}^{+}}. \quad (3.71)
\]

Similarly, we then get

\[
\left| \int_{f} (\sigma^{-}(u,p) \cdot n) \times [v_{h} \times n] \, ds \right| \lesssim \mu^{-} h |u|_{2,T_{f}^{-}} |v_{h}|_{1,T_{f}^{-}}. \quad (3.72)
\]

From the above two estimates (3.71) and (3.72), it follows that

\[
\left| \int_{f} (\sigma(u,p) \cdot n) \times [v_{h} \times n] \, ds \right|
\]

\[
\lesssim h \left( \mu^{+} |u|_{2,T_{f}^{+}}^{2} + \mu^{-} |u|_{2,T_{f}^{-}}^{2} \right)^{1/2} \left( \mu^{+} |v_{h}|_{1,T_{f}^{+}}^{2} + \mu^{-} |v_{h}|_{1,T_{f}^{-}}^{2} \right)^{1/2}.
\]
Applying the Cauchy-Schwarz inequality again, gives this consistency error estimate:

\[
|E_h(u, p, v_h)| \lesssim h \left( \sum_{f \in \mathcal{F}(T)} \left( \mu^+ |u_{2,T_f}^2 + \mu^- |u_{2,T_f}^2 \right) \right)^{1/2} \\
\cdot \left( \sum_{f \in \mathcal{F}(T)} \left( \mu^+ |v_h|_{1,T_f}^2 + \mu^- |v_h|_{1,T_f}^2 \right) \right)^{1/2} \\
\lesssim h \mu^{1/2} \nabla u_{1,h} \|v_h\|_h.
\]

For the 2D case, on the edge \( e \), decompose the vector \( \sigma(u, p) n \) and \( v_h \) along the normal direction \( n \) and along the tangential direction \( t \), i.e., \( \sigma(u, p) n = (\sigma(u, p) n \cdot n) n + \sigma(u, p) n \cdot t ) t \) and \( v_h = (v_h \cdot n) n + (v_h \cdot t) t \). Then, we get

\[
E_h(u, p, v_h) = \sum_{e \in \mathcal{E}(T)} \int_e (\sigma(u, p) n \cdot t) [v_h \cdot t] ds. \tag{3.73}
\]

Similar to the 3D case, the following uniform consistency error estimate holds for all the two 2D elements.

**Lemma 3.3.10.** For \( u \in H^1_0 \), \( \forall v_h \in V_h^{(i)} \), \( i = 1, 2 \),

\[
|E_h(u, p, v_h)| \lesssim h \mu^{1/2} \nabla u_{1,h} \|v_h\|_h. \tag{3.74}
\]

### 3.3.3 Stabilized formulation and families of stable Stokes elements

Brezzi, Fortin, and Marini [17] studied the mixed form of the Poisson equation and modified the equation such that the coercivity condition is automatically preserved on
the discrete level. Here, we can apply a similar technique for our equation. We multiply
the second equation of (3.7) by \( M \) (defined in (3.10)), and add to the first equation of
(3.7), then we get the equivalent formulation of (3.7): Find \( \{u, p\} \in V \times W \) such that

\[
\begin{aligned}
\left\{ \begin{aligned}
a(u,v) + M(\text{div}u, \text{div}v) - (p, \text{div}v) &= \langle f, v \rangle + M \langle g, \text{div}v \rangle \quad \forall v \in V, \\
(\text{div}u, q) &= \langle g, q \rangle 
\end{aligned} \right.
\end{aligned}
\]  

(3.75)

Correspondingly, we have the following the discrete weak formulations. Find \( \{u_h, p_h\} \in V_h \times W_h \) such that, for all \( v_h \in V_h \) and \( q_h \in W_h \),

\[
\begin{aligned}
\left\{ \begin{aligned}
a_h(u_h, v_h) + M(\text{div}u_h, \text{div}v_h) - (p_h, \text{div}v_h) &= \langle f, v_h \rangle + M \langle g, \text{div}v_h \rangle, \\
(\text{div}u_h, q_h) &= \langle g, q_h \rangle.
\end{aligned} \right.
\end{aligned}
\]  

(3.76)

We shall show that any pair of stable Stokes elements that satisfy the inf-sup condition

\[
\sup_{v_h \in V_h} \frac{\langle \text{div}v_h, q_h \rangle}{\|v_h\|_{1,h}} \gtrsim \|q_h\|_0 \quad \forall q_h \in W_h,
\]  

(3.77)

is uniformly stable with the norms given in (3.21) and (3.9) to the modified problem
(3.76).
Lemma 3.3.11. Suppose that (3.77) is fulfilled, then the following uniform stability conditions hold:

\[ a_h(v_h, v_h) + M(\text{div}v_h, \text{div}v_h) = \|v_h\|^2, \quad \forall v_h \in V_h, \quad (3.78) \]

\[ \sup_{v_h \in V_h} \frac{(\text{div}v_h, q_h)}{\|v_h\|_h} \gtrsim \|q_h\|, \quad \forall q_h \in W_h, \quad (3.79) \]

\[ a_h(u_h, v_h) + M(\text{div}u_h, \text{div}v_h) \lesssim \|u_h\|_h \|v_h\|_h, \quad \forall u_h, v_h \in V_h, \quad (3.80) \]

\[ (\text{div}v_h, q_h) \lesssim \|v_h\|_h \|q_h\|, \quad \forall v_h \in V_h, \quad \forall q_h \in W_h. \quad (3.81) \]

Proof. We note that the coercivity condition (3.78) is automatically satisfied (independent of \( Z_h \)) by the definition. Using the fact that \( \|v_h\|_h \leq M^{1/2} \|v_h\|_{1,h} \), the inf-sup condition (3.79) follows immediately from (3.77): For all \( q_h \in W_h \),

\[ \sup_{v_h \in V_h} \frac{(\text{div}v_h, q_h)}{\|v_h\|_h} \gtrsim M^{-1/2} \sup_{v_h \in V_h} \frac{(\text{div}v_h, q_h)}{\|v_h\|_{1,h}} \gtrsim M^{-1/2} \|q_h\|_0 = \|q_h\|. \]

Finally, the Cauchy-Schwarz inequality implies the other two conditions (3.80) and (3.81).

\[ \square \]

The consistency error of a nonconforming finite element approximation to the problem (3.76) is defined by

\[ E_h(u, p, v_h) = \sum_{T \in T_h} \int_{\partial T} (\sigma(u, p) \mathbf{n} \cdot v_h - \text{div}v_h \cdot \mathbf{n}) \, ds. \quad (3.82) \]

Furthermore, by the saddle point theory [13, 16, 31], we have the following theorem.
Theorem 3.3.12. Assume that a pair of finite element spaces $V_h$ and $W_h$ satisfies the condition (3.77). Then the discrete problem (3.76) has a unique solution. In addition,

$$
\|u-u_h\|_h + \|p-p_h\|_h \lesssim \inf_{v_h \in V_h} \|u-v_h\|_h + \inf_{q_h \in W_h} \|p-q_h\|_h + \sup_{v_h \in V_h} \frac{|E_h(u,p,v_h)|}{\|v_h\|_h}.
$$

(3.83)

3.4 New discrete de Rham complexes with extra smoothness

In Section 3.3.2, we discussed modified $H(\text{div})$-conforming elements leading to uniformly stable discretizations to the Darcy-Stokes-Brinkman problem (3.3) with respect to the viscosity, permeability, and their jumps. In fact, the finite element spaces $V_h(\text{div}) := V_h$ and $L^2_h := W_h$ in Section 3.3.2 form an exact sequence.

$$
V_h(\text{div}) \xrightarrow{\text{div}} L^2_h.
$$

(3.84)

The sequence is exact in the sense that the range of each map is equal to the null space of the succeeding map. Furthermore, we have the following commutative diagram:

$$
\begin{array}{ccc}
H^1 & \xrightarrow{\text{div}} & L^2 \\
\downarrow \Pi_h^{\text{div}} & & \downarrow \Pi_h^0 \\
V_h(\text{div}) & \xrightarrow{\text{div}} & L^2_h \\
\end{array}
$$

(3.85)

in the sense that $\text{div}\Pi_h^{\text{div}} = \Pi_h^0 \text{div}$, where $\Pi_h^{\text{div}} := \Pi_h$ and $\Pi_h^0 := Q_h$. Recall that the degree of freedoms in Table 3.1 in Section 3.3.2 defines the canonical interpolation operator $\Pi_h$ by Definition 3.3.5. $Q_h$ is an $L^2$-orthogonal projection to the finite element space $W_h$ (3.63).
The purpose of this section is to construct several stable finite element spaces for $V_h(\text{grad})$ and $V_h(\text{curl})$ (these spaces will be defined later) to complete the sequence (3.84) to be exact in regard to the de Rham complexes. The de Rham complex of $\Omega$ is the sequence of maps in the sense that the composition of two consecutive maps is zero. If $\Omega$ is contractible, these complexes are exact in the sense that the range of each map is equal to the null space of the succeeding map.

These exact sequences and the corresponding commutative diagrams are important tools for the design and analysis of multigrid methods [4, 49] and nodal auxiliary preconditioners [35] to the discrete problems arising from compatible discretizations of $V_h(\text{grad}), V_h(\text{div})$ and $V_h(\text{curl})$. This is the motivation to present such complexes here. As another application, these finite element spaces in the discrete de Rham complex can be used to discretize a family of singularly perturbed high-order equations.

### 3.4.1 Preliminaries

If $\Omega$ is a simply connected 3D domain, it is well-known that the following sequence is exact:

$$
\mathbb{R} \longrightarrow H^1 \xrightarrow{\text{grad}} H(\text{curl}) \xrightarrow{\text{curl}} H(\text{div}) \xrightarrow{\text{div}} L^2 \longrightarrow 0. \quad (3.86)
$$

As discussed in Section 3.3.2, $H(\text{div})$ denotes the Sobolev space consisting of all vectors $u$ with $u \in L^2$ and $\text{div} u \in L^2$. Similarly, $H(\text{curl}) := \{ u \mid u \in L^2, \text{curl} u \in L^2 \}$. 
At the discrete level, it is well-known that the following sequence is exact:

\[
\mathbb{R} \longrightarrow V_h(\text{grad}) \xrightarrow{\text{grad}} V_h(\text{curl}) \xrightarrow{\text{curl}} V_h(\text{div}) \xrightarrow{\text{div}} L^2_h \longrightarrow 0. \quad (3.87)
\]

Here, \(V_h(\text{grad}) \subset H^1\), \(V_h(\text{curl}) \subset H(\text{curl})\), \(V_h(\text{div}) \subset H(\text{div})\), and \(L^2_h \subset L^2\). There are four possible choices for the above sequence [5]:

\[
\mathbb{R} \longrightarrow P_{r+1} \xrightarrow{\text{grad}} N_r^{(1)} \xrightarrow{\text{curl}} RT_r \xrightarrow{\text{div}} P_{r-1} \longrightarrow 0, \quad (3.88)
\]

\[
\mathbb{R} \longrightarrow P_{r+2} \xrightarrow{\text{grad}} N_{r+1}^{(2)} \xrightarrow{\text{curl}} RT_r \xrightarrow{\text{div}} P_{r-1} \longrightarrow 0, \quad (3.89)
\]

\[
\mathbb{R} \longrightarrow P_{r+2} \xrightarrow{\text{grad}} N_{r+1}^{(1)} \xrightarrow{\text{curl}} BDM_{r+1} \xrightarrow{\text{div}} P_{r-1} \longrightarrow 0, \quad (3.90)
\]

\[
\mathbb{R} \longrightarrow P_{r+3} \xrightarrow{\text{grad}} N_{r+2}^{(2)} \xrightarrow{\text{curl}} BDM_{r+1} \xrightarrow{\text{div}} P_{r-1} \longrightarrow 0. \quad (3.91)
\]

Here, \(P_r\) is the classical continuous piecewise polynomial finite element space of degree \(r\), and the degrees of freedom are defined in [62]; \(N_r^{(1)}\) and \(N_r^{(2)}\) are Nedelec’s first and second family of \(H(\text{curl})\)-conforming finite element spaces of order \(r\) [66, 67]; \(RT_r\) is the \(r\)-th order Raviart-Thomas \(H(\text{div})\)-conforming finite element space [66]; \(BDM_r\) is the \(r\)-th order Brezzi-Douglas-Duran-Fortin \(H(\text{div})\)-conforming finite element space [14]; and \(P_{r-1}^{-1}\) is the discontinuous piecewise polynomial finite element space with degree \(r\).
Furthermore, the following diagram commutes for the above four possible choices [5].

\[
\begin{array}{ccccccccc}
\mathbb{R} & \rightarrow & C^\infty & \xrightarrow{\text{grad}} & C^\infty & \xrightarrow{\text{curl}} & C^\infty & \xrightarrow{\text{div}} & C^\infty & \rightarrow & 0 \\
\downarrow & & \Pi_h^{\text{grad}} & & \Pi_h^{\text{curl}} & & \Pi_h^{\text{div}} & & \Pi_h^0 \\
\mathbb{R} & \rightarrow & V_h(\text{grad}) & \xrightarrow{\text{grad}} & V_h(\text{curl}) & \xrightarrow{\text{curl}} & V_h(\text{div}) & \xrightarrow{\text{div}} & L^2_h & \rightarrow & 0.
\end{array}
\] (3.92)

Here, degrees of freedom in \( V_h(\text{grad}) \), \( V_h(\text{curl}) \), and \( V_h(\text{div}) \) define \( \Pi_h^{\text{grad}} \), \( \Pi_h^{\text{curl}} \), and \( \Pi_h^{\text{div}} \) respectively by Definition 3.3.5; \( \Pi_h^0 \) is the \( L^2 \)-orthogonal projection to \( L^2_h \).

In the two-dimensional situation, we have similar properties. Let \( \Omega \) be a simply connected 2D domain, it is well-known [5] that the following sequences in both continuous and discrete levels are also exact:

\[
\begin{array}{ccccccccc}
\mathbb{R} & \rightarrow & H^1 & \xrightarrow{\text{curl}} & H(\text{div}) & \xrightarrow{\text{div}} & L^2 & \rightarrow & 0, \\
\downarrow & & \Pi_h & & \Pi_h & & \Pi_h & & \\
\mathbb{R} & \rightarrow & V_h(\text{grad}) & \xrightarrow{\text{curl}} & V_h(\text{div}) & \xrightarrow{\text{div}} & L^2_h & \rightarrow & 0.
\end{array}
\] (3.93) (3.94)

For this discrete sequence, there are two possible choices for the finite element spaces [5]:

\[
\begin{array}{ccccccccc}
\mathbb{R} & \rightarrow & P_{r+1} & \xrightarrow{\text{curl}} & RT_r & \xrightarrow{\text{div}} & P_r^{-1} & \rightarrow & 0, \\
\downarrow & & \Pi_h & & \Pi_h & & \Pi_h & & \\
\mathbb{R} & \rightarrow & P_{r+2} & \xrightarrow{\text{curl}} & BDM_{r+1} & \xrightarrow{\text{div}} & P_r^{-1} & \rightarrow & 0.
\end{array}
\] (3.95) (3.96)

Here, \( RT_r \) and \( BDM_r \) are the two-dimensional \( r \)-th order Raviart-Thomas [78] and Brezzi-Douglas-Marini [15] \( H(\text{div}) \)-conforming finite element spaces respectively. In addition, it is also well-known [5] that the following diagram commutes for the above
choices:

\[
\begin{array}{cccccc}
\mathbb{R} & \longrightarrow & C^\infty & \xrightarrow{\text{curl}} & C^\infty & \xrightarrow{\text{div}} & C^\infty & \longrightarrow & 0 \\
& & \downarrow \Pi^\text{curl}_h & & \downarrow \Pi^\text{div}_h & & \downarrow \Pi^0_h & & \\
\mathbb{R} & \longrightarrow & V_h(\text{grad}) & \xrightarrow{\text{curl}} & V_h(\text{div}) & \xrightarrow{\text{div}} & L^2_h & \longrightarrow & 0.
\end{array}
\]  

(3.97)

3.4.2 3D discrete de Rham complexes with extra smoothness

A three-dimensional example of a de Rham complex with extra smoothness, corresponding to (3.86) is

\[
\begin{array}{cccccc}
\mathbb{R} & \longrightarrow & H^2 & \xrightarrow{\text{grad}} & H^1(\text{curl}) & \xrightarrow{\text{curl}} & H^1 & \xrightarrow{\text{div}} & L^2 & \longrightarrow & 0.
\end{array}
\]  

(3.98)

Here, \(H^1(\text{curl})\) denotes the Sobolev space in which \(\text{curl}u \in H^1\). In addition, if \(\Omega\) is a convex polyhedron then the sequence is exact (see Section I.3.5 of [31]).

In Section 3.3.2, we discussed four possible choices (in 3D) for the pair of spaces \(\left( V_h(\text{div}), L^2_h \right) \), by modifying \(H(\text{div})\)-conforming finite element spaces \(RT_1\) and \(BDM_1\), and choosing two different polynomial spaces \(Y\) for 3D case as in (3.54). We rewrite those four finite element spaces as follows.

The first finite element triple (corresponding to \(V_h(\text{div})\)) is given by

- \(T\) is tetrahedron.
- The polynomial space restricted on \(T\) is \(V_T := RT_1 + \text{curl}(bY_2)\).
- The degrees of freedom are:

\[
\begin{align*}
& - \int_f (v \cdot n)q, \quad q \in P_1(f), \\
& - \int_T v \cdot q, \quad q \in P_0^3(T), \\
& - \int_f (v \times n) \cdot q, \quad q \in RT_0(f).
\end{align*}
\]
The second finite element triple (corresponding to $V_h(\text{div})$) is given by

- $T$ is tetrahedron.
- The polynomial space restricted on $T$ is $V_T := RT_1 + \text{curl}(bY_3)$.
- The degrees of freedoms are
  
  $- \int_f (v \cdot n)q, \quad q \in P_1(f)$.
  $- \int_T v \cdot q, \quad q \in P^3_0(T)$.
  $- \int_f (v \times n) \cdot q, \quad q \in P^2_0(f)$.

In above two cases, $L^2_h$ is a piecewise discontinuous linear polynomial space.

The third finite element triple (corresponding to $V_h(\text{div})$) is given by

- $T$ is tetrahedron.
- The polynomial space restricted on $T$ is $V_T := BDM_1 + \text{curl}(bY_2)$.
- The degrees of freedom are
  
  $- \int_f (v \cdot n)q, \quad q \in P_1(f)$.
  $- \int_f (v \times n) \cdot q, \quad q \in RT^2_0(f)$.

Finally, the fourth finite element triple (corresponding to $V_h(\text{div})$) is given by

- $T$ is tetrahedron.
- The polynomial space restricted on $T$ is $V_T := BDM_1 + \text{curl}(bY_3)$.
- The degrees of freedom are
  
  $- \int_f (v \cdot n)q, \quad q \in P_1(f)$.
  $- \int_f (v \times n) \cdot q, \quad q \in P^2_0(f)$. 
For the last two cases, $L^2_h$ is a piecewise discontinuous constant polynomial.

In what follows, we complete the exact sequence (3.84) by finding appropriate finite element spaces for $V_h(\text{grad})$ and $V_h(\text{curl})$. Based on the well-known four types, (3.88)-(3.91), of 3D discrete de Rham complexes in Section 3.4.1, we found eight discrete de Rham complexes with extra smoothness for the 3D case (two for each type). One of eight complexes has been also proposed by Tai and Winther in [87]. We give the detailed discussion for two new discrete de Rham complexes with extra smoothness by modifying the first type well-known de Rham complex (3.88).

**First type exact sequence**

When $r = 1$, the first type exact sequence (3.88) has the following form:

$$
\mathbb{R} \longrightarrow P_2 \xrightarrow{\text{grad}} N^{(1)}_1 \xrightarrow{\text{curl}} RT_1 \xrightarrow{\text{div}} P^{-1}_1 \longrightarrow 0 \quad (3.99)
$$

Based on this, we construct two exact sequences for two different choices of polynomial spaces of $Y$ in (3.54). One is the case that $Y = Y_2$. The finite element triple corresponding $V_h(\text{grad})$ is given by

- $T$ is tetrahedron.
- The polynomial space restricted on $T$ is $S_T := P_2 + bP_1$.
- The degrees of freedom are
  - $s(x_i), \quad x_i(i = 1, 2, 3, 4)$ are the vertices of $T$.
  - $\int e s dx$,
  - $\int f \frac{\partial s}{\partial n} dx$. 
The finite element triple corresponding to $V_h(\text{curl})$ is given by

- $T$ is tetrahedron.
- The polynomial space restricted on $T$ is $U_T := N_1^{(1)} + \text{grad}(bP_1) + bY_2$.
- The degrees of freedom are
  
  \[
  \begin{align*}
  & - \int_e (u \cdot t) q \, dx, \quad q \in P_1(e), \\
  & - \int_f (u \times n) \cdot q \, dx, \quad q \in P_0^2(f), \\
  & - \int_f u \cdot n \, dx, \\
  & - \int_f (\text{curl} u \times n) \cdot q \, dx, \quad q \in RT_0(f).
  \end{align*}
  \]

The finite element triple corresponding to $V_h(\text{div})$ is given by

- $T$ is tetrahedron.
- The polynomial space restricted on $T$ is $V_T := RT_1 + \text{curl}(bY_2)$.
- The degrees of freedom are

  \[
  \begin{align*}
  & - \int_f (v \cdot n) q, \quad q \in P_1(f), \\
  & - \int_T v \cdot q, \quad q \in P_0^3(T), \\
  & - \int_f (v \times n) \cdot q, \quad q \in RT_0(f).
  \end{align*}
  \]

$L_h^2$ is a piecewise discontinuous constant polynomial space.

For the other case, we choose $Y = Y_3$ in (3.54). $V_h(\text{grad})$ remains the same. $V_h(\text{curl})$ and $V_h(\text{div})$ are slightly different by modifying corresponding degrees of freedom. The finite element triple corresponding to $V_h(\text{curl})$ is given by

- $T$ is tetrahedron.
- The polynomial space restricted on $T$ is $U_T := N_1^{(1)} + \text{grad}(bP_1) + bY_3$. 
• The degrees of freedom are

\[- \int_e (\mathbf{u} \cdot \mathbf{t}) q dx, \quad q \in P_1(e),\]
\[- \int_f (\mathbf{u} \times \mathbf{n}) \cdot q dx, \quad q \in P_0^2(f),\]
\[- \int_f \mathbf{u} \cdot n dx.\]
\[- \int_f (\text{curl}\mathbf{u} \times \mathbf{n}) \cdot q dx, \quad q \in P_0^2(f).\]

The finite element triple corresponding to \( V_h(\text{div}) \) is given by

• \( T \) is tetrahedron.

• The polynomial space restricted on \( T \) is \( V_T := RT_1 + \text{curl}(bY_3) \).

• The degrees of freedom are

\[- \int_f (\mathbf{v} \cdot \mathbf{n}) q, \quad q \in P_1(f),\]
\[- \int_T \mathbf{v} \cdot q, \quad q \in P_0^3(T),\]
\[- \int_f (\mathbf{v} \times \mathbf{n}) \cdot q, \quad q \in P_0^2(f).\]

\( L^2_h \) is a piecewise discontinuous linear polynomial space.

In \( V_h(\text{grad}) \), \( V_h(\text{curl}) \), and \( V_h(\text{div}) \), we classify the degrees of freedom into two types. The first type of degrees of freedom is from the ones in the standard \( H(\text{grad})^- \), \( H(\text{curl})^- \), and \( H(\text{div})^- \)-conforming finite element spaces. The second type arises from the space \( Y (Y = Y_2 \text{ or } Y = Y_3) \) in order to have certain weak continuity as discussed in Section 3.3.2.

The other three types of exact sequences

We take \( r = 1 \) in the second type of standard exact sequence (3.89), \( r = 0 \) in the third type (3.90) and the fourth type (3.91). Then the exact sequences have the
following forms:

\[ \mathbb{R} \rightarrow P_3 \xrightarrow{\text{grad}} N_2^{(2)} \xrightarrow{\text{curl}} RT_1 \xrightarrow{\text{div}} P_1^{-1} \rightarrow 0, \quad (3.100) \]

\[ \mathbb{R} \rightarrow P_2 \xrightarrow{\text{grad}} N_1^{(1)} \xrightarrow{\text{curl}} BDM_1 \xrightarrow{\text{div}} P_0^{-1} \rightarrow 0, \quad (3.101) \]

\[ \mathbb{R} \rightarrow P_3 \xrightarrow{\text{grad}} N_2^{(2)} \xrightarrow{\text{curl}} BDM_1 \xrightarrow{\text{div}} P_0^{-1} \rightarrow 0. \quad (3.102) \]

Based on the above each type of sequence, we have two exact sequences (when \( Y = Y_2 \) and \( Y = Y_3 \)), by taking a similar approach as in the first type of exact sequence. The first type of degrees of freedom are standard ones for the corresponding standard \( H(\text{grad}) \)-, \( H(\text{curl}) \)-, and \( H(\text{div}) \)-conforming spaces. The degrees of freedom of the second type are determined from the space \( Y_2 \) and \( Y_3 \) as in the first type exact sequence.

Before we prove that these discrete de Rham complexes with extra smoothness are exact, we first prove that the finite elements proposed above are all unisolvent.

**Lemma 3.4.1.** All above elements in \( V_h(\text{grad}) \), \( V_h(\text{curl}) \) and \( V_h(\text{div}) \) are unisolvent.

**Proof.** For \( V_h(\text{div}) \), we have four different elements. A unified proof is given in the Lemma 3.3.8 in Section 3.3.2.

For \( V_h(\text{curl}) \), we also have four different elements. The proof for \( V_h(\text{curl}) \) follows a similar argument. \( \mathbf{u} \in U_T \), i.e.,

\[ \mathbf{u} = \mathbf{u}^0 + \text{grad}(bp) + bq, \quad \mathbf{u}^0 \in N_1, \quad p \in P_1, \quad q \in Y. \]
Here, $N_1$ is either $N_1^{(1)}$ or $N_1^{(2)}$. Assume the degrees of freedom are all zeros for each element. Since $bq \cdot t = 0$ and $\text{grad}(bq) \times n = 0$ on the face $f$, the first type of degrees of freedom for $u^0$ are also zeros. By the unisolvence of the first and second family of the Nedelec element, we have $u^0 = 0$. Furthermore, $\text{grad}(bp) \cdot n = cb_f p$, on $f$. Here, $b_f$ is the bubble function with respect to the face $f$; and $c$ is some positive constant. Then,

$$0 = \int_f (u \cdot n) = \int_f \text{grad}(bp) \cdot n dx = c \int_f b_f p. \quad (3.103)$$

Thus, $p = 0$. Finally, in Lemma 3.3.8 in Section 3.3.2, we have shown that if $\int_f (\text{curl}(bq) \times n) \times n \cdot r ds = 0$, $r \in RT_0(f)$ (when $Y = Y_2$) and $r \in P^2_0(f)$ (when $Y = Y_3$), then $q = 0$.

For $V_h(\text{grad})$, we have two elements. When $S(T) = P_2 + bP_1$, the unisolvence is given in [87]. The proof for the second one is similar. If $s \in S(T), s = p + bq, p \in P_3, q \in P_1$. Since $b = 0$ on edge $e$ and face $f$, the first type of degrees of freedom for $p$ is also zero. By the unisolvence of standard $P_3$ element, $p = 0$. Furthermore, $\int_f \frac{\partial (bq)}{\partial n} dx = 0$, by (3.103) we get $q = 0$.

**Theorem 3.4.2.** The eight 3D sequences are all complex and exact.

**Proof.** The proofs for the eight sequences are very similar. We only give a proof for the first type based on the classical discrete exact de Rham complex (3.99). From this standard complex sequence, it is straightforward to check that $\text{grad}V_h(\text{grad}) \subseteq V_h(\text{curl}), \text{curl}V_h(\text{curl}) \subseteq V_h(\text{div}),$ and $\text{div}V_h(\text{div}) \subseteq L^2_h$. This implies that the sequence is complex.
Next, we shall show that the sequence is exact. For \( v \in V_h(\text{div}) \), the restriction \( v_T \) on \( T \) is
\[
v_T = v^0_T + \text{curl}(bq_T), \quad v^0_T \in RT_1(T), \quad q_T \in P^3_0(T).
\]

Note \( \text{curl}(bq_T) \cdot n = 0 \) on \( f \) and \( \int_T \text{curl}(bq_T) \cdot q = 0, \forall q \in P^3_0(T) \). Thus \( v^0 \) is an element of \( RT_1 \). Assume \( \text{div} v = 0 \). We want to show that there exists \( u \in V_h(\text{curl}) \) such that \( v = \text{curl} u \). If \( \text{div} v = 0 \), then \( \text{div} v^0 = 0 \). Since the corresponding classical sequence is exact, there exists \( u^0 \in N_1^{(1)} \) such that \( v^0 = \text{curl} u^0 \) and \( v^0_T = \text{curl} u^0_T \).

Furthermore, \( \text{curl} \left( \text{grad}(bp_T) \right) = 0, p_T \in P_1(T) \). Therefore,
\[
v_T = \text{curl} \left( u^0_T + \text{grad}(bp_T) + bq_T \right).
\]

In \( V_h(\text{div}) \), \( \int_f [v \times n] \cdot q = 0, \forall q \in RT_0(f) \). So that
\[
\int_f \left[ \text{curl}(u^0 + \text{grad}(bp) + bq) \times n \right] \cdot q = 0, \forall q \in RT_0(f).
\]

Since \( b = 0 \) on the face \( f \) and edge \( e \), it follows that \( \text{grad}(bp_T) \times n = 0 \) on \( f \), and \( \text{grad}(bp_T) \cdot t = 0 \) on \( e \). As a result,
\[
\int_f [(u^0 + \text{grad}(bp) + bq) \times n] \cdot q dx = \int_f [u^0 \times n] \cdot q dx = 0, \forall q \in P^2_0(f),
\]
\[
\int_e [(u^0 + \text{grad}(bp) + bq) \cdot t] q dx = \int_e [u^0 \cdot t] q dx = 0, \forall q \in P_1(e).
\]
Furthermore, from the exactness of the standard sequence, we have $u^0 = \text{grad}s^0$. Then,

$$\int_f [(u^0 + \text{grad}(bp) + bq) \cdot n] dx = \int_f [\text{grad}(s^0 + bp) \cdot n] dx = 0. \quad (3.108)$$

Let $u = u^0 + \text{grad}(bp) + bq$. From (3.105)-(3.108), we conclude that $u \in V_h(\text{curl})$.

We can use a similar argument to show that curl-free elements of $V_h(\text{curl})$ are gradients of functions in $V_h(\text{grad})$. For $u \in V_h(\text{curl})$, the restriction of $u_T$ on $T$ is

$$u_T = u_T^0 + \text{grad}(b_T p_T) + b_T q_T. \quad (3.109)$$

Here, $u_T^0 \in N_1^{(1)}(T)$, $p_T \in P_1(T)$, and $q_T \in P_3^1(T)$. Since $u_T \cdot t = u_T^0 \cdot t$ on $e$, and $(u_T \times n) \cdot q = (u_T^0 \times n) \cdot q$ on $f$, we can see that $u^0$ is an element of $N_1^{(1)}$. Assume $\text{curl} u = 0$, then $\text{curl} u^0 = 0$ and $\text{curl}(bq) = 0$. If $\text{curl}(bq) = 0$, by the degrees of freedom in $V_h(\text{curl})$, the element $bq$ of $V_h(\text{curl})$ is zero. By the exactness of the classical sequence (3.100), there is $s^0 \in P_2$ such that $u^0 = \text{grad}s^0$ and $u_T^0 = \text{grad}s_T^0$.

Therefore,

$$u_T = \text{grad}(s_T^0 + b_T p_T). \quad (3.110)$$

Note that $s^0$ is a continuous piecewise polynomial space $P_2$, then

$$\int_e [s^0 + bp] dx = \int_e [s^0] dx = 0 \quad (3.111)$$

and

$$[s^0 + bp]_{x_i} = [s^0]_{x_i} = 0. \quad (3.112)$$
Since \( u \in V_h(\text{curl}) \), then \( \int f[u \cdot n]dx = 0 \), and therefore

\[
\int f\left[ \frac{\partial}{\partial n}(s^0 + bp) \right] dx = \int f[u \cdot n]dx = 0.
\]  
(3.113)

Let \( s = s^0 + bp \), then \( u = \text{grad} s \) and \( s \in V_h(\text{grad}) \) from (3.111)-(3.113).

Let \( \Pi^\text{grad}_h : H^2 \rightarrow V_h(\text{grad}) \), \( \Pi^\text{curl}_h : H^1(\text{curl}) \rightarrow V_h(\text{curl}) \), and \( \Pi^\text{div}_h : H^1 \rightarrow V_h(\text{div}) \) be the canonical interpolation operators given in Definition 3.3.5, and \( \Pi^0_h : L^2 \rightarrow L^2_h \) be the \( L^2 \)-orthogonal projection.

For all eight discrete de Rham complexes with extra smoothness, we have the corresponding eight commutative diagrams as follows:

\[
\begin{array}{ccccccc}
\mathbb{R} & \longrightarrow & H^2 & \xrightarrow{\text{grad}} & H^1(\text{curl}) & \xrightarrow{\text{curl}} & H^1 & \xrightarrow{\text{div}} & L^2 & \longrightarrow & 0 \\
\downarrow \Pi^\text{grad}_h & & \downarrow \Pi^\text{curl}_h & & \downarrow \Pi^\text{div}_h & & \downarrow \Pi^0_h \\
\mathbb{R} & \longrightarrow & V_h(\text{grad}) & \xrightarrow{\text{grad}} & V_h(\text{curl}) & \xrightarrow{\text{curl}} & V_h(\text{div}) & \xrightarrow{\text{div}} & L^2_h & \longrightarrow & 0.
\end{array}
\]  
(3.114)

**Theorem 3.4.3.** The diagram (3.114) is commutative. This means that the following identities hold:

\[
\text{grad}\Pi^\text{grad}_h = \Pi^\text{curl}_h \text{grad}, \quad \text{curl}\Pi^\text{curl}_h = \Pi^\text{div}_h \text{curl}, \quad \text{div}\Pi^\text{div}_h = \Pi^0_h \text{div}.
\]

**Proof.** The proofs for the eight diagrams are all very similar. We give a proof for a diagram of the first type.

To show that \( \text{grad}\Pi^\text{grad}_h = \Pi^\text{curl}_h \text{grad} \), it then suffices to show that all degrees of freedom in \( V_h(\text{curl}) \) for \( \text{grad}\Pi^\text{grad}_h s \) and \( \Pi^\text{curl}_h \text{grad} \) agree element by element.
Here, $s \in H^2$. We start with the edge degrees. \( \forall q \in P_1(e)\),

\[
\int_e \left( \nabla \Pi_h^{\text{grad}} s - \Pi_h^{\text{curl}} \nabla s \right) \cdot t q = \int_e \nabla \Pi_h^{\text{grad}} (s - s) \cdot t q \\
= - \int_e \Pi_h^{\text{grad}} (s - s) (\nabla q \cdot t) + \int_{\partial e} \Pi_h^{\text{grad}} (s - s) q = 0.
\]

Next, consider the first set of degrees of freedom on faces. \( \forall q \in P_0^2(f)\),

\[
\int_f \left( \nabla \Pi_h^{\text{grad}} s - \Pi_h^{\text{curl}} \nabla s \right) \times n \cdot q = 0.
\]

Here, $\nabla f$ is the gradient operator on the face; and $n_{\partial f}$ is a unit normal vector on the edge of the face $f$. Further, consider the second set of degrees of freedom on the face.

\[
\int_f \left( \nabla \Pi_h^{\text{grad}} s - \Pi_h^{\text{curl}} \nabla s \right) \cdot n = 0.
\]

Finally, consider the third set of degrees of freedom on the face. \( \forall q \in RT_0(f)\),

\[
\int_f \left( \text{curl} \nabla \Pi_h^{\text{grad}} s - \Pi_h^{\text{curl}} \nabla s \right) \times n \cdot q = 0.
\]

This completes the proof of the first commutativity $\nabla \Pi_h^{\text{grad}} = \Pi_h^{\text{curl}} \nabla$. 
To show that \( \text{curl}^h \Pi^h = \Pi^h \text{div} \), it then suffices to show that all degrees of freedom in \( V_h(\text{div}) \) for \( \text{curl}^h \Pi^h u \) and \( \Pi^h \text{div} \) \( \text{curl} u \) agree element by element. Here, \( u \in H^1(\text{curl}) \). We start with the first face degrees. \( \forall q \in P_1(f) \),

\[
\int_f \left( \text{curl}(\Pi^h \text{curl} u) - \Pi^h \text{div} \text{curl} u \right) \cdot n_q = \int_f \text{rot}(\Pi^h \text{curl} u - u) f q
\]

\[
\begin{align*}
\int_f (\Pi^h \text{curl} u - u) f \cdot \text{curl} q f q + \int_{\partial f} (\Pi^h \text{curl} u - u) f \cdot t q &= 0.
\end{align*}
\]

Next, consider the second volume degrees of freedom. \( \forall q \in P_3^0(T) \),

\[
\int_T \left( \text{curl}(\Pi^h \text{curl} u) - \Pi^h \text{div} \text{curl} u \right) \cdot q = \int_T \text{curl} \left( \Pi^h \text{curl} u - u \right) \cdot q
\]

\[
\begin{align*}
\int_T (\Pi^h \text{curl} u - u) \cdot \text{curl} q + \int_{\partial T} (\Pi^h \text{curl} u - u) \times n \cdot q &= 0.
\end{align*}
\]

Then, consider the third set of degrees of freedom on the face. \( \forall q \in RT_0(f) \),

\[
\int_f \left( \text{curl}(\Pi^h \text{curl} u) - \Pi^h \text{div} \text{curl} u \right) \times n \cdot q = \int_f \text{curl}(\Pi^h \text{curl} u - u) \times n \cdot q = 0.
\]

This completes the proof of the second commutativity \( \text{curl}^h \Pi^h = \Pi^h \text{div} \).

Lastly, we show that \( \text{div}^h \Pi^h = \Pi^h \text{div} \). For \( v \in H^1 \), \( \forall w \in P_1(T) \),

\[
\int_T \left( \text{div}(\Pi^h \text{div} v) - \Pi^h \text{div} v \right) w = \int_T \text{div}(\Pi^h \text{div} v - v) w
\]

\[
\begin{align*}
\int_T (\Pi^h \text{div} v - v) \cdot \nabla w + \int_{\partial T} (\Pi^h \text{div} v - v) \cdot n w &= 0.
\end{align*}
\]

This completes the proof of the last commutativity \( \text{div}^h \Pi^h = \Pi^h \text{div} \). \( \square \)
3.4.3 2D discrete de Rham complexes with extra smoothness

A two-dimensional example of a complex with extra smoothness, corresponding to (3.93) is

\[ \mathbb{R} \longrightarrow H^2 \xrightarrow{\text{curl}} H^1 \xrightarrow{\text{div}} L^2 \longrightarrow 0. \]  \hspace{1cm} (3.115)

Its analogy to the discrete level is

\[ \mathbb{R} \longrightarrow V_h(\text{grad}) \xrightarrow{\text{curl}} V_h(\text{div}) \xrightarrow{\text{div}} L_h^2 \longrightarrow 0. \]  \hspace{1cm} (3.116)

The following commutative diagram is given in Section 3.3.2:

\[
\begin{array}{ccc}
H^1 & \xrightarrow{\text{div}} & L^2 \\
\downarrow \Pi_h^{\text{div}} & & \downarrow \Pi_h^0 \\
V_h(\text{div}) & \xrightarrow{\text{div}} & L_h^2
\end{array}
\]  \hspace{1cm} (3.117)

Here, \( V_h(\text{div}) \) and \( L_h^2 \) have two cases.

Firstly, the finite element triple corresponding to \( V_h(\text{div}) \) is given by

- \( T \) is triangle.
- The polynomial space restricted on \( T \) is \( V_T := RT_1 + \text{curl}(bP_1) \).
- The degrees of freedom are
  - \( \int_e (\mathbf{v} \cdot \mathbf{n})q, \quad q \in P_1(e) \).
  - \( \int_T \mathbf{v} \cdot \mathbf{q}, \quad \mathbf{q} \in P_0^2(T) \).
  - \( \int_e (\mathbf{v} \cdot \mathbf{t})q, \quad q \in P_0(e) \).
\(L^2_h\) is a piecewise discontinuous linear polynomial.

Secondly, the finite element triple corresponding to \(V_h(\text{div})\) is given by

- \(T\) is triangle.
- The polynomial space restricted on \(T\) is \(V_T := BDM_1 + \text{curl}(bP_1)\).
- The degrees of freedom are
  
  \[- \int_e (\mathbf{v} \cdot \mathbf{n})q, \quad q \in P_1(e). \]
  \[- \int_e (\mathbf{v} \cdot \mathbf{t})q, \quad q \in P_0(e). \]

\(L^2_h\) is a piecewise discontinuous constant polynomial.

In what follows, we complete the discrete exact sequence in (3.117) by finding appropriate finite element spaces for \(V_h(\text{grad})\).

**First type exact sequence**

Based on this standard exact sequence, when \(r = 1\) in (3.95),

\[
\begin{array}{cccccc}
\mathbb{R} & \longrightarrow & P_2 & \xrightarrow{\text{curl}} & RT_1 & \xrightarrow{\text{div}} & P_1 & \longrightarrow & 0,
\end{array}
\]

we have one exact sequence. The finite element triple corresponding to \(V_h(\text{grad})\) is given by

- \(T\) is triangle.
- The polynomial space restricted on \(T\) is \(S_T := P_2 + bP_1\).
- The degrees of freedom are
  
  \[- s(x_i), \quad x_i(i = 1, 2, 3) \text{ are the vertices of } T. \]
\[- \int_c s \, dx. \]

\[- \int_c \frac{\partial s}{\partial n} \, dx. \]

This \( V_h(\text{grad}) \) together with the first type \( V_h(\text{div}) \) and \( L^2_h \) form an exact sequence.

**Second type exact sequence**

Based on this standard exact sequence, when \( r = 0 \) in (3.96),

\[
\mathbb{R} \rightarrow P_2 \xrightarrow{\text{curl}} \text{BDM}_1 \xrightarrow{\text{div}} P_1 \rightarrow 0,
\]

\( V_h(\text{grad}) \) together with the second type \( V_h(\text{div}) \) and \( L^2_h \) also form an exact sequence.

**Theorem 3.4.4.** All the above elements in \( V_h(\text{grad}) \) and \( V_h(\text{div}) \) are unisolvent.

**Proof.** We have two different \( V_h(\text{div}) \) elements. A unified proof is given in Lemma 3.3.8 in Section 3.3.2. For \( V_h(\text{grad}) \), the proof is given [70]. \( \square \)

**Theorem 3.4.5.** The two 2D sequences (3.116) are all complex and exact.

**Proof.** The proofs of two types of sequences are very similar. We, therefore, give proof for the first type only. For the classical conforming element \( V_h(\text{grad}) \) and \( V_h(\text{div}) \), we have the discrete de Rham complex:

\[
\mathbb{R} \rightarrow P_2 \xrightarrow{\text{curl}} \text{RT}_1 \xrightarrow{\text{div}} P_1 \rightarrow 0.
\]

Based on this complex, it is straightforward to check \( \text{curl} V_h(\text{grad}) \subseteq V_h(\text{div}) \) and \( \text{div} V_h(\text{div}) \subseteq L^2_h \). This implies that the sequence (3.116) is a complex.
Now we show that the sequence is exact. For \( \mathbf{v} \in V_h(\mathbf{div}) \), the restriction of \( \mathbf{v}_T \) on \( T \) is

\[
\mathbf{v}_T = \mathbf{v}_T^0 + \text{curl}(bq_T), \quad \mathbf{v}_T^0 \in RT_1(T), \quad q_T \in P_1(T).
\]

Note that \( \text{curl}(bq_T) \cdot \mathbf{n} = 0 \) on \( e \) and \( \int_T \text{curl}(bq_T) \cdot \mathbf{q} = 0, \forall \mathbf{q} \in P^2_0(T) \). Thus \( \mathbf{v}_T^0 \) is an element of \( RT_1 \). Assume \( \text{div}\mathbf{v} = 0 \). We need to show that there exists \( s \in V_h(\mathbf{grad}) \) such that \( \mathbf{v} = \text{curl}s \). If \( \text{div}\mathbf{v} = 0 \), then \( \text{div}\mathbf{v}_T^0 = 0 \). Since the classical sequence is exact, there exists \( s^0 \in P_2 \) such that \( \mathbf{v}_T^0 = \text{curl}s^0 \) and \( \mathbf{v}_T^0 = \text{curl}s^0_T \). Therefore,

\[
\mathbf{v}_T = \text{curl}(s_T^0 + bq_T).
\]

In \( V_h(\mathbf{div}) \), \( \int_e [\mathbf{v} \cdot \mathbf{t}] = 0, \forall \mathbf{q} \in P_0(e) \). Then

\[
\int_e [\text{curl}(s^0 + bq) \cdot \mathbf{t}] dx = \int_e \left[ \frac{\partial}{\partial n}(s^0 + bq) \right] dx = 0. \tag{3.118}
\]

Notice \( b = 0 \) on \( e \), so

\[
\int_e [s^0 + bq] = \int_e [s^0] = 0, \tag{3.119}
\]

and

\[
[s^0 + bq]_{x_i} = [s^0]_{x_i} = 0. \tag{3.120}
\]

Let \( s = s^0 + bq \), then \( \mathbf{v} = \mathbf{grad}s \). Furthermore from (3.118)-(3.120), we get \( s \in V_h(\mathbf{grad}) \).

Let \( \Pi^\text{grad}_h : H^2 \to V_h(\mathbf{grad}) \), \( \Pi^\text{div}_h : H^1 \to V_h(\mathbf{div}) \), and \( \Pi^0_h : L^2 \to L^2_h \) be the canonical interpolation operators given in Definition 3.3.5. For the two different discrete
de Rham complexes with extra smoothness, we have the corresponding commutative diagrams as follows:

\[ \begin{array}{cccccc}
\mathbb{R} & \longrightarrow & H^2 & \xrightarrow{\text{curl}} & H^1 & \xrightarrow{\text{div}} & L^2 & \longrightarrow & 0 \\
\downarrow \Pi_h^{\text{grad}} & & \downarrow \Pi_h^{\text{div}} & & \downarrow \Pi_h^0 & & & & \\
\mathbb{R} & \longrightarrow & V_h(\text{grad}) & \xrightarrow{\text{curl}} & V_h(\text{div}) & \xrightarrow{\text{div}} & L^2_h & \longrightarrow & 0.
\end{array} \]

(3.121)

**Theorem 3.4.6.** The diagram (3.121) is commutative. This means that the following identities hold:

\[ \text{curl} \Pi_h^{\text{grad}} = \Pi_h^{\text{div}} \text{curl}, \quad \text{div} \Pi_h^{\text{div}} = \Pi_h^0 \text{div} \]

**Proof.** The proofs for the two types of diagrams are very similar. We, therefore, give proof for the diagram of the first type only.

To show that \( \text{curl} \Pi_h^{\text{grad}} = \Pi_h^{\text{div}} \text{curl} \), it suffices to show that all degrees of freedom in \( V_h(\text{div}) \) for \( \text{curl} \Pi_h^{\text{grad}} s \) and \( \Pi_h^{\text{div}} \text{curl}s \) agree element by element. Here, \( s \in H^2 \). We start with the first edge degrees of freedom. For all \( q \in P_1(e) \),

\[ \int_e \left( \text{curl} \Pi_h^{\text{grad}} s - \Pi_h^{\text{div}} \text{curl}s \right) \cdot \mathbf{n} = \int_e \text{curl} \left( \Pi_h^{\text{grad}} s - s \right) \cdot \mathbf{n} \\
= \int_e \text{grad} \left( \Pi_h^{\text{grad}} s - s \right) \cdot \mathbf{t} = - \int_e [\Pi_h^{\text{grad}} s - s] d\mathbf{x} + \left[ \Pi_h^{\text{grad}} s - s \right]_{\partial e} = 0. \]

Next, consider the second set of edge degrees of freedom:

\[ \int_e \left( \text{curl} \Pi_h^{\text{grad}} s - \Pi_h^{\text{div}} \text{curl}s \right) \cdot \mathbf{t} = \int_e \text{curl} \left( \Pi_h^{\text{grad}} s - s \right) \cdot \mathbf{t} \\
= \int_e \text{grad} \left( \Pi_h^{\text{grad}} s - s \right) \cdot \mathbf{n} = 0. \]
Finally, consider the set of degrees of freedom on triangle. For all \( q \in P_0^2(T) \),

\[
\int_T \left( \text{curl} \Pi_h \text{grad} s - \Pi_h \text{div} \text{curl} s \right) \cdot q = \int_T \text{curl} \left( \Pi_h \text{grad} s - s \right) \cdot q
\]

\[
= \int_e \left( \Pi_h \text{grad} s - s \right) (q \cdot t) = 0.
\]

This completes the proof for the first identity.

Now we show that \( \text{div} \Pi_h \text{div} = \Pi_h^0 \text{div} \). For all \( v \in H^1 \) and \( w \in P_1(T) \),

\[
\int_T \left( \text{div} (\Pi_h \text{div} v) - \Pi_h^0 \text{div} v \right) w = \int_T \text{div} (\Pi_h^0 \text{div} v - v) w
\]

\[
= - \int_T (\Pi_h^0 \text{div} v - v) \cdot \nabla w + \int_{\partial T} (\Pi_h^0 \text{div} v - v) \cdot \mathbf{n} w = 0.
\]

This completes the proof of the second commutativity.

3.4.4 Applications to the singularly perturbed high-order equations

In this section, we consider a family of singularly perturbed high-order equations on a three-dimensional convex polygonal domain. For given \( f \in V' \), find \( u \in V \), \( \forall v \in V \), such that

\[
\epsilon^2 a(u, v) + b(u, v) = \langle f, v \rangle.
\] (3.122)
Here,

\[
\begin{align*}
a(u, v) &= \begin{cases} 
(\Delta u, \Delta v), & V = V(\text{grad}) := \epsilon H_0^2 \cap H_0^1, \\
(\text{curl}u, \text{curl}v), & V = V(\text{curl}) := \epsilon H_0^1(\text{curl}) \cap H_0(\text{curl}), \\
(\text{grad}u, \text{grad}v), & V = V(\text{div}) := \epsilon H_0^1 \cap H_0(\text{div}),
\end{cases} 
\end{align*}
\]

(3.123)

and

\[
\begin{align*}
b(u, v) &= \begin{cases} 
(\text{grad}u, \text{grad}v), & V = V(\text{grad}), \\
(\text{curl}u, \text{curl}v) + (u, v), & V = V(\text{curl}), \\
(\text{div}u, \text{div}v) + (u, v), & V = V(\text{div}).
\end{cases} 
\end{align*}
\]

(3.124)

As \( \epsilon \) approaches zero, the high-order term \( \epsilon^2 a(u, v) \) vanishes, and the equation (3.122) reduces to a low-order one: \( b(u, v) = < f, v > \). Define the norm in \( V \) as:

\[
\|v\|^2 := \epsilon^2 a(v, v) + b(v, v), \quad \forall v \in V.
\]

It is easy to see that the problem (3.122) has a unique solution by the Lax-Milgram Lemma.

The finite element spaces developed in Section 3.4.2 satisfy that \( V_h(\text{grad}) \subset H^1 \), \( V_h(\text{curl}) \subset H(\text{curl}) \), and \( V_h(\text{div}) \subset H(\text{div}) \). Thus, we have conforming discretizations for the low-order term, \( b(u, v) \), of the equation (3.122). However, we note \( V_h(\text{grad}) \not\subset V(\text{grad}) \), \( V_h(\text{curl}) \not\subset V(\text{curl}) \), and \( V_h(\text{div}) \not\subset V(\text{div}) \). This implies that we have nonconforming discretizations for the high-order term \( a(u, v) \).
The finite element solution $u_h \in V_h$ is defined as

$$
\epsilon^2 a_h(u_h, v_h) + b(u_h, v_h) = \langle f, v_h \rangle, \quad \forall v_h \in V_h.
$$

(3.125)

Here, $a_h(u_h, v_h)$ is defined element by element (because of nonconforming discretizations to the high-order term):

$$
a_h(u_h, v_h)|_T := a(u_h|_T, v_h|_T),
$$

(3.126)

and the inner product $b(u_h, v_h)$ remains the same as the continuous one.

Define the mesh dependent norm in $V_h$, for $v_h \in V_h$,

$$
\|v_h\|_h^2 := \epsilon^2 a_h(v_h, v_h) + b(v_h, v_h).
$$

Clearly, we have the coercivity:

$$
\epsilon^2 a_h(v_h, v_h) + b(v_h, v_h) \geq \|v_h\|_h, \quad \forall v_h \in V_h,
$$

and the continuity:

$$
\left| \epsilon^2 a_h(u_h, v_h) + b(u_h, v_h) \right| \leq \|u_h\|_h \|v_h\|_h, \quad \forall u_h, v_h \in V_h.
$$
Thus, the discrete problem (3.125) also admits a unique solution by Lax-Milgram Lemma.

Furthermore, by the second Strang Lemma [83, 77, 16], we have

$$\|u - u_h\|_h \lesssim \inf_{v \in V_h} \|u - v_h\|_h + \sup_{v_h \in V_h} \frac{|E_h(u, v_h)|}{\|v_h\|_h},$$

(3.127)

where the consistency error reads as follows:

$$E_h(u, v_h) = \epsilon^2 \sum_{\partial T} \begin{cases} \int_{\partial T} \Delta u \frac{\partial v}{\partial n} \, ds, & V_h = V_h(\text{grad}), \\
\int_{\partial T} (\text{curl}\, \text{curl}\, u) \cdot [\text{curl}\, v \times n] \, ds, & V_h = V_h(\text{curl}), \\
\int_{\partial T} (\nabla u \cdot n) \cdot [v] \, ds, & V_h = V_h(\text{div}). \end{cases}$$

(3.128)

The following consistency error estimates hold.

**Lemma 3.4.7.** Let $u \in V$ be the solution of the problem (3.122). Then $\forall v_h \in V_h$,

$$E_h(u, v_h) \lesssim \epsilon^2 \begin{cases} |u|_3 \|v\|_h, & V_h = V_h(\text{grad}), \\
|u|_3 \|v\|_h, & V_h = V_h(\text{curl}), \\
|u|_2 \|v\|_h, & V_h = V_h(\text{div}). \end{cases}$$

(3.129)

**Proof.** The proof is similar to that for Lemma 3.3.9. By the construction of the degrees of freedom in $V_h(\text{grad}), V_h(\text{curl}),$ and $V_h(\text{div}),$ the integrals $\int_{\partial T} \frac{\partial v}{\partial n} \, ds, \int_{\partial T} \text{curl}\, v \times n \, ds,$ and $\int_{\partial T} v \, ds$ are all continuous across $\partial T$. Further, using the standard trace theorem, the Cauchy-Schwarz inequality, and the scaling argument, we get the desired result.

We also have the interpolation error estimate.
Lemma 3.4.8. Let \( u \in V \), then

\[
\inf_{v_h \in V_h} \| u - v_h \|_h \lesssim (h^2 + \epsilon h)
\begin{align*}
|u|_3, & \quad V_h = V_h(\text{grad}), \\
|u|_3, & \quad V_h = V_h(\text{curl}), \\
|u|_2, & \quad V_h = V_h(\text{div}).
\end{align*}
\] (3.130)

Finally, we have the following error estimate by applying the interpolation error estimate (3.130) and the consistency error estimate (3.129) to the second Strang Lemma (3.127).

Theorem 3.4.9. The finite element solution \( u_h \) of the problem (3.125) admits the following error estimate:

\[
\| u - u_h \|_h \lesssim (h^2 + \epsilon h)
\begin{align*}
|u|_3, & \quad V_h = V_h(\text{grad}), \\
|u|_3, & \quad V_h = V_h(\text{curl}), \\
|u|_2, & \quad V_h = V_h(\text{div}).
\end{align*}
\] (3.131)
Table 3.1. Six modified $H(\text{div})$-conforming elements

<table>
<thead>
<tr>
<th>Elements</th>
<th>$V^D_T$</th>
<th>$Y$</th>
<th>Degrees of Freedom (DOF)</th>
<th># of DOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>First 2D Element</td>
<td>$RT_1(T)$</td>
<td>$Y_1$</td>
<td>( \int_e \mathbf{v} \cdot \mathbf{n} , dq, \quad \forall q \in P_1(e), ) [\int_T \mathbf{v} \cdot \mathbf{q} , dx, \quad \forall \mathbf{q} \in P_0^2(T) ] [\int_e \mathbf{v} \cdot \mathbf{t} , ds ]</td>
<td>11</td>
</tr>
<tr>
<td>Second 2D Element</td>
<td>$BDM_1(T)$</td>
<td>$Y_1$</td>
<td>( \int_e \mathbf{v} \cdot \mathbf{n} , dq, \quad \forall q \in P_1(e), ) [\int_e \mathbf{v} \cdot \mathbf{t} , ds ]</td>
<td>9</td>
</tr>
<tr>
<td>First 3D Element</td>
<td>$RT_1(T)$</td>
<td>$Y_2$</td>
<td>( \int_f \mathbf{v} \cdot \mathbf{n} , dq, \quad \forall q \in P_1(f) ) [\int_T \mathbf{v} \cdot \mathbf{q} , ds, \quad \forall \mathbf{q} \in P_0^3(T) ] [\int_f (\mathbf{v} \times \mathbf{n}) \cdot \mathbf{r} , ds, \quad \forall \mathbf{r} \in RT_0(f) ]</td>
<td>27</td>
</tr>
<tr>
<td>Second 3D Element</td>
<td>$BDM_1(T)$</td>
<td>$Y_2$</td>
<td>( \int_f \mathbf{v} \cdot \mathbf{n} , dq, \quad \forall q \in P_1(f) ) [\int_f (\mathbf{v} \times \mathbf{n}) \cdot \mathbf{r} , ds, \quad \forall \mathbf{r} \in RT_0(f) ]</td>
<td>24</td>
</tr>
<tr>
<td>Third 3D Element</td>
<td>$RT_1(T)$</td>
<td>$Y_3$</td>
<td>( \int_f \mathbf{v} \cdot \mathbf{n} , dq, \quad \forall q \in P_1(f) ) [\int_T \mathbf{v} \cdot \mathbf{q} , ds, \quad \forall \mathbf{q} \in P_0^3(T) ] [\int_f (\mathbf{v} \times \mathbf{n}) \cdot \mathbf{r} , ds, \quad \forall \mathbf{r} \in P_0^2(f) ]</td>
<td>23</td>
</tr>
<tr>
<td>Fourth 3D Element</td>
<td>$BDM_1(T)$</td>
<td>$Y_3$</td>
<td>( \int_f \mathbf{v} \cdot \mathbf{n} , dq, \quad \forall q \in P_1(f) ) [\int_f (\mathbf{v} \times \mathbf{n}) \cdot \mathbf{r} , ds, \quad \forall \mathbf{r} \in P_0^2(f) ]</td>
<td>20</td>
</tr>
</tbody>
</table>
Chapter 4

MULTIPHYSICS DIRECT METHANOL
FUEL CELL SIMULATIONS

The work presented in this chapter is based on the collaborative work in [86].

4.1 Introduction

A direct methanol fuel cell (DMFC) is another kind of fuel cell that converts methanol and oxygen fuel energy into electricity based on chemical reactions. A liquid methanol solution is fed from the anode gas channel and diffuses through the backing layer. Once the methanol solution reaches the reaction site at the catalyst layer, the following global chemical reaction occurs:

\[ \text{MeOH} + \text{H}_2\text{O} = 6\text{H}^+ + 6\text{e}^- + \text{CO}_2. \]  

(4.1)

The backing layer and catalyst layer collect the electrons and form an outer circuit toward the anode side. Simultaneously, the proton diffuses through the proton exchange membrane to reach the cathode reaction site. The carbon dioxide, as a byproduct of the oxidation reaction, forms bubbles and is removed by the flow field toward the anode gas channel outlet.

On the cathode side, air is pumped into the gas channel. By a similar mechanism, air reaches the reaction site of the catalyst layer, where it combines with electrons and
protons from the anode side to form water. This chemical reaction is given by

\[ \frac{3}{2}O_2 + 6H^+ + 6e^- = 3H_2O. \] (4.2)

Overall, the cell reaction is

\[ MeOH + \frac{3}{2}O_2 = CO_2 + 2H_2O. \] (4.3)

Compared to the hydrogen PEFC, the DMFC’s fuel storage is easier and its design is simpler. Also, there is no need for cooling or humidification in the DMFC. As a result, the DMFC is considered to be a leading contender for next-generation portable and micropower sources, as it offers a combination of simplicity, robustness, and high-energy density due to the use of liquid methanol [93].

As discussed in Chapter 2, in the porous media part of the PEFC, the coexistence of a gas-phase zone and a two-phase zone induces a nonlinear discontinuous degenerate diffusion-coefficient for the water transport equation. For the liquid feed DMFC, we do not have such a situation. In fact the two-phase zone are all over the porous part of the DMFC. This means that the water diffusion-coefficient is a smooth function. Thus, in our numerical simulation of DMFC, we do not need special techniques developed in Chapter 2. In this chapter, we mainly put efforts on the simulation of fully coupled 3D model equations in the DMFC.

Extensive reviews of DMFC research have been published in recent years [63, 64, 68, 3, 45, 32, 106, 53]. A two-phase mixture multicomponent model was first developed

Because of the complicated nature of multi-physicochemical phenomena in fuel cells, in the steady-state simulation, it is challenging to make the nonlinear iteration converge in a robust manner. It is typical that, with standard numerical techniques, the nonlinear iteration converges (but slowly) under certain parameters. However, under different operating conditions, the iteration may diverge without adjusting some parameters. Therefore, developing efficient numerical methods to achieve fast convergence towards solutions of 3D fully coupled multiphysics DMFC models is the main purpose of this chapter.

We design new numerical methods for the 3D DMFC simulation, by applying the combined finite element-upwind finite volume method, proper linearization, coupling and decoupling strategies of governing equations, finding an optimal sequence of solution unknowns in the nonlinear iterative procedure, and intensively investigating the multi-component two-phase transport model in the existing DMFC model. Our numerical results demonstrate that fast convergence towards the solutions can be achieved for the steady-state simulation of the full 3D DMFC model.

We begin with a discussions of modeling equations.

4.2 Model description

The present 3D model is essentially from Liu and Wang [52]. It is an extension from Wang and Wang [101] and is based on the multiphase mixture model discussed in
Section 2.2.3. The primal variables for species in the present model are mass concentrations compared to molar ones in [52]. For the model assumptions, we refer to [52]. We begin our discussion with electrochemical kinetics, which are incorporated into the source terms of various species conservation equations.

**Electrochemical Kinetics**

Electrochemical reactions are treated as source or sink terms in methanol, water, oxygen, proton, electron, and energy conservation equations. In the anode side, the volumetric transfer current density derived by Meyers and Newman [61, 60, 59] has the following form:

\[
j_a = \frac{a_{j0,a} c_{MeOH} |_{cata} \exp \left[ \frac{\alpha_a F}{R T} \eta_a \right]}{c_{MeOH} |_{cata} + K_j \exp \left[ \frac{\alpha_a F}{R T} \eta_a \right]},
\]

where the anode over-potential is defined from the electron potential \( \Phi_s \), the proton potential \( \Phi_e \), and the anodic potential under the thermodynamic equilibrium \( U_{0,a} \). It has the form:

\[
\eta_a = \Phi_s - \Phi_e - U_{0,a}.
\]

In (4.4), \( a_{j0,a} \) is the total exchange current density at the reference condition; \( c_{MeOH} |_{cata} \) is the local liquid methanol molar concentration at the anode catalyst layer; \( K_j \) is the reaction constant; \( \alpha_a \) is an anodic transfer coefficient; \( F \) is Faraday’s constant; and \( R \) is the gas constant.
In the cathode side, the volumetric transfer current density is expressed by the Tafel equation:

\[ j_c = a_j^{ref} \frac{C^{O_2}_{\text{cata}}}{C^{O_2}_{g,ref}} (1 - s) \exp \left( -\frac{\alpha_c F}{RT} \eta_c \right), \]  

(4.6)

which is a linear approximation of the Butler-Volmer equation. In the above equation, \(1 - s\) counts for the volume fraction of the gas phase in a two-phase mixture; \(a_j^{ref}\) is the total exchange current density at the reference condition; \(C^{O_2}_{\text{cata}}\) is the local oxygen molar concentration at the cathode catalyst layer; \(C^{O_2}_{g,ref}\) is the oxygen molar concentration at the reference condition; and \(\alpha_c\) is a cathodic transfer coefficient. The cathodic over-potential is defined by

\[ \eta_c = \Phi_s - \Phi_e - U_{0,c}. \]  

(4.7)

Here, \(U_{0,c}\) is the cathodic potential under the thermodynamic equilibrium.

**Mass conservation of the multiphase mixture**

A generic mass conservation equation, valid for all components (channels, backing layers, catalyst layers, and the membrane) except bipolar plates, can be written as

\[ \nabla \cdot (\rho u) = \dot{m}, \]  

(4.8)
where

\[ \dot{m} = \begin{cases} 
M_{MeOH} S_{MeOH} + M_{H_2O} S_{H_2O} + M_{CO_2} \frac{j_a}{6F} & \text{anode catalyst layer,} \\
M_{H_2O} S_{H_2O} + M_{O_2} S_{O_2} + M_{CO_2} \frac{j_{cross}}{6F} & \text{cathode catalyst layer,} \\
0 & \text{other subdomains.} 
\end{cases} \]

Here, \( j_a \) is the volumetric transfer current density at the anode side given in (4.4); \( j_{cross} \) is the current density caused by the net methanol (MeOH) crossover flux from the anode to the cathode side through the membrane via electro-osmotic drag and diffusion. Detailed discussions regarding \( j_{cross} \) will be provided shortly in (4.20). \( M^\alpha \) and \( S^\alpha \) (superscript \( \alpha \) denotes the species \( H_2O, MeOH, O_2, CO_2, \) etc.) denote the molecular weight of each species and the source term of each species in the conservation equations respectively. In the anode catalyst layer, we have methanol and water sink because of the chemical reactions and crossover fluxes to the cathode side through the membrane. In addition, carbon dioxide is generated because of the chemical reactions. In the cathode catalyst layer, oxygen sink occurs because of the chemical reactions; water is generated due to chemical reactions and crossover flux from the anode side; and carbon dioxide is generated by the chemical reaction of the crossover methanol flux.

**Momentum equation**

The momentum equation is the same as the first equation in (2.66), which is valid in both the porous media regions and viscous fluid regions of fuel cells:

\[ -\nabla \cdot (\mu \nabla \mathbf{u}) + \frac{1}{\varepsilon^2} \nabla \cdot (\rho \mathbf{uu}) + \frac{\mu}{K} \mathbf{u} + \nabla p = 0, \]  

(4.10)
where the Darcy’s drag term exerted by porous media is given by $S_u = -\frac{\mu}{K} u$. When the position-dependent permeability function $K$ approaches infinity in channels, the momentum equation (4.10) together with the continuity equation reduces to the steady-state Navier-Stokes equations. When the permeability $K$ is small in porous media regions, the momentum equation approaches the two-phase mixture Darcy’s law (2.31) derived in Section 2.2.3. The equations (4.10) and (4.8) are called Navier-Stokes/Brinkman equations. They model the coupling between porous media flow and viscous channel flow in a single computational domain through channels, backing layers, and catalyst layers in both anode and cathode sides. This system of equations is also related to Darcy-Brinkman-Forchheimer models [44, 29]. The specific values for the permeability $K$ at different subdomains are given by

$$K = \begin{cases} 
10^{-12} \text{ m}^2 & \text{backing layers}, \\
10^{-12} \text{ m}^2 & \text{catalyst layers}, \\
10^{30} \text{ m}^2 & \text{channels}.
\end{cases}$$

(4.11)

**General species conservation equation**

In Section 2.2.3, we derived the general species conservation (2.39) in the multiphase mixture framework [95] as follows:

$$\nabla \cdot (\gamma \rho u Y^\alpha) = \nabla \cdot \left[ (Y_{g}^\alpha - Y_{l}^\alpha) j_l \right] + \nabla \cdot \left[ \rho_l D_{l,eff}^\alpha \nabla Y_{l}^\alpha + \rho_g D_{g,eff}^\alpha \nabla Y_{g}^\alpha \right] + \dot{m}^\alpha. \quad (4.12)$$

Recall that $Y^\alpha$ denotes the mixture mass fraction of species $\alpha$, the advection correction factor $\gamma$ is equal to unity in the channel regions due to the homogeneous flow assumptions.
[52]; however, it is non-unity in backing and catalyst layers based on the multiphase-mixture models. In addition, the effective diffusion coefficients in the liquid and gas phases are given by

\[ D_{l,eff}^{\alpha} = (\varepsilon s)^{1.5} D_{l}^{\alpha} \quad \text{and} \quad D_{g,eff}^{\alpha} = (\varepsilon (1 - s))^{1.5} D_{g}^{\alpha}, \quad (4.13) \]

considering the tortuosity factor of the electrodes. The first term on the right side of (4.12) represents species diffusive-flux across phases caused by the relative motion of the liquid to gas phase under capillary action in the porous backing and catalyst layers. As defined in (2.49) in Section 2.2.3, the capillary diffusion flux of the liquid phase \( j_l \) is directly proportional to the gradient of capillary pressure:

\[ j_l = \frac{\lambda_l \lambda_g K \rho}{\mu} \nabla p_{cl}. \]

In the following, we derive each species equation in terms of the mass fraction from the general species transport equation (4.12) under appropriate assumptions for each species in our liquid-feed DMFC model. In particular, compared to other species, methanol obeys Henry’s Law, i.e., assuming liquid and vapor methanol equilibrium.

**Methanol conservation equation**

We assume equilibrium between the liquid and gas phase methanol at the anode side. Based on Henry’s Law, it holds that

\[ C_{l}^{MeOH} = K_H C_{g}^{MeOH}. \quad (4.14) \]

Here, \( C_{l}^{MeOH} \) and \( C_{g}^{MeOH} \) are the liquid and gas phase methanol molar concentrations; and \( K_H \) is Henry’s constant. From the following relationships between species molar
concentration and mass fraction:

\[ \rho_l Y_{MeOH}^l = C_{MeOH}^l M_{MeOH}^l, \quad \rho_g Y_{MeOH}^g = C_{MeOH}^g M_{MeOH}^g, \]

and (4.14), we obtain

\[ Y_{MeOH}^g = \frac{\rho_l}{\rho_g k_H} Y_{MeOH}^l. \quad \text{(4.15)} \]

Furthermore, from the two-phase mixture property (2.20) in Section 2.2.3, we obtain

\[ \rho Y_{MeOH} = \rho_l \left( s + \frac{1 - s}{k_H} \right) Y_{MeOH}^l. \quad \text{(4.16)} \]

Substitute (4.15) and (4.16) into the general species conservation equation (4.12), and we get

\[
- \nabla \cdot \left( \rho_l \left( D_{MeOH}^{l, eff} + \frac{D_{MeOH}^{g, eff}}{k_H} \right) \nabla Y_{MeOH}^l \right) + \nabla \cdot (\tilde{\gamma} \rho u Y_{MeOH}^l) = - \nabla \cdot \left( 1 - \frac{\rho_l}{\rho_g k_H} \right) Y_{MeOH}^l j_l + M_{MeOH} S_{MeOH}, \quad \text{(4.17)}
\]

where the modified advection factor is given by

\[
\tilde{\gamma} = \gamma \frac{\rho_l}{\rho} \left( s + \frac{1 - s}{k_H} \right) = \gamma \frac{\rho_l}{\rho_l s + \rho_g (1 - s)} = \lambda_l + \lambda_g \frac{\rho_l}{\rho_g k_H}. \quad \text{(4.18)}
\]

In (4.17), the capillary diffusion flux of the liquid phase, \( j_l \), is given by (2.49). It will be further derived in terms of the gradient of the water mass fraction \( Y_{H_2O} \) in (4.28).
In the anode catalyst layer, the source term is caused by the chemical reaction and the methanol crossover flux, and is given by

\[ S^{MeOH} = -\frac{j_a}{6F} - S_{cross}^{MeOH}. \]  

(4.19)

The methanol crossover flux through the membrane is caused by electro-osmotic drag and diffusion. It is given as follows:

\[ S_{cross}^{MeOH} = \frac{j_{cross}}{6F} = N_a^{MeOH} + N_a^{MeOH}. \]  

(4.20)

The electro-osmotic drag flux is given by

\[ N_{a,EOD}^{MeOH} = n_d^{MeOH} \frac{j_a}{F}. \]  

(4.21)

Here, \( n_d^{MeOH} \) and \( n_d^{H_2O} \) denote the number of methanol and water molecules per proton in the electro-osmotic drag. Their relation is given as

\[ n_d^{MeOH} = n_d^{H_2O} \frac{C_1^{MeOH}}{C_1^{H_2O}}. \]  

(4.22)

In the cathode side, we assume that all of the methanol crossover flux from the anode side is consumed by the chemical reaction with oxygen. Then we assign the average diffusive methanol flux only to the elements of mesh adjacent to the membrane, by the following:

\[ N_{a,diff}^{MeOH} = \frac{D_m^{MeOH} C_1^{MeOH}|_{cata}}{d_\delta|_{acl}}. \]  

(4.23)
Here, $d\delta_{acl}$ is the length of one element size, along the through-plane direction (from anode to cathode), in the anode catalyst layer; $D_m^{MeOH}$ is the methanol diffusivity in the membrane; and $\delta_m$ is the membrane thickness along the through-plane direction.

**Water conservation equation**

In the water conservation equation, we assume that the gas phase is always saturated since sufficient amount of water is provided in both the anode and cathode sides. In addition, we assume that the gradient of mass fraction in the liquid phase is zero. Then from the general species equation (4.12), we get

$$\nabla \cdot (\gamma \rho u Y_{H_2O}) = \nabla \cdot \left( (Y_{H_2O}^g - Y_{H_2O}^l) j_l \right) + M_{H_2O} S_{H_2O}. \quad (4.24)$$

In Section 2.3, we derived the liquid diffusive flux relative to the two-phase mixture $j_l$ in terms of gradient of saturation (2.49):

$$j_l = \frac{\sigma \cos(\theta_c) (\epsilon K)^{1/2} \lambda_l \lambda_g \nu}{\nu} \nabla J(s). \quad (4.25)$$

Based on the mixture variable relationships (2.18) and (2.20) in Section 2.2.3, we get

$$s = \frac{\rho_g Y_{H_2O}^g - \rho_g Y_{H_2O}^l}{\rho_l Y_{H_2O}^l - \rho_l Y_{H_2O}^g + \rho_g Y_{H_2O}^g - \rho_g Y_{H_2O}^l}. \quad (4.26)$$
From our assumptions $\nabla Y_l^H2O = 0$ and $\nabla Y_g^H2O = 0$, we obtain

$$\nabla s = \frac{\rho_l(\rho_g Y_l^H2O - \rho_g Y_g^H2O)}{(\rho_l Y_l^H2O - \rho_l Y_g^H2O + \rho_g Y_l^H2O - \rho_g Y_g^H2O)^2} \nabla Y^H2O. \quad (4.27)$$

As a result, $j_l$ can be expressed in terms of the water mass fraction $Y^H2O$ as follows:

$$j_l = \frac{\lambda_l \lambda_g \sigma \cos(\theta_c)(\epsilon K)^{\frac{1}{2}}}{\nu} \frac{\rho_l(\rho_g Y_l^H2O - \rho_g Y_g^H2O)}{(\rho_l Y_l^H2O - \rho_l Y_g^H2O + \rho_g Y_l^H2O - \rho_g Y_g^H2O)^2} \nabla Y^H2O. \quad (4.28)$$

Finally, we can rewrite the water conservation equation as the following convection-diffusion-reaction type equation:

$$-\nabla \cdot (D_{cap} \nabla Y^H2O) + \nabla \cdot (\gamma \rho u Y^H2O) = M^H2O S^H2O, \quad (4.29)$$

where the capillary diffusivity $D_{cap}$ is defined as

$$D_{cap} = \frac{(Y_g^H2O - Y_l^H2O) \lambda_g \lambda_l \sigma \cos(\theta_c)(K \epsilon)^{\frac{1}{2}}}{\nu} \frac{\rho_l(\rho_g Y_l^H2O - \rho_g Y_g^H2O)}{(\rho_l Y_l^H2O - \rho_l Y_g^H2O + \rho_g Y_l^H2O - \rho_g Y_g^H2O)^2}. \quad (4.30)$$

This capillary diffusivity under the mass fraction equation has a similar form as the one in (2.54) under the molar concentration equation.
The source term in (4.24) is defined by

\[
S_{H_2O} = \begin{cases} 
-j_a \frac{H_2O}{6F} - \left( N_{a,EOD}^H + N_{a,diff}^H + N_{a, mpl}^H \right), & \text{anode catalyst layer}, \\
2j_c + N_{c,cross}^H + \left( N_{c,EOD}^H + N_{c,diff}^H + N_{c, mpl}^H \right), & \text{cathode catalyst layer}. 
\end{cases}
\]  

(4.31)

The first source term \(j_a\) in the anode catalyst layer is the water consumption because of the oxidation reaction. The anodic volumetric transfer current density \(j_a\) is given in (4.4). The other source terms in the anode catalyst layer are caused by three fluxes through the membrane: the electro-osmotic drag \(N_{a,EOD}^H\), the diffusion \(N_{a,diff}^H\), and the hydraulic permeation \(N_{a, mpl}^H\) due to the difference of hydraulic pressure between the anode and cathode sides. They are given as

\[
\begin{align*}
N_{a,EOD}^H &= \frac{n_d^H j_a}{F}, \\
N_{a,diff}^H &= \frac{\rho_m}{EW_m} D_m^{H_2O} \frac{s_a - s_c}{s_a} \delta_m, \\
N_{a, mpl}^H &= \frac{-\rho_1 K_m}{M^{H_2O} \mu_1 \delta_m} \left[ \frac{2\sigma_a \cos \theta_a}{r_a} J(s_a, \theta_a) - \frac{2\sigma_c \cos \theta_c}{r_c} J(s_c, \theta_c) \right] \delta_c^{CL}. 
\end{align*}
\]

(4.32)

Similar to \(N_{a,diff}^{MeOH}\) in (4.23), we assign \(N_{a,diff}^{H_2O}\) only to the elements (in the mesh) adjacent to the membrane. In addition, \(d\delta_{cl}\) is chosen as one element size (along the through-plane direction) of the anode catalyst layer. Further, \(EW_m\) is the equivalent weight of the membrane; \(\rho_m\) is the membrane density; \(D_m^{H_2O}\) is the water diffusivity in the membrane; and \(s_a/s_c\) is the saturation at the interface between the anode/cathode catalyst layer and the membrane. In the flux \(N_{a, mpl}^{H_2O}\), the hydraulic pressure is proportional to the hydraulic permeability \(K_m\) of the membrane, and it is inversely proportional to the
membrane thickness $\delta_m$; the Leverett function $J$ is given in (2.15) of Section 2.2.2; $\theta_a/\theta_c$ is the contact angle at anode/cathode side; and $r_a/r_c$ is a pore radius of anode/cathode microporous layer (MPL).

In the cathode side, the first source term $\frac{j_c}{2F}$ is the water production because of the reduction reaction. The cathodic volumetric transfer current density $j_c$ is given by (4.6). Alternatively, we can also assign $j_c$ by the following average calculation of the anode transfer current density:

$$j_c = \int_{L_{acl}} j_a dx / \delta_{acl}. \quad (4.33)$$

Here, $L_{acl}$ denotes the one-dimensional line along the through-plane direction across the entire anode catalyst layer; and $\delta_{acl}$ is the thickness of the anode catalyst layer along that direction. Thus, we have the conservation of current through the entire cell. $N_{H_2O}^{c,\text{cross}}$ is the water production due to the chemical reaction caused by the methanol crossover. It is defined as follows:

$$N_{H_2O}^{c,\text{cross}} = \frac{j_{\text{cross}}}{3F}. \quad (4.34)$$

Here, $j_{\text{cross}}$ is given in (4.20). We assign the net water flux from the anode side as follows:

$$\begin{align*}
N_{c,\text{EOD}}^{H_2O} &= \int_{L_{acl}} N_{a,\text{EOD}}^{H_2O} dx / \delta_{acl}, \\
N_{c,\text{diff}}^{H_2O} &= N_{a,\text{diff}}^{H_2O}, \\
N_{c,\text{mpl}}^{H_2O} &= N_{a,\text{mpl}}^{H_2O}. \quad (4.35)
\end{align*}$$

As a result, we also have the conservation of the new water flux through the entire cell.
Remark 2.2.1. As stated above, we assume that the water in the gas phase is always saturated. This means that water always presents in two phase in backing layers and catalyst layers of both the anode and cathode sides. From a computational point of view, this constitutes a significant difference between the liquid-feed DMFC and the hydrogen-feed polymer electrolyte fuel cell (PEFC) \[102, 97, 93\], where single- and two-phase regions may coexist. This makes the diffusion-coefficient of the water conservation equation in the porous media highly discontinuous and even degenerate (see the definition of the diffusivity \(2.54\) and Fig. 2.2 in Section 2.3). In our DMFC model, we do not have such difficulties, since the diffusion coefficient \(4.30\) for the water equation is a smooth function.

Oxygen concentration equation

Since oxygen solubility in the liquid water is very low, we assume that \(Y_{l}^{O_2} = 0\). Then the advection correction factor \(\gamma\) in \(2.37\) can be simplified as

\[
\gamma = \left( \frac{\rho \sum_k \lambda_k Y_{k}^{\alpha}}{(\rho Y^{\alpha})} \right) = \lambda_g. \tag{4.36}
\]

As a consequence, the general species equation \(4.12\) for the methanol reads

\[
\nabla \cdot \left( \lambda_g \rho u Y_{g}^{O_2} \right) = \nabla \cdot \left( \rho_g D_{g,eff}^{O_2} \nabla Y_{g}^{O_2} \right) + \nabla \cdot \left( Y_{g}^{O_2} j_l \right) + M^{O_2} S^{O_2}. \tag{4.37}
\]
The source term in this oxygen equation is given by the anode reduction reaction and the methanol crossover from the anode side:

\[ \dot{S}^O_2 = -\frac{j_c + j_{cross}}{4F}. \] (4.38)

Here, the cathodic volumetric transfer current density \( j_c \) and the volumetric current density \( j_{cross} \) caused by the methanol crossover are given in (4.6) and (4.20) respectively.

**Proton conservation equation**

The proton conservation is given by the following reaction-diffusion equation:

\[ -\nabla \cdot (\kappa_{eff} \nabla \Phi_e) = S^{\Phi_e}, \] (4.39)

where the \( \kappa_{eff} \) is the effective proton conductivity, and the source term is defined as

\[ S^{\Phi_e} = \begin{cases} j_a, & \text{anode catalyst layer,} \\ -j_c + j_{cross}, & \text{cathode catalyst layer.} \end{cases} \] (4.40)

**Electron conservation equation**

The electron conservation equation is also given by the following reaction-diffusion equation

\[ -\nabla \cdot (\sigma_{eff} \nabla \Phi_s) = S^{\Phi_s}, \] (4.41)
where $\sigma_{s}^{eff}$ is the effective electron conductivity, and the source term is defined as:

$$S_{\Phi s} = \begin{cases} 
-j_a, & \text{anode catalyst layer}, \\
-j_c - j_{cross}, & \text{cathode catalyst layer}.
\end{cases}$$ \hspace{1cm} (4.42)

**Energy conservation equation**

The energy conservation equation in terms of temperature can be derived from (2.43). It has the following convection-diffusion-reaction form:

$$-\nabla \cdot \left( k^{eff} \nabla T \right) + \nabla \cdot \left( \rho C_p u T \right) = S^T.$$ \hspace{1cm} (4.43)

Here, $k^{eff}$ and $C_p$ denote the effective heat conductivity and heat capacity respectively. The source term is caused by the irreversible heat of the electrochemical reaction, the reversible entropic heat, and the Joule heating:

$$S^T = \begin{cases} 
-j_a \left( \eta_a + T \frac{dU_{0,a}}{dT} \right) + \frac{I^2}{\kappa^{eff}}, & \text{anode catalyst layer}, \\
\frac{I^2}{\kappa^{eff}}, & \text{membrane}, \\
-j_c \left( \eta_c + T \frac{dU_{0,c}}{dT} \right) + \frac{I^2}{\kappa^{eff}} - j_{cross} \left( \eta_c + T \frac{dU_{0,c}}{dT} \right), & \text{cathode catalyst layer}.
\end{cases}$$ \hspace{1cm} (4.44)

The current density is given by

$$I = -\kappa^{eff} \frac{\partial \Phi_e}{\partial x}.$$ \hspace{1cm} (4.45)
Useful current density is only present in the through-plane direction (from anode to cathode). Thus it is important to minimize the current densities for the other directions. In this source term, the influence of the methanol crossover on the energy balance is also considered in the cathode catalyst later. The definitions for the anode over-potential $\eta_a$ and cathode over-potential $\eta_c$ are given in (4.5) and (4.7) respectively.

In summary, we get a full system of conservation equations: continuity (4.8), momentum (4.10), methanol (4.17), water (4.29), oxygen (4.37), proton (4.39), electron (4.41), and energy (4.43) equations. They are strongly coupled through various terms and coefficients in the equations.

**Physical parameters**

Two phase relationships are given in Section 2.2.3. Physical parameters used in the above governing equations and constitutive equations are given below in Tables 4.1 - 4.3.

### 4.3 Computational domain and boundary conditions

Fig. 4.1. shows the computational domain of the 3D DMFC model. It is divided into nine subdomains along the through-plane direction ($x$-axis): the anode bipolar plate (ABP, anode current collector), anode gas channel (AGC), anode backing layer (ABL), anode catalyst layer (ACL), membrane (MEM), cathode catalyst layer (CCL), cathode backing layer (CBL), cathode gas channel (CGC), and cathode bipolar plate (CBP, cathode current collector). The thickness in the through-plane direction of each subdomain: $\delta_{ABP} = 5 \times 10^{-4} m$, $\delta_{AGC} = 10^{-3} m$, $\delta_{ABL} = 3 \times 10^{-4} m$, $\delta_{ACL} = 10^{-5} m$. 
\[ \delta_{MEM} = 5 \times 10^{-5} m, \quad \delta_{CCL} = 10^{-5} m, \quad \delta_{CBL} = 3 \times 10^{-4} m, \quad \delta_{CGC} = 10^{-3} m, \quad \text{and} \quad \delta_{CBP} = 5 \times 10^{-4} m. \]

The widths of the in-plane direction (z-axis) of the cell and the channel are \( w_{cell} = 2 \times 10^{-3} m \) and \( w_{channel} = 10^{-3} m \) respectively. The length of the cell in the along-channel direction (y-axis) is \( l_{cell} = 2.5 \times 10^{-2} m \).

As shown in Fig. 4.1, we extend the two gas channels to both sides for the half length of the cell in order to better approximate the true physical boundary conditions for the momentum equations.

All governing equations of the 3D model are summarized in Section 4.2, with ten unknowns: \( \mathbf{u} \) (three components), \( p, Y_l^\text{MeOH}, Y_g^\text{O}_2, Y^\text{H}_2\text{O}, \Phi_e, \Phi_s \) and \( T \). Their corresponding boundary conditions are given as follows:
Inlet boundaries. The constant inlet velocity $u_{\text{in}}$ in a flow channel is expressed by the stoichiometric flow ratios in the anode and cathode sides, i.e., $\xi_a$ or $\xi_c$, defined at a reference current density, $i_{\text{ref}}$, as

$$\xi_a = \frac{C_{l,\text{in}}^{\text{MeOH}} u_{\text{in}} A_{\text{cross},a}}{i_{\text{ref}} A} \quad \text{and} \quad \xi_c = \frac{C_{l,\text{in}}^{\text{O}_2} u_{\text{in}} A_{\text{cross},c}}{i_{\text{ref}} A}$$

(4.46)

where $u_{\text{in}}$ is the along-channel direction ($y$-axis) component of $u_{\text{in}}$, and $A_{\text{cross},a}$ and $A_{\text{cross},c}$ are the cross-sectional ($x$-$z$ plane) areas of the anode and cathode flow channels, respectively. The area of the cell ($y$-$z$ plane) is denoted by $A$. The other two components of $u_{\text{in}}$ are given by zeros.

The anode inlet methanol concentration $C_{l,\text{in}}^{\text{MeOH}}$ is given as an operating parameter, and the cathode oxygen molar concentration $C_{l,\text{in}}^{\text{O}_2}$ is determined by the cathode inlet pressure, temperature, and relative humidity according to the ideal gas law. At the anode inlet, pure liquid fuel is provided so that $s = 100\%$. The liquid methanol mass fraction is computed from the methanol inlet concentration by $Y_{l}^{\text{MeOH}} = \frac{C_{l,\text{in}}^{\text{MeOH}} M_{\text{MeOH}}}{\rho_l}$; here $C_{l,\text{in}}^{\text{MeOH}} = 2000 \text{ mol/m}^3$. Then the water mass fraction is $Y_{l}^{\text{H}_2\text{O}} = Y_{l}^{\text{H}_2\text{O}} = 1 - Y_{l}^{\text{MeOH}}$ since $s = 100\%$. At the cathode inlet, pure gas fuel is provided so that $s = 0\%$. Then $Y_{g}^{\text{O}_2}$ and $Y_{g}^{\text{H}_2\text{O}} = Y_{g}^{\text{H}_2\text{O}}$ are determined by the ideal gas law.

By the above calculations, we write inlet boundary conditions as follows:

- Anode inlet methanol mass fraction: $Y_{l}^{\text{MeOH}} = 6.4\%$,
- Anode inlet water mass fraction: $Y_{l}^{\text{H}_2\text{O}} = 93.6\%$,
- Cathode inlet oxygen mass fraction: $Y_{g}^{\text{O}_2} = 20.21\%$,
• Cathode inlet water mass fraction: $Y_{H_2O} = 13.24\%$.

The temperature, at both anode and cathode inlets, is given as $T = 333.15 \, K$.

**Outlet boundaries.** We impose a traction-free boundary condition for the momentum equation and no diffusive flux condition for the other variables.

- Traction-free boundary condition for the momentum equation at the outlet channel:

$$(-\mu \nabla \mathbf{u} + p I) \cdot \mathbf{n} = 0.$$

- No diffusive flux condition for the methanol, oxygen, and water at the outlet channel:

$$\nabla Y_{l \, MeOH} \cdot \mathbf{n} = 0, \quad \nabla Y_{g \, O_2} \cdot \mathbf{n} = 0, \quad \nabla Y_{H_2O} \cdot \mathbf{n} = 0.$$

- No flux condition for the electron potential at the outlet of the bipolar plate:

$$\nabla \Phi_s \cdot \mathbf{n} = 0.$$

- $T = 333.15k$

**Walls.** No-slip and no-flux conditions are applied.

- No slip condition: $\mathbf{u} = 0$.

- No flux conditions for the methanol, oxygen, water, and proton potential:

$$\nabla Y_{l \, MeOH} \cdot \mathbf{n} = 0, \quad \nabla Y_{g \, O_2} \cdot \mathbf{n} = 0, \quad \nabla Y_{H_2O} \cdot \mathbf{n} = 0, \quad \nabla \Phi_s \cdot \mathbf{n} = 0.$$
• Temperature:

\[
\begin{aligned}
\nabla T \cdot \mathbf{n} &= 0, \quad \text{top and bottom walls,} \\
T &= 333.15 \text{k}, \quad \text{other walls.}
\end{aligned}
\]  

\[\text{(4.47)}\]

• Electron potential:

\[
\begin{cases}
\Phi_s = 1, & \text{at the anode current collector,} \\
\Phi_s = V_{cell} = 1.4, & \text{at the cathode current collector,} \\
(\text{or } \sigma^s_{eff} \nabla \Phi_s \cdot \mathbf{n} = 2000) & \\
\frac{\partial \Phi_s}{\partial n} = 0, & \text{at other walls.}
\end{cases}
\]

\[\text{(4.48)}\]

The cell operating voltage is 0.4 V, which is the difference between the value of $\Phi_s$ at the cathode and anode current collectors.

**Internal boundary conditions.** The computational domains of each variable are not the same. For example, the species (methanol, water, and oxygen) cannot transport through bipolar plates which are solid phases, while electrons transport through bipolar plates. We use Table 4.4 to indicate whether each governing equation is solved in each specific subdomain. We use the check mark notation "✓" to denote if the governing equation is solved in the specific subdomain. Otherwise, we use the notation "×".

Then we give the internal boundary conditions for each variable.

• Momentum equation:

We impose no slip condition at the interface between ACL (or CCL) and MEM,

\[\mathbf{u} = 0.\]  

\[\text{(4.49)}\]
• Methanol equation:

At the interface between ACL and MEM,

\[ \nabla Y_{\text{MeOH}} \cdot \mathbf{n} = 0. \]  
(4.50)

This implies that there is no diffusive flux. In fact, the convective flux is also zero because of the no-slip condition (4.49).

• Water equation:

At the interface between ACL (or CCL) and MEM, we impose no flux condition:

\[ \nabla Y_{\text{H}_2\text{O}} \cdot \mathbf{n} = 0. \]  
(4.51)

• Oxygen equation:

At the interface between CCL and MEM, we impose no flux condition:

\[ \nabla Y_{\text{O}_2} \cdot \mathbf{n} = 0. \]  
(4.52)

• Proton potential equation:

At the interface between ACL (or CCL) and ABL (or CBL), we impose no flux condition:

\[ \nabla \Phi_e \cdot \mathbf{n} = 0. \]  
(4.53)
So far we have discussed the 3D steady-state two-phase full DMFC model equations with boundary conditions in a computational domain shown in Fig. 4.1 that contain continuity (4.8) and momentum (4.10), species equations of methanol (4.17), water (4.29) and oxygen (4.37), potential equations of proton (4.39) and electron (4.41), and the energy equation (4.43). In the following section, we will discuss numerical methods to solve this coupled system of equations.

4.4 Numerical simulation techniques

4.4.1 Investigation of water source terms

In our numerical simulations, we detect the tough nonconvergent phenomena that occurs in the water equation. This strongly influence other equations’ numerical performance. After having conducted plenty of numerical experiments and analyses, we are convinced of the importance of modification of water source terms based on the following.

The water source term $S^{H_2O}$ (4.31) at the anode catalyst layer is more reasonable if a sufficient amount of water is provided. In particular the volumetric current transfer density $j_a$ in (4.4) is defined with this assumption [61, 60, 59]. Physically, this is guaranteed because sufficient water is always provided through the anode inlet. This is shown in Section 4.3, where the boundary condition of the water mass fraction at the anode inlet is assigned the high value of 93.6%.

What if during the iteration of numerical simulations, the water mass fraction is not large enough? In the literature, this situation is avoided by under relaxation
(choosing a small relaxation parameter) with respect to a sufficiently large initial guess. However, for the purpose of fast convergence, we should consider that during the iterative procedure the not-yet-converged solution might be small. In such a case, because of the large negative water source term (sink), \( S_{H_2O}, Y_{H_2O} \) will be numerically continuously decreased once the small values of \( Y_{H_2O} \) emerge in nonlinear iterations. This runs counter to what we would expect in the DMFC system: a sufficient amount of water needs to be carried in the anode. Therefore, a modification of the water source term (4.31) is important for this consideration. We give the modified water source term as follows:

\[
\hat{S}_{H_2O}(Y_{H_2O}) = \begin{cases} 
S_{H_2O} f_a(Y_{H_2O}) & \text{at anode catalyst layer,} \\
S_{H_2O} f_c(Y_{H_2O}) & \text{at cathode catalyst layer,}
\end{cases}
\]  

(4.54)

where

\[
f_a(Y_{H_2O}) = 0.5 \tanh\left(\frac{Y_{H_2O} - b_a}{\varepsilon_a}\right) + 0.5, \\
f_c(Y_{H_2O}) = 0.5 \tanh\left(\frac{b_c - Y_{H_2O}}{\varepsilon_c}\right) + 0.5.
\]  

(4.55)

We choose \( b_a = 92\% \), \( b_c = 54\% \), and \( \varepsilon_a = \varepsilon_c = 10^{-4} \) in the expression of the \( \tanh \) function. This allows \( \hat{S}_{H_2O}(Y_{H_2O}) \) to approximate the original water source term \( S_{H_2O} \) when the water mass fraction \( Y_{H_2O} \) is greater than \( b_a \) at the anode and less than \( b_c \) at the cathode. Otherwise, \( \hat{S}_{H_2O}(Y_{H_2O}) \) is forced to approach zero immediately. Then little water is consumed if \( Y_{H_2O} \) is smaller than \( b_a \), and little water is generated if \( Y_{H_2O} \) is bigger than \( b_c \).

By the property of the \( \tanh \) function, it is easy to see that \( \hat{S}_{H_2O}'(Y_{H_2O}) < 0 \) for both the anode and cathode sides. Thus we use Newton’s method to linearize this source term and get a positive definite matrix, which contributes to the linearized stiffness matrix of the water equation and stabilizes the iteration process.
4.4.2 Sequence of unknowns in the nonlinear iterative procedure

The 3D steady-state two-phase full DMFC model consists of 8 nonlinear governing equations: momentum (4.10) and continuity (4.8) equations, species conservation equations for water (4.29), methanol (4.17) and oxygen (4.37), proton (4.39) and electron (4.41) potential equations, and energy transport (4.43). There are 10 unknowns in the equations: $u, p, Y_{H_2O}, Y_{MeOH}^l, Y_{O2}^g, \Phi_e, \Phi_s$, and $T$. These equations couple with each other through various terms. In particular, two potential equations exhibit a strong coupling to each other by a pair of volumetric transfer current densities in the source terms: $j_a$ and $j_c$. Thus we solve these two potentials simultaneously. In addition, we solve the coupled momentum and continuity equations as a saddle-point system. Other than these equations, we decouple the oxygen, methanol, water, and temperature equations, and solve them individually. In the remaining section, we will discuss the importance of the sequence of unknowns in the nonlinear iteration procedure for the full DMFC simulation, and then arrange the sequence of unknowns appropriately to get a better iterative performance.
Consider the Jacobian system of the fully coupled system of the full DMFC model.

\[ A\Phi = F, \] with \( \Phi = (\Phi_1, \Phi_2, \Phi_3, \Phi_4, \Phi_5, \Phi_6)^\top, \) \( F = (b_1, b_2, b_3, b_4, b_5, b_6)^\top, \) and

\[
A = \begin{pmatrix}
A_{11} & A_{12} & A_{13} & A_{14} & A_{15} & A_{16} \\
A_{21} & A_{22} & A_{23} & A_{24} & A_{25} & A_{26} \\
A_{31} & A_{32} & A_{33} & A_{34} & A_{35} & A_{36} \\
A_{41} & A_{42} & A_{43} & A_{44} & A_{45} & A_{46} \\
A_{51} & A_{52} & A_{53} & A_{54} & A_{55} & A_{56} \\
A_{61} & A_{62} & A_{63} & A_{64} & A_{65} & A_{66}
\end{pmatrix}.
\]

Let \( A = D - L - U, \) where \( D \) is the diagonal block matrix of \( A; \) \( L \) and \( U \) are the strictly lower and upper triangular blocks of \( A. \) We let \( \Phi = (\Phi_1, \Phi_2, \Phi_3, \Phi_4, \Phi_5, \Phi_6)^T = (D - L)^{-1}F, \) then by backward substitution we have

\[
\Phi_1 = A_{11}^{-1}b_1, \\
\Phi_2 = A_{22}^{-1}(b_2 - A_{21}\Phi_1), \\
\Phi_3 = A_{33}^{-1}(b_3 - A_{31}\Phi_1 - A_{32}\Phi_2), \\
\Phi_4 = A_{44}^{-1}(b_4 - A_{41}\Phi_1 - A_{42}\Phi_2 - A_{43}\Phi_3), \\
\Phi_5 = A_{55}^{-1}(b_5 - A_{51}\Phi_1 - A_{52}\Phi_2 - A_{53}\Phi_3 - A_{54}\Phi_4), \\
\Phi_6 = A_{66}^{-1}(b_6 - A_{61}\Phi_1 - A_{62}\Phi_2 - A_{63}\Phi_3 - A_{64}\Phi_4 - A_{65}\Phi_5).
\]

Thus, this decoupling procedure can be viewed as a fully coupled implicit nonlinear solution method by applying one step of the block Gauss-Seidel iteration instead of solving the Jacobian system exactly. The efficiency of the block Gauss-Seidel method
depends on the arrangement of the unknowns. If we reorder the unknowns so that entries
in the upper triangular block are smaller in some sense, then \((D - L)^{-1}A\) is closer to
the identity matrix \(I\).

Now we will consider the ordering of unknowns in the above decoupling procedure. Proton potential \(\Phi_e\) and electron potential \(\Phi_s\) have the strongest effect on other
unknowns through over-potentials (4.5) and (4.7), which contribute to the driving force
of the chemical reactions in fuel cells. Many coefficients in the governing equations de-
pend on temperature, thus we choose \(T\) as the second unknown in the sequence. All
species convective flow transport are driven by the flow field, with the velocity \(u\) and
pressure \(p\) acting as the next strongest pair of unknowns. Among the remaining three
unknowns \(Y_{MeOH}^l\), \(Y_{H_2O}^g\), and \(Y_{O_2}^g\), we choose \(Y_{MeOH}^l\) the next strongest one due
to the methanol crossover flux \(j_{cross}\) and anodic volumetric current density \(j_a\). Lastly,
compared to oxygen, water appears in not only cathode side but also anode side; thus,
\(Y_{H_2O}^g\) has a stronger influence than \(Y_{O_2}^g\). In conclusion, the following sequence of un-
knowns
\[
\begin{pmatrix}
\Phi_e \\
\Phi_s
\end{pmatrix}
\to T
\to
\begin{pmatrix}
u \\
p
\end{pmatrix}
\to Y_{MeOH}^l
\to Y_{H_2O}^g
\to Y_{O_2}^g
\]
is the right one in order
that the lower block triangular part of the Jacobian matrix \(A\) is dominant.

### 4.4.3 Linearization method

We use Newton’s method to linearize the source term and use Picard linearization
for the other terms in each conservation equation. In the following, we present the
linearization method for the 3D steady-state two-phase DMFC model. Provided

\[ \begin{pmatrix} \Phi_n^e \\ \Phi_n^s \\ T_n^e \\ p_n^e \end{pmatrix}, \begin{pmatrix} u_n^e \\ Y_{\text{MeOH},n}^l \\ Y_{\text{H}_2\text{O},n}^l \\ Y_{\text{O}_2,n}^g \end{pmatrix}, \begin{pmatrix} u_n^s \\ Y_{\text{MeOH},n+1}^l \\ Y_{\text{H}_2\text{O},n+1}^l \\ Y_{\text{O}_2,n+1}^g \end{pmatrix}, \begin{pmatrix} \Phi_{n+1}^e \\ \Phi_{n+1}^s \\ T_{n+1}^e \\ p_{n+1}^e \end{pmatrix} \]

we define the next iterative solution

\[ \begin{pmatrix} \Phi_{n+1}^e \\ \Phi_{n+1}^s \\ T_{n+1}^e \\ p_{n+1}^e \end{pmatrix}, \begin{pmatrix} u_{n+1}^e \\ Y_{\text{MeOH},n+1}^l \\ Y_{\text{H}_2\text{O},n+1}^l \\ Y_{\text{O}_2,n+1}^g \end{pmatrix} \]

as the solution of the following linearized problems \((n = 0, 1, 2, \cdots)\):

1. Linearization of the coupled proton and electron potential equations:

\[
\begin{align*}
-\nabla \cdot (\kappa_{\text{eff}} \nabla \Phi_{n+1}^e) - \partial S_{\Phi_e,n} \Phi_{n+1}^e - \partial S_{\Phi_s,n} \Phi_{n+1}^s &= S_{\Phi_e,n} - \partial S_{\Phi_e,n} \Phi_{n}^e \\
-\nabla \cdot (\sigma_{\text{eff}} \nabla \Phi_{n+1}^s) - \partial S_{\Phi_s,n} \Phi_{n+1}^s - \partial S_{\Phi_e,n} \Phi_{n+1}^e &= S_{\Phi_s,n} - \partial S_{\Phi_s,n} \Phi_{n}^s
\end{align*}
\]

(4.56)

2. Linearization of the energy equation:

\[
-\nabla \cdot (k_{\text{eff}} \nabla T_{n+1}^e) + \nabla \cdot \left( \rho C_p u_{n+1} T_{n+1}^e \right) - \frac{\partial S_{T,n}}{\partial T} T_{n+1}^e = S_{T,n} - \frac{\partial S_{T,n}}{\partial T} T_{n}^e.
\]

(4.57)
3. Linearization of the momentum and continuity equations:

\[
\begin{align*}
-\nabla \cdot (\mu^n \nabla \mathbf{u}^{n+1}) + \frac{2}{\varepsilon} \nabla \cdot (\rho^n \mathbf{u}^n \mathbf{u}^{n+1}) + \nabla p^{n+1} + \frac{\mu^n}{K} \mathbf{u}^{n+1} &= \frac{1}{\varepsilon^2} \nabla \cdot (\rho^n \mathbf{u}^n \mathbf{u}^n), \\
\nabla \cdot \mathbf{u}^{n+1} &= \frac{\dot{m}^n}{\rho_{\text{fr}}} - \frac{\nabla \rho^n}{\rho_{\text{fr}}} \cdot \mathbf{u}^n.
\end{align*}
\]

(4.58)

4. Linearization of the methanol equation:

\[
\begin{align*}
-\nabla \cdot \left[ \rho_l \left( D_{l,\text{eff}}^{\text{MeOH},n} + \frac{D_{g,\text{eff}}^{\text{MeOH},n}}{K_H} \right) \nabla Y_{\text{MeOH},n}^{n+1} \right] \\
+\nabla \cdot \left[ \gamma^n \rho^n \mathbf{u}^{n+1} Y_{\text{MeOH},n}^{n+1} \right] - \frac{\partial S_{\text{MeOH},n}^{\text{MeOH},n}}{\partial Y_{l}^{\text{MeOH}}} M_{\text{MeOH}} Y_{\text{MeOH},n}^{n+1}
\end{align*}
\]

\[
= \nabla \cdot \left( \left( \frac{\rho_l}{\rho_{g,H}} - 1 \right) Y_{\text{MeOH},n}^{n+1} \right)
\]

\[
+ M_{\text{MeOH}} \left( S_{\text{MeOH},n}^{\text{MeOH},n} - \frac{\partial S_{\text{MeOH},n}^{\text{MeOH},n}}{\partial Y_{l}^{\text{MeOH}}} Y_{\text{MeOH},n}^{n+1} \right).
\]

(4.59)

5. Linearization of the water equation:

\[
\begin{align*}
-\nabla \cdot \left( D_{\text{cap}}^{\text{H}_2\text{O},n} (Y_{\text{H}_2\text{O},n}^{n+1}) \nabla Y_{\text{H}_2\text{O},n}^{n+1} \right) + \nabla \cdot \left( \gamma^n \rho^n \mathbf{u}^{n+1} Y_{\text{H}_2\text{O},n}^{n+1} \right)
\end{align*}
\]

\[
- \frac{\partial S_{\text{H}_2\text{O},n}^{\text{H}_2\text{O},n}}{\partial Y_{l}^{\text{H}_2\text{O}}} M_{\text{H}_2\text{O}} Y_{\text{H}_2\text{O},n}^{n+1}
\]

\[
= M_{\text{H}_2\text{O}} \left( S_{\text{H}_2\text{O},n}^{\text{H}_2\text{O},n} - \frac{\partial S_{\text{H}_2\text{O},n}^{\text{H}_2\text{O},n}}{\partial Y_{l}^{\text{H}_2\text{O}}} Y_{\text{H}_2\text{O},n}^{n+1} \right).
\]

(4.60)
6. Linearization of the oxygen equation:

\[
\begin{align*}
-\nabla \cdot \left( \rho g D_{g,\text{eff}}^O Y_{g}^{O_2,n+1} \right) &+ \nabla \cdot \left( \lambda_g^n \rho^n u^{n+1} Y_{g}^{O_2,n+1} \right) \\
- \frac{\partial S_{O_2,n}^O m_{O_2}^O}{\partial Y_{g}^{O_2}} Y_{g}^{O_2,n+1} &+ \nabla \cdot \left( Y_{g}^{O_2,n} j^n_{l} \right) + M_{O_2}^O \left( S_{O_2,n}^O - \frac{\partial S_{O_2,n}^O}{\partial Y_{g}^{O_2}} Y_{g}^{O_2,n} \right). \\
\end{align*}
\]

(4.61)

4.4.4 Coupled finite element and upwind finite volume discretizations

To discretize the dominant convection arising in flow channels and possibly in other subdomains, we employ coupled finite element–finite volume upwind discretization methods. First of all, we discuss how to use a upwind finite volume method to discretize the convection term of the form \( \nabla \cdot (u p) \), where \( p \) is a general scalar variable and \( u \) is a vector.

Let \( T_h \) be a triangular or rectangular mesh of the computational domain \( \Omega \). In \( T_h, T \) denotes a triangle or rectangle, and \( P_i (i = 1, 2, \ldots, N) \) means the nodal points in the mesh. \( N \) is number of nodes. By \( \omega_i \), we denote the set of nodes that share an edge with the point \( P_i \). A piecewise continuous finite element space \( V_h \) on \( T_h \) is defined as

\[
V_h := \{ q \in C^0(\bar{\Omega}) \mid q \in P_1(T), \quad \forall T \in T_h \}. 
\]

(4.62)

Then the finite element discretization of the above convection term reads

\[
(\nabla \cdot (u p_h), q_h). 
\]

(4.63)
Here, \( p_h, q_h \in V_h \).

Next we need a dual mesh for the finite volume discretization. The dual mesh \( \mathcal{D}_h \) consists of a control volume \( \Omega_i \in \mathcal{D}_h \) associated with each vertex \( P_i \). It is constructed as follows. Connect the gravitational center of \( T \) (which has the vertex \( P_i \)) to the mid-point of edges (which have vertex \( P_i \)). Then the polygonal domain surrounding \( P_i \) obtained in this way is the control volume \( \Omega_i \). In this control volume, \( \Gamma_{ij} \) denotes the part of boundary \( \partial \Omega_i \) that intersects with the line segment \( P_i P_j \ (j \in \omega_i) \). It could be a line segment or a union of segments. Based on this dual mesh, we define the space

\[
W_h := \{ w \in L^2(\Omega) \mid w \in P_0(\Omega_i), \ \forall \Omega_i \in \mathcal{D}_h \}. \tag{4.64}
\]

Further, we introduce an interpolation operator \( S_h : C^0(\bar{\Omega}) \to W_h \):

\[
q \to S_h(q) := \sum_{\omega_i \in \mathcal{D}_h} q(P_i) \chi_{\Omega_i} \tag{4.65}
\]

Here, \( \chi_{\Omega_i} \) is the characteristic function of \( \Omega_i \).

The upwind finite volume discretization can be derived as

\[
(\nabla \cdot (u p_h), S_h(q_h)) = \sum_{i=1}^{N} q_i \int_{\partial \Omega_i} (u \cdot n) p_h ds = \sum_{i=1}^{N} q_i \sum_{j \in \omega_i} \int_{\Gamma_{ij}} (u \cdot n) p_h ds
\]

\[
\approx \sum_{i=1}^{N} q_i \sum_{j \in \omega_i} \int_{\Gamma_{ij}} (u \cdot n)(r_{ij} p_i + (1-r_{ij}) p_j) ds. \tag{4.66}
\]
Here, \( q_i := q_h(P_i) \) and \( r_{ij} \) is the upwind parameter determined by the following:

\[
\begin{align*}
  r_{ij} = \begin{cases} 
    1 & \text{if } F_{ij} > 0, \\
    0 & \text{if } F_{ij} < 0, \\
    0.5 & \text{if } F_{ij} = 0.
  \end{cases}
\end{align*}
\] (4.67)

In the above, \( F_{ij} := \int_{\Gamma_{ij}} (\mathbf{u} \cdot \mathbf{n}) ds \) is called a numerical flux. Clearly, (4.67) implies \( r_{ij} + r_{ji} = 1 \). By numerical flux \( F_{ij} \), (4.66) can be rewritten as

\[
(\nabla \cdot (u p_h), S_h(q_h)) \approx \sum_{i=1}^{N} q_i \sum_{j \in \omega_i} F_{ij} \left( r_{ij} p_i + (1 - r_{ij}) p_j \right).
\] (4.68)

Apparently, then, \( F_{ij} = -F_{ji} \).

Similarly, we can derive the finite volume discretization for the three-dimensional case. By applying the coupled finite element method (FEM) and the upwind finite volume method (FVM) to the linearized systems (4.56)–(4.61), we obtain the following discretizations in the continuous piecewise trilinear finite element space \( V_h \).

For any \( \begin{pmatrix} \Phi_e \\ \Phi_s \end{pmatrix}, \begin{pmatrix} \bar{U} \\ \bar{P} \end{pmatrix}, \begin{pmatrix} Y_{MeOH}^l \\ Y_{H_2O}^l \\ Y_{O_2}^l \end{pmatrix}, \begin{pmatrix} Y_{MeOH}^h \\ Y_{H_2O}^h \\ Y_{O_2}^h \end{pmatrix} \in V_h \), find \( \begin{pmatrix} \Phi_{e,h} \\ \Phi_{s,h} \end{pmatrix}, T_h, \begin{pmatrix} U_h \\ P_h \end{pmatrix} \in V_h \) such that \( (n = 0, 1, 2, \ldots) \),
1. FEM discretization of the coupled proton and electron potential equations:

\[
\begin{align*}
\left\{ \begin{array}{l}
\left( \kappa_{\text{eff}} \nabla \Phi^{n+1}_{e,h}, \nabla \Phi_e \right) - \left( \partial S_{\Phi_e,\text{e,n}} \Phi^{n+1}_{e,h}, \Phi_e \right) - \left( \partial S_{\Phi_s,\text{s,n}} \Phi^{n+1}_{s,h}, \Phi_s \right) \\
= \left( S_{\Phi_e,n}^{\text{e,n}} \Phi_e \right) - \left( \partial S_{\Phi_e,\text{e,n}} \Phi^{n+1}_{e,h}, \Phi_e \right) - \left( \partial S_{\Phi_s,\text{s,n}} \Phi^{n+1}_{s,h}, \Phi_s \right)
\end{array} \right. \\
\left( \sigma_{\text{eff}}^s \nabla \Phi^{n+1}_{s,h}, \nabla \Phi_s \right) - \left( \partial S_{\Phi_s,\text{s,n}} \Phi^{n+1}_{s,h}, \Phi_s \right) - \left( \partial S_{\Phi_e,\text{s,n}} \Phi^{n+1}_{s,h}, \Phi_e \right) \\
= \left( S_{\Phi_s,n}^{\text{s,n}} \Phi_s \right) - \left( \partial S_{\Phi_s,\text{s,n}} \Phi^{n+1}_{s,h}, \Phi_s \right) - \left( \partial S_{\Phi_e,\text{s,n}} \Phi^{n+1}_{s,h}, \Phi_e \right)
\end{align*}
\]

(4.69)

2. Coupled FEM and upwind FVM discretization of the energy equation:

\[
\begin{align*}
\left( k_{\text{eff}} \nabla T^{n+1}_h, \nabla \tilde{T} \right) - \left( \partial S_{T,\text{e,n}} \Phi^{n+1}_h, \tilde{T} \right) \\
+ \sum_{i=1}^{N} \tilde{T}_i \sum_{j \in \omega_i} \int_{\Gamma_{ij}} \left( \rho^n C_p u^n_h \cdot \mathbf{n} \right) ds \left( r_{ij} T^{n+1}_{h,i} + (1 - r_{ij}) T^{n+1}_{h,j} \right) \\
= \left( S_{T,\text{e,n}} \Phi_h \right) - \left( \partial S_{T,\text{e,n}} \Phi^{n+1}_h, \tilde{T} \right)
\end{align*}
\]

(4.70)

Here, the upwind parameter \( r_{ij} \) is determined by the numerical flux \( F_{ij} = \int_{\Gamma_{ij}} (\rho^n C_p u^n_h \cdot \mathbf{n}) ds \) according to (4.67); \( \tilde{T}_i := \tilde{T}(P_i) \), and similar notations hold for the remaining equations.
3. Coupled FEM and upwind FVM discretization of the momentum and continuity equations:

\[
\begin{cases}
\left( \mu^n \nabla \mathbf{u}_h^{n+1}, \nabla \tilde{\mathbf{u}} \right) - \left( p_h^{n+1}, \nabla \cdot \tilde{\mathbf{u}} \right) + \left( \frac{K^n}{\kappa} \mathbf{u}_h^{n+1}, \tilde{\mathbf{u}} \right) \\
+ \sum_{i=1}^{N} \tilde{u}_i \sum_{j \in \omega_i} \frac{1}{2} \int_{\Gamma_{ij}} \left( \rho^n \mathbf{u}_h^n \cdot \mathbf{n} \right) ds \left( r_{ij} \mathbf{u}_{h,i}^{n+1} + (1 - r_{ij}) \mathbf{u}_{h,j}^{n+1} \right) \\
+ \delta(h^2) \left( \nabla p_h^{n+1}, \nabla \tilde{p} \right)
\end{cases}
\]

(4.71)

Here, \( r_{ij} \) is determined by \( F_{ij} = \int_{\Gamma_{ij}} \left( \rho^n \mathbf{u}_h^n \cdot \mathbf{n} \right) ds \) according to (4.67). After splitting the right hand side of continuity equation (4.8) as (4.71b) does, a saddle point system is then obtained from above finite element based discretization. On the other hand, although \( Q_1-Q_1 \) finite element spaces (continuous trilinear velocity and pressure) do not directly satisfy the inf-sup stability condition, they can be stabilized by properly adding a pressure stabilizing term, \( \delta(h^2)(\nabla p_h, \nabla \tilde{p}) \), into the momentum equation [18, 38, 88], as shown in its weak form.
4. FEM and upwind FVM discretization of the methanol equation:

\[
\begin{align*}
&\left(\rho_l \left(D_{MeOH,n}^{l,eff} + D_{g,eff}^{MeOH,n} \right) \nabla Y_{MeOH,n}^{l,h} + \nabla \tilde{\nabla}^{MeOH}\right) \\
&- \left(\frac{\partial S_{MeOH,n}^{MeOH}}{\partial Y_{MeOH}^{l,h}} M_{MeOH} Y_{MeOH,n}^{l,h}, \tilde{\nabla}^{MeOH}\right) \\
&+ \sum_{i=1}^{N} Y_{MeOH}^{l,i} \sum_{j \in \omega_i} \int_{\Gamma_{ij}} \left(\gamma^n \rho^n u^n \cdot n\right) ds \left(r_{ij} Y_{MeOH,n}^{l,h,i} \right) \\
&+ \left(1 - r_{ij}\right) Y_{MeOH,n}^{l,h,j} \\
&= \sum_{i=1}^{N} Y_{MeOH}^{l,i} \sum_{j \in \omega_i} \int_{\Gamma_{ij}} \left(\left(\frac{\rho_l}{\rho_g H} - 1\right) j^n \cdot n\right) ds. \\
&\left(\tilde{\gamma}^{l,h,i} Y_{MeOH,n}^{l,h,i} + \left(1 - \tilde{\gamma}^{l,h,i}\right) Y_{MeOH,n}^{l,h,j}\right) \\
&+ M_{MeOH} \left(S_{MeOH}^{H,n} - \frac{\partial S_{MeOH,n}^{MeOH}}{\partial Y_{MeOH}^{l,h}} Y_{MeOH,n}^{l,h}, \tilde{\nabla}^{MeOH}\right). \\
\end{align*}
\]

(4.72)

Here, \(r_{ij}\) is determined by \(F_{ij} = \int_{\Gamma_{ij}} \left(\gamma^n \rho^n u^n \cdot n\right) ds\), and \(\tilde{r}_{ij}\) is determined by \(\tilde{F}_{ij} = \int_{\Gamma_{ij}} \left(\left(\frac{\rho_l}{\rho_g H} - 1\right) j^n \cdot n\right) ds\) according to (4.67).

5. FEM and upwind FVM discretization of the water equation:

\[
\begin{align*}
&\left(D_{cap}(Y_{h} H_2 O,n) \nabla Y_{h} H_2 O,n+1, \nabla \tilde{\nabla}^{H_2 O}\right) \\
&- \left(\frac{\partial \bar{S}_{H_2 O}^n}{\partial Y_{h} H_2 O} M_{H_2 O} Y_{h} H_2 O,n+1, \tilde{\nabla}^{H_2 O}\right) \\
&+ \sum_{i=1}^{N} Y_{H_2 O}^{i} \sum_{j \in \omega_i} \int_{\Gamma_{ij}} \left(\gamma^n \rho^n u^n \cdot n\right) ds \left(r_{ij} Y_{h} H_2 O,n\right) \\
&+ \left(1 - r_{ij}\right) Y_{h} H_2 O,n+1 \\
&= \sum_{i=1}^{N} Y_{H_2 O}^{i} \sum_{j \in \omega_i} \int_{\Gamma_{ij}} \left(\left(\frac{\rho_l}{\rho_g H} - 1\right) j^n \cdot n\right) ds. \\
&\left(S_{H_2 O}^{H,n} - \frac{\partial \bar{S}_{H_2 O}^n}{\partial Y_{h} H_2 O} Y_{h} H_2 O,n, \tilde{\nabla}^{H_2 O}\right). \\
\end{align*}
\]

(4.73)

Here, \(r_{ij}\) is determined by \(F_{ij} = \int_{\Gamma_{ij}} \left(\gamma^n \rho^n u^n \cdot n\right) ds\) according to (4.67).
6. FEM and upwind FVM discretization of the oxygen equation:

\[
\left( \rho g D_{O_2}^{n,eff} \nabla \tilde{Y}_{O_2}^{g,h,n} , \tilde{Y}_{O_2}^g \right) - M_{O_2} \left( \frac{\partial S_{O_2}^{n}}{\partial Y_{O_2}^{g,h,n}} Y_{O_2}^{g,h,n+1} , \tilde{Y}_{O_2}^g \right) \\
+ \sum_{i=1}^{N} \tilde{Y}_{O_2}^{g,i} \sum_{j \in \omega_i} \int_{\Gamma_{ij}} \left( \lambda_g^n \rho^n u^n h \cdot n \right) ds \left( r_{ij} Y_{O_2}^{g,h,i,n+1} + (1 - r_{ij}) Y_{O_2}^{g,h,j,n+1} \right) \\
= \sum_{i=1}^{N} \tilde{Y}_{O_2}^{g,i} \sum_{j \in \omega_i} \int_{\Gamma_{ij}} j^n_l \cdot n ds \left( \tilde{r}_{ij} Y_{O_2}^{g,h,i,n} + (1 - \tilde{r}_{ij}) Y_{O_2}^{g,h,j,n} \right) \\
+ M_{O_2} \left( S_{O_2}^{h,n} , \tilde{Y}_{O_2}^g \right) - M_{O_2} \left( \frac{\partial S_{O_2}^{n}}{\partial Y_{O_2}^{g,h,n}} Y_{O_2}^{g,h,n} , \tilde{Y}_{O_2}^g \right). 
\]

(4.74)

Here, \( r_{ij} \) is determined by \( F_{ij} = \int_{\Gamma_{ij}} \left( \lambda_g^n \rho^n u^n h \cdot n \right) ds \), and \( \tilde{r}_{ij} \) is determined by \( \tilde{F}_{ij} = \int_{\Gamma_{ij}} j^n_l \cdot n ds \).

4.5 Numerical results

As shown in Fig. 4.2, there are totally around 52,000 grid points and 47,000 hexahedra elements in the mesh, and around 333000 degrees of freedom altogether. The number of mesh intervals at each subdomain in each direction are displayed in Table 4.5. For the initial guesses of the above iterative method, we simply choose uniform initial electron and proton potentials, temperature, velocity, and species mass fractions everywhere in terms of their Dirichlet boundary conditions.

In the following discussion, we focus on the numerical results for the 3D DMFC model. The cell is operated at the environment temperature of 333.15K and operating voltage 1.4V, with 6.4% \((2000mol/m^3)\) methanol solution and 93.6% liquid water at the anode inlet, and partially humidified air \((13.2% \text{ water vapor and } 20.2% \text{ oxygen})\) at the
cathode inlet. The stoichiometric flow ratios (4.46) at the anode and cathode channels are all set to be three.

We employ the numerical algorithms discussed in Section 4.4.4, for the 3D DMFC model with the above boundary conditions in a hexahedra 3D mesh shown in Fig. 4.2 and Table 4.5. We get the solution

$$\begin{pmatrix}
\Phi_{e,h} \\
\Phi_{s,h} \\
u_h \\
p_h \\
Y_{l,h}^{MeOH} \\
Y_{h}^{H_2O} \\
Y_{g,h}^{O_2}
\end{pmatrix}$$

within about 130 nonlinear iteration steps, under the stopping criteria that the relative error in two successive iterative steps is less than $10^{-6}$. Fig. 4.3 demonstrates the convergence history of the nonlinear iterative procedure in the steady-state DMFC simulation.
Figs. 4.4–4.8 demonstrate the numerical solutions we obtained. The distribution of each species’ numerical solution is similar to those in [52], thus similar elucidations for Figs. 4.4–4.7 are referred to [52] and do not require repeating here.

The temperature profile on the left of Fig. 4.8 shows that the highest temperature occurring in the membrane electrode assembly (MEA), and the gradual decay of the environment temperature $333.15K$ at the circumference of the DMFC. The maximum temperature increase in this case is about $0.3K$. The temperature variation depends strongly on the thermal conductivities of backing layers and bipolar plates as well as thermal boundary conditions.
In our numerical simulation of the 3D DMFC model, we designed a new source term that took into account that during the iterative procedure the current iterative step solution might be small as discussed in Section 4.4.1. In addition, Newton’s linearization method for this new source term stabilizes the linear system because of the negative sign of the derivative of the source term with respect to the water mass fraction. For other species, we also used Newton’s method to linearize corresponding source terms for the same purpose. To discretize the dominant convection arising in flow channels and possibly in other subdomains, we employed coupled finite element–finite volume upwind discretization methods.

In addition to discretization and linearization methods, an appropriate sequence of unknowns in the numerical simulation plays an important role as discussed in Section 4.4.2. We arrange the unknowns in terms of decreasing dependency interrelationship, such that the lower block triangular part of the Jacobian matrix is dominant. Then the resulting decoupled iteration procedure is equivalent to solve the fully implicit system.
Fig. 4.5. Oxygen $Y_g^{O_2}$ in the $xz$-plane: (left) near the inlet, (middle) near the middle of the cell length, (right) near the outlet, in the cathode.

with the lower block triangular part of the Jacobian matrix. Finally, we are able to get the fast convergence towards the solutions for the 3D steady-state two-phase DMFC model.
Fig. 4.6. Water $Y^{{H_2O}}$ in the $xz$-plane: (left) near the inlet, (right) near the middle of the cell length, (bottom) near the outlet, in both the anode and cathode.

Fig. 4.7. (left) Methanol $Y^{{{MeOH}_l}}$ in the anode; (middle) Oxygen $Y^{{{O_2}_g}}$ in the cathode; (right) Water $Y^{{H_2O}}$ in both the anode and cathode, in the $xy$-plane through the cell center.
Table 4.1. Transport properties

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Physical quantity and its value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_g$: Gas dynamic viscosity</td>
<td>$2.03 \times 10^{-5}$ kg/m s anode side</td>
</tr>
<tr>
<td></td>
<td>$1.8842 \times 10^{-5}$ kg/m s cathode side</td>
</tr>
<tr>
<td>$\mu_l$: Liquid water dynamic viscosity</td>
<td>$4.8211 \times 10^{-4}$ kg/m s</td>
</tr>
<tr>
<td>$D^\text{MeOH}_l$: Liquid methanol diffusivity</td>
<td>$4.83 \times 10^{-9}$ m$^2$/s</td>
</tr>
<tr>
<td>$D^\text{MeOH}_g$: Gas methanol diffusivity</td>
<td>$6.617754 \times 10^{-6}$ m$^2$/s</td>
</tr>
<tr>
<td>$k_H$: Methanol solubility</td>
<td>$607.75$ A/m$^2$</td>
</tr>
<tr>
<td>$\rho_{m}$: Membrane density</td>
<td>$1.98 \times 10^4$ kg/m$^3$</td>
</tr>
<tr>
<td>$D^\text{MeOH}_m$: Liquid methanol diffusivity in membrane</td>
<td>$3.077 \times 10^{-11}$ m$^2$/s</td>
</tr>
<tr>
<td>$D^\text{H}_2\text{O}_m$: Water diffusivity in membrane</td>
<td>$9.5499 \times 10^{-11}$ m$^2$/s</td>
</tr>
<tr>
<td>$K_m$: Hydraulic permeability of membrane</td>
<td>$2 \times 10^{-20}$ m$^2$</td>
</tr>
<tr>
<td>$D^\text{O}_2_g$: Oxygen diffusivity</td>
<td>$2.9339 \times 10^{-5}$ m$^2$/s</td>
</tr>
<tr>
<td>$\kappa_{\text{eff}}$: Proton conductivity</td>
<td>$10$ S/m membrane</td>
</tr>
<tr>
<td></td>
<td>$2.5298$ S/m catalyst layers</td>
</tr>
<tr>
<td></td>
<td>$10^{-30}$ S/m backing layers and channels</td>
</tr>
<tr>
<td>$\sigma_{\text{eff}}$: Electron conductivity</td>
<td>$2 \times 10^4$ S/m bipolar plates</td>
</tr>
<tr>
<td></td>
<td>$300$ S/m backing layers and catalyst layers</td>
</tr>
<tr>
<td></td>
<td>$10^{-30}$ S/m channels and membrane</td>
</tr>
<tr>
<td>$k_{\text{eff}}$: Heat conductivity</td>
<td>$0.6324$ W/m K anode gas channel</td>
</tr>
<tr>
<td></td>
<td>$10$ W/m K backing layers and catalyst layers</td>
</tr>
<tr>
<td></td>
<td>$0.95$ W/m K membrane</td>
</tr>
<tr>
<td></td>
<td>$0.02863$ W/m K cathode gas channel</td>
</tr>
<tr>
<td></td>
<td>$20$ W/m K bipolar plates</td>
</tr>
<tr>
<td>$C_p$: Heat capacity</td>
<td>$4109$ J/kg K anode side</td>
</tr>
<tr>
<td></td>
<td>$1142$ J/kg K cathode side and membrane</td>
</tr>
<tr>
<td>$n_d$: Electro-osmotic drag coefficient of water</td>
<td>$2.5$</td>
</tr>
</tbody>
</table>
### Table 4.2. Electrochemical properties

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Physical quantity and its value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{\text{j}0}^{\text{ref}}$: Exchange current density</td>
<td>$a_{\text{j}0,a}^{\text{ref}} = 4.551 \times 10^6$ anode side</td>
</tr>
<tr>
<td>$\alpha$: Reaction transfer constant</td>
<td>$\alpha_a = 0.239$ anode side</td>
</tr>
<tr>
<td>$U_0$: Thermodynamic equilibrium potential</td>
<td>$U_{0,a} = 0$ anode side</td>
</tr>
</tbody>
</table>

### Table 4.3. Material properties

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Physical quantity and its value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon$: Porosity</td>
<td>$\epsilon = 0.6$ backing layers</td>
</tr>
<tr>
<td>$\sigma$: Surface tension</td>
<td>$\sigma = 0.0625 \text{ N/m}$</td>
</tr>
<tr>
<td>$\theta$: Contact angle</td>
<td>$\theta_a = 0$ anode side</td>
</tr>
<tr>
<td>$EW_m$: Membrane equivalent weight</td>
<td>$EW_m = 1.1 \text{ kg/mol}$</td>
</tr>
<tr>
<td>$r$: Pore radius of MPL</td>
<td>$r_a = 1 \times 10^{-7} \text{ m}$ anode side</td>
</tr>
</tbody>
</table>
Table 4.4. Computational subdomains of the DMFC for each variable

<table>
<thead>
<tr>
<th>Variable</th>
<th>ABP</th>
<th>AGC</th>
<th>ABL</th>
<th>ACL</th>
<th>MEM</th>
<th>CCL</th>
<th>CBL</th>
<th>CGC</th>
<th>CBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(u, p)_l</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>y_{MeOH}</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>y_{H_2O}</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>y_{O_2}</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>$\Phi_e$</td>
<td>✓</td>
<td>×</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>$\Phi_s$</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>T</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Table 4.5. Number of mesh intervals at each subdomain of the 3D DMFC

<table>
<thead>
<tr>
<th>Subdomain</th>
<th>x-direction</th>
<th>y-direction</th>
<th>z-direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABP</td>
<td>5</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>AGC</td>
<td>10</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>ABL</td>
<td>10</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>ACL</td>
<td>5</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>MEM</td>
<td>6</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>CCL</td>
<td>5</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>CBL</td>
<td>10</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>CGC</td>
<td>10</td>
<td>45</td>
<td>10</td>
</tr>
<tr>
<td>CBP</td>
<td>5</td>
<td>25</td>
<td>20</td>
</tr>
</tbody>
</table>
Fig. 4.8. Temperature $T$ (left), Proton potential $\Phi_e$ (middle), and Electron potential $\Phi_s$ (right) in the $xy$-plane through the cell center.
CONCLUSIONS AND FUTURE WORK

Conclusions. The focus of this thesis is on efficient numerical methods for obtaining accurate numerical solutions to the model problems arising in fuel cells. The contributions to this thesis are as follows:

Under the multiphase-mixture modeling framework, we found that the two-phase water transport equation is the bottleneck that slows down the convergence of the steady-state simulation of polymer electrolyte fuel cells (PEFC), because of the nonlinear, discontinuous, and degenerate diffusion-coefficient. We overcame this difficulty by using our new numerical techniques based on the Kirchhoff transformation and nonlinear alternating Dirichlet-Neumann domain decomposition methods.

We designed three uniformly stable finite element methods for the Darcy-Stokes-Brinkman models with strongly discontinuous coefficients, arising from the momentum equation of fuel cells. In particular, the new modified $H(\text{div})$-conforming elements are related to the discrete de Rham complex, which is an important tool for designing and analyzing optimal linear solvers.

We developed a numerical simulation package for the multiphysics, multiphase, and multicomponent models arising in direct methanol fuel cells (DMFC). Our new method is based on the coupling and decoupling strategies of governing equations, proper linearizations and discretizations, optimal sequence of unknowns, and modification of
the water source term. Our method demonstrated the fast convergence of the nonlinear
iteration of the steady state DMFC simulation.

Future Work. Some of the future research directions are as follows:

- Optimal linear solvers for the Darcy-Stokes-Brinkman models.
- Optimal linear solvers for the DMFC simulations.
- Development of numerical simulation packages for the PEFC.

For the Darcy-Stokes-Brinkman models, we aim to design and analyze efficient
solvers (such as multigrid methods and uniform preconditioners) for the linear system
of equations arising from our new compatible discretizations in Section 3.3.2. A useful
tool to achieve this goal is the discrete de Rham complexes obtained in Section 3.4.

In Chapter 4, we focused on the nonlinear solver of the steady-state simulation
of full DMFC models. In order to speed up computational time, it is essential to have
the optimal linear solvers. We aim to develop multigrid methods (or as preconditioners)
to solve species convection-diffusion-reaction type equations, as well as the momentum
equations.

In the PEFC, we aim to develop numerical simulation packages for the full mul-
tiphysics simulations, by applying techniques in Section 2.4.
References


Vita

Guangri Xue was born on October 11th, 1979, in Yanji city, Jilin province, P. R. China. He received a B. S. degree in mathematics from Peking University in June 2002. He married Ji Xuan in July 2002. He enrolled in the Ph.D. program in mathematics at the Pennsylvania State University in August 2002.