MULTIPHYSICAL SIMULATION OF CO₂ ENHANCED OIL RECOVERY IN UNCONVENTIONAL RESERVOIRS: FROM FUNDAMENTAL PHYSICS TO SIMULATOR DEVELOPMENT

by

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ABSTRACT

The economic recovery of unconventional reservoirs is demanding yet challenging. Traditional enhanced oil recovery (EOR) techniques face difficulty when being applied to unconventional reservoirs. In this PHD study, we aim to deepen the understanding of the transport mechanisms and the phase behavior in unconventional reservoirs. Moreover, we aim to develop numerical tools to simulate the multiphysical process occurring in the carbon dioxide enhanced oil recovery (CO$_2$-EOR) process. Based on the developed simulator, we plan to investigate the potential of applying cold CO$_2$ flooding in unconventional reservoirs.

We have developed a novel transport model for the gas slippage effect of multicomponent gases in unconventional reservoirs. The model is essentially a second-order slippage boundary condition, based on kinetic theory of gases. The model has been validated with respect to both physical experimental data and numerical simulation data and has shown accuracy up to 90%.

We have developed a compositional reservoir simulator named MSFLOW-CO$_2$, which adopts integral finite difference method to simulate the coupled thermal-hydraulic-mechanical processes during CO$_2$-EOR. In our method, the governing equations of the multiphysical processes are solved fully coupled on the same unstructured grid. An algebraic multiscale linear solver is adopted to speed up the non-isothermal simulation. In order to simulate the phase behavior of the three-phase system, a flash calculation module based on direct minimization of Gibbs energy is implemented in the simulator.

We have investigated the impact of cold CO$_2$ injection on injectivity as well as phase behavior. We conclude that cold injection is an effective way to increase the injectivity in tight
intact reservoirs. We have also observed and studied the temperature decreasing phenomenon near the production well, known as the Joule-Thomson effect, induced by expansion of in-situ fluids.

Moreover, we aim to speed up compositional modeling by stochastic training. In traditional compositional simulators, the phase behavior is simulated using flash calculation techniques on each grid block within each iteration, which results in a huge amount of computational time. In this work, based on the developed standalone flash calculation module, we have trained two fully connected neural networks, namely the phase classification and the concentration determination, using Keras to conduct proxy flash calculation and have implemented the proxy module into the simulator. The networks are trained with stochastic gradient method optimizer and are used as the preconditioner of the physical flash calculation module. The accuracy of the phase classification step is above 99%. The accuracy of the concentration determination step is up to 98%. Therefore, the overall accuracy of our proxy flash calculator is above 97%. With the implementation of the proxy flash calculation module as a preconditioner, the number of iterations of the flash calculation module is reduced by more than 50%.

To sum up, the novelty of this work lies in the transport mechanism in unconventional reservoirs, the multiphysical simulation framework, the flash calculation module, and the proxy simulation module.
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LIST OF SYMBOLS

$A$ ................................................................. area of a connection

$A_q$ ................................................................................ aqueous phase

$a_{ij}$ ................................................................. parameter in equation of state

$b$ ......................................................................... Klinkenberg factor

$b_{ij}$ ................................................................. parameter in equation of state

$C$ ........................................................................... slippage coefficient

$D_{\beta}$ ................................................................. objective function for phase $\beta$

$D$ ............................................................................... channel diameter

$E$ ............................................................................... Young’s modulus

$E_i$ ................................................................................ exponential integral function

$E_{\beta}$ ................................................................. objective function for phase $\beta$

$F$ ............................................................................... flux term

$F_b$ ............................................................................... body force

$F_{\beta}$ ................................................................. objective function for phase $\beta$

$f_i$ ............................................................................... fugacity of the $i$th component

$G$ ............................................................................... Gibbs energy

$G_s$ ............................................................................... shear modulus

$g$ ............................................................................... gravity terms

$h$ ............................................................................... enthalpy

$i$ ............................................................................... integer index

$j$ ............................................................................... integer index
\( \mathbf{J} \) Jacobian matrix
\( j \) integer index
\( K \) equilibrium ratio
\( K_a \) apparent permeability
\( K_i \) equilibrium ratio of component \( i \)
\( K_N \) Knudsen number
\( K_r \) relative permeability
\( K_R \) formation heat conductivity
\( K_\beta \) phase heat conductivity
\( K_\infty \) absolute permeability
\( k \) integer index
\( k_{ij} \) binary interaction coefficient
\( k_B \) Boltzmann constant
\( L_i \) fracture spacing on the \( i \)th direction
\( M \) accumulation term
\( M_1 \) momentum transported by Type 1 molecules
\( M_2 \) momentum transported by Type 2 molecules
\( M_b \) momentum transported by molecules from below
\( M_R \) mobility ratio
\( M_u \) momentum transported by molecules from above
\( m \) molecular weight
\( N \) number of molecules
\( N_t \) total number of moles
\( n_t \)............................................................total number density
\( P \)......................................................................pore pressure
\( P_{C} \).....................................................................critical pressure
\( P_{c} \)......................................................................capillary pressure
\( P_{inlet} \)....................................................................inlet pressure
\( P_{outlet} \)....................................................................outlet pressure
\( P_r \)........................................................................reduced pressure
\( p \)..........................................................................iteration index
\( Q \)..................................................................................generation term
\( Q_D \)....................................................................dimensionless flow rate
\( \bar{R} \)........................................................................residual vector
\( R \)................................................................................gas constant
\( S \)............................................................................flow rate enhancement factor
\( S_i^* \)................................................................intermediate parameter in equation of state
\( S_{gr} \)..................................................................residual gas saturation
\( S_{or} \)..................................................................residual oil saturation
\( S_{wr} \)..................................................................residual water saturation
\( S_{\beta} \)...................................................................phase saturation
\( T \)............................................................................temperature
\( T_{C} \)...................................................................critical temperature
\( T_r \)........................................................................reduced temperature
\( T_{ref} \)...................................................................reference temperature
\( t \)........................................................................time
Δt.................................time step length
\overline{u}.................................displacement vector
u...........................................horizontal velocity
u_\beta..................................phase specific internal energy
V...........................................volume
\overline{V}.............................mole volume
v.............................................thermal velocity
x..........................................coordinate
x_i........................................mass concentration of the i\textsuperscript{th} component
Z.............................................compressibility factor
z.........................................coordinate
z_i........................................mole fraction of the i\textsuperscript{th} component
Ψ.........................................primary variable of flash calculation
\phi.....................................porosity
α...........................................Biot’s coefficient
α_\beta....................................mole fraction of phase \beta
β.........................................phase index
β_T.........................................thermal expansion coefficient
δ............................................collision (kinetic) diameter
ε_k......................................diagonal strain component
ε_v......................................volumetric strain
ε_{kk}.................................diagonal strain component
ζ.........................................primary variable of optimization
η.................................................................learning rate
Θ.................................................................object function of optimization
θ_β.............................................................stability indicator of phase β
λ.................................................................mean free path
λ_{im}.........................................................mean free path of mixture
λ_i.............................................................mobility of phase i
λ_L.............................................................Lame’s coefficient
Λ_β..........................................................Lagrange multiplier
μ.............................................................viscosity
μ_i............................................................chemical potential of the i-th component
ν_{max,hor}................................................maximum horizontal stress
ν_{min,hor}................................................minimum horizontal stress
ρ.............................................................density
τ.............................................................unit volume
σ.............................................................stress
σ’............................................................effective stress
σ_k..........................................................normal stress at the k-th direction
σ_{kk}........................................................diagonal stress component
σ_m........................................................mean stress
σ_n..........................................................normal effective stress
φ.............................................................spherical angle
ω.............................................................radial angle
LIST OF ABBREVIATIONS

Artificial Intelligence.................................................................AI
American Petroleum Institute...................................................API
Central Processing Unit..............................................................CPU
Deep Learning.............................................................................DL
Direct Simulation Monte Carlo..................................................DSMC
Enhanced Oil Recovery...............................................................EOR
Equation of State.........................................................................EOS
Graphic Processing Unit.............................................................GPU
Generalized Minimal Residual Method.......................................GMRES
Integral Finite Difference.............................................................IFD
Improved Oil Recovery.................................................................IOR
Lattice Boltzmann Method..........................................................LBM
Multiple Interacting Continua......................................................MINC
Minimum Miscible Pressure.........................................................MMP
Multiscale Restriction Smoothed Basis method..........................MsRSB
Pressure-Volume-Temperature.....................................................PVT
Scanning Electron Microscope.....................................................SEM
Stochastic Gradient Descent.........................................................SGD
Stimulated Reservoir Volume.......................................................SRV
Support Vector Machine.............................................................SVM
Thermal-Hydraulic-Mechanical......................................................THM
Tangential Momentum Accommodation Coefficient......................TMAC
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At last, I want to express my deepest love to my fiancée Siyuan Lin, who casts light into my life!

Thank you all!
CHAPTER 1
INTRODUCTION

1.1 Background

CO₂ injection has been proven to be an effective enhanced recovery approach for conventional reservoirs. Knowing that the accurate quantification and prediction of the CO₂ flooding process is demanding yet challenging for petroleum engineers, in this dissertation we propose to numerically investigate the thermal-hydraulic-mechanical processes during the CO₂ injection. We aim to investigate state-of-the-art techniques, including transport mechanisms, proxy calculation and multiphysical coupling scheme, to incorporate more relevant physics and improve the numerical performance of the proposed program. We will also investigate the potential of extending CO₂ injection to unconventional reservoirs. The outcome of this PhD work will include a comprehensive simulation software that is ready-to-use in field applications.

1.2 Objectives

The purpose of this work is to develop new techniques for the accurate simulation of carbon dioxide enhanced oil recovery (CO₂-EOR). To achieve this goal, the objectives of this work are as follows:

- Review and compare the existing EOR techniques.
- Investigate the transport mechanisms and phase behavior in unconventional reservoirs.
- Develop a fully coupled thermal-hydraulic-mechanical compositional reservoir simulator
- Investigate the temperature impacts on the fluid properties as well as recovery performance of CO₂-EOR.
Speed up the compositional simulation by proxy flash calculation techniques.

1.3 Dissertation layout

This dissertation is organized as follows:

In Chapter 2, we will review the physical model as well as the numerical approaches for the simulation of the multiphysical processes during CO₂-EOR.

In Chapter 3, we will introduce the mathematical model developed in this work, including the governing equation and the phase behavior model.

In Chapter 4, we will investigate the transport mechanisms in unconventional reservoirs, specially focusing on the gas slippage (Klinkenberg) effect

In Chapter 5, we will discuss our numerical methods, including the integrated finite difference method and the multiscale linear solver.

In Chapter 6, we will validate our developed simulator, with respect to data from literature as well as commercial software.

In Chapter 7, we will present our numerical results, including the phase equilibrium calculation and the multiphysical coupling simulation.

In Chapter 8, we will present our proxy flash calculation module, to speed up the compositional modeling.

In Chapter 9, we will summarize our work and suggest for future work.
CHAPTER 2
BACKGROUND

2.1 Introduction of unconventional reservoirs

Unconventional reservoirs, such as shale and tight reservoirs, are rich resources of natural oil/gas. In unconventional reservoirs, a huge amount of hydrocarbon is trapped in the location where it is generated, without the primary migration process, as shown in Figure 2.1. According to the report by U.S. Energy Information Administration (U.S. Energy Information Administration (EIA) 2016), unconventional reservoirs will soon contribute the major part of world’s fossil energy consumption, as shown in Figure 2.2 and Figure 2.3. Therefore, it is of great importance to understand and enhance the production performance of unconventional reservoirs.

In general, unconventional reservoirs are very low in permeability and porosity. The pore throat diameter of tight gas formulations is usually between 1µm to 0.01µm (Holditch 2006; Nelson 2009), while the pore throat diameter of shale reservoirs varies from tens of nanometers to as low as about 5 nanometers (Nelson 2009). Recent studies (Collell et al. 2015; Falk et al. 2015) even reveal the existence of small pores inside shale reservoirs that are beyond the scope of scanning electron microscope (SEM). The diameters of such small pores are less than 5 nanometers, resulting in very low rock permeability (Wang 2018; Wang and Bhattacharya 2018).

Because of their extremely narrow pores, the transport mechanism inside unconventional reservoirs turns out to be significantly different from that inside the conventional reservoirs (Xu et al. 2017a; Xu et al. 2017b). Since hydrocarbons flow extremely slowly by natural driving forces in unconventional reservoirs, the economic development of unconventional reservoirs highly relies on improved oil recovery (IOR) and enhanced oil recovery (EOR) approaches (L.
Wang et al. 2017a). One proven IOR approach is the hydraulic fracturing technique. Originally applied in conventional reservoirs, the hydraulic fracturing operation fracks formation rocks by injection proppant-bearing liquids into the formation through vertical or horizontal wells. Therefore, the engineered fractures create formation-wellbore flow channels and effectively improves the productivity of the well (production capability). Although the hydraulic fracturing technique has widely used in unconventional reservoirs, other IOR/EOR techniques rarely achieve any successes. Especially, since the unconventional reservoirs are very tight, the injectivity (injection capability) of them is relatively lower compared to conventional reservoirs, which increases difficulties of applying traditional EOR approaches to unconventional reservoirs.

Figure 2.1 Conceptual model of the difference between unconventional reservoirs and conventional reservoirs.
2.2 Review of EOR techniques

In this section, we briefly review and compare the currently existing EOR techniques.
2.2.1 Water flooding

Water flooding has been used for decades as the main energy supplement and secondary recovery technique in the oil/gas industry. The benefits of water flooding operation with horizontal wells has also been proven (Taber and Seright 1992). The sweep efficiency of water flooding should be investigated microscopically and macroscopically.

In the micro-scale, the sweep efficiency can be quantified by the mobility ratio and the capillary number. The mobility ratio \( M_R \) is defined as the ratio between the mobility \( \lambda_d \) of the displacing fluids (water in this case) to the mobility \( \lambda_i \) of the in-situ fluid.

\[
M_R = \frac{\lambda_d}{\lambda_i} = \frac{K_{rd} \mu_i}{\mu_d K_{ri}}
\]  

(2.1)

In the above formulation, \( K_{rd} \) and \( \mu_d \) denotes the relative permeability and viscosity of the displacing fluid, respectively, while \( K_{ri} \) and \( \mu_i \) denotes the relative permeability and viscosity of the displaced fluid, respectively. Theoretically speaking, the lower the mobility ratio is, the higher the microscopic sweep efficiency is.

As water and oil are hardly mutual soluble, capillary forces exist at the interface between the two phases. According to the Young-Laplace equation, the capillary pressure \( P_C \) between two phases is inversely proportional to the pore (throat) diameter \( D \), as follows.

\[
P_C \propto \frac{1}{D}
\]

(2.2)

The magnitude of the capillary effect is quantified by the capillary number, which is the ratio of the viscous force to the capillary force. Because of the capillary forces, oil droplets require higher pressure gradient to flow through pore throats. Therefore, oil may be trapped inside pores, as shown in Figure 2.2.
The microscopic sweep efficiency of water flooding directly affects the macroscopic sweep efficiency. At the macro scale, water flooding suffers channeling problems, resulting in the early breakthrough of injected water. The sweep efficiency and breakthrough time for simple 1-D problems without capillary forces can be analytically estimated by Buckley-Leverett method (Wu 2015). The sweep efficiency of 3D problems with the complex physical process has, in general, to be numerically calculated by reservoir simulators.

Figure 2.4 Mechanism of capillary-forces induced oil (non-wetting phase) trapping. Upper figure: the water phase tries to push an oil droplet through a pore throat. Lower figure: the oil droplet breaks into two and is trapped in a continuous water phase.

The heterogeneity and natural fractures of the reservoirs may further reduce the macroscopic sweep efficiency of water, because water will channel through the highly permeable portion of the reservoir and form a preferable flow pathway, leaving a huge amount of oil behind.

### 2.2.2 Low-salinity water flooding

Another type of water flooding is to inject water with electrolytes, especially brine. Particularly, when the concentration of electrolytes of the injected brine is lower to a certain
level (one-hundredth-strength) with respect to the formation liquids, such kind of water flooding is called low-salinity water flooding. The idea of low-salinity water flooding was first brought out by Tang and Morrow (1997). According to the experimental investigations conducted by McGuire et al. (2005) and Lager et al. (2008a; 2008b), the recovery factor of water flooding can be increased by 2% to 40%.

The mechanisms of the improving sweep efficiency achieved by low-salinity water flooding are still in debate. So far widely accepted explanations are as follows

- Wettability alteration induced by clay migration (Tang and Morrow 1999). Clay exchanges ions with the injected brine, and the rock thus tends to be more water wet.
- Multiple-component ion exchange (MIE) (Lager et al. 2008a). The formation oil exchanges ions with the injected brine and becomes more mobile.
- pH change induced by CaCO₃ dissolution (McGuire et al. 2005). The dissolute CaCO₃ increases the pH value of the pore-filling fluids and thus reduces interfacial tension forces.

### 2.2.3 Gas injection

Gas injection refers to techniques that inject gas, such as carbon dioxide (CO₂), nitrogen and natural gas, into reservoirs to displace the *in-situ* oil. Gas injection is a major EOR approach, particularly, in the United States. Figure 2.5 shows the fraction of different kinds of EOR projects undergoing in the U.S. According to Figure 2.5, gas injection projects account for more than half of the EOR projects. Compared to water flooding, gas injection could have much higher microscopic sweep efficiency and can be applied to wider range of reservoirs, especially
heavy oil reservoirs. Gas injection can be adopted as either a secondary recovery operation or a tertiary recovery operation.

![Diagram showing distribution of EOR projects in the U.S. (Department of Energy 2013)](image)

Figure 2.5 Distribution of the EOR projects in the U.S. (Department of Energy 2013)

There are two types of gas injection EOR, namely, immiscible gas injection and miscible gas injection. In immiscible injection, the injected gas does not fully dissolve into the in-situ oil phase, while in miscible injection, the injected gas and the in-situ oil dissolve into each other and become one single phase. Immiscible gas injection requires the density of in-situ oil to be between 20 to 40 °API. For reservoirs with oil that is heavier than 20 °API, immiscible gas injection cannot fully mobilize the oil and miscible gas injection technique has to be adopted. In the case of immiscible injection, the injected gas will extract certain components from the oil phase, making the oil more mobile. Meanwhile, the injected gas maintains the pressure and drives the oil to the production well. Since capillary effect still exists in the immiscible flooding system, immiscible gas injection suffers from similar problems as water flooding, i.e., fingering and channeling. Madathil et al. (2015) reported the successful application of immiscible gas injection in a reservoir locating in offshore Abu Dhabi. According to their observation,
immiscible gas injection maintains the pressure of the reservoir as well as increases oil recovery. They conclude that updip injection with low injection rate has higher sweep efficiency. The miscible flooding requires the downhole pressure to be higher than a certain value. The minimum value of the pressure to achieve miscible condition is called Minimum Miscible Pressure (MMP), which can be determined experimentally by slim tube test (Elsharkawy et al. 1996; Wu and Batycky 1990). In some reservoirs, injected gas cannot be miscible at the first contact with the reservoir fluids. Instead, the injected gas gradually extracts heavier components from the oil phase during flow time and finally becomes miscible with the oil after multiple contacts. Such a process is called multiple-contact miscible flooding. Since a two-phase zone still exists between the pure injected gas zone and the miscible zone during the multiple-contact miscible flooding process, considerable oil may still be trapped during the flooding. As to the selection of injection gas, the comparison of the MMP, sweep efficiency, cost and required density of in-situ oil among the three major types of miscible gas injection techniques is listed in Table 2.1. More thorough criteria to screen reservoirs for miscible gas injection are listed in Teletzke et al. (2005).

<table>
<thead>
<tr>
<th></th>
<th>MMP</th>
<th>Sweep efficiency</th>
<th>Cost</th>
<th>In-situ oil (Taber and Seright 1992)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td>Lowest</td>
<td>Highest</td>
<td>Highest</td>
<td>&gt;30 °API</td>
</tr>
<tr>
<td>CO₂</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>&gt;25 °API</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Highest</td>
<td>Lowest</td>
<td>Lowest</td>
<td>&gt;40 °API</td>
</tr>
</tbody>
</table>
2.2.4 Natural gas injection and recycling gas injection

Natural gas injection is of the best sweep efficiency, because of similarity between the injected gas and the in-situ formation liquids. However, natural gas may be much more expensive than CO\textsubscript{2} and nitrogen. Therefore, unless rich gas sources are available, natural gas is seldom injected as a displacing fluid. One effective natural gas injection technique is the recycling gas injection technique for condensate gas reservoirs. In condensate gas reservoirs, it is of great importance to maintain the reservoir pressure above the dew point pressure. In recycling gas injection, the produced gas from condensate gas is processed at the surface by removing the heavy components (C3+) and water. The resulting lighter gas is then reinjected into the reservoir for pressure maintenance.

2.2.5 CO\textsubscript{2} flooding

CO\textsubscript{2} flooding is a proven and promising EOR technique for tertiary recovery. The injected CO\textsubscript{2} has a variety of impacts on the in-situ oil-water system, including the expansion of oil volume and the reduction of oil viscosity as well as capillary forces (Grigg and Schechter 1997). During the past three decades, the number of active CO\textsubscript{2} flooding projects in the United States has increased by more than 300% (Manrique et al. 2010). CO\textsubscript{2} flooding has brought many water-flooded reservoirs back to life by increasing the recovery factor by up to 30%, as summarized in (Rao 2001). For immiscible CO\textsubscript{2} flooding, CO\textsubscript{2} usually turns into the supercritical phase in the high-pressure high-temperature downhole environment, as shown by the phase diagram of CO\textsubscript{2} in Figure 2.6. The density of injected supercritical CO\textsubscript{2} is usually lighter than that of the in-situ hydrocarbons, therefore supercritical CO\textsubscript{2} may override oil.
Meanwhile, as the viscosity of injection CO$_2$ is much smaller than that of the oil phase, viscous fingering and channeling is likely to occur in immiscible CO$_2$ flooded reservoirs.

Miscible CO$_2$ flooding technique can be used to recover oil that is heavier than 25 °API to 30 °API. If the gas source is available, miscible CO$_2$ flooding is also much more cost-effective than natural gas flooding. After CO$_2$ dissolves, the viscosity of oil phase gets reduced and the volume of oil significantly expands, therefore the residual oil becomes mobile. (This is also true for immiscible flooding.) The sweep efficiency of CO$_2$ flooding highly depends on the purity of the injected CO$_2$ (Zhang et al. 2004). Therefore, a pre-treatment of the injected CO$_2$ to reduce impurity is required.

Although the capillary forces have been removed microscopically, miscible flooding still cannot achieve ‘perfect’ sweep efficiency. Reservoir heterogeneity in the macro scale may induce fingering and channeling. This is because the less viscous miscible phase may form preferable flow pathways in the local higher permeable zone. Moortgat et al. (2012) developed three-phase compositional models to numerical study the impact of local heterogeneity on miscible gas flooding. Their results are shown in Figure 2.7, according to which even for a slightly heterogeneous reservoir, obvious fingering of miscible gas flooding can be observed.
Figure 2.7 Numerical simulation results of gas flow channeling. Plot (a) and plot (b) refer to homogeneous formations, while plot (c) and plot (d) refer to heterogeneous formation. Figure from Moortgat (2012).

2.3 Transport mechanisms in unconventional reservoirs

Unconventional reservoirs have some unique transport mechanisms, including gas slippage effect, Knudsen diffusion effect, adsorption/desorption effect and pore confinement effect, as follows.

2.3.1 Gas slippage effect and Knudsen diffusion effect

The molecules of the reservoir fluids are constantly moving in random motions under high velocity (thermal velocity). Due to the narrow pores in the unconventional reservoirs, the fluid molecules frequently interact with the pore wall, which is a rough surface. When the molecules hit the wall, they lose momentum and may reflect into a random direction. The loss of
the momentum leads to the reduction of the viscosity of the reservoir fluids, increasing the ‘apparent’ permeability. Therefore, the reservoir fluids behave like ‘slipping’ in the unconventional reservoirs. Commonly called the ‘slippage effect’, this phenomenon is more significant in the gas phase, whose freely moving path (or known as ‘mean free path’) is relatively longer. The molecular-wall interaction also varies the number density of diffusing molecules, resulting in the Knudsen diffusion effect. Therefore, the gas slippage effect and the Knudsen diffusion effect are resulted from the same physical process, as shown in Figure 2.8. More discussions on the gas slippage effect and Knudsen diffusion effect will be presented in Chapter 4.

![Figure 2.8 Conceptual model of the gas slippage effect and the Knudsen diffusion effect (Wang et al. 2019c).](image)

**2.3.2 Adsorption/desorption**

As stated in Chapter 2.1, in the unconventional reservoirs, the reservoir fluids are stored in the organic matter (kerogen) without migration. The organic matter has a certain preference for the reservoir fluid components. The fluid component may adsorb to the surface of the organic
matter. The amount of the adsorption is subject to the property of the organic matter, the species of the reservoir fluids, the temperature as well as the pressure (Mosher et al. 2013). In certain shale formations, methane and CO$_2$ have competence in the adsorption effect (Zhou et al. 2018). Moreover, the adsorbed components form a liquid-like ‘phase’ on the surface of the organic matter and the transport of the components in the adsorption layer is called as the surface diffusion, according to the study of (Barrer and Barrie 1952; Malek and Coppens 2001; Wu et al. 2015).

![An example of the kerogen in shale formations](image)

Figure 2.9 An example of the kerogen in shale formations (Curtis et al. 2010).

2.3.3 Large capillary pressure and pore confinement effect

Since the capillary pressure between two phases is inversely proportional to the pore (throat) diameter as shown in Equation (2.2), the narrow pores of unconventional reservoirs result in larger capillary pressure (Li et al. 2014; 2016). Also, the confinement of the narrow pores causes the ‘shift’ of the critical properties. The large capillary pressure in unconventional
reservoirs leads to the variation of phase behavior, as studied in the work of (Haider and Aziz 2017; Pitakbunkate et al. 2016; Rahmani and Akkutlu 2015; Travalloni et al. 2014). In general, the temperature of bubble points and dew points will tend to decrease, subject to the capillary pressure effect. A conceptual model of the dual-phase system in the nano-pores of unconventional reservoirs is shown in Figure 2.10.

L. Wang et al. (2017b) have thoroughly reviewed the transport processes in unconventional reservoirs.

2.4 Multiphysical process and coupled simulation

The recovery of petroleum/geothermal reservoirs typically involves complex thermal-hydraulic-mechanical (THM) processes. For instance, problems with rock failure in the vicinity of the injection well induced by cold water injection and permeability-porosity change during production require the simulator to be able to accurately predict the transient pressure, temperature and stress fields of the reservoir (Wang et al. 2014).

The above-mentioned mechanical coupling frameworks are either sequentially or iteratively coupled framework, where the pressure-temperature field and the stress field are solved separately. Kim (2009) analyzed that for linear problems, the sequentially coupled framework could be unconditionally stable. However, for highly nonlinear problems, the stability and accuracy of the sequentially coupled framework are still questionable. Therefore, fully coupled THM frameworks that solve all physical fields simultaneously are in demand for industrial applications, where the problems are usually highly nonlinear. For fully coupled frameworks, ‘mean stress’ method, which solves the volumetric stress of the system, is a simple yet accurate approach. The sequentially-coupled and fully-coupled mean stress method has been presented in Zhang et al. (2015) and Wang (2015) respectively.

Figure 2.11 Conceptual model of the interaction among the THM processes (Wang 2015).
2.5 Compositional modeling and flash calculation

To accurately simulate the CO$_2$-hydrocarbon-water system in the CO$_2$ flooded reservoir, compositional modeling with flash calculation is needed. The compositional simulator tracks the migration of each component. Within each iteration step, the compositional simulator conducts flash calculation to predict the phase behavior of the system. The flash calculation outputs the phase combination as well as the concentration distribution at a given temperature and pressure. The first trial of flash calculation and compositional modeling for two-phase system dates back to the 1960s (Hoffman 1968). The flash calculation approach brought out by Michelsen (1982a, 1982b) has been widely adopted. Michelsen’s approach has two steps. It first conducts a phase stability test to determine whether a phase exists. It then solves the Rachford-Rice equations (Leibovici and Neoschil 1992, 1995; Okuno et al. 2010a) using Newton iteration based on the equilibrium ratio (K-value) of each component. Although Michelsen’s method has been successfully used in two-phase flash calculation, it has several drawbacks which prevent it from being extended to three-phase flash calculation. Firstly, Michelsen’s method has convergence issues, due to the discontinuity of Rachford-Rice equation. Secondly, Michelsen’s method requires multiple iterations and complex phase stability calculation, which causes it to be impractical for multiphase flash calculation.

Recently, Okuno et al. (2010b, 2010c) brought out a reduced model for multiphase flash calculation. Although the reduced model is more efficient compared to traditional K-value approach, its input parameters are relatively hard to be determined. Moreover, the reduced model is only faster than the classic K-value method when the number of components is above 15 to 20, which is not the usual cases for real applications.
K-value based flash calculation has been widely adopted in the simulation of CO₂-EOR by research code (Pan and Oldenburg 2016) and commercial simulators (Computer Modelling Group LTD. 2010; Schlumberger 2009). In practice, people adopt a ‘hybrid’ framework for K-value based flash calculation, in which a Newton’s method is combined with the bi-section method. When Newton’s method fails to converge, the algorithm switches to the bi-section method to search for the solution.

Besides the K-value approach, direct minimization of the Gibbs energy is another effective approach for flash calculation. Direct minimization of the Gibbs energy approach is based on the fact that at the equilibrium state, the Gibbs energy of the system is at its minimum. In the direct minimization of the Gibbs energy approach, the objective function is the total Gibbs free energy of the system. By iteratively tuning the concentration distribution, the approach searches the global minima of the objective function with Newton’s method. Therefore, the flash calculation becomes an optimization problem and global optimization techniques, such as Branch and Bound method (Cheung et al. 2002), tunneling (Nichita et al. 2002), linear programming (Rossi et al. 2009) and heuristic algorithm (Bhargava et al. 2013; Bonilla-Petriciolet and Segovia-Hernández 2010; Walton et al. 2011), can be used to globalize the optimization process. Zhang et al. (2011) thoroughly reviewed the global optimization techniques for the direct minimization of the Gibbs energy method.

Compared to the K-value approach, the direct minimization of the Gibbs energy method can be more easily applied to multiphase systems. Moreover, this approach is also suitable for the calculation of phase behavior in unconventional reservoirs, in which the capillary pressure has larger impact on the phase equilibrium. To account for the capillary pressure impact, the direct minimization of the Gibbs energy approach adds a surface energy term in its formulation.
(Rossi et al. 2009). Therefore, this approach has the flexibility to handle the capillary pressure impact in a three-phase system, in which capillary exist both in the gas-liquid phase interface and the liquid-water interface. Recently, Ma (2013) adopts a similar approach to investigate the capillary pressure impact on PV-flash by minimizing Helmholtz free energy.

To quantify the properties, such as density and fugacity, of the multiphase system, several equation of state (EOS) models have been brought out. The widely used EOS are cubic equations, such as Soave-Redlich-Kwong equation of state (SRK EOS) (Soave et al. 1972) and Peng-Robinson equation of state (PR EOS) (Peng and Robinson 1972, 1976). SRK EOS and PR EOS have been proven to be successful in light hydrocarbon systems. However, their accuracy is not satisfactory in systems containing polar components. To overcome this shortness, Cubic-plus-association equation of state (CPA EOS) (Folas et al. 2005; Tsivintzelis et al. 2011) and Perturbed Chain form of the Statistical Associating Fluid Theory equation of state (PC-SAFT) (Panuganti et al. 2012; Tumakaka et al. 2005) have been developed to simulate more complex systems. CPA EOS has also been used to simulate CO$_2$-EOR (Moortgat et al. 2012).

### 2.6 Injectivity increase induced by cold liquid injection

The permeability and porosity of the formation rock are sensitive to the stress change induced by temperature variation. When the temperature increases, the rock expands and the pore becomes smaller, resulting in the decrease of the permeability and porosity. Such a process is called the thermal loading process. When the temperature decreases, the rock shrinks, causing the permeability and porosity to increase. Such a process is commonly called the thermal unloading process. The conceptual model of the thermal loading and unloading processes is shown in Figure 2.12.
According to the mechanism of the thermal unloading process, when cold liquids are injected into the reservoir, the injectivity of the injector should increase. In practice the injectivity increase phenomenon near the cold water injector has been widely observed in geothermal reservoirs (Kaya et al. 2011; Stefansson 1997). In Geyser geothermal field, people have recorded and studied micro-earthquake events in the vicinity of the cold water injection wells (Rutqvist and Tsang 2003; Majer and Peterson 2007). According to the studies, the micro-earthquake can be explained by the thermal unloading process. In fractured reservoirs, the increase in fracture permeability could be more significant, because that the fractured rocks tend to be more sensitive to stress change. As the fracture permeability is approximately the cubic power of the fracture aperture, the increase of fracture permeability could be considerable.

As shown in Figure 2.13, the injectivity of well 4R1 in the Tongonan field was significantly increased after the cold waste water reinjection. Wang et al. (2016) have brought out a semi-analytical correlation to quantify the injectivity increase phenomenon. The permeability variation predicted by their correlation is as shown in Figure 2.14. Based on these
observations, in this work, we propose to simulate the effect of cold CO₂ injection on the injectivity.

Figure 2.13 Variation of injectivity subject to the injection of cold water in Tongonan field, after (Sarmiento 1986).

Figure 2.14 A numerical study of the permeability change induced by cold water injection (Wang et al. 2016)
2.7 Data-driven proxy flash calculation

The prediction of the complex phase behavior in unconventional reservoirs requires compositional modeling, of which the flash calculation is an essential yet time-consuming portion. To improve the speed as well as the stability of the flash calculation, several techniques have been adopted, including reduction method (Okuno et al. 2010c), phase stability test (Nichita and Petitfrere 2013) and so on. Recently, the fast arising artificial intelligence (AI) techniques have drawn attentions of researchers. There are several trials of combing AI with flash calculation.

El-Sebakhy (2009) and Rafiee-Taghanaki et al. (2013) used the support vector machine technique (Burges 1998; Kobayashi and Komaki 2006; Schölkopf and Smola 2002; Vapnik 2000) to predict the PVT properties of crude oil, including gas oil ratio, oil volume factor, density and so on. Artificial neural network has also been used to predict the PVT behavior of crude oil (Gharbi et al. 1999) and gas mixtures (Kamyab et al. 2010). Habiballah et al. (1996) adopted neural networks to predict the phase equilibrium ratio of hydrocarbons (Habiballah et al. 1996). Recently, Kashinath et al. (2018) brought out a novel framework to conduct isothermal flash calculation. In their work, they combine relevance vector machine (Tipping 1999) with artificial neural network. The former technique is used to classify phase condition, while the latter is used to determine the concentration distribution. Nikravesh et al. (2003) reviewed the applications of artificial intelligence techniques in the exploration and development of petroleum reservoirs.

In recent years, the fast development of algorithm as well as hardware infrastructure has greatly promoted the advance of stochastic learning techniques. The rapid development of GPU especially enables the training the deep neural networks (LeCun et al. 2015). In this work, we
have developed a deep learning based flash calculation module for the prediction of phase behavior of oil and gas in unconventional reservoirs.
CHAPTER 3
MATHEMATICAL MODEL

In this chapter, we describe the mathematical models used in our developed simulator, MSFLOW_CO2. MSFLOW_CO2 is a compositional simulator. It aims to simulate the fully coupled thermal-hydraulic-mechanical (THM) processes and track the migration of each component in the reservoir. To fulfill this task, MSFLOW_CO2 solves the governing partial differential equations describing the THM process and conducts flash calculation to predict the concentration distribution as well as phase behavior of the system. In the following sections, we will present the governing equations, the flash calculation module along with the equation of state used by MSFLOW_CO2.

3.1 Formulation of Fluid and Heat Flow

Based on the conservation of mass and energy, the governing equations of the thermal-hydraulic simulation module in MSFLOW_CO2 describes the fluid and heat transport in the porous media of the reservoir. For a compositional system consisting of $N_c$ components, the mass/energy conservation equation for component $k$ is as follows

$$\frac{\partial M^k}{\partial t} = \nabla \cdot \vec{F}^k + q^k$$

(3.1)

In the above equation, the term $M$ is the accumulation term for mass or energy. $\vec{F}$ is the flux term. $t$ is the time term and $q$ is the sink/source term. $k$ could refer to an aqueous (water) component, a hydrocarbon component or an energy ‘component’. In MSFLOW_CO2, $k = 1$ refers to the aqueous (water) component. $k = 2, \ldots, N_c$ denote hydrocarbon components.
\( k = N_C + 1 \) denotes the internal energy. For aqueous and hydrocarbon components, the accumulation term is calculated as

\[
M^k = \phi \sum_{\beta} S_{\beta} \rho_{\beta} x_{\beta}^k, \quad \beta = L, G, A, \quad k = 1, \ldots, N_C
\]

(3.2)

Where \( \phi \) is the porosity, \( \beta \) is the phase index. \( G \) refers to the gas (vapor) hydrocarbon phase; \( L \) refers to the liquid hydrocarbon phase and \( A \) refers to the aqueous phase. \( S_{\beta} \) and \( \rho_{\beta} \) is the saturation and density of phase \( \beta \) respectively. \( x_{\beta}^k \) is the mass fraction of component \( k \) inside phase \( \beta \). Since the solubility of hydrocarbon in the aqueous phase is very low, in this work we set

\[
x_{A}^k = 0, \quad k = 2, \ldots, N_C
\]

(3.3)

For the energy ‘component’,

\[
M^{N_C+2} = (1 - \phi) C_R \rho_R T + \phi \sum_{\beta} S_{\beta} \rho_{\beta} U_{\beta}
\]

(3.4)

where \( C_R \) and \( \rho_R \) are the specific heat and density of the rock, respectively. \( U_{\beta} \) is the internal energy of phase \( \beta \). \( T \) is the temperature of the system.

In Equation (3.1), the flux term \( \bar{F}^k \) is calculated as

\[
\bar{F}^k = \sum_{\beta} \bar{F}_{\beta} x_{\beta}^k, \quad k = 1, \ldots, N_C
\]

(3.5)

In the above equation, \( x_{\beta}^k \) is the mass fraction of component \( k \) inside phase \( \beta \). The phase flux \( \bar{F}_{\beta} \) is calculated by the multiphase Darcy’s law, as shown in Equation (3.6), where \( K_a \) is the apparent permeability of the rock. \( K_{\beta} \) is the relative permeability of phase \( \beta \), \( \mu_{\beta} \) is the viscosity of \( \beta \), and \( g \) is the gravity vector.

\[
\bar{F}_{\beta} = -K_a \frac{K_{\beta} \rho_{\beta}}{\mu_{\beta}} (\nabla P_{\beta} - \rho_{\beta} g)
\]

(3.6)
For the liquid and aqueous phase, $K_a$ is identical to the absolute permeability of the rock $K_\infty$. For the gas phase, $K_a = K_\infty (1 + b/p)$, where $b$ is the Klinkenberg parameter, which will be discussed in the next chapter.

The energy flux has heat conduction and convection as

$$ F^{N_c+1}_\beta = -k_t \nabla T + \sum_{\beta} h_\beta F_\beta $$

where $k_t$ is thermal conductivity and $h_\beta$ is the specific enthalpy of phase $\beta$.

### 3.2 Formulation of geomechanical simulation

The mechanical simulation module of MSFLOW_CO2 is based on mean stress method, as discussed in (Wang et al. 2016). In MSFLOW_CO2, the formation rock is assumed to be a linear thermo-poro-elastic material. To derive the governing stress equation of MSFLOW_CO2, we start from the Hooke’s law of linear elastic material, as shown in the equation below.

$$ \bar{\tau} = 2G_s \bar{\varepsilon} + \lambda_L (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \bar{I} $$

where $\bar{\tau}$ is the stress tensor, $\bar{\varepsilon}$ is the strain tensor, and $\bar{I}$ is a unit tensor. $G_s$ is the shear modulus and $\lambda_L$ is Lame’s coefficient. $\varepsilon_{kk} = x, y, z$ is the diagonal terms of the strain tensor.

Equation (3.8) was extended to non-isothermal materials by Nowacki (2013) and Norris (1992). Moreover, McTigue (1986) brought out the poro-thermo-elastic version of the above equation, as shown below

$$ \sigma_{kk} - \left[ \alpha P + 3\beta_L K_B (T - T_{ref}) \right] = \lambda_L \varepsilon_v + 2G_s \varepsilon_{kk} $$

where $\sigma_{kk} = x, y, z$ is the diagonal terms of the stress tensor. In Equation (3.9), $\beta_T$ and $K_B$ are the thermal expansion coefficient and the bulk modulus respectively. $\varepsilon_v$ is the volumetric strain, which is defined as shown in Equation (3.10).
\[ \varepsilon_v = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz} \]  

(3.10)

By summing over the \( x, y \) and \( z \) component of Equation (3.10) and rearranging the resulting terms, we can get

\[ \sigma_m - \alpha P - 3\beta_t K_b \left( T - T_{ref} \right) = \left( \lambda + \frac{2}{3} G_S \right) \varepsilon_v \]  

(3.11)

in which

\[ \sigma_m = \frac{\sigma_{xx} + \sigma_{yy} + \sigma_{zz}}{3} \]  

(3.12)

is the mean stress.

Meanwhile, the conservation of momentum for the thermo-poro-elastic process can be described by Navier’s equation (Eslami et al. 2013), as follow

\[ \alpha \nabla \cdot P + 3 \beta_t K_b \nabla T + \left( \lambda^2 + G_S \right) \nabla \left( \nabla \cdot \vec{u} \right) + G_S \nabla^2 \vec{u} + \vec{F}_b = 0 \]  

(3.13)

In the above equation, \( \vec{u} \) and \( \vec{F}_b \) is the displacement vector and body force respectively. By implementing divergence operations to Equation (3.13), we can get

\[ \alpha \nabla^2 P + 3 \beta_t K_b \nabla^2 T + \left( \lambda^2 + 2 G_S \right) \nabla^2 \left( \nabla \cdot \vec{u} \right) + \nabla \cdot \vec{F}_b = 0 \]  

(3.14)

Moreover, we have the following relationship between the displacement vector and the volumetric strain

\[ \nabla \cdot \vec{u} = \varepsilon_v \]  

(3.15)

By combing Equation (3.11) and Equation (3.15) with Equation (3.14) and rearranging them, we can get the following equation,

\[ \frac{3(1-\nu)}{(1+\nu)} \nabla^2 \sigma_m + \nabla \cdot \vec{F} = \frac{2(1-2\nu)}{(1+\nu)} \left( \alpha \nabla^2 P + 3 \beta_t K_b \nabla^2 T \right) \]  

(3.16)

The above equation is the governing equation of the mechanical simulation of MSFLOW_CO2. The relationships among the mechanical modulus are as follows.
\[ E = 2G_s (1 + \nu) \quad (3.17) \]
\[ E = 3K_b (1 - 2\nu) \quad (3.18) \]
\[ \lambda_L = \frac{2\nu G_s}{1 - 2\nu} \quad (3.19) \]

3.3 Phase behavior

In this chapter, we present the phase equilibrium (flash) calculation module of MSFLOW_CO2. The purpose of conducting flash calculation is to obtain the phase combination as well as the component distribution of the CO₂-hydrocarbon-water system. According to thermodynamic principles, at the equilibrium state the Gibbs free energy of the system should be minimized, if the surface energy induced by capillary forces is ignored. The flash calculation in MSFLOW_CO2 is based on the direct minimization of Gibbs energy, following the work of Ballard (Ballard and Sloan 2004; Ballard 2002) and Di et al. (2015). The Gibbs free energy of a multicomponent system is as follows

\[ G = \sum_{\beta=1}^{N_P} \sum_{i=1}^{N_C} n_{i\beta} \mu_{i\beta} \quad (3.20) \]

In the above equation, \( \mu_{i\beta} \) is the chemical potential of component \( i \) in phase \( \beta \), \( n_{i\beta} \) is the number of moles of component \( i \) in phase \( \beta \), \( N_P \) is the number of phases and \( N_C \) is the number of components. In this study, \( N_P = 3 \).

In every flash calculation, we need to define a reference phase \( r \) and assume that phase \( r \) always exits in the system. If a reference phase disappears, then an alternative phase will be chosen as the reference phase. By introducing the reference phase, we can rearrange Equation (3.20) as
\[ G = \sum_{\beta=1}^{N_p} \sum_{i=1}^{N_C} n_{i\beta} \mu_{i\beta} + \sum_{\beta=1}^{N_p} \sum_{\beta \neq r}^{N_C} n_{i\beta} \left( \mu_{i\beta} - \mu_{ir} \right) \]  

(3.21)

Meanwhile, the fraction of phase $\beta$ among all the phases is calculated as

\[ \alpha_\beta = \sum_{i=1}^{N_C} n_{i\beta} / N_t \quad \beta = 1, ..., N_P; \beta \neq r \]  

(3.22)

In the above equation, $N_t$ is the total number of moles in the whole system, as follows

\[ N_t = \sum_{i=1}^{N_C} \sum_{\beta=1}^{N_P} n_{i\beta} \]  

(3.23)

The mole fraction of the reference phase is

\[ \alpha_r = 1 - \sum_{\beta=1}^{N_P} \alpha_\beta \]  

(3.24)

We then define the Lagrange function and the Lagrange multipliers as follows

\[ G^* = G + \sum_{\beta=1}^{N_p} \lambda_{\beta} \left( \alpha_\beta - \sum_{i=1}^{N_C} N_{i\beta} / N_t \right) \]  

(3.25)

To achieve the minimum Gibbs free energy, the derivative of the above function with respect to all variables should be zero, as

\[ \frac{\partial G^*}{\partial n_{i\beta}} = 0, i = 1, ..., N_C; \beta = 1, ..., N_P; \beta \neq r \]  

(3.26)

\[ \frac{\partial G^*}{\partial \lambda_{\beta}} = 0, \beta = 1, ..., N_P; \beta \neq r \]  

(3.27)

\[ \frac{\partial G^*}{\partial \alpha_{\beta}} = \lambda_{\beta}, \beta = 1, ..., N_P; \beta \neq r \]  

(3.28)

Based on the above equations, when phase $\beta$ exists ($\alpha_k > 0$), $\lambda_{\beta}$ should be 0. Therefore, the condition for phase $\beta$ to exist is

\[ \alpha_\beta \lambda_{\beta} = 0, \beta = 1, ... N_P; \beta \neq r \]  

(3.29)
Moreover, it can be solved that

$$\lambda_{i, \beta} / N_i = \mu_{i, \beta} - \mu_{i, r} = RT \ln \left( f_{i, \beta} / f_{i, r} \right) \quad i = 1, ..., N_C; \beta = 1, ..., \pi; \beta \neq r$$  \hspace{1cm} (3.30)

where $f_{i, \beta}$ and $f_{i, r}$ is the fugacity of component $i$ in an arbitrary phase $\beta$ and the reference phase $r$ respectively.

$$\begin{cases} 
\frac{f_{i, \beta}}{f_{i, r}} = 1 & \text{phase } \beta \text{ exists} \\
\frac{f_{i, \beta}}{f_{i, r}} < 1 & \text{phase } \beta \text{ disappears} 
\end{cases} \hspace{1cm} (3.31)$$

The $K$ value of component $i$ in phase $\beta$ with respect to that in the reference phase $r$ is defined as the ratio of the fugacity coefficient, as follows

$$K_{i, \beta r} = \frac{\phi_{i, \beta}}{\phi_{i, r}} = \frac{x_{i, \beta}}{x_{i, r}} \frac{f_{i, \beta}}{f_{i, r}} = \frac{x_{i, \beta}}{x_{i, r}} \exp(- \ln \frac{f_{i, \beta}}{f_{i, r}})$$  \hspace{1cm} (3.32)

We introduce a variable $\theta$ to quantify the stability of phase $\beta$ as

$$\theta_{\beta} = \ln \frac{f_{i, \beta}}{f_{i, r}}, \beta = 1, ..., N_p$$  \hspace{1cm} (3.33)

Therefore, the concentration of component $i$ in phase $\beta$ is

$$x_{i, \beta} = K_{i, \beta r} x_{i, r} e^{\theta_{\beta}} \quad i = 1, ..., N_C; \beta = 1, ..., N_p; \beta \neq r$$  \hspace{1cm} (3.34)

Moreover, Equation (3.30) can be rewritten as

$$\alpha_{i, \beta} \theta_{\beta} = 0, \beta = 1, ..., N_p; \beta \neq r$$  \hspace{1cm} (3.35)

The total number of moles of component $i$ can be expressed as

$$\alpha_{i, r} x_{i, r} + \sum_{\beta=1}^{\pi} \alpha_{i, \beta} x_{i, \beta} = z_i \quad i = 1, ..., N_C$$  \hspace{1cm} (3.36)

By combining Equation (3.35), (3.36) and (3.37), we can obtain that
\[ x_{ir} = \frac{z_i}{1 + \sum_{\beta=1}^{\pi} \alpha_{\beta} (K_{i,\beta r} e^{\theta_{\beta}} - 1)} \quad i = 1, \ldots, N_C \]  

Moreover, the total concentration of component \( i \) among all phases should be one, as follows

\[ \sum_{i=1}^{C} x_{i\beta} = 1, \beta = 1, \ldots, N_P \]  

We then define the objective functions for each component as

\[ D_{i\beta} = x_{i\beta} [1 + \sum_{j=1}^{\pi} \alpha_j (K_{i,j\beta} e^{\theta_j} - 1)] - z_i K_{i,\beta r} e^{\theta_{\beta}} = 0 \quad i = 1, \ldots, N_C; \beta = 1, \ldots, N_P; \beta \neq r \]  

\[ E_{\beta} = \sum_{i=1}^{C} \frac{z_i (K_{i,\beta r} e^{\theta_{\beta}} - 1)}{1 + \sum_{j=1}^{\pi} \alpha_j (K_{i,j\beta} e^{\theta_j} - 1)} = 0 \quad \beta = 1, \ldots, N_P \]  

\[ F_{\beta} = \frac{\alpha_{\beta} \theta_{\beta}}{\alpha_{\beta} + \theta_{\beta}} = 0 \quad \beta = 1, \ldots, N_P \]  

Therefore, to minimize \( G^* \) is to minimize \( D, E \) and \( F \) simultaneously. The minimization of \( G^* \) is essentially an optimization process. By finding the global minima of the objective functions, we can get the phase behavior of the multiphase system.

### 3.4 Equation of state and fugacity models

As shown in the previous section, the calculation of the Gibbs energy requires the calculation of the fugacity of the component, which is achieved by the reformulation of an equation of state. In MSFLOW\_CO2, Soave-Redlich-Kwong equation of state (SRK EOS) is used for the calculation of the density as well as fugacity of the vapor hydrocarbon and the liquid hydrocarbon phase. The fugacity of the vapor hydrocarbon and the liquid hydrocarbon phase is shown in Equation (3.42) and (3.43) respectively.
In the above equation, the parameter $a$ is defined as

$$a = \sum_{i=1}^{N_c} \sum_{j=1}^{N_c} x_i x_j a_{ij}$$  \hspace{1cm} (3.44)$$

$a_{ij}$ is defined as

$$a_{ij} = (1 - k_{ij}) \sqrt{\alpha_i \alpha_j}$$  \hspace{1cm} (3.45)$$

where $k_{ij}$ is the interaction parameter. $\alpha_i$ and $\alpha_j$ are defined as

$$\alpha_i = \left[ 1 + S_i^* \left( 1 - \sqrt{T_i} \right) \right]^2$$  \hspace{1cm} (3.47)$$

where

$$S_i^* = 0.48508 + 1.55151 \omega_i - 0.15613 \omega_i^2$$  \hspace{1cm} (3.48)$$

The reduced temperature and pressure is defined as
\[ T_r = \frac{T}{T_{c_i}} \quad (3.49) \]

\[ P_r = \frac{P}{P_{c_i}} \quad (3.50) \]

In the above equation, \( \omega_i \) is the acentric parameter of component \( i \)

\[ b = \sum_{i=1}^{N_C} x_i b_i \quad (3.51) \]

\[ b_i = 0.08664 \frac{RT_{c_i}}{P_{c_i}} \quad (3.52) \]

In SRK EOS, the compressibility factor \( Z \) is expressed as a cubic function, as below.

\[ f(Z) = Z^3 - Z^2 + (A - B - B^2) Z - A \cdot B = 0 \quad (3.53) \]

In the above equation,

\[ A = \frac{aP}{(RT)^2} \quad (3.54) \]

\[ B = \frac{bP}{RT} \quad (3.55) \]

Equation (3.53) is solved analytically. For the three solved compressibility factor, the largest factor and the smallest factor is assigned to the gas phase and the liquid phase respectively.

The aqueous (water) phase properties are calculated based on Shock and Helgeson’s (1988) approach. The chemical potential \( \mu_{i,aq} \) of the \( i \)th dissolved component (non-water component) in the water phase is calculated as

\[ \frac{\mu_{i,aq}}{RT} = \frac{g_i^*}{RT_0} - \int_{T_0}^{T} \frac{h_i^*}{RT^2} dT + \int_{P_0}^{P} \frac{y_i^*}{RT} dP + \ln a_{i,aq} \quad (3.56) \]
In the above equation, \( T_0 \) and \( P_0 \) is the standard temperature and pressure respectively. \( \bar{g}_i^* \), \( \bar{h}_i^* \) and \( \bar{v}_i^* \) is the partial molar Gibbs energy, partial molar enthalpy and partial molar volume of a hypothetical solution, respectively. The detailed formulation of \( \bar{g}_i^* \), \( \bar{h}_i^* \) and \( \bar{v}_i^* \) can be found in Shock and Helgeson (1988). The chemical potential of water component in the water phase is calculated as

\[
\frac{\mu_{w,\text{aq}}}{RT} = \frac{g_{w_0,\text{pure}}}{RT_0} - \frac{h_{w,\text{pure}}}{RT^2} dT + \frac{\nu_{w,\text{pure}}}{RT} dP + \ln a_{w,\text{aq}} \tag{3.57}
\]

where the subscript ‘pure’ refers to the pure water phase. The details of the implementation of water fugacity can be found in Bromley (1973) and Jager et al. (2003).

We use Newton’s method to minimize Equation (3.39), (3.40), and (3.41), as follows.

\[
\begin{bmatrix}
\frac{\partial \Psi}{\partial X_j} \\
\end{bmatrix}_p \{\Delta X_j\}_{p+1} = -\{\Psi_i\}_p 
\tag{3.58}
\]

In the above equation, \( \Psi \) is the objective function, \( X \) is the primary variable and \( \left[\frac{\partial \Psi_i}{\partial X_j}\right]_p \) is the Jacobian matrix. Therefore, Newton’s method is a gradient-based optimization approach. More details of Newton’s method will be described in the next chapter. The Newton’s approach requires an initial guess. In this work, the initial guess of the equilibrium ratio for the hydrocarbon component in the oil and gas phase \( K^0_i \) is estimated by Wilson’s equation, as

\[
K^0_i = \frac{P_{ci}}{P} \exp \left( 5.37 (1 + \omega) \left( 1 - \frac{T_{ci}}{T_i} \right) \right) 
\tag{3.59}
\]

The initial guess of the equilibrium ratio of the water component in the oil and the gas phase. Moreover, the solubility of the hydrocarbon components in the aqueous phase is set to be 0.
3.5 Mechanical properties

The mechanical properties have impacts on the permeability as well as the porosity of the formation rock. In general, the porosity and permeability can be expressed as the function of the pressure, temperature, and mean stress, as

\[ \phi = \phi (P, T, \sigma_m) \]  
\[ K = K (P, T, \sigma_m) \]

MSFLOW_CO2 has implemented several correlations of the permeability and porosity, from literature (Rutqvist et al. 2002b; Taron et al. 2009; Wang et al. 2016). Moreover, MSFLOW_CO2 allows the users to input a table of permeability and porosity with respect to the primary variables. One example of the correlations is as follows (Wang 2015b). The porosity of the rock can be calculated as

\[ \phi = \phi_0 \left( 1 + c_p \left( P - P_{ref} \right) + 3 \beta_T \left( T - T_{ref} \right) \right) \]

In the above equation, \( c_p \) and \( \beta_T \) is the compressibility and the thermal expansion coefficient, respectively. \( P_{ref} \) is a reference pressure, while \( T_{ref} \) is a reference temperature. \( \phi_0 \) and \( \phi \) are the initial porosity and the transient porosity of the rock, respectively. Based on the calculated porosity, the permeability can be calculated by the Kozeny-Carman equation (Carman, 1956; Kruczek, 2014) as

\[ K = K_0 \left( \frac{1 - \phi_0}{1 - \phi} \right)^3 \left( \frac{\phi}{\phi_0} \right)^3 \]

The pore diameter changes as the stress condition varies. The change of the pore diameter results in the variation of the capillary pressure of the multiphase system. In MSFLOW_CO2, the capillary pressure is correlated with the permeability and porosity as follows (Leverett 1941)
where $P_{c0}$ and $P_c$ is the initial and the transient capillary pressure, respectively. Moreover, the mechanical impact on the volume of the grid block is quantified via the volumetric strain $\varepsilon_r$ as

$$V = V_0 \left(1 - \varepsilon_r \right)$$  \hspace{1cm} (3.65)

Where $V_0$ and $V$ are the initial and the transient volume of the grid block, respectively.

### 3.6 Fluid properties

The fluid properties are secondary variables in the simulation of THM processes. In this section, we present the calculation of fluid properties in MSFLOW_CO2, including water properties and hydrocarbon properties.

#### 3.6.1 Water properties

In MSFLOW_CO2, the aqueous phase is treated as a mixture, whose properties, including the density, viscosity and enthalpy, are calculated based on the properties of pure water phase and dissolved CO$_2$ component, after (Pan and Oldenburg 2016). The properties of the pure water phase are primarily based on the NIST Standard Reference Databases (Lemmon 2002). Since the property correlations of the pure water phase either have lengthy formulations or have no explicit formulations at all, we just plot them as the function of pressure and temperature, as shown in Figure 3.1 (density), Figure 3.2 (enthalpy), Figure 3.3 (viscosity) and Figure 3.4 (saturation pressure). According to the results, the water properties, especially the viscosity tend to be more sensitive to temperature than to pressure. Therefore, the simulation of multiphysical processes in reservoirs should take the thermal impact on the water properties into consideration.
Figure 3.1 Density of the pure water phase at reservoir temperature and pressure conditions.

Figure 3.2 Enthalpy of the water phase at reservoir temperature and pressure conditions.
Figure 3.3 Viscosity of the water phase at reservoir temperature and pressure conditions.

Figure 3.4 Saturation pressure of the water phase at reservoir temperature and pressure conditions.
3.6.2 Hydrocarbon properties

In MSFLOW\_CO2, the densities of the hydrocarbon phases are calculated from the flash calculation based on SRK EOS, as described in Section 3.3 and 3.4. Once the compressibility factor $Z$ of phase $\beta$ is solved from SRK EOS, the mole volume of the phase $\overline{V}_\beta$ (mol/m$^3$) is solved as follows

$$\overline{V}_\beta = \frac{Z\beta RT}{P}, \quad \beta = G, L$$  \hspace{1cm} (3.66)

The phase mole density $\rho_\beta$ (m$^3$/mol) is then solved as

$$\rho_\beta = \frac{1}{\overline{V}_\beta}, \quad \beta = G, L$$  \hspace{1cm} (3.67)

The saturation of each phase is calculated based on the phase ratio $\alpha_\beta$ and the phase mole density $\rho_\beta$, as follows.

$$S_\beta = \frac{\alpha_\beta / \rho_\beta}{\sum_{i=1}^{N_p} \alpha_i / \rho_i}, \quad \beta = G, L, A$$  \hspace{1cm} (3.68)

In the above equation, the phase ratio for each phase is obtained from the flash calculation described in Section 3.4. The density of the hydrocarbon phase is obtained from Equation (3.68), while the density of the aqueous phase is obtained from Equation (3.67).

The enthalpy of the hydrocarbon phases $h_\beta$ is calculated using a simple mixing rule based on the enthalpy of the pure components, as follows.

$$h_\beta = \sum_{i=1}^{N_c} x_{\beta i} h_i, \quad \beta = G, L$$  \hspace{1cm} (3.69)

In the above equation, $h_i$ is retrieved from the NIST database (Lemmon 2002). We use a linear function of temperature to regress the data, as follows.
\( h_i = a_0 + a_1 (T-275) \)  \hspace{1cm} (3.70)

The critical temperature \((T_c)\), critical pressure \((P_c)\), acentric factor \((\omega)\), molecular weight \((M_w)\) as well as the two parameters \((a_0, a_1)\) to the enthalpy of all the components are listed in Table 3.1. The binary interaction parameters between each pair of components are listed in Table 3.2.

**Table 3.1 Parameters for the calculation of component properties**

<table>
<thead>
<tr>
<th>Component</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (MPa)</th>
<th>( \omega )</th>
<th>( M_w ) (g·mol(^{-1}))</th>
<th>( a_0 ) (KJ·(kg·K)(^{-1}))</th>
<th>( a_1 ) (KJ·(kg·K)(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>190.56</td>
<td>4.599</td>
<td>0.0115</td>
<td>16.043</td>
<td>2.191</td>
<td>0.002672</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>305.32</td>
<td>4.872</td>
<td>0.0995</td>
<td>30.07</td>
<td>1.651</td>
<td>0.004384</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>369.83</td>
<td>4.248</td>
<td>0.1523</td>
<td>44.096</td>
<td>0.79</td>
<td>0.00468</td>
</tr>
<tr>
<td>n-C(<em>4)H(</em>{10})</td>
<td>408.14</td>
<td>3.648</td>
<td>0.2002</td>
<td>58.123</td>
<td>0.818</td>
<td>0.004255</td>
</tr>
<tr>
<td>n-C(<em>5)H(</em>{12})</td>
<td>469.7</td>
<td>3.37</td>
<td>0.2515</td>
<td>72.15</td>
<td>-0.218</td>
<td>0.001895</td>
</tr>
<tr>
<td>n-C(<em>6)H(</em>{14})</td>
<td>507.6</td>
<td>3.025</td>
<td>0.3013</td>
<td>86.177</td>
<td>-0.491</td>
<td>0.007187</td>
</tr>
<tr>
<td>n-C(<em>7)H(</em>{16})</td>
<td>540.2</td>
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<td>0.3495</td>
<td>100.204</td>
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</tr>
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<td>n-C(<em>8)H(</em>{18})</td>
<td>568.7</td>
<td>2.49</td>
<td>0.3996</td>
<td>114.231</td>
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<tr>
<td>n-C(<em>9)H(</em>{20})</td>
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<td>n-C(<em>{10})H(</em>{22})</td>
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<td>CO(_2)</td>
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<td>0.003722</td>
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<td>H(_2)O</td>
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<td>22.06</td>
<td>0.3440</td>
<td>18.015</td>
<td>___</td>
<td>___</td>
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Table 3.2 Binary interaction coefficients for the calculation of properties

<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>C₂H₆</th>
<th>C₃H₈</th>
<th>n-C₄H₁₀</th>
<th>n-C₅H₁₂</th>
<th>n-C₆H₁₄</th>
<th>n-C₇H₁₆</th>
<th>n-C₈H₁₈</th>
<th>n-C₉H₂₀</th>
<th>n-C₁₀H₂₂</th>
<th>CO₂</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
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<td>CH₄</td>
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<td>0</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
<td>0.04</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
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<td>0.02</td>
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3.6.3 Relative permeability and capillary pressure

In MSFLOW_CO₂, the three-phase relative permeability is calculated using the Brooks-Corey model (Delshad and Pope 1989) as follows.

\[
k_{ro} = k_{ro, \text{max}} \left( \frac{S_o - S_{or}}{1 - S_{or} - S_{wr} - S_{gr}} \right)^{n_o}
\]  (3.71)

\[
k_{rw} = k_{rw, \text{max}} \left( \frac{S_w - S_{wr}}{1 - S_{or} - S_{wr} - S_{gr}} \right)^{n_w}
\]  (3.72)

\[
k_{rg} = k_{rg, \text{max}} \left( \frac{S_g - S_{gr}}{1 - S_{or} - S_{wr} - S_{gr}} \right)^{n_g}
\]  (3.73)

Where \( k_{ro, \text{max}} \), \( k_{rw, \text{max}} \) and \( k_{rg, \text{max}} \) is the maximum relative permeability for the liquid hydrocarbon phase, the aqueous phase and the gas phase, respectively, while \( S_{or} \), \( S_{wr} \) and \( S_{gr} \) are the residual relative permeability for each phase, respectively.

The capillary pressure between the phases is calculated using the Young-Laplace equation as below.
\[ P_c = \frac{2\gamma \cos \theta}{r} \]  

(3.74)

In the above equation, \( \gamma \) is the surface tension; \( \theta \) is the contact angle and \( r \) is the pore radius. The surface tension between the aqueous phase and the liquid hydrocarbon phase is calculated from temperature as (Tolman 1949)

\[
\gamma_{L-A} = 0.2358 \left( \frac{T_{c,\text{water}}}{T_{c,\text{water}}} \right)^{1.256} \left[ 1 - 0.625 \left( \frac{T_{c,\text{water}}}{T_{c,\text{water}}} \right) \right]
\]  

(3.75)

where \( T_{c,\text{water}} \) is the critical temperature of water. For water, \( T_{c,\text{water}} \) is 647.15 K. The surface tension between the aqueous phase and the liquid hydrocarbon phase

\[
\gamma_{V-L} = \left( \rho_L \sum_{i}^{N_c} x_L^i P_a^i - \rho_V \sum_{i}^{N_c} x_V^i P_a^i \right)^\nu
\]  

(3.76)

where \( \rho_L \) and \( \rho_V \) is the density of the liquid and vapor hydrocarbon phase respectively. \( x_L^i \) and \( x_V^i \) is the mole concentration of component \( i \) in the liquid and vapor hydrocarbon phase respectively. \( \nu \) is a constant parameter, which is by default set as 3.6. \( P_a^i \) is the parachor of component \( i \), as listed in Table 3.3.

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CHAPTER 4
TRANSPORT MECHANISMS

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Shihao Wang¹, Alexander A. Lukyanov², and Yu-Shu Wu¹

4.1 Introduction

As discovered by Maxwell (1879), when gas flows through narrow channels, the mass transfer rate increases due to momentum loss on the wall of the channel. In the microscale, the gas becomes rarefied, and Navier-Stokes equation that is based on continuous assumptions is no longer valid (Hadjiconstantinou 2006). In this case, the gas flow should be investigated from a kinetic viewpoint (Chapman and Cowling 1970; Present 1958), and Boltzmann equation (Cercignani 1988) should be adopted. In the rarefied gases, the average distance that a gas molecular can move without any collisions is defined as the mean free path. The ratio between the mean free path and the flow channel diameter is defined as the Knudsen number, which is for quantification of the magnitude of the gas-wall interaction effect.

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The gas-wall interaction results in the enhancement of mass transfer rate and is observed as an ‘apparent’ boundary slippage phenomenon. Maxwell (1879) brought out the very first slippage boundary condition, as shown in Equation (4.1)

\[ u_{slip} = \frac{2 - \sigma}{\sigma} \cdot \lambda \left( \frac{\partial u}{\partial n} \right)_s \]  

(4.1)

In this equation, \( u \) is the flux velocity at the boundary, \( \sigma \) is the Tangential Momentum Accommodation Coefficient (TMAC), which quantifies the ratio of momentum transfer on the boundary and \( \lambda \) is the mean free path of the gas. \( n \) denotes normal direction and \( s \) denotes (flat) surface. The detailed explanations of symbols used in this paper can be found in the Nomenclature list. A general form of the slippage boundary condition can be expressed as

\[ u_{slip} = C_1 \left( K_N \right) \cdot \lambda \left( \frac{\partial u}{\partial n} \right)_s - C_2 \left( K_N \right) \cdot \lambda^2 \left( \frac{\partial^2 u}{\partial n^2} \right)_s \ldots \]  

(4.2)

As shown in Equation (4.2), the boundary slippage velocity is a multiple order function of the velocity gradient. In Equation (4.2), the term \( C_1 \) and \( C_2 \) are the coefficients of first-order velocity gradient and second-order velocity gradient, respectively. By comparing Equation (4.1) and (4.2), Maxwell’s slippage boundary condition is a first-order boundary condition with a constant coefficient.

In the petroleum reservoirs, the gas slippage effect exists in the flow of gas through the pores of unconventional reservoir rocks, which ranges from several nanometers to several micrometers. Klinkenberg first discovered that the apparent gas permeability \( K_a \) could be larger than absolute rock permeability \( K_\infty \) and brought out a general model to quantify such effect, which was later named after him, as shown in Equation (4.3).

\[ K_a = K_\infty \left( 1 + \frac{b}{P} \right) \]  

(4.3)
In the above equation, $b$ is an empirical parameter. Since $\lambda \propto 1/P$, Klinkenberg’s correlation can be viewed as an empirical first-order slippage model.

Knudsen (1910, 1934) investigated the diffusion effect induced by molecular-wall interaction for high Knudsen numbers and brought out the Knudsen diffusion effect along with the Knudsen diffusion coefficient. Pollard and Present (1948) later studied the gas diffusion process in a long channel. According to Pollard and Present’s model, Knudsen diffusion coefficient is the ‘extreme’ value for very high Knudsen numbers (extremely narrow flow channel). The diffusion coefficient decreases from the Knudsen diffusion coefficient continuously to the molecular diffusion coefficient as the Knudsen number decreases from infinitely large to infinitely small. Recently, the impact of surface geometry on Knudsen diffusion has also been investigated (Guo et al. 2016).

Rarefied gas flow and its associated gas slippage model has a wide range of applications in vacuum science (Dushman and Brown 1962), the design of microfluidics (Wleklinski 2001; Wu et al. 2017b), aerospace engineering (Kogan 1992), microelectromechanical systems (MEMS) (Ho and Tai 1998; Wu et al. 2017a) and unconventional gas formations (Moghadam and Chalaturnyk 2014; Fathi et al. 2012; Wang and Reed 2009; S. Wang et al. 2017b; Wang et al. 2018; Wang et al. 2015). To simulate the rarefied gas flow, many numerical approaches have been proposed and applied. Direct Simulation Monte Carlo (DSMC) (Bird 1998; Bird 1976 1981; Kroese et al. 2014; Oran et al. 1998) directly tracks the motion of molecules. Therefore, DSMC is able to obtain accurate results. DSMC has been used to obtain slippage boundary conditions (Pan et al. 1999) and to study the flow inside microchannels (Ho et al. 2016). The limitation of DSMC is also obvious, that it is in need of huge computational capability.
Lattice Boltzmann Method (LBM) (Chen and Doolen 1998; He and Luo 1997) solves Boltzmann equation on a grid-like lattice. LBM has been successfully applied to ‘mesoscale’ microfluid simulation for low to moderately high Knudsen number (Li et al. 2011; Nie et al. 2002; Tang et al. 2005). However, it should be noticed that LBM itself still requires a slippage boundary condition (Silva and Semiao 2017).

DSBGK method (direct simulation based on Bhatnagar–Gross–Krook equation) (Li 2011) is a promising method for rarefied gas dynamics. Compared with DSMC, DSBGK is less computationally intensive. Li and Sultan (2017) adopted DSBGK method to study the Klinkenberg effect with a two-dimensional digital rock and benchmarked against the traditional empirical Klinkenberg’s correlation.

Gas kinetic scheme (Liu et al. 2018; Xu 2001, 2002) is another appealing approach to numerically simulate the rarefied gas flow. Ohwada and Xu (2004) combined gas-kinetic scheme with Burnett equation, which is a higher order approach (Chapman and Cowling 1970), to solve for the velocity profile as well as pressure/temperature distribution of gas flow inside microchannels.

Besides Burnett equation, numerous higher order continuum hydrodynamics approaches, including super-Burnett equation (Xu 2003), Eu’s generalized hydrodynamics approach (Myong 1999), BGK-Burnett equation (Balakrishnan 2004), 13-moment approach (Grad 1949) and many more, have been proposed and studied. However, as pointed out by Lockerby et al. (Lockerby et al. 2005b), these approaches may have instability issues and in general, fail to match DSMC results well.

In recent years, more physical factors have been taken into the consideration of numerical approaches, such as the surface geometry (Dinler et al. 2013; Guo et al. 2016), and the near-
surface viscosity effect (Vo et al. 2015). The flow in unconventional oil/gas formations is typically under high-temperature high-pressure conditions (Deng et al. 2017). Moreover, in shale/clay reservoirs, when hydrocarbon molecules flow through the micro/nano-scale channels in kerogen, the surface of the kerogen (as organic matter) has certain preference to gas components, which leads to the surface preference effect (Ho et al. 2016; Ho et al. 2018) as well as gas adsorption/desorption processes. Therefore, the slippage model in unconventional reservoirs involves more complex multiphysical processes, including the surface diffusion in the adsorption layer (Wu et al. 2015), the impact of the pore-network geometry (Shi et al. 2012), the impact of the surface roughness (Shi et al. 2012), the real (dense) gas effect (Wu et al. 2017b; Wu et al. 2016), and the mechanical impact (Wu et al. 2016). Song et al. (2016) brought out a comprehensive model for the calculation of gas apparent permeability of shale by considering stress effect, slippage effect and surface diffusion effect. Song’s model can also be combined with our proposed model. The pore-network geometry of unconventional reservoirs can be reconstructed by digital rock techniques. Yang et al. (2015) presented a novel approach to characterize the pore space geometry, in which the inorganic pore digital core and the organic pore digital core is constructed by the multiple point statistics method, and the Markov chain Monte Carlo method, respectively.

As discussed above, the slippage boundary condition is of great importance in the quantification of rarefied gas flow. During the past few years, numerous boundary conditions, including first order and second order conditions, have been proposed. Among the proposed formulation, some representative models are as follows. Cercignani (1964) derived a second order boundary condition from the linearized Boltzmann equation. This boundary condition was later validated by Hadjiconstantinou (2003). Beskok and Karniadakis (1999) proposed an
empirical correlation to quantify the flow within multiple geometries for a wide range of Knudsen numbers. Wu and Bogy (2003) used gas kinetic theory to address this problem and derived a simple yet accurate second-order model for relatively low Knudsen numbers that is below one. They investigated the momentum loss on the pore wall with the kinetic theory of gases. Their model was later extended to higher Knudsen numbers (Wu 2008). Zhang et al. (2012) have conducted thorough reviews and comparisons on the slippage effect and Klinkenberg phenomenon, respectively. From their observation, Wu (2008)’s model is the most accurate non-empirical slippage boundary condition. Recently, S. Wang et al. (2017b; 2019b) presented a novel second-order slippage model, which accurately calculates the mass transfer enhancement in micro-channels and matches the numerical results (Li et al. 2011) as well as physical experiment (Colin et al. 2004) data very well.

As for the slippage model for multiple component gas mixtures, Loyalka (1971), Takata (2001), Garcia et al. (2007), and (Sharipov et al. 2004; Sharipov and Kalempa 2003, 2004a, 2004b, 2005) have studied the slippage of binary gas mixtures by solving the linearized Boltzmann equation. Hyakutake et al. (Hyakutake et al. 2005) and Arcidiacono et al. (Arcidiacono et al. 2007) conduct DSMC simulation and LBM simulation for binary gas mixtures. Bentz et al. (1999) and Yamaguchi et al. (2016) conduct spinning rotor gauge experiments and tube flooding experiments respectively to measure the slippage coefficient of binary gas mixtures.

Based on the above literature review, although the slippage model of single component gas flow has been investigated in-depth, the non-empirical slippage model for multicomponent gas mixtures, however, has not yet been well developed. In this work, we proposed a non-
empirical gas slippage for multicomponent gas mixtures. Our work is based on the published research (Wu 2008; Wu and Bogy 2003) about single component gas slippage.

4.2 Background

In this section, we present the essential background for the proposed model, including basic kinetic theory of gases.

4.2.1 Mean free path of the near-ideal gas mixture

By definition, the mean free path is the ‘average’ distance that a gas molecule can travel before it hits another gas molecule. The mean free path of gas can be calculated in several ways, resulting in slightly different values (Bird 1976; Chapman and Cowling 1970; Present 1958). In this work, we follow Kennard’s method (Kennard 1938) to calculate the mean free path of the $i$th component in a gas mixture with $N_C$ components as follows

$$
\lambda_i = \frac{4k_B T}{\pi P \sum_{j=1}^{N_C} n_j \left( \delta_i + \delta_j \right)^2 \left( 1 + m_i/m_j \right)^{3/2}}
$$

(4.4)

In the above equation, $n_j$ is the number density of the $j$th type of molecules. $\delta_i$ and $m_i$ are the collision diameter (kinetic diameter) and molecular weight of the $i$th type of molecules respectively. $k_B$ and $T$ are the Boltzmann constant and temperature respectively. The ‘average’ mean free path of the gas mixture can be defined as

$$
\lambda_{fm} = \sum_{j=1}^{N_C} x_j \lambda_j
$$

(4.5)

Where $x_j$ is the mole fraction of the $j$th type of molecules.
In Equation (4.5), \( \lambda_{jm} \) is calculated via a simple mixing rule and is used only for calculation of Knudsen number to make comparison easier. From \( \lambda_{jm} \), we can define Knudsen number for the gas mixture as

\[
K_N = \frac{\lambda_{jm}}{d}
\]  

(4.6)

In our work, we will use the above Knudsen number to calculate the mass rate enhancement factor of the gas slippage model. It should be pointed out that the above definition of Knudsen number is only for convenience (to be consistent with the formulation of single-component gases). The definition of the Knudsen number does not affect our derivation.

### 4.2.2 Diffuse reflection and momentum loss

The impinging molecules reflect on the wall of the porous media. A certain amount of reflections are specular, in which the molecules maintain their horizontal momentum. The rest of the molecules diffusively reflect into a random direction, causing a loss of momentum, as shown in Figure 4.1. The diffuse reflection can be analogous to light scattering on rough surfaces and can be quantified by the method proposed by Bennett and Porteus (1961); Davies (1954); and Harvey et al. (2012). The percentage of the loss of the momentum is defined as Tangential Momentum Accommodation Coefficient (TMAC), ranging from 0 to 1. The rougher the surface is, the higher the TMAC is.

The diffusively reflected molecules will lose their horizontal momentum after the reflection. Since the momentum gradient is the origin of shear stress, the loss of horizontal momentum will reduce the shear stress and thus reduce the viscosity of fluid that is in the
vicinity of the pore wall, causing the fluid to ‘slip.’ In this work, we aim to quantify the slippage effect by quantifying the amount of lost momentum.

![Figure 4.1](image)

Figure 4.1 The conceptual model of gas molecular reflection on the rough surface (wall) of porous media. The solid arrow line represents the specular reflection, while the dash arrow lines represent the diffuse reflection.

### 4.2.3 Kinetic theory of gasses and viscosity of gas mixtures

In the bulk flow, consider a spherical coordinate system in which a small volume $d\tau$ of the gas is in a position $(r, \varphi, \omega)$, as shown in Figure 4.2. According to the kinetic theory of gasses (Present, 1958), in unit time the number of the $i$th type of molecules that collide once in $d\tau$, then leave $d\tau$ and reach a small area $dS$ at $(0,0,0)$ without any other collisions is

$$dN_i = x_i \frac{\bar{v}_i n_i}{\lambda_i} \cdot d\tau \cos \varphi \exp \left( -\frac{r}{\lambda_i} \right) \cdot dS \tag{4.7}$$

In the above formulation, $x_i$ is the mole concentration of component $i$. $n$ is the number density of the gas mixture. $r$ is the traveling distance. The average momentum of the molecules transport
can be calculated by multiplying their flux velocity (in the mean moving distance controlled by mean free path) by their number density and mass.

For laminar flow (along x-direction as shown in Figure 4.3), supposing there is no wall and no boundary reflection, given an imaginary plane at $z = z_0$ with unit area in the space, molecules that impinge into the unit area from position $(r, \varphi, \omega)$ have the flux velocity at $z = z_0 + r\cos\varphi$, as shown in Table 4.4. Therefore, assuming a simple mixing rule, the amount of horizontal momentum transported by $i$th type of molecules impinge into the imaginary plane from the above is

$$M_{ui} = \chi_i \frac{\bar{v}_i m_i n}{4\pi \lambda_i} \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \int_0^{z_0} u(z_0 + r\cos\varphi) \cos\varphi \sin\varphi \exp\left(-\frac{r}{\lambda_i}\right) r \, dr \, d\varphi \, d\omega \quad (4.8)$$
where $u$ is the flux velocity. In the case of laminar flow, $u$ is the function of $z$ only. Since the space is open, the traveling distance of the molecular may range from 0 to infinity. Therefore, the lower and upper limit of the inner integral is 0 and $\infty$, respectively. (This will be different for rarefied gases within microchannels). Similarly, the horizontal momentum carried by $i$th of molecules from bottom along direction ($\pi-\varphi$) is

$$M_{bi} = x_i \frac{\nu m_i n_i}{4\pi \lambda_i} \int_{0}^{2\pi} \int_{0}^{\pi/2} \int_{0}^{\infty} u(z_0 - r \cos \varphi) \cos \varphi \sin \varphi \exp \left( -\frac{r}{\lambda_i} \right) dr d\varphi d\omega$$  \hspace{1cm} (4.9)\

**Figure 4.3** The velocity profile of the laminar flow system.

Based on the net momentum, by summing up all $Nc$ types of molecules, the total momentum from the above direction and bellow direction can be calculated and expanded with respect the $z$-coordinate into the second order in Equation (4.10) and Equation (4.11), respectively. The second-order term of the velocity refers to the ‘non-local’ nature of the flow. Therefore, Equation (4.10) and Equation (4.11) are the estimates of the momentum carried by impinging molecules in an open space without any restrictions from the boundary.
\[ M_n = \sum_{i=1}^{N_c} M_{ni} \]
\[ = \sum_{i=1}^{N_c} x_i \frac{\overline{v}_i m_i n_i}{4\pi \lambda_i} \int_0^{2\pi} \int_0^{\pi/2} u(z_0 + r \cos \varphi) \cos \varphi \sin \varphi \exp \left( -\frac{r}{\lambda_i} \right) dr \varphi d\omega \]  \hspace{1cm} (4.10)

\[ = \sum_{i=1}^{N_c} x_i \frac{\overline{v}_i m_i n_i}{4\pi \lambda_i} \int_0^{2\pi} \int_0^{\pi/2} \left[ u \bigg|_{z_0} + r \cos \varphi \frac{\partial u}{\partial z} \bigg|_{z_0} + \frac{1}{2} r^2 \cos^2 \varphi \frac{\partial^2 u}{\partial z^2} \bigg|_{z_0} \right] \cos \varphi \sin \varphi \exp \left( -\frac{r}{\lambda_i} \right) dr \varphi d\omega \]

---

**Figure 4.4** The conceptual model of the \( i \)th type of molecules that impinge into an imaginary plane in an open space within a laminar flow field. \( x \)-direction is the flux direction, meaning that the flux velocity vector only has non-zero components along the \( x \)-direction.

\[ M_b = \sum_{i=1}^{N_c} M_{bi} = \sum_{i=1}^{N_c} x_i \frac{\overline{v}_i m_i n_i}{4\pi \lambda_i} \int_0^{2\pi} \int_0^{\pi/2} u(z_0 - r \cos \varphi) \cos \varphi \sin \varphi \exp \left( -\frac{r}{\lambda_i} \right) dr \varphi d\omega \]

\[ = \sum_{i=1}^{N_c} x_i \frac{\overline{v}_i m_i n_i}{4\pi \lambda_i} \int_0^{2\pi} \int_0^{\pi/2} \left[ u \bigg|_{z_0} - r \cos \varphi \frac{\partial u}{\partial z} \bigg|_{z_0} + \frac{1}{2} r^2 \cos^2 \varphi \frac{\partial^2 u}{\partial z^2} \bigg|_{z_0} \right] \cos \varphi \sin \varphi \exp \left( -\frac{r}{\lambda_i} \right) dr \varphi d\omega \]  \hspace{1cm} (4.11)
The shear force on the plane is just the difference between $M_u$ and $M_b$ as

$$\tau = M_u - M_b = \frac{1}{3} \sum_{i=1}^{N_c} x_i \bar{v}_i m_i n_i \lambda_i \left( \frac{\partial u}{\partial z} \right)_{z=0} \quad (4.12)$$

Based on the definition of viscosity, we can obtain the viscosity of gas mixture as

$$\mu_{\text{ideal}} = \frac{1}{3} \sum_{i=1}^{N_c} x_i \bar{v}_i m_i n_i \lambda_i \quad (4.13)$$

According to (Present 1958), the accuracy of the above approach is up to 90% for light molecules. Therefore, we can use this mean free path method originated from the kinetic theory of gases to estimate the viscosity of ideal gas mixtures. In a system that is confined by walls, gas molecules cannot travel freely as they do in the open-boundary flow. The molecules will frequently collide with the walls losing momentum, which causes the reduction of viscous shear stress and the slippage of the flow. Based on this model, we can further calculate the slippage boundary condition of gas mixtures by putting the mixture into a confined flow channel.

4.3 ‘Equivalent’ non-empirical slippage model for multicomponent gas

In this section, we present the derivation of an ‘equivalent’ non-empirical gas slippage model of gas mixtures. This correlation is under the assumption of a parabolic velocity profile within the flow channel. As mentioned in the previous sections, the existence of walls and diffuse reflection are the origin of viscosity reduction as well as boundary slippage. We consider two types of molecules. For the first type (Type 1), these molecules have a molecular collision at $(r, \varphi, \omega)$, then directly impinge on a point of interest (of unit area) on the boundary ($z=0$) along direction $\varphi$, as shown in Figure 4.5.
According to our previous discussion, the flux velocity transported by these molecules is the flux velocity at $z = r \cdot \cos \varphi$. Because of the confinement of the upper wall, the traveling distance of Type 1 molecules ranges from $0$ to $d / \cos \varphi$. All the effective momentum transported by all types of molecules can be calculated as

$$M_1 = \sum_{i=1}^{N_r} M_{1i}$$

$$= \sum_{i=1}^{N_r} \frac{\nu_i m_i n_i}{4\pi} \int_0^{\pi/2} \int_0^{2\pi} \int_0^r u(r \cos \varphi \cos \varphi \sin \varphi dr \exp \left( -\frac{r}{\lambda_i} \right)} dr d\varphi d\omega$$

The above formulation can be expanded to the second order as

$$M_1 = \sum_{i=1}^{N_r} M_{1i}$$

$$\approx \sum_{i=1}^{N_r} \frac{\nu_i m_i n_i}{4\pi} \int_0^{\pi/2} \int_0^{2\pi} \int_0^r \left[ u \left| w \right| + r \cos \varphi \frac{\partial u}{\partial z} \right]_{w} \cos \varphi \sin \varphi \exp \left( -\frac{r}{\lambda_i} \right)} dr d\varphi d\omega$$

Equation (4.15) can be calculated analytically as
Another type of molecules hit the upper wall before impinging, as shown in Figure 4.6. Because of the confinement of the upper wall, Type 2 molecules have momentum loss at the upper wall. The traveling distance of Type 2 molecules ranges from \( d/\cos \varphi \) to \( 2d/\cos \varphi \).

Consider the symmetric feature of specular reflection, the \( z \) coordinate of Type 2 molecules whose traveling distance is \( r \) is \( 2d - r \cdot \cos \varphi \). The effective momentum transported by Type 2 molecules is shown in Equation (4.17). Similar to the treatment of Type 1 molecules, Equation (4.17) can be expanded to the second order, as shown in Equation (4.18).

![Figure 4.6 The conceptual model of Type 2 molecules.](image)
\[ M_2 = (1 - \sigma) \sum_{i=1}^{N_i} x_i \frac{\bar{v}_i m_n}{4 \pi \lambda_i} \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{\phi_{\cos \phi}} u (2d - r \cos \phi) \cos \phi \sin \phi \exp \left( -\frac{r}{\lambda_i} \right) dr d\phi d\omega \quad (4.17) \]

\[ M_2 \approx (1 - \sigma) \sum_{i=1}^{N_i} x_i \frac{\bar{v}_i m_n}{4 \pi \lambda_i} \int_{0}^{2\pi} \int_{0}^{\phi_{\cos \phi}} \left[ u \left|_w + (2d - r \cos \phi) \left( \frac{\partial u}{\partial z} \right) \right|_w \right] \cos \phi \sin \phi \exp \left( -\frac{r}{\lambda_i} \right) dr d\phi d\omega \quad (4.18) \]

The above formulation can be evaluated analytically as follows

\[ M_2 = (1 - \sigma) \sum_{i=1}^{N_i} x_i \frac{\bar{v}_i m_n}{48 \lambda_i} \left( \frac{\partial^2 u}{\partial z^2} \right)_w \left\{ \begin{align*} &-11K_{N_i}^{-3} E_i (-K_{N_i}^{-1}) + \exp(-K_{N_i}^{-1}) \left[ -10K_{N_i}^{-3} + 11K_{N_i}^{-2} \right] \\ &+16K_{N_i}^{-3} E_i (-2K_{N_i}^{-1}) - \exp(-2K_{N_i}^{-1}) \left[ -8K_{N_i}^{-3} + 4K_{N_i}^{-2} \right] \\ &\quad \vdots \end{align*} \right\} \quad (4.19) \]

\[ \vdots + (1 - \sigma) \sum_{i=1}^{N_i} x_i \frac{\bar{v}_i m_n}{48 \lambda_i} \left( \frac{\partial u}{\partial z} \right)_w \left\{ \begin{align*} &-12K_{N_i}^{-2} E_i (-K_{N_i}^{-1}) + \exp(-K_{N_i}^{-1}) \left[ -12K_{N_i}^{-1} + 12 \right] \\ &+48K_{N_i}^{-2} E_i (-2K_{N_i}^{-1}) + \exp(-2K_{N_i}^{-1}) \left[ 24K_{N_i}^{-1} - 12 \right] \end{align*} \right\} \]

Considering the diffuse reflection on the lower wall and equaling the net (actual) momentum on the lower wall to the ‘ideal’ momentum shown in Equation (4.12).

\[ \sigma (M_1 + W_2) = \sum_{i=1}^{N_i} x_i \frac{\bar{v}_i m_n}{3} \lambda_i \left( \frac{\partial u}{\partial z} \right)_w \quad (4.20) \]

By reorganizing the above equation and considering \( \bar{v}_i \propto \left( \sqrt{m_i} \right)^{-1} \), the slippage boundary condition can be obtained as
Compared with Equation (4.12), the two coefficients $C_1$ and $C_2$ in our model are as follows

$$
C_1 = 2\sum_{i=1}^{N_c} x_i \sqrt{m_i} \lambda_i \left\{ \frac{2 - \sigma - \sigma (1 - \sigma) \exp(-2K_{Ni}^{-1}) \left[ 4K_{Ni}^{-3} + 2K_{Ni}^{-2} \right]}{1 + \sigma K_{Ni}^{-2} Ei(-K_{Ni}^{-1}) + \sigma \exp(-K_{Ni}^{-1}) \left[ K_{Ni}^{-1} - 1 \right]} \right\}
$$

$$
C_2 = 3\sigma \sum_{i=1}^{N_c} x_i \sqrt{m_i} \lambda_i \left\{ \frac{6 + (-8 + 11\sigma) K_{Ni}^{-4} Ei(-K_{Ni}^{-1}) + 16(1 - \sigma) K_{Ni}^{-4} Ei(-2K_{Ni}^{-1})}{1 + \sigma K_{Ni}^{-2} Ei(-K_{Ni}^{-1}) + \sigma \exp(-K_{Ni}^{-1}) \left[ K_{Ni}^{-1} - 1 \right]} \right\}
$$


\[
C_z = \frac{1}{12} \sum_{i=1}^{N_c} x_i \sqrt{m_i \lambda_i^2} \left\{ \sum_{j=1}^{N_c} x_j \sqrt{m_j \lambda_j^2} \right\} \frac{\left( 1+ \sigma K_{Ni}^{-1} Ei(-K_{Ni}^{-1}) + \sigma \exp(-K_{Ni}^{-1}) \right)^2}{\left( \sum_{j=1}^{N_c} x_j \lambda_j \right)^2}
\]

4.4 Validation of the slippage model

In this section, we validate our proposed model using data in the literature. We compare our model with the work of Bentz et al. (1999), Sharipov et al. (2004a), Hyakutake et al. (2005), and Yamaguchi et al. (2016). Bentz et al. measure the mass transfer of rarefied gas mixtures using spinning rotor gauge. Sharipov et al. calculate the mass transfer of several combinations of binary gas mixtures by solving the linearized Boltzmann equation. To quantify the interaction between different gas molecules, Sharipov et al. consider both hard sphere gas molecules and Lennard-Johns potential. The results of the two models are slightly different. Hyakutake et al. conduct combined molecular dynamics (MD) simulation with DSMC to simulate the transport of binary gas mixtures in micro-channels. Yamaguchi et al. conduct microtube flooding to measure the slippage coefficient of binary gas mixtures. The above work has been widely adopted as benchmarks in the study of the rarefied gas flow of multicomponent gases.

4.4.1 Single component case

We first use Li et al. (2011)’s and Shen et al. (2003)’s numerical results to as benchmark data to validate our results for the single-component case. Li et al. used the Lattice Boltzmann Method (LBM) with a combined bounce-back/specular-reflection boundary to simulate gas transport in microchannels. In both of the two referred studies, purely diffuse reflection on the
boundary is assumed (TMAC=1). In this paper, we compared the dimensionless flow rate $Q_D$ predicted by the slippage models. The dimensionless flow rate is defined as follows

$$Q_D = -\int_0^h \rho u dz \sqrt{2RT} / \left( h^2 \frac{\partial p}{\partial x} \right)$$  \hspace{1cm} (4.24)$$

For our proposed correlation, $Q_D$ can be explicitly expressed as

$$Q_D = \frac{\sqrt{\pi}}{12K_N} + \frac{\sqrt{\pi}}{2} C_1 + \sqrt{\pi} K_N C_2$$ \hspace{1cm} (4.25)$$

When reduced to single component cases, our kinetic model is independent of molecular type. However, Yamaguchi et al. (2016) and Bentz et al. (1999) ’s model are slightly impacted by the type of components. Regarding this, we compare the mass transfer rate predicted by the above two models with both Helium (He) and Argon (Ar). The comparison of mass transfer is shown in Figure 4.7, indicating that our proposed model matches numerical experimental results very well. Especially, when Knudsen number is above 0.5, our model yields more accurate results than the other four models. This is partly attributed to the second-order correction term in our correlation.

We also compare our results with Maurer et al. (2003)’s experimental data. The experiment is based on microchannel flooding using Helium with Knudsen number up to 0.8. The TMAC was determined as 0.91±0.03. The microchannel used for the flow rate measurement was shallow enough so that the flow channel can be viewed as two infinite long parallel plates. Maurer et al.’s experiment has been widely adopted as benchmark data for the validation of gas slippage models. In this work, we compare the flow rate enhancement factor predicted by our model with that predicted by Maurer et al.’s experiment. The flow rate enhancement factor can be calculated analytically by our model, as shown in the equation below.

$$S = 1 + 6C_1 K_N + 12C_2 K_N^2$$ \hspace{1cm} (4.26)$$
The comparison with Knudsen number up to 0.8 is shown in Figure 4.8, indicating that our model is with 90% accuracy.

Figure 4.7 Comparison between LBM results, DSMC results, physical experimental data and the proposed kinetic model for single component gas flow with TMAC being 1.

Figure 4.8 Comparison of flow rate enhancement factor between our model and Maurer et al.’s microchannel flooding experiment with TMAC being 0.91.
4.4.2 Multiple component cases

In this section, we validate our model for multiple component (binary gas mixtures) cases. We use the binary mixture of Helium-Argon (He-Ar) and Helium-Xenon (He-Xe). The collision diameter of Helium, Argon, and Xenon is 260 pm, 341 pm and 398 pm respectively (Yampolskii et al. 2006). Diffuse reflection (TMAC=1) is used for the validation. The comparison of the dimensionless flow rate for binary He-Ar gas mixture and binary He-Xe gas mixture with different mole fraction of He is shown in Figure 4.9 and Figure 4.10 respectively. (The work of Yamaguchi et al. (2016) and Bentz et al. (1999) only has data for He-Ar mixtures.)

As shown in Figure 4.9 and Figure 4.10, our model predicts the same trend with literature data. The average difference between our model with literature data is less than 10%. The Knudsen number used for this calculation is 0.4. When Knudsen number varies within the range from 0 to 1, the difference between our model with literature data varies from 0.9% (Kn <0.01) to 12% (Kn =0.18).

The maximum value of the mass transfer rate is at x_{He}=0.6~0.8. This is because heavier components have larger impact on the slippage than lighter components. It should be mentioned that in Hyakutake et al.’s work, TMAC is not 1. Instead, the TMAC (at T=300K) of Ar and Xe, is respectively, 0.89 and 0.95. In our work, we assume the TMAC of all components are the same. Such an assumption can be easily relaxed in the future work. Typically, smaller TMAC leads higher mass transfer rate. If we substitute the TMAC used in Hyakutake et al.’s work, the mass transfer rate predicted by our model will increase by less than 5%.

The above comparisons of single and multiple component cases validate the accuracy of our proposed model.
Figure 4.9 Comparison of the dimensionless flow rate for binary He-Ar gas mixture with varying mole fraction of He.

Figure 4.10 Comparison of the dimensionless flow rate for binary He-Xe gas mixture with varying mole fraction of He.
4.5 Results of multicomponent cases

In this section, we present the flow rate enhancement factor $S$ of binary and ternary gas mixtures predicted by our proposed correlation. The properties of gases used in this work are all from widely cited literature (Reid et al. 1976, 1977).

4.5.1 Slippage of air (a binary mixture of nitrogen-oxygen)

In this section, we present the impact of compositional distribution on the flow rate enhancement factor, shown in Equation (4.26), of binary mixtures of nitrogen and oxygen, which is a mimic of air. The summary of the concentration combinations is listed in Table 4.1. The pressure ranges from 0.4 bar to 10 bar. The width of the flow channel is 100 nm. The flow rate enhancement factor is shown in Figure 4.11 in the next page. As pressure increases, the flow rate enhancement factor decreases from above 20 to 1.

<table>
<thead>
<tr>
<th>Case</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1 (100 nm)</td>
<td>78%</td>
<td>22%</td>
</tr>
<tr>
<td>4-2 (100 nm)</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>4-3 (100 nm)</td>
<td>0%</td>
<td>100%</td>
</tr>
</tbody>
</table>

4.5.2 Slippage of a binary mixture of hydrogen-oxygen

In this section, we analyze the impact of compositional distribution on the flow rate enhancement factor of binary mixtures of hydrogen and oxygen. The study of hydrogen-oxygen mixtures is crucial to the determination of explosion limit in micro devices (Law 2006). We
compare the flow rate enhancement factor of the binary mixture with that of pure components. The summary of the concentration combinations is listed in Table 4.2.

The flow rate enhancement factors of the three cases are shown in Figure 4.12, according to which gases with smaller molecular weight have higher slippage effect. On the other hand, in a mixture, the slippage effect prone to the component with higher molecular weight.

<table>
<thead>
<tr>
<th>Case</th>
<th>Hydrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-4 (100 nm)</td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>4-5 (100 nm)</td>
<td>100%</td>
<td>0%</td>
</tr>
<tr>
<td>4-6 (100 nm)</td>
<td>0%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Figure 4.11 Comparison of the dimensionless flow rate for binary He-Xe gas mixture with varying mole fraction of He.
4.5.3 Ternary mixtures of light hydrocarbon

In this section, we discuss the impact of compositional distribution on the ternary mixture of light hydrocarbons. For hydrocarbons in unconventional gas reservoirs, the flow rate enhancement factor is also known as the permeability enhancement factor. In this work, we calculate the permeability enhancement factor of a ternary mixture of methane (C1), ethane (C2) and propane (C3). The summary of the compositional combinations is listed in Table 4.3. The permeability enhancement factor with respect to pressure for the 25 nm wide channel and the 15 nm wide channel is shown in Figure 4.13 and Figure 4.14, respectively. According to the two figures, when pressure is above 2000 psi, the permeability enhancement factor is below 2. This indicates that Klinkenberg effect is more important in the near-well region of a reservoir and also in the late-production regime during production. As can be seen from the results, our proposed correlation is able to capture the compositional impact for ternary gas mixtures. Moreover, there

![Slippage Phenomena in H₂ - O₂ Binary Mixtures](image)
should be not much difficulty for our correlation to predict the permeability enhancement effect of more complex gas mixtures consisting of light components.

Table 4.3 Summary of concentration combinations of ternary mixture cases

<table>
<thead>
<tr>
<th>Case</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-7 (25 nm)</td>
<td>10%</td>
<td>20%</td>
<td>70%</td>
</tr>
<tr>
<td>4-8 (25 nm)</td>
<td>33.3%</td>
<td>33.3%</td>
<td>33.3%</td>
</tr>
<tr>
<td>4-9 (25 nm)</td>
<td>70%</td>
<td>20%</td>
<td>10%</td>
</tr>
<tr>
<td>Case 10 (15 nm)</td>
<td>10%</td>
<td>20%</td>
<td>70%</td>
</tr>
<tr>
<td>Case 11 (15 nm)</td>
<td>33.3%</td>
<td>33.3%</td>
<td>33.3%</td>
</tr>
<tr>
<td>Case 12 (15 nm)</td>
<td>70%</td>
<td>20%</td>
<td>10%</td>
</tr>
</tbody>
</table>

Figure 4.13 Permeability enhancement factor for different composition distribution of methane-ethane-propane mixtures within 25 nm channel with respect to pressure. Both of the two axes are in log scale.
4.6 Discussions

As can be seen from the validation and results, our model can accurately capture the multicomponent slippage effect with finite Knudsen numbers up to 1. For higher Knudsen numbers, our model may show larger errors because the gas-wall interaction becomes more complex. In higher Knudsen number conditions (transient regime), the molecules collide with the wall more frequently, and the behavior of the gases can no more be described by viscosity-shear force relationship. For that condition, more ‘discrete’ models need to be adopted. Moreover, we now consider two types of molecules. As Knudsen number becomes larger, more molecules will hit the wall more than once before impinging into the point of interest. Hence the contribution of these currently-ignored molecules will become larger, especially when TMAC is not 1.

Admittedly, our model has several limitations. First, it can only be used to low-speed gas flow, because it assumes near-steady conditions in its derivation. Secondly, it should only be
applied to light gas components in near-ideal (low pressure) conditions, since it is based on the assumption of hard-sphere gas collisions among different gas specifies. For high-pressure condition, as pointed on by Long et al. (2012), the confinement effect cannot be ignored, and our model cannot handle this condition. For heavier components, the molecular-molecular interaction becomes more complex, and the hard-sphere collision assumption is no longer validate. Lennard-Jones potential should be taken into consideration (Bird 1976). Thirdly, it does not take account for the surface force impact (Barisik and Beskok 2014), surface shape impact (Dinler et al. 2013) and dense gas effect (Wu et al. 2016). The model can be further improved by considering the variation of gas density near the boundary. Without the incorporation of multiphase slippage effect (Wu et al. 2017a; Zerpa et al. 2017), The applications of the model should be limited to single-phase flow for the time being.

In practice, our model could either be combined with digital rock techniques (Yang et al. 2015) for small-scale simulation or be directly used as a gas apparent permeability correlation in reservoir scale simulation. In the former case, our model provides the boundary condition for the governing equations (Navier-Stokes equation, Burnett equation, etc.). In the latter case, our model serves as a Klinkenberg-type correlation, as shown in Equation (4.26), for the calculation of gas apparent permeability. Since the model is non-empirical, it only requires the effective rock diameter, TMAC and gas component concentration as the input parameters, making it convenient for applications.

4.7 ‘Real’ velocity on the boundary

In the previous sub-chapter, we have presented an ‘equivalent’ slippage model. This model assumes that the velocity profile within the flow channel is parabolic. Based on the results
of the validation, the equivalent model is accurate enough for engineering applications. However, in the real situation, the velocity profile within the flow channel may not be parabolic. In the forthcoming chapters, we will discuss a more accurate model, which directly calculates the velocity profile, without pre-assuming the shape of it. We first start with the velocity boundary on the wall. Without the loss of generality, we only consider single component cases in this chapter.

The velocity on the boundary $U_W$ is calculated by calculating the total flux velocity carried by the molecules that impinge into the boundary and the total number of impinging molecules, as follows.

$$U_W = \frac{(V_M + W_M) + (1 - \sigma)(V_M + W_M)}{(N_M + N_W) + (N_M + N_W)}$$

(4.27)

In the above equation, $V_M$ is the total velocity carried by all impinging molecules after one time of molecular collision, while $W_M$ is the total velocity carried by all impinging molecules after one time of wall collision. $N_M$ is the total number of molecules that impinges into the boundary molecules after one molecular collision, while $N_W$ is the number of molecules that impinges into the boundary after one wall collision. Therefore, $U_W$ is calculated by directly averaging the velocity on the boundary, without assuming the shape of the velocity profile.

Similar to the previous chapters, the velocity, and molecular quantity can be calculated as

$$V_M = \sum_{i=1}^{N_c} \frac{N_i}{4\pi} \int_{0}^{\pi/2} \int_{0}^{\sin \phi} u(r \cos \phi) \cos \phi \sin \phi dr d\phi d\omega$$

(4.28)

$$W_W = (1 - \sigma) \sum_{i=1}^{N_c} \frac{N_i}{4\pi \lambda_i} \int_{0}^{\pi/2} \int_{0}^{2\sin \phi} u(2d - r \cos \phi) \cos \phi \sin \phi \exp \left( -\frac{r}{\lambda_i} \right) dr d\phi d\omega$$

(4.29)

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Equation (4.28) to (4.31) can be also expanded to the second order. Therefore, \( U_w \) can be expressed as

\[
U_w = \sum_{j=1}^{N_c} x_j \lambda_j \left\{ \begin{array}{l}
2 - \sigma - \sigma (1 - \sigma) \exp(-2K_{Ni}^{-1}) \left[ 4K_{Ni}^{-3} + 2K_{Ni}^{-2} + \frac{2}{\cos \phi} \right] \\
+ \sigma (1 - 2\sigma) K_{Ni}^{-3} Ei(-K_{Ni}^{-1}) \\
+ \sigma \exp(-K_{Ni}^{-1}) \left[ (1 - 2\sigma) K_{Ni}^{-2} - (1 - 2\sigma) K_{Ni}^{-1} \right] \\
+ (2 - \sigma) \left( \sum_{j=1}^{N_c} x_j \lambda_j \right)
\end{array} \right.
\]

\[
3\sigma \sum_{i=1}^{N_c} x_i \lambda_i \left\{ \begin{array}{l}
[1 + \sigma K_{Ni}^{-2} Ei(-K_{Ni}^{-1}) + \sigma \exp(-K_{Ni}^{-1}) K_{Ni}^{-1}] + 16(1 - \sigma) K_{Ni}^{-4} Ei(-2K_{Ni}^{-1}) \\
+ 6 + (-8 + 11\sigma) K_{Ni}^{-2} Ei(-K_{Ni}^{-1}) \\
- (1 - \sigma) \exp(-2K_{Ni}^{-1}) \left[ -8K_{Ni}^{-3} + 4K_{Ni}^{-2} - 4K_{Ni}^{-1} + 6 \right] \\
+ \exp(-K_{Ni}^{-1}) \left[ (-8 + 11\sigma) K_{Ni}^{-3} + (8 - 11\sigma) K_{Ni}^{-2} \right] \\
+ (16 + 10\sigma) K_{Ni}^{-4} - 6\sigma
\end{array} \right. \left\{ \begin{array}{l}
\sum_{j=1}^{N_c} x_j \lambda_j \\
\lambda_{jm} \left( \frac{\partial^2 u}{\partial z^2} \right)_w
\end{array} \right. \right.
\]

\[
12 \sum_{i=1}^{N_c} x_i \left\{ \begin{array}{l}
[1 + \sigma K_{Ni}^{-2} Ei(-K_{Ni}^{-1}) + \sigma \exp(-K_{Ni}^{-1}) K_{Ni}^{-1}] + 12(1 - \sigma) K_{Ni}^{-4} Ei(-2K_{Ni}^{-1}) \\
+ (1 - \sigma) \exp(-2K_{Ni}^{-1}) \left[ 2K_{Ni}^{-1} - 1 \right]
\end{array} \right. \left\{ \begin{array}{l}
\sum_{j=1}^{N_c} x_j \lambda_j \\
\lambda_{jm} \left( \frac{\partial^2 u}{\partial z^2} \right)_w
\end{array} \right. \right.
\]

\[
4.8 \text{ Velocity profile inside the Knudsen layer}
\]

In this section, we present a kinetic model to capture the velocity profile inside the Knudsen layer. Our approach is similar to that used in Chapter 4.3. In literature, there are mainly
three types of existing velocity profiles models, namely the wall-function model (Lockerby et al. 2005b; O’Hare et al. 2007), the higher-order continuum model (Lockerby et al. 2005a) and the power-law model (Aidun and Clausen 2010). The wall-function model is an empirical model of the following form (Cercignani 2000)

\[
 u(z) = k_u \left[ z + 1.146\lambda - \lambda I \left( \frac{z}{\lambda} \right) \right]
\]  

(4.33)

In the above formulation, \( k_u \) is the velocity gradient of the bulk flow. \( z \) is the position inside the micro-channel and \( I \) is a function of \( z/\lambda \), which is the ‘dimensionless’ distance away from the wall. The higher-order continuum model is derived from fluid mechanics governing equations, such as the Burnett and the super-Burnett equations. Such equations are of higher order accuracy compared to Navier-Stokes equation. The power-law model is another type of empirical model, according to which the velocity inside the Knudsen’s layer is a power function of the distance from the wall, as

\[
 u(z) = U_w + \xi \cdot z^{\alpha_p}
\]  

(4.34)

Where \( U_w \) is the boundary velocity, \( \xi \) and \( \alpha_p \) are empirical parameters obtained by fitting data from Direct Simulation Monte Carlo method (DSMC) or Lattice Boltzmann Method (LBM).

The power-law model itself cannot calculate the velocity on the boundary and the term \( U_w \) in Equation (4.34) has to be obtained by certain boundary velocity models.

Based on the above discussion, the three existing models are mostly empirical models and can only handle flow with low Knudsen number. Besides, the existing models are not unified models, meaning that they can only capture the velocity profile inside the Knudsen layer, but not on the boundary (wall). To be applied, they have to be combined with the flow velocity boundary
models. In this work, we bring out a novel kinetic model to fully capture the flow velocity both inside the Knudsen layer as well as on the boundary.

For an imaginary plane as shown by the dotted line in Figure 4.15, we calculated the total momentum carried by molecules impinging into an arbitrary point A on the plane. We assume that there are four types of molecules hit the imaginary plane, as shown in Figure 4.15. Type 1 molecules, denoted by circle number 1 in Figure 4.15, impinge into the plane from above after a molecular collision only and without any wall collision. The coordinate of Type 2 molecules is shown in Figure 4.16.

Figure 4.15 Conceptual model of the momentum difference at an imaginary plane in the micro-channel.

Figure 4.16 Coordinates of Type 1 molecules.
The momentum carried by these molecules is

\[ M'_{wp} = \frac{\bar{v}mn}{4\pi\lambda} \int_0^2 \int_0^{\pi/2} \int_0^{l_i} u(z + r \cos \varphi) \cos \varphi \sin \varphi \exp \left(-r / \lambda\right) dr d\varphi d\omega \quad (4.35) \]

where the upper limit of the distance is

\[ l_i = \frac{d - z}{\cos \varphi} \quad (4.36) \]

The momentum can be expanded to the second order with respect to the flux velocity as

\[ M'_{wp} \approx \frac{\bar{v}mn}{4\pi\lambda} \int_0^2 \int_0^{\pi/2} \int_0^{l_i} \left[ u(z) + r \cos \varphi \frac{du}{dz} (z) \right] \cos \varphi \sin \varphi \exp \left(-r / \lambda\right) dr d\varphi d\omega \quad (4.37) \]

Type 2, denoted by circle number 2 in Figure 4.15, impinge into the plane after hitting the upper wall of the micro-channel. During the collision, the portion of momentum loss is \( \sigma \), due to the diffuse reflection. Therefore, \((1-\sigma)\) of the total Type 2 molecules keep their original flux velocity as well as the flux momentum. The coordinate of Type 2 molecules is shown in Figure 4.17. The momentum carried by these molecules is

\[ W'_{wp} = (1-\sigma) \frac{\bar{v}mn}{4\pi\lambda} \int_0^2 \int_0^{\pi/2} \int_0^{l_i} u(2d - r \cos \varphi - 2z) \cos \varphi \sin \varphi \exp \left(-r / \lambda\right) dr d\varphi d\omega \quad (4.38) \]

In which

\[ l_z = \frac{2d - z}{\cos \varphi} \quad (4.39) \]

The momentum can be expanded to the second order with respect to the flux velocity as

\[ W'_{wp} \approx (1-\sigma) \frac{\bar{v}mn}{4\pi\lambda} \int_0^2 \int_0^{\pi/2} \int_0^{l_i} \left[ u(z) + (2d - r \cos \varphi - 2z) \frac{du}{dz} (z) \right] \cos \varphi \sin \varphi \exp \left(-r / \lambda\right) dr d\varphi d\omega \quad (4.40) \]
Similarly, Type 3 and Type 4 are molecules impinge from below after molecular collision and wall collision respectively. The momentum carried by them is shown as follows.

\[
M'_{\text{down}} = \frac{\bar{v}m}{4\pi \lambda} \int \int \int u(z - r \cos \varphi) \cos \varphi \sin \varphi \exp\left(-\frac{r}{\lambda}\right) dr d\varphi d\omega
\]  
(4.41)

\[
W'_{\text{down}} = (1 - \sigma) \frac{\bar{v}m}{4\pi \lambda} \int \int \int u(r \cos \varphi - z) \cos \varphi \sin \varphi \exp\left(-\frac{r}{\lambda}\right) dr d\varphi d\omega
\]  
(4.42)

Where

\[
l_3 = \frac{z}{\cos \varphi}
\]  
(4.43)

\[
l_4 = \frac{d + z}{\cos \varphi}
\]  
(4.44)

The above momentum can be expanded as follows

\[
M'_{\text{down}} \approx \frac{\bar{v}m}{4\pi \lambda} \int \int \int \left[ u(z) - r \cos \varphi \frac{du}{dz}(z) \right] \cos \varphi \sin \varphi \exp\left(-\frac{r}{\lambda}\right) dr d\varphi d\omega
\]

\[
+ \frac{1}{2} r^2 \cos^2 \varphi \frac{d^2 u}{dz^2}(z) \]  
(4.45)
\[
W_{\text{down}} \approx (1-\sigma) \frac{\tilde{v}_{mn}}{4\pi \lambda} \int_0^{\pi/2} \int_0^1 \left[ u(z) + \left( r \cos \phi - 2z \right) \frac{du}{dz}(z) \right] \cos \phi \sin \phi \exp \left( -r / \lambda \right) dr \phi d\omega \quad (4.46)
\]

Then the horizontal shear stress on the imaginary plane is just the net momentum across the plane along the vertical direction.

\[
T = W'_{\text{up}} + M'_{\text{up}} - W'_{\text{down}} - M'_{\text{down}} \quad (4.47)
\]

The shear stress should be balanced with the pressure gradient in order to maintain laminar flow. Therefore, the stress balance equation along the imaginary plane is as follows

\[
\frac{dT}{dz} = \frac{dP}{dL} \quad (4.48)
\]

The above equation is the ‘governing’ equation for calculation of the velocity profile. For extremely small Knudsen number, \(d\) is much larger compared to the mean free path. Therefore the model can be reduced to

\[
M'_{\text{up}} - M'_{\text{down}} + W'_{\text{up}} - W'_{\text{down}} = \frac{\tilde{v}_{mn}}{48} \frac{\lambda}{d} \frac{du}{dz} \{16\} = \frac{\tilde{v}_{mn}}{3} \frac{\lambda}{d} \frac{du}{dz} \quad (4.49)
\]

which is just the normal expression of the viscous force (shear stress).

### 4.9 ‘Real’ velocity profile

In this section, we combine Chapter 4.7 and Chapter 4.8 and present the numerical results, including the velocity profile as well as the permeability enhancement factor. The pressure is 4000 Pa, the diameter of the microchannel is 200 nm. The temperature is set at 373K. Therefore, the Knudsen number of this case is 0.84. The length of the channel is 0.1m, which is much larger than the width (diameter) of it. We change the pressure ratio from 1.1 to 1.5 and
solve the equations using the finite difference method to get the velocity profile. The pressure ratio $\Pi$ is defined as

$$\Pi = \frac{P_{\text{inlet}}}{P_{\text{outlet}}} \quad (4.50)$$

Where $P_{\text{inlet}}$ and $P_{\text{outlet}}$ is the pressure at the inlet and the outlet respectively.

The velocity profiles with respect to different pressure ratios are shown in Figure 4.18.

The comparison between the velocity profile obtained from our model with that obtained from non-slippage boundary condition is shown in Figure 4.19. According to Figure 4.19, with the slippage taken into consideration, both the magnitude of the flux velocity and the velocity profile have been significantly changed.

Figure 4.18 Velocity profile at $K_N = 0.84$ with respect to different pressure ratios.
4.10 Effects of pressure ratio and pressure gradient

In this section, we analyze the effects of the pressure gradient. It is common belief that the permeability enhancement factor is the only function of pressure (Knudsen number). In this work, we show that the pressure gradient can also affect the permeability enhancement. We conduct four cases for comparison, the parameters of which are shown in Table 4.4. The pressure of Case 4-13 and Case 4-14 are both 4000 Pa, while the length of the tube in Case 4-14 is 5 times that in Case 4-13. Therefore, Case 4-13 and Case 4-14 have the same Knudsen number but different values of the pressure gradient. Compare to the first pair of cases, Case 4-15 and Case 4-16 are with higher pressure and thus, lower Knudsen number. Similar to the first pair, the pressure gradient of Case 4-16 is 20% of that of Case 4-15.

The detailed parameters and results of Case 4-13 and Case 4-14 are shown in Table 4.5 and Table 4.6, respectively. The comparison between their permeability enhancement factors
with respect to the pressure ratio is shown in Figure 4.20. According to the comparison, when the pressure ratio increases from 1.1 to 1.5, the permeability enhancement factor of Case 4-13 (higher pressure gradient case) increases by 54% from 5.84 to 8.97, while that of Case 4-14 increases only 5% from 5.72 to 6.00.

The results of the second pair of cases are shown in Table 4.7 and Table 4.8. The comparison of the permeability enhancement factor is shown in Figure 4.21, according to which in these two cases with lower Knudsen number, the permeability enhancement effect is not sensitive to the pressure gradient. By comparing the four cases, we can draw two conclusions. Firstly, the permeability enhancement factor (Klinkenberg factor) is not only the function of pressure, but also the function of the pressure gradient, as

$$K_a = S \left( P, \frac{\partial P}{\partial x} \right) \cdot K_e$$

(4.51)

Secondly, the impact of pressure gradient depends on the Knudsen number range. When Knudsen number is higher, the permeability enhancement factor tends to increase significantly as pressure gradient grows. When Knudsen number is relatively lower, the enhancement factor is not sensitive to the pressure gradient.

<table>
<thead>
<tr>
<th>Case Index</th>
<th>Average Pressure (Pa)</th>
<th>Tube Length (m)</th>
<th>Knudsen Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-13</td>
<td>4000</td>
<td>0.1</td>
<td>0.84</td>
</tr>
<tr>
<td>4-14</td>
<td>4000</td>
<td>0.5</td>
<td>0.84</td>
</tr>
<tr>
<td>4-15</td>
<td>8000</td>
<td>0.1</td>
<td>0.42</td>
</tr>
<tr>
<td>4-16</td>
<td>8000</td>
<td>0.5</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Table 4.5 Parameters and results of Case 4-13

<table>
<thead>
<tr>
<th>Inlet pressure (Pa)</th>
<th>Outlet pressure (Pa)</th>
<th>Pressure gradient (Pa/m)</th>
<th>Pressure ratio</th>
<th>Enhancement factor</th>
</tr>
</thead>
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<tr>
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<td>3860</td>
<td>1.1</td>
<td>5.84</td>
</tr>
<tr>
<td>4421</td>
<td>3684</td>
<td>7369</td>
<td>1.2</td>
<td>7.73</td>
</tr>
<tr>
<td>4581</td>
<td>3524</td>
<td>10573</td>
<td>1.3</td>
<td>8.43</td>
</tr>
<tr>
<td>4728</td>
<td>3377</td>
<td>13510</td>
<td>1.4</td>
<td>8.77</td>
</tr>
<tr>
<td>4863</td>
<td>3242</td>
<td>16212</td>
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</tr>
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</table>

Table 4.6 Parameters and results of Case 4-14

<table>
<thead>
<tr>
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<th>Outlet pressure (Pa)</th>
<th>Pressure gradient (Pa/m)</th>
<th>Pressure ratio</th>
<th>Enhancement factor</th>
</tr>
</thead>
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Table 4.7 Parameters and results of Case 4-15

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<th>Pressure ratio</th>
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<tr>
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<td>2.886</td>
</tr>
</tbody>
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Table 4.8 Parameters and results of Case 4-16

<table>
<thead>
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<th>Outlet pressure (Pa)</th>
<th>Pressure gradient (Pa/m)</th>
<th>Pressure Ratio</th>
<th>Enhancement Factor</th>
</tr>
</thead>
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</tr>
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<td>1.4</td>
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</tr>
<tr>
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<td>3242</td>
<td>16212</td>
<td>1.5</td>
<td>2.893</td>
</tr>
</tbody>
</table>

Figure 4.20 Comparison of the permeability enhancement factor between Case 1 (red line) and Case 2 (blue line).

Figure 4.21 Comparison of the permeability enhancement factor between Case 4-15 (red line) and Case 4-16 (blue line).
5.1 Solution of governing equations

In MSFLOW_CO2, all the governing equations described in the previous chapter are solved by the integrated finite difference (IFD) method (Narasimhan and Witherspoon 1976). Similar to the finite volume method, the integrated finite difference method divides the computational domain into numerous grid blocks. After being integrated over grid blocks, the governing equations are converted to accumulation terms on each grid blocks and flux terms on each pair of neighboring grid blocks using the Gaussian divergence theorem. The details of the IFD method used in MSFLOW_CO2 are as follows.

Firstly, the governing equations can be expressed as the following general conservation form

\[
\frac{\partial M^k}{\partial t} = \nabla \cdot \vec{F}^k + q^k
\]  

(5.1)

where \( k \) is the component index. \( M \) is the accumulation term, which is the quantity per unit volume. \( \vec{F} \) is the flux term, which is the flux per unit area. \( q \) is source/sink term and \( t \) is the time variable. Integrating the above equation over the volume of the \( n \)th grid block \( V_n \) yields

\[
\frac{\partial}{\partial t} \int_{V_n} M^k dV = \int_{\Gamma_n} \vec{F}^k \cdot \hat{n} d\Gamma + \int_{V_n} q^k dV
\]  

(5.2)

In the above equation, \( \hat{n} \) is the normal vector and \( \Gamma \) is the area. The accumulation term can be then expressed as

\[
\int_{V_n} M^k dV = M^k_{n} V_n
\]  

(5.3)
In the above equation, $M^k_n$ is the discrete accumulation term of component $k$ on grid block $n$.

Meanwhile, the flux term can be express as

$$\int_{\Gamma_n} \vec{F}^k \cdot \vec{n} \, d\Gamma = \sum_m A_{nm} \vec{F}^k_{nm}$$

(5.4)

where $m$ loops through all the neighboring grid blocks of grid block $n$. $A_{nm}$ and $\vec{F}^k_{nm}$ is the area and flux term of component $k$ between grid block $m$ and grid block $n$, respectively. The time derivative is approximated by the first-order finite difference scheme. Therefore, Equation (5.2) becomes

$$\left[ M^k_n \right]^{l+1} - \left[ M^k_n \right]^l = -\frac{\Delta t}{\rho} \sum_m A_{nm} F^k_{nm} + V_n q_n$$

(5.5)

where $\Delta t$ is the time step length and $l$ is time level. MSFLOW_CO2 is fully implicit, which guarantees the best stability of the computation. In calculating the flux terms between two neighboring grid blocks, MSFLOW_CO2 adopts the harmonic weighting technique for the rock-related properties and the upwind weighting technique for the phase (fluid)-related properties.

By rearranging the terms, Equation (5.5) can be expressed in the residual vector form as

$$R(x^{l+1}) = 0$$

(5.6)

where $R$ is the residual vector form and $x^{l+1}$ is the primary variable vector at time level $l+1$. The above equation is a nonlinear equation and is solved iteratively by the Newton-Raphson method. A conceptual model of the IFD method is shown in Figure 5.1.

The Newton-Raphson method has been widely used in solving the nonlinear equations arising in scientific computing. The basic idea of the Newton-Raphson method is to use the gradient of the equation to calculate the searching direction of the iteration. The gradient of a
vector equation is expressed by the Jacobian matrix. The formulation of the Newton-Raphson method is as shown in Equation (5.7).

\[ \mathbf{J} \cdot \Delta \mathbf{x} = - \mathbf{R}(\mathbf{x}) \]  

(5.7)

In the above equation, \( \mathbf{J} \) is the Jacobian matrix and \( \Delta \mathbf{x} \) is the update the primary variable of each iteration. The Jacobian matrix of a vector equation with \( N \) unknowns is defined as follows

\[
\mathbf{J} = \begin{bmatrix}
\frac{\partial R_1}{\partial x_1} & \cdots & \frac{\partial R_1}{\partial x_N} \\
\vdots & \ddots & \vdots \\
\frac{\partial R_N}{\partial x_1} & \cdots & \frac{\partial R_N}{\partial x_N}
\end{bmatrix}
\]  

(5.8)

In MSFLOW_CO2, the partial derivatives are calculated by the numerical derivative.

Until convergence, the above equation is iteratively constructed. Within each nonlinear iteration, the above equation is linearized and is solved by a multiscale linear solver (Hajibeygi and Jenny 2009). More details of the Newton-Raphson method used in MSFLOW_CO2 can be found in (Wang et al. 2016).
5.2 **Solution of the linear system**

In this section, we present the algorithm of the linear solver for the solution of the linear system that is resulted from the IFD discretization.

5.2.1 **Introduction of multiscale linear solver**

The most time-consuming part for obtaining a solution of subsurface flow problems relates to the solution of elliptic/parabolic pressure equation. In recent decades considerable research has undergone in the domain of two-level multiscale solvers (MS) (Hou and Wu 1997) as an alternative to AMG or SA-AMG solvers for the pressure system, which is of ‘global’ impact compared to the saturation system.

Traditionally, the multiscale methods have split into three main groups: multiscale finite element methods (MsFE) (Hou and Wu 1997), (Hughes et al. 1998), multiscale mixed finite elements (MsMFE) (Aarnes 2004; Aarnes et al. 2005); Chen and Hou 2002) and multiscale finite volume (MsFV) (Jenny et al. 2003, 2005, 2006; Lunati and Jenny 2006), methods. The aforementioned methods all use numerically computed basis functions that capture local flow characteristics by solving local flow problems that restrict the fine grid onto the coarse grid. Then, after solving the coarse problem, the bases can again be used to prolongate back onto the fine grid. MsMFE, MsFE and MsFV all have received varying amounts of attention over the years (Hajibeygi and Jenny 2009; Hajibeygi and Tchelepi 2014; Lunati and Jenny 2006, 2008) for example: fractured media (Bosma et al. 2017; Hajibeygi et al. 2011; Shah et al. 2016; Ṭene et al. 2016) and unstructured grids (Cortinovis and Jenny 2017; Hajibeygi et al. 2008; Hajibeygi and Jenny 2011; Kippe et al. 2008; Møyner and Lie 2014). Additionally, the MsFV method has been used in a fully implicit solver (Cusini et al. 2014; Cusini et al. 2015), later being extended.
to incorporate an adaptive grid (Cusini et al. 2016). In addition, MsFV was formulated in the algebraic form (AMS) (Ţene et al. 2016; Tene et al. 2014; Wang et al. 2014).

The multiscale methods can be described by local and global stages. The global stage corresponds to the sequence of aggressive restriction, coarse-grid correction, and prolongation operators which effectively handles low-frequency modes on the coarse grid. The local stage or smoother resolves high-frequency modes. The local and global stages lead to direct comparisons between multiscale, multigrid, and deflation strategies (Lukyanov and Vuik 2016). More recently the multiscale restriction smoothed basis method (MsRSB) was developed (Møyner and Lie 2016; Shah et al. 2016), which, unlike traditional MsFV methods can be used effectively on unstructured and stratigraphic grids. This method is also formulated algebraically and constructs its coarse grid using ideas from deflation and SA-AMG, while using a traditional smoother such as Gauss-Seidel or ILU(0) (Wang et al. 2019b).

The iterative methods are the good candidates to solve SLAEs with matrices of general form. The multigrid methods (Trottenberg et al. 2001) or Krylov subspace methods (e.g., BiCGStab (van der Vorst 1992), GMRES (Saad and Schultz 1986)) with multigrid (e.g., AMG) preconditioners are popular to solve the systems with elliptic matrices. The advantages of these methods are related to their robustness and excellent scalability potential (Baker et al. 2011). In this paper, we provide a mathematical formulation of Algebraic Smoothing Aggregation Multiscale (ASAM) preconditioned GMRES iterative techniques for solving a system of linear algebraic equations (SLAEs).

5.2.2 Algorithm of the multiscale solver

We rewrite the linear system in Equation (5.7) as
\[ Ay = b \]  

(5.9)

in which \( A \) is a \( N \times N \) sparse block matrix resulted from the discretization of governing partial differential equations in reservoir simulation. \( y \) is the \( N \times 1 \) primary variable vector (unknown vector) and \( b \) is the \( N \times 1 \) residual vector. We use multiscale linear solver to solve Equation (5.9). The algorithm of the linear solver is as follows.

Step 1, divide the computational domain \( \Omega \) into \( M \) subdomains \( \overline{\Omega}_1, \ldots, \overline{\Omega}_M \). We can try to use the method and divide the variable space into subspaces which we can use to construct our basis functions. So we do not have to define our reservoirs in the subdomains.

Step 2, define the \( N \times M \) restrictor matrix \( Z^0 \) as

\[
Z^0 = \begin{bmatrix} Z^0 \end{bmatrix}_{N \times M} = \begin{bmatrix} Z^0_1 & \cdots & Z^0_M \end{bmatrix}
\]  

(5.10)

In which \( Z^0_i \) is a \( N \times 1 \) vector as

\[
(Z^0_i)_j = \begin{cases} 1 & j \in \Omega_i \\ 0 & j \notin \Omega_i \end{cases}, \quad j = 1, \ldots, N
\]  

(5.11)

Step 3, from \( k=1 \), iteratively calculate \( Z^k_i \) as shown in Equation (5.11) until \( k \) is large enough (e.g., \( k=5:10 \)). This process creates the basis vector \( Z^k_i \)

\[
Z^k_i = \left( I - \omega M^{-1} A \right) Z^{k-1}_i
\]  

(5.12)

where \( \omega \) is the relation parameter and

\[
M_i = \text{diag} \left( A \right)
\]  

(5.13)

We may also need to do the localization step using any partition of unity (PU) functions \( \{ \phi_i \} \) with \( \Omega_i = \text{supp}(\phi_i) \) at any level \( k \) as follows

\[
\tilde{Z}^k_i = \phi_i Z^k_i
\]  

(5.14)
where functions $\varphi_i$ play the role of “glue” and $\hat{Z}_i^k$ are the final basis functions. Therefore, we can obtain the $N \times M$ restrictor matrix $Z$ as

$$Z = [Z]_{N \times M} = [Z_1, \ldots, Z_M]$$

(5.15)

Step 4, define the $M \times M$ coarse scale coefficient matrix $A_c$ as

$$A_c = Z^T A Z = \begin{bmatrix} \hat{Z}_i^k \\ \vdots \\ \hat{Z}_M^k \end{bmatrix} A \begin{bmatrix} \hat{Z}_i^k \\ \vdots \\ \hat{Z}_M^k \end{bmatrix}$$

(5.16)

Step 5, in this step, the original fine-scale problem is solved in the coarse scale to eliminate the low-frequency terms, as

$$X^* = Z \cdot \begin{bmatrix} A_c^{-1} \cdot Z^T \cdot b \end{bmatrix}$$

(5.17)

where the $N \times 1$ vector $X^*$ is the initial guess of the smoothing step in Step 6. The inverse of $A_c$ can be calculated by preconditioned GMRES method.

Step 6, in this step, the unknown vector is iteratively updated by a smoothing matrix $M_2$ until converged. The iterative computation is shown in Equation (5.18) to (5.20). It should be noticed that, in this step, ILU(0) preconditioner is used to precondition the updated system.

$$y^0 = X^*$$

(5.18)

Until converged, iterate as

$$y^k = y^{k-1} + M_2^{-1} \left( A y^{k-1} - b \right)$$

(5.19)

Where $M_2$ is the smoother, as

$$M_2 = ILU(0)[A]$$

(5.20)
In general, this approach is essentially a two-stage multiscale approach. It is fully algebraic, which enables it to handle complex fields with unstructured grids.

5.3 Data structure and simulator framework

Within a simulation run, MSFLOW_CO2 first reads in input data and conduct initialization of the simulation. Then for each grid block, MSFLOW_CO2 conducts flash calculation to obtain fluid properties. Using the calculated the fluid properties, MSFLOW_CO2 computes the accumulation term for each grid block and the flux term of each two neighboring grid blocks (connections). Then MSFLOW_CO2 shifts the primary variables and repeats the process of the calculation of the accumulation terms and flux terms using the shifted primary variables. Based on the shifted and unshifted accumulation terms and flux terms, MSFLOW_CO2 constructs the Jacobian matrix and the residual vector. MSFLOW_CO2 constructs the Jacobian matrix in a way that is similar to that of MSFLOW, a multiphase simulator (Wu 1998). In MSFLOW_CO2, for each element, all of its neighbors are looped and the derivatives are calculated. Therefore, the Jacobian is built in the order of columns and the memory of the ‘shifted’ primary and secondary variables is released immediately after the variables are used, so that the memory can be significantly saved.

The Jacobian matrix as well as the residual vector are sent to the linear solver to get the solution of linear system, which is for updating the primary variable in the Newton-Raphson method. When the Newton-Raphson method is converged according to a preset convergence criterion, the time step is moving forward.
MSFLOW_CO2 uses all ‘nature’ variables as the primary variable. The primary and secondary variables of MSFLOW_CO2 are listed in Figure 5.1.

To store the parameters for the multiphysical simulation, MSFLOW_CO2 adopts an extensible data structure. The data used for the thermal (T), hydraulic (H) and mechanical (M) simulation is classified as element-based data (data used for each grid block) and connection-based data (data used between two neighboring grid blocks). All the data is grouped into according modules and all modules are connected by pointers. Therefore, the source code of the simulator can be relatively easily maintained, compared to the previous data structure, which is based on common blocks. As an example, the conceptual model of the data structure of element-based data types is shown in Figure 5.2. A conceptual model of MSFLOW_CO2 is shown in Figure 5.3. MSFLOW_CO2 also has a comprehensive visualization module, which is capable of plotting the 2D simulation results. The plotting module is based on OpenGL (Kessenich et al. 2016). It adopts shading techniques to plot 2D variable tables with arbitrary geometry. A comparison of the shading effect of MSFLOW_CO2 with respect to a commercial plotting software is shown in Appendix A.

![Figure 5.2 Data structure of element-based data types.](image)
Figure 5.3 Flow chart of the simulation run of MSFLOW_CO2.
Table 5.1 List of primary and secondary variables of MSFLOW_CO2

<table>
<thead>
<tr>
<th>Primary variables</th>
<th>Secondary variables</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H</td>
</tr>
<tr>
<td>pressure</td>
<td>density</td>
</tr>
<tr>
<td>temperature</td>
<td>permeability</td>
</tr>
<tr>
<td>( Z_i ) (mole fraction), ( i=1, Nc-1 )</td>
<td>porosity</td>
</tr>
<tr>
<td>mean stress</td>
<td>viscosity</td>
</tr>
<tr>
<td></td>
<td>saturation</td>
</tr>
</tbody>
</table>
In this chapter, we present the validation of our numerical model.

6.1 Performance of flash calculation

In this section, we present the validation as well as the results of the flash calculation module. We first present a seven-component case and compare it with experimental data. The feed mole fraction of the seven-component acid gas system is shown in Table 6.1. The feed contains H$_2$S, making it acid gas. We calculate the variation of gas-liquid equilibrium ratio at 338.71 K and compare the results with experimental data (Yarborough 1972). The comparison is shown in Figure 6.1. The comparison shows that our proposed flash calculation module matches well with experimental data.

Table 6.1 Feed mole fraction of a seven-component acid gas system

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed mole fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>77.43</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>5.74</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>2.99</td>
</tr>
<tr>
<td>C$<em>5$H$</em>{12}$</td>
<td>4.66</td>
</tr>
<tr>
<td>C$<em>7$H$</em>{16}$</td>
<td>3.59</td>
</tr>
<tr>
<td>C$<em>{10}$H$</em>{22}$</td>
<td>2.63</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>2.96</td>
</tr>
</tbody>
</table>
6.2 Two-dimensional Mandel-Cryer effect

In this example, we benchmark the hydraulic-mechanical module of MSFLOW_CO2 with the two-dimensional Mandel-Cryer effect. The Mandel-Cryer effect states as follows. A constant force is first applied on the two ends of a piece of saturated poro-elastic rock (z-direction). Then the rock is allowed to drain on the lateral sizes (x-direction). It is observed that, after the drainage starts, the pore pressure in the center of this rock will first increase before decreasing. This interesting phenomenon was first studied by Mandel (1953) and is named as the Mandel-Cryer effect. Later, Abousleiman et al. (1996) provided an analytical solution for the Mandel-Cryer effect. Figure 6.2 shows a conceptual model of the Mandel-Cryer effect.

The physical reason behind the Mandel-Cryer effect is that mechanical impact propagates much faster within the rock framework than the hydraulic pressure. This results in that the center
of the rock frame gets compressed before the pore gets compressed. Clearly, the Mandel-Cryer effect is essentially a coupled hydraulic-mechanical problem and can be used for the validation of the multiphysical simulation module of MSFLOW_CO2. In this work, we use MSFLOW_CO2 to study the Mandel-Cryer effect and compare our results to the analytical solution with different rock properties. The rock properties we use for the comparison are listed in Table 6.2. For all the four cases, the computational domain is discretized into 90*90 grid blocks. Our simulation consists of two steps. At first, we only apply the compressive force on the rock for a sufficiently long time (2 years in this case). We then allow the rock to drain on the lateral sizes and record the change of the pore pressure in the center of the rock. The variation of the pore pressure in the center of the rock is shown in Figure 6.3, according to which our numerical results match the analytical solution very well for all the four cases. This case study validates the multiphysical simulation of MSFLOW_CO2. Moreover, when permeability increases, the pressure in the center of the rock declines faster. This is because the pore pressure changes propagate faster in higher permeable rocks.

![Figure 6.2 Problem description of two-dimensional compaction.](image)

Figure 6.2 Problem description of two-dimensional compaction.
Table 6.2 Rock properties for 2-D Mandel-Cryer effects

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.15</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Young's modulus</td>
<td>15.0</td>
<td>GPa</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.3</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Biot's coefficient</td>
<td>1.0</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Water viscosity</td>
<td>0.001</td>
<td>Pa·S</td>
</tr>
<tr>
<td>Permeability of case #1</td>
<td>100</td>
<td>md</td>
</tr>
<tr>
<td>Permeability of case #2</td>
<td>70</td>
<td>md</td>
</tr>
<tr>
<td>Permeability of case #3</td>
<td>50</td>
<td>md</td>
</tr>
<tr>
<td>Permeability of case #4</td>
<td>10</td>
<td>md</td>
</tr>
</tbody>
</table>

Figure 6.3 Comparison between numerical results and analytical results of two-dimensional compaction.
6.3 Heat sweep in a vertical fracture

In this session, we validate the thermal-hydraulic simulation module of MSFLOW_CO2 with commercial non-isothermal reservoir simulator CMG-STARS (Computer Modelling Group LTD. 2010).

We simulate the non-isothermal problem of injecting cold liquid into a vertical fracture, which is initially of in-situ reservoir temperature. This problem was first investigated by Pruess and Bodvarsson (1984) in a geothermal reservoir. We compare the results of MSFLOW_CO2 with the thermal-hydraulic module of CMG-STARS (Pruess and Bodvarsson 1984). In a given vertical fracture sandwiched by semi-infinite half-spaces of impermeable rock, we set a cold liquid injector and a constant pressure producer at the two ends of it, as shown in Figure 6.4. The fracture is bounded by semi-infinite half-spaces of impermeable rock, which serves as a heat supply source. The initial temperature of the fracture is 100 °C. Cold water with 51 °C is injected at a constant rate of 3.75 kg/s. The water is produced at 10 MPa.

The temperature field at the end of the simulation without and with the heat gain from the surrounding rock is shown in Figure 6.5 and Figure 6.6 respectively. The temperature fields indicate that when there is no heat supply, the final temperature is much lower. Moreover, the lower part of the fracture tends to be cooler than the upper part. This is because cold fluids become denser and tend to accumulate at the bottom. The comparison of the temperature of the produced fluid between MSFLOW_CO2 and CMG-STARS without and with the heat supply from the surrounding rock is shown in Figure 6.7 and Figure 6.8 respectively. Based on the comparison, the results of MSFLOW_CO2 match those from the commercial simulator very well.
Figure 6.4 Conceptual model of the heat sweep problem.

Table 6.3 Input parameters for the heat sweep problem

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock grain density</td>
<td>2600</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Specific heat</td>
<td>1000</td>
<td>J/kg°C</td>
</tr>
<tr>
<td>Heat conductivity</td>
<td>2</td>
<td>W/m°C</td>
</tr>
<tr>
<td>Fracture height</td>
<td>240</td>
<td>m</td>
</tr>
<tr>
<td>Fracture length</td>
<td>240</td>
<td>m</td>
</tr>
<tr>
<td>Fracture aperture</td>
<td>0.04</td>
<td>m</td>
</tr>
<tr>
<td>Fracture permeability</td>
<td>200</td>
<td>Darcy</td>
</tr>
<tr>
<td>Fracture porosity</td>
<td>0.5</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>10</td>
<td>MPa</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>100</td>
<td>°C</td>
</tr>
</tbody>
</table>
Figure 6.5 Temperature field at the end of the simulation without heat gain from the surrounding rock.

Figure 6.6 Temperature field at the end of the simulation with heat gain from the surrounding rock.
Figure 6.7 Comparison of the temperature of the produced fluid between MSFLOW_CO2 and CMG-STARS (without heat gain from surrounding rocks).

Figure 6.8 Comparison of the temperature of the produced fluid between MSFLOW_CO2 and CMG-STARS (with heat gain from surrounding rocks).
CHAPTER 7

NUMERICAL SIMULATION RESULTS

In this chapter, we present the numerical results of our study. We have conducted five numerical studies. The first is to present the capability of the newly developed flash calculation module. The second case is a coupled hydraulic-mechanical simulation case study of a reservoir whose permeability is stress-sensitive. The third and the fourth are about the thermal impact on the fluid properties as well as rock properties. The last case is a reservoir scale cold CO$_2$ injection problem. These five cases systemically investigate the coupled thermal-hydraulic-mechanical processes during the CO$_2$ flooding processes.

7.1 Flash calculation for three phase systems

In this session, we present the results of the flash calculation module. We run two three-component three-phase cases. The first case is a ternary mixture of CO$_2$, water and nonane (n-C$_9$H$_{20}$). Figure 7.1 shows the mole fraction of the aqueous phase at 333 K and 30 MPa. According to Figure 7.1, the distribution of the mole fraction of the aqueous phase is almost proportional to the water component fraction. The second case is a ternary mixture of methane, water and nonane (n-C$_9$H$_{20}$). Figure 7.2 shows the distribution of the mole fraction of the liquid hydrocarbon phase at 333 K and 30 MPa. According to Figure 7.2, our flash calculation module is able to capture the transition between the gas and the liquid hydrocarbon phase. Based on the validation and the numerical results, it can be concluded that our flash calculation module is able to handle complex multi-phase systems.
Figure 7.1 Mole fraction of aqueous phase of the CO2/n-C9H20/H2O mixture at 333 K and 30 MPa.

Figure 7.2 Mole fraction of liquid hydrocarbon phase of the CH4/n-C9H20/H2O mixture at 333 K and 30 MPa.

7.2 Stress-sensitive permeability problem

In this problem, we use MSFLOW_CO2 to simulate a reservoir whose permeability is sensitive to stress changes. The geometry we use is shown in Figure 7.3.
In this case, a well is injecting water at the center of a reservoir, as shown in Figure 7.3. The reservoir zone (2 m thick) is below a caprock zone (1000 m thick), but only 20 m of the caprock zone is taken into consideration. According to the simulation results, the pressure variation only propagates 5 m into the caprock zone, due to its low permeability. The initial temperature of the reservoir is 140 °C.

The permeability of the reservoir is subject to the following correlation

\[ K = K_0 \exp \left( \frac{c \cdot dP}{\sigma_m} \right) \]  

In the above correlation, the permeability is an exponential function of the pressure change. In the above equation, \( K_0 \) is the initial permeability of the reservoir. \( dP \) is the pressure change. \( \sigma_m \) is the mean stress. The parameter \( c \) is a constant.
Table 7.1 Input parameters of the stress-sensitive permeability case

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial permeability of the reservoir</td>
<td>1.0*10^{-13}</td>
<td>m^2</td>
</tr>
<tr>
<td>Initial permeability of the caprock</td>
<td>1.0*10^{-18}</td>
<td>m^2</td>
</tr>
<tr>
<td>Porosity of the reservoir zone</td>
<td>0.0001</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Porosity of the caprock</td>
<td>0.01</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Young’s modulus of the caprock</td>
<td>600</td>
<td>GPa</td>
</tr>
<tr>
<td>Young’s modulus of the reservoir</td>
<td>180</td>
<td>GPa</td>
</tr>
<tr>
<td>Poisson’s ratio of the caprock</td>
<td>0.1</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Biot’s coefficient of the caprock</td>
<td>0.7</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Poisson’s ratio of the reservoir zone</td>
<td>0.1</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Biot’s coefficient of the caprock</td>
<td>0.7</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Thermal conductivity of the caprock</td>
<td>4.0</td>
<td>W/(m K)</td>
</tr>
<tr>
<td>Thermal conductivity of the reservoir rock</td>
<td>4.0</td>
<td>W/(m K)</td>
</tr>
<tr>
<td>Constant $c$</td>
<td>10</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Stress $\sigma_m$</td>
<td>45</td>
<td>MPa</td>
</tr>
<tr>
<td>Injection rate</td>
<td>80</td>
<td>kg/s</td>
</tr>
<tr>
<td>Injection temperature</td>
<td>140</td>
<td>°C</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>20</td>
<td>MPa</td>
</tr>
</tbody>
</table>

The transient pressure curves at (1 m, 1 m, 2000 m), (2.5 m, 2.5 m, 2000 m), (5 m, 5 m, 2000 m), (10 m, 10 m, 2000 m), (50 m, 50 m, 2000 m), (500 m, 500 m, 2000 m) are shown in Figure 7.4. Along the diagonal of the reservoir, the permeability profiles at 100 s, 1000 s, 10000 s, 50000 s and 100000 s are shown in Figure 7.5.
Figure 7.4 Transient pressure curves at different points of the reservoir.

Figure 7.5 Permeability profiles along the diagonal of the reservoir at 100 s, 1000 s, 10000 s, 50000 s and 100000 s.
7.3 Compaction and low-temperature effects

In this section, we investigate the effects of the compaction and temperature change on the rock permeability and apparent gas permeability. The compaction effect is essentially the stress change induced by fluids produced from the reservoir. The low-temperature effect is the stress change of cold liquid injection into the reservoir.

We use the following correlation to calculate the porosity (Davies and Davies 1999; Rutqvist et al. 2002)

\[
\phi = \phi_r + (\phi_0 - \phi_r) e^{-a\Delta\sigma_m}
\]  
(7.2)

In which \(\phi_r\) is the residual porosity at maximum stress. \(\phi_0\) is the porosity when the stress is zero. \(\sigma_m\) is the mean effective stress. The change of the mean effect stress is calculated by

\[
\Delta\sigma_m = 3\beta K_B (T - T_{ref}) - \alpha (P - P_{ref})
\]  
(7.3)

Where \(\beta\) is the linear thermal expansion coefficient. \(K_B\) is the bulk modulus calculated by Equation (3.18). The absolute permeability is calculated from porosity using Equation (3.63).

The calculation of the gas apparent permeability requires the pore radius, which in this work is obtained by the Aguilera’s correlation (Aguilera 2002), as

\[
D = 2r = 2 \times 2.665 \left(\frac{k_\infty}{100\phi}\right)^{0.45}
\]  
(7.4)

In the above, \(D\) and \(r\) is the diameter and radius of the pore throat in μm respectively. The absolute permeability \(k_\infty\) is in md.

The input parameters used for this study are listed in Table 7.2. The variation of rock absolute permeability and porosity with respect to pressure and temperature change is shown in
Figure 7.6. From these results, the absolute permeability is very sensitive to the thermal unloading effect induced by temperature reduction. If the reservoir temperature decreases from 100 °C to 20 °C, the permeability rapidly increases. Meanwhile, the absolute permeability is also sensitive to pressure change. However, in practice the pressure changes in the reservoir will not be too large, subject to the limitation of the facilities. The variation of the pore diameter and the gas apparent permeability with respect to pressure and temperature are shown in Figure 7.7. According to this analysis, the diameter of the pore is sensitive to the thermal loading process and thermal unloading process, however the gas apparent permeability is not sensitive to the thermal processes in the normal reservoir environment.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear thermal expansion coefficient</td>
<td>11.2</td>
<td>$10^{-6}$ m/(m K)</td>
</tr>
<tr>
<td>Young’s modulus $E$</td>
<td>12.0</td>
<td>GPa</td>
</tr>
<tr>
<td>Poisson’s ratio $\nu$</td>
<td>0.25</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Initial permeability $k_0$</td>
<td>0.001</td>
<td>md</td>
</tr>
<tr>
<td>Biot’s coefficient $\alpha$</td>
<td>1.0</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Residual porosity $\phi_r$</td>
<td>0.009</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Zero stress porosity $\phi_0$</td>
<td>0.1</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Reference temperature $T_{ref}$</td>
<td>100</td>
<td>°C</td>
</tr>
<tr>
<td>Reference pressure $P_{ref}$</td>
<td>20</td>
<td>MPa</td>
</tr>
<tr>
<td>TMAC $\sigma$</td>
<td>1</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>
Figure 7.6 Variation of rock absolute permeability and porosity with respect to pressure and temperature change. Left: absolute permeability. Right: porosity.

Figure 7.7 Variation of rock absolute permeability and porosity with respect to pressure and temperature change.

7.4 Low-temperature effects on capillary pressure

In this section, we argue that the cold water can reduce the capillary pressure, therefore reduce the imbibition effect. From Young-Laplace’s equation, as shown in Equation (3.74). In this case study, the contact angle $\theta$ is set to be 0. The surface tension or the surface energy will
increase as temperature decreases. At the same time, the pore throat radius will also increase as the temperature drops down, because of the shrinkage of rock grain induced by the change of the thermal stress. In the following work, we aim to quantify the low-temperature effect. We use Leverett’s formulation (Leverett 1941) to calculate the capillary pressure, as shown in Equation (3.64). We use the Kozeny-Carman equation to correlate permeability and porosity, as shown in Equation (3.63). By substituting Equation (3.63) into Leverett’s formulation, we get the following formulation which directly correlates between porosity and capillary pressure.

\[
P_c = P_{c0} \frac{(1 - \phi_0) \phi_0}{(1 - \phi) \phi}
\]

(7.5)

Note that Leverett’s correlation is based on isothermal condition. To take into temperature effect into consideration, we should also include the change of surface tension in our analysis. The calculation of surface tension is shown in Equation (3.75). The surface tension profile is shown in the following figure. According to the results, when temperature decrease from 423 K (150 °C) to 373 K (100 °C), the surface tension increases by about 20%.

Figure 7.8 The surface tension of water versus reservoir temperature. Note that the reservoir temperature is in reserve sequence.
We use the following correlation to calculate the porosity

\[ \phi = \phi_r + (\phi_0 - \phi_r)e^{-\sigma_n} \]  

(7.6)

In which \( \phi_r \) is the residual porosity. \( \phi_0 \) is the zero stress porosity. \( \sigma_n \) is the mean effective stress.

The change of \( \sigma' \) is calculated by

\[ \Delta \sigma' = \beta K_B \left( T - T_{ref} \right) \]  

(7.7)

Where \( \beta \) is the linear thermal expansion coefficient. \( K_B \) is the bulk modulus calculated by Equation (3.18).

By combing all the above equations, we can eventually quantify the temperature effect on the capillary behavior, as shown in the following figures. To better present the results, we scale the capillary pressure by calculating the dimensionless ratio

\[ \gamma_D = \frac{P_c(T)}{P_c(T_{ini})} \]  

(7.8)

Where \( T_{ini} \), the original reservoir temperature, is set as 110 °C. We let the reservoir temperature decrease from 110 °C to 60 °C and plot \( \gamma_D \) versus temperature in Figure 7.9 and Figure 7.10. The parameters used in this analysis are as follows.

Table 7.3 Parameters used in the analysis of capillary behavior

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial porosity of the matrix</td>
<td>0.02</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Linear thermal expansion coefficient</td>
<td>11.2</td>
<td>10(^{-6}) m/(m K)</td>
</tr>
<tr>
<td>Young’s modulus E</td>
<td>12.0</td>
<td>GPa</td>
</tr>
<tr>
<td>Poisson’s ratio ( \nu )</td>
<td>0.25</td>
<td>dimensionless</td>
</tr>
</tbody>
</table>
According to the results, as the reservoir temperature decreases from 110 °C to 60 °C, the capillary pressure decreases. For the rocks that are more sensitive to change of thermal stress (with higher bulk modulus), the low-temperature effects are more significant.

Figure 7.9 Capillary pressure ratio versus reservoir temperature with different Young’s modulus.
In this case, we present a cold CO\textsubscript{2} injection study (Wang et al. 2019a). Cold CO\textsubscript{2} is injected at a rate of 0.3 kg/s into a 100 m by 100 m reservoir for 1 year. One production well is producing at a constant bottom hole pressure of 16.2 MPa. The initial temperature of the reservoir is 85 \textdegree C. The conceptual model of this case is shown in Figure 7.11. The three-phase relative permeability is calculated using the Brooks-Corey model (Delshad and Pope 1989), as shown in Equation (3.72) to Equation (3.74). The capillary pressure is calculated according to Equation (3.75). The initial distribution of component is shown in Table 7.4 and Figure 7.12. The rest input parameters are listed in Table 7.5. We run three cases, in which the injection temperature (temperature of CO\textsubscript{2} when it arrives at the formation) is 20 \textdegree C, 40 \textdegree C and 60 \textdegree C.
respectively. The length and width of the domain is 100 m * 100 m. The domain is discretized uniformly into 50*50 grid blocks.

![Figure 7.11 Conceptual model of the cold CO2 injection case.](image)

Table 7.4 Initial distribution of component for cold CO2 injection case

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>0.16736</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>0.04885</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>C₇H₁₆</td>
<td>0.09334</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>C₉H₂₀</td>
<td>0.05751</td>
</tr>
<tr>
<td>n-Decane</td>
<td>C₁₀H₂₂</td>
<td>0.33736</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
<td>0.05854</td>
</tr>
</tbody>
</table>
Table 7.4 Continued

<table>
<thead>
<tr>
<th>Water</th>
<th>H₂O</th>
<th>0.23704</th>
</tr>
</thead>
</table>

Table 7.5 Input parameters for cold CO₂ injection case

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus</td>
<td>26 GPa</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.25</td>
</tr>
<tr>
<td>Rock permeability</td>
<td>1 md</td>
</tr>
<tr>
<td>Rock porosity</td>
<td>0.2</td>
</tr>
<tr>
<td>Biot’s coefficient</td>
<td>1.0</td>
</tr>
<tr>
<td>Grid block length</td>
<td>4 m</td>
</tr>
<tr>
<td>Injection temperature</td>
<td>50 °C</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>85 °C</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>35.2 MPa</td>
</tr>
<tr>
<td>Production pressure</td>
<td>16.2 MPa</td>
</tr>
<tr>
<td>Initial mean stress</td>
<td>80.6 MPa</td>
</tr>
<tr>
<td>Residual gas saturation</td>
<td>0.1 dimensionless</td>
</tr>
<tr>
<td>Residual oil saturation</td>
<td>0.1 dimensionless</td>
</tr>
<tr>
<td>Residual water saturation</td>
<td>0.1 dimensionless</td>
</tr>
</tbody>
</table>

The distribution of gas phase saturation and temperature after 1 year of injection is shown in Figure 7.13 and Figure 7.14 respectively. According to Figure 7.13, the gas phase saturation increases near the injector. Therefore, this is immiscible flooding. Moreover, the gas saturation
decreases in certain region near the saturation front. This is because of pressure impact propagates faster than saturation impact. The buildup of pressure decreases the gas saturation in the region near the saturation front. According to Figure 7.14, the temperature in the vicinity the producer slightly decreases. The reduction of the temperature is because the energy of the system is consumed by the expansion of the in-situ fluids, known as the Joule-Thomson effect. From this phenomenon, we can conclude that our simulator is capable of capturing many aspects of the complex behavior of the multiphysical system. The variation of scaled permeability (transient permeability to initial permeability) at the injector with respect to time is shown in Figure 7.15, according to which the injected cold CO₂ effectively increases the injectivity near the injector. When the injection temperature decreases from 60 ºC to 20 ºC, the eventual increase of the permeability increases from 170% to 280%. Based on this observation, we can conclude that cold CO₂ injection can be adopted improve the EOR performance of unconventional reservoirs.

Figure 7.12 The fraction of initial concentration of the for cold CO₂ injection case.
Figure 7.13 Gas phase saturation distribution after 1 year of injection (injection temperature = 60 °C).

Figure 7.14 Temperature distribution after 1 year of injection (injection temperature = 60 °C).
Figure 7.15 Variation of scaled permeability at the injector with respect to time.
CHAPTER 8
PROXY FLASH CALCULATION

8.1 Introduction

It has been observed that the flash calculation consumes a significant portion of CPU time during the compositional simulation (Cao et al. 2005), since the flash calculation is conducted for every grid block within every Newton-Raphson iteration. Meanwhile, as described in Chapter 3, the flash calculation approach we use in this study is essentially an optimization algorithm, the performance of which highly depends on the selection of initial guess. A sound initial guess will help speed up the convergence. In the algorithm presented in Chapter 3, the initial guess is calculated by the Wilson’s equation, which is not satisfactory in many cases. In this work, we aim to speed up the flash calculator by using initial guess predicted by a proxy flash calculator based on deep learning technique.

8.2 General background

In this work, we have developed a data-driven flash calculation module based on deep learning techniques to improve the speed and convergence performance. In the new framework, the initial guess of the flash calculation is obtained from a stochastically trained neural network instead of Wilson’s equation. We use deep-learning (DL) based stochastic training technique to develop the proxy simulator. We have trained a neural network, which has an input layer, an output layer, and four hidden layers. Within each layer, there are several neurons elements. All neurons belong to two neighboring layers are fully connected with each other, as shown in Figure 8.1.
The neural network adopts fully connected (dense) layers and is trained on by a standalone module. Once trained, the neural network predicts the phase condition, capillary pressure as well as concentration distribution by simple interpolations. As shown later, the accuracy of the developed network is above 95%. Therefore, a much more accurate initial guess for the flash calculation can be obtained.

The fully connected layers are an imitation of human’s neural system. Each element within the network has one weight value and one bias value, indicating the ‘contribution’ of the element. In the fully connected layers, each element is connected to all elements belonging to its neighboring layers. Activation functions are used between layers. For a given set of input parameters, the network predicts the output results by interpolating from the weight values, the bias values and the activation functions.

During the training process, the weight and the bias of the elements are optimized by certain optimization algorithms to achieve the best prediction. Then in the prediction step as shown in Figure 8.2, the simulator only needs to load the trained weight and bias values into the memory and conduct simple interpolation, which is very cheap in terms of computational time.

In this work, the training process consists of two steps. The first step, which is named as the phase classification step, determines the phase condition of the system under the given condition. In the second step, which is named as the concentration determination step, the phase ratio, component concentration and capillary pressure are determined. Therefore, the neural network replaces the physical flash calculation module in the simulator. The input parameters for both of the two steps include pressure, temperature, feed concentration and pore radius. The input parameters are all normalized to [0,1] scale before being substituted into the network. The normalization is done by scaling the parameters with their maximum and minimum values.
8.3 Phase classification

The network for the phase classification step consists of five layers, including the input layer (layer 1), the output layer (layer 5) and three hidden layers (layer 2 to 4). The number of
input parameters is $N_c + 2$. The input parameters $X$ include the feed concentration ($Z$), pressure ($P$) and temperature ($T$), as shown in Equation (8.1).

$$X = \left[ P, T, Z_1, \ldots, Z_N \right]^T$$  \hspace{1cm} (8.1)

All input parameters are normalized to $[0,1]$ scale. The output parameters $Y$ include the seven possible phase conditions, including pure liquid phase (L), pure gas phase (G), pure aqueous phase (A), coexisting liquid-gas phases (L+G), coexisting liquid-aqueous phases (L+A), coexisting gas-aqueous phases (G+A) and coexisting liquid-gas-aqueous phases (L+G+A). In the network, the dimension of layer 1 to layer 4 is 64 and the dimension of the output layer is seven. Therefore, the network classifies the phase condition into seven types, as listed in Table 8.1. For layer 1, 2, 3, 4 we use ReLU function as the activation function, which is defined as

$$ReLU(x) = \begin{cases} 
0 & \text{for } x < 0 \\
& \text{for } x \geq 0 
\end{cases}$$  \hspace{1cm} (8.2)

For the output layer (layer 5), the softmax function is chosen as the activation function, defined as

$$\text{softmax}(x)_j = \frac{e^{x_j}}{\sum e^{x_i}}$$  \hspace{1cm} (8.3)

Where $e^x$ is the exponential function. The cross-entropy function (Boer et al. 2005; Szita and Lörincz 2006) is chosen as the loss function, to quantify the error during the training process. A detailed structure of the network is as shown in Figure 8.3 in Page 126.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Phase Combination</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_f$</td>
<td>L</td>
</tr>
</tbody>
</table>
Table 8.1 Continued

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_2$</td>
<td>G</td>
</tr>
<tr>
<td>$I_3$</td>
<td>A</td>
</tr>
<tr>
<td>$I_4$</td>
<td>L+G</td>
</tr>
<tr>
<td>$I_5$</td>
<td>L+A</td>
</tr>
<tr>
<td>$I_6$</td>
<td>G+A</td>
</tr>
<tr>
<td>$I_7$</td>
<td>L+G+A</td>
</tr>
</tbody>
</table>

### 8.4 Concentration determination

The network for the concentration determination step consists of five layers, including the input layer (layer 1), the output layer (layer 5) and three hidden layers (layer 2 to 4). The dimension, as well as the physical meanings of the input parameters of this step, is the same as those of the phase classification step.

The dimension of layer 1 to layer 4 is 64 and the dimension of the output layer is $3 \times N_c + 3$, including the phase ratio (the mole fraction of each phase) and component concentration (the concentration of each component in each phase), as listed in Table 8.2. The activation function for layer 1 to 4 is ReLU function, as shown in Equation (8.2). The activation function for the output layer is the sigmoid equation, as shown in Equation (8.4).

$$
\text{sigmoid}(x) = \frac{1}{1 + e^{-x}}
$$

During the training process, we found that ReLU function effectively releases the overfitting issue.
Figure 8.3 Structure of the fully connected neural network for the phase classification step. The numbers refer to the dimension of the layers.

Table 8.2 Summary of the output parameters in the concentration determination step

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Physical meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha_L)</td>
<td>liquid phase ratio</td>
</tr>
<tr>
<td>(\alpha_V)</td>
<td>vapor phase ratio</td>
</tr>
<tr>
<td>(\alpha_W)</td>
<td>aqueous phase ratio</td>
</tr>
</tbody>
</table>
Table 8.2 Continued

| $x_i, i = 1, \ldots, N_c$ | component concentration in the liquid phase |
| $y_i, i = 1, \ldots, N_c$ | component concentration in the vapor phase |
| $w_i, i = 1, \ldots, N_c$ | component concentration in the aqueous phase |

![Diagram](image)

Figure 8.4 Structure of the fully connected neural network for the concentration determination step. The numbers refer to the dimension of the layers.
8.5 Network training

We have investigated five cases with different combinations of hydrocarbon components. For each case, we use 1,000,000 training samples generated from the standalone flash calculation module described in Chapter 3. The samples are generated randomly using Latin Hypercube Sampling (Pebesma and Heuvelink 1999; Zhang and Pinder 2003) technique. The range of the input parameters is listed in Table 8.3.

Table 8.3 Range of the parameters of the training samples

<table>
<thead>
<tr>
<th>Unit</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>MPa</td>
<td>10</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>20</td>
</tr>
<tr>
<td>Feed concentration</td>
<td>dimensionless</td>
<td>0</td>
</tr>
</tbody>
</table>

We use stochastic gradient descent (SGD) algorithm (Bottou 2010) to train the network on Keras (Chollet 2015) with a GPU of 11 GB in memory. The algorithm of SGD can be briefly described as follows (Bottou 2012). For an objective function $\Theta$ with the primary variable $\mathbf{w}$ of $n$ dimensions,

$$\Theta(\xi) = \frac{1}{n} \sum_{i=1}^{n} \Theta_i(\xi_i)$$\hspace{1cm} (8.5)

Instead of optimizing all $n$ dimensions at the same time, SGD randomly optimizes a randomly chosen group (batch) of the variables using gradient descent optimization, as below

$$\xi_{t+1} = \xi_t - \eta \nabla_j \Theta(\xi_t)$$\hspace{1cm} (8.6)
where $t$ is the number of iteration steps. $j$ is the index of batch. $\eta$ is the learning rate. After the completion of one epoch, all the training samples are shuffled. Therefore, the optimization of one high-dimensional problem is effectively converted to the optimization of numerous low-dimensional problems. In this work, the learning rate is 0.001. The neural network for the phase classification step and the concentration determination step is trained with 100 epochs, respectively.

We use the mean absolute percentage error as a metric (loss function) during the training. The error metric for each of the six cases are listed in Table 8.4. According to the results, the accuracy of our neural network is above 97% for the cases we run. As expected, when the number of hydrocarbon components increases, the accuracy decreases according, due to the increase of the dimensions in the parameter space. In general, the proxy flash calculator based on deep learning techniques is much more accurate than any other existing techniques.

As an example, the variation of the loss function during the training epochs of the phase classification step for Case 8-3 is shown in Figure 8.5.

<table>
<thead>
<tr>
<th>Case Index</th>
<th>Feed Component</th>
<th>Phase Classification Error</th>
<th>Concentration Determination Error</th>
<th>Overall Error</th>
<th>Overall Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-1</td>
<td>C1+CO2+N2</td>
<td>0.01%</td>
<td>0.82%</td>
<td>0.83%</td>
<td>99.17%</td>
</tr>
<tr>
<td>8-2</td>
<td>C1+C2+C3+CO2</td>
<td>0.02%</td>
<td>0.65%</td>
<td>0.67%</td>
<td>99.33%</td>
</tr>
</tbody>
</table>
Table 8.4 Continued

<table>
<thead>
<tr>
<th></th>
<th>C1+C2+C4+C7</th>
<th>C1+C2+C3+C4+C5</th>
<th>C1+C2+C10+C10+CO2+H2O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8-3</strong></td>
<td>0.03%</td>
<td>1.63%</td>
<td>1.66%</td>
</tr>
<tr>
<td><strong>8-4</strong></td>
<td>0.07%</td>
<td>1.86%</td>
<td>1.93%</td>
</tr>
<tr>
<td><strong>8-5</strong></td>
<td>0.11%</td>
<td>2.02%</td>
<td>2.13%</td>
</tr>
<tr>
<td><strong>8-6</strong></td>
<td>0.11%</td>
<td>2.87%</td>
<td>2.98%</td>
</tr>
</tbody>
</table>

Figure 8.5 Variation of the loss function during the training epochs of the phase classification step.

8.6 Deep learning based flash calculator

The trained deep learning (DL) network is implemented in our flash calculation module. The proxy flash calculator provides the initial guess of the equilibrium ratio as well as the
capillary pressure, replacing Wilson’s equation. Since the phase classification step is of very high accuracy, the phase condition predicted by that step is adopted as the ‘final’ result, and all components go into the predicted phase. Therefore, if the phase classification step predicts that only one phase exists in the system, the DL proxy calculator directly output the results. If, however, the phase classification step makes the prediction that multiple phases exist in the system, the flash calculator will start the K-value based iteration using the predicted equilibrium ratio and capillary pressure, until globally convergent. A flowchart of the deep leaning based flash calculator is shown in Figure 8.6. The comparison between the average number of iterations of the flash calculation with and without DL preconditioning is shown in Table 8.5 and Figure 8.7. According to the comparison of the numerical performance, the number of iterations has been cut by above 50%. According to the results, DL based proxy calculation effectively reduces the number of iterations of flash calculation and, thus accelerates the reservoir simulation. The reason of the overwhelming performance of DL based proxy calculation lies in the elaborated designed neural network, which provides a highly accurate initial guess of the flash calculation.

Table 8.5 Comparison between the average number of iterations of the flash calculation with and without DL preconditioner (convergence criteria = 10^{-6})

<table>
<thead>
<tr>
<th>Case index</th>
<th>Feed component</th>
<th>Average number of iterations without DL preconditioner</th>
<th>Average number of iterations with DL preconditioner</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-1</td>
<td>C1+CO2+ H20</td>
<td>7.8</td>
<td>1.1</td>
</tr>
<tr>
<td>8-2</td>
<td>C1+C2+C3+CO2</td>
<td>9.2</td>
<td>1.2</td>
</tr>
<tr>
<td>8-3</td>
<td>C1+C2+C4+C7</td>
<td>9.5</td>
<td>2.1</td>
</tr>
</tbody>
</table>
Table 8.5 Continued

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-4</td>
<td>C1+C2+C3+C4+C5</td>
<td>10.2</td>
<td>3.3</td>
</tr>
<tr>
<td>8-5</td>
<td>C1+C2+C10+CO2+N2+H2O</td>
<td>15.6</td>
<td>3.9</td>
</tr>
<tr>
<td>8-6</td>
<td>C1+C2+C3+C7+C9+C10+CO2+H2O</td>
<td>19.4</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Figure 8.6 Flowchart of the proxy flash calculation in a reservoir simulator.
Figure 8.7 Comparison of the average number of iterations of flash calculation with and without the deep-learning based preconditioner.

8.7 Deep learning based compositional reservoir simulation

We have implemented the deep-learning based flash calculator into our simulator MSFLOW_CO2. We have conducted several case studies to investigate the performance of the deep learning based compositional simulator. In this chapter, all numerical cases are executed by an Intel i7-6700 processor with 3.40 GHz.

We first compare the cold CO\textsubscript{2} injection case presented in Section 7.5. We test cases with a different number of grid blocks. The comparison of the CPU time with 25*25, 50*50, and 100*100 grid blocks with and without the deep-learning based preconditioner is shown in Figure 8.8. The comparison shows that the CPU time has been effectively reduced by 30% to 40% by the deep learning based preconditioner.
We have also investigated the compositional simulation of a fractured reservoir. The reservoir is naturally fractured. A horizontal well is drilled through the reservoir, and a hydraulic fracture is engineered within the reservoir, creating a stimulated reservoir volume (SRV) in the vicinity of the hydraulic fracture. The conceptual model of the problem is shown in Figure 8.9, in which the green and the orange part indicates the area within and outside the SRV, respectively.

The natural fractured reservoir part and the SRV are both modeled as dual-porosity dual-permeability systems. The length of the entire reservoir along $x$ and $y$ direction is 540 m and the 400 m, respectively, while the length of the SRV along $x$ and $y$ direction is 120 m and 160 m, respectively. The conceptual model of the case is shown in Figure 8.9. The initial distribution of components of this case is shown in Table 8.6. The mechanical impact is not considered in this case. The input parameters, including the rock properties, are listed in Table 8.7. We run this
case with three different grid block sizes, namely 10 m*10 m, 8 m*8 m and 4 m*4 m for eight years.

As the results, the oil pressure fields of the fracture system and the matrix rock at the end of the production are shown in Figure 8.10. The comparison of the oil saturation fields of the matrix rock system at the end of the first year of production and at the end of the eighth year of production is shown in Figure 8.11. According to the results, the fractures in the vicinity of the hydraulic fracture get quickly drained by the production, while the pressure inside the matrix rock system declines much slower. As the pressure decreases, the gas phase expands and the oil saturation decreases.

The comparison of the CPU time of this case with and without the deep-learning based preconditioner is shown in Figure 8.12. According to the comparison, the CPU time of the simulation has been effectively cut by 20% to 30%. Based on the above results, we can conclude that our DL based reservoir simulator effectively speeds up the simulation.
Table 8.6 Initial distribution of components for deep leaning based compositional reservoir simulation case

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Mole fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>0.40</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>0.15</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>0.15</td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>0.05</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>C₅H₁₂</td>
<td>0.05</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>C₇H₁₆</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 8.7 Input parameters for fractured reservoir case

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability of the matrix rock</td>
<td>0.1</td>
<td>μd</td>
</tr>
<tr>
<td>Porosity of the matrix rock</td>
<td>0.01</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Permeability of the hydraulic fracture</td>
<td>100</td>
<td>md</td>
</tr>
<tr>
<td>Porosity of the hydraulic fracture</td>
<td>0.2</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Permeability of the fractures in SRV</td>
<td>50</td>
<td>md</td>
</tr>
<tr>
<td>Porosity of the fractures in SRV</td>
<td>0.1</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Permeability of the fractures outside SRV</td>
<td>20</td>
<td>md</td>
</tr>
<tr>
<td>Porosity of the fractures outside SRV</td>
<td>0.05</td>
<td>dimensionless</td>
</tr>
<tr>
<td>Initial pressure</td>
<td>21.2</td>
<td>MPa</td>
</tr>
<tr>
<td>Initial temperature</td>
<td>120</td>
<td>°C</td>
</tr>
<tr>
<td>Production pressure</td>
<td>10.2</td>
<td>MPa</td>
</tr>
</tbody>
</table>
Table 8.7 Continued

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>dimensionless</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual gas saturation ($S_{gr}$)</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Residual oil saturation ($S_{or}$)</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Residual water saturation ($S_{wr}$)</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

Figure 8.10 Comparison of the oil pressure fields of the matrix rock system and the fracture system at the end of the 8-years production. Left: matrix rock system. Right: fracture system.

Figure 8.11 Comparison of the oil saturation fields of the matrix rock system at the end of the first year of production and at the end of the eighth year of production. Left: end of the first year. Right: end of the eighth year.
Figure 8.12 Comparison of the CPU time of the compositional reservoir simulation case with and without the deep-learning based preconditioner.
CHAPTER 9

CONCLUSION AND DISCUSSION

In this chapter, we summarize and conclude this work.

9.1 Summary and Conclusion

In this dissertation,

- We have reviewed the transport mechanism and phase behavior in unconventional oil/gas formations. We have also reviewed the history as well as the recent development of EOR techniques.

- We have developed a comprehensive non-isothermal compositional simulator, named as MSFLOW_CO2, to simulate CO2-EOR processes. The simulator is based on the Integrated Finite Difference (IFD) method, which is able to simulate multiphysical flow and transport processes in reservoirs using an unstructured grid. To accelerate the computation, the simulator has been equipped with the state-of-the-art multiscale linear solver.

- We have implemented a fully coupled thermal-hydraulic-mechanical framework in MSFLOW_CO2 to simulate the multiphysical processes during CO2-EOR. The hydraulic-mechanical module of MSFLOW_CO2 has been verified against analytical solutions with sufficient accuracy. The mean stress method used in this simulator is able to capture the poroelastic effect during the recovery of petroleum reservoirs. Moreover, the thermal-hydraulic module of MSLOW_CO2 has been benchmarked with a commercial simulator. The results yielded by the two simulators show a good match.
Therefore, the accuracy of the multiphysical simulation framework of MSFLOW_CO2 is validated.

- We have investigated the transport mechanisms in the unconventional reservoirs during CO2-EOR, with focus on the gas slippage effect. We have developed a novel second-order slippage model for both single and multiple component gases based on kinetic theory of gases. We discovered that the slippage effect of a binary mixture could be higher than any of the two pure components, depending on the molecular weights of the components. Moreover, we have simulated the velocity profile of the nano-pores in the unconventional reservoirs and investigated the impact of the pressure ratio on the slipp flow.

- To simulate the complex phase behavior in the REV, we have developed a novel flash calculation module based on minimization of the Gibbs energy method. We have benchmarked the flash calculation module with respect to experimental results. The minimization of the Gibbs energy method shows the flexibility in capturing the phase transition during CO2 flooding. Moreover, this method can be potentially applied to simulate even more complex systems, for instance, systems with four or more phases.

- Based on the developed simulator, we have studied the impact of cold CO2 injection on the production performance of unconventional reservoirs. Such impact is ignored by existing commercial simulators. We discovered that, cold CO2 injection effectively increases the injectivity of unconventional reservoirs.

- At last, we also developed a data-based proxy flash calculator to speed up the time-consuming flash calculation. The proxy flash calculator adopts an initial guess obtained from the deep neural network, the accuracy of which is above 95%. With the
implementation of the proxy calculator, the number of iterations of the flash calculation has been effectively reduced by 50%. This work is among the first trials in this area.

9.2 Suggestions for future work

- As a simplified approach, the currently-used mean stress method fails to compute all the components of the stress tensor. Recently, the mean stress method has been extended to fully solve the entire stress tensor, which could be adopted in the future (S. Wang et al. 2017c; Winterfeld and Wu 2016).
- The CO$_2$ huff-and-puff (Abedini and Torabi 2014; Gondiken 1987; Torabi and Asghari 2010) operation is becoming more and more popular in the recent years. The huff-and-puff operation injects and produces in the same well, instead of forming a hydraulic doublet between neighboring wells, which makes it suitable to be carried out in extremely low-permeable formations. As a future plan, MSFLOW_CO2 can also be used to investigate the multiphysical process involved in the CO$_2$ huff-and-puff operations.
- So far the phase behavior calculation is limited to three phase systems. Theoretically speaking, the method can also be applied to systems with even more phases, as reported by Ballard (Ballard and Sloan 2004). In the future, the method may be extended to simulate the CO$_2$-oil-water-asphaltene systems.
- The flash calculation module can also be extended to incorporate the large capillary pressure effect (Sobecki et al. 2019). The capillary pressure is essentially surface energy and can be added to the formulation of the Gibbs free energy of the system.
- The current gas slippage model can be applied to low to moderate Knudsen numbers. It could be extended to higher Knudsen number ranges by including more elaborated
models of the molecular-wall interactions and also by taking Knudsen diffusion effect into considerations.

- To further improve the stability of the simulator, especially to improve the capability of the simulator in handling rapid phase transition, some advanced numerical techniques may be tried, for instance, the hybrid upwind weighting scheme (Lee et al. 2015).

- The economic recovery of unconventional reservoirs highly relies on the success of hydraulic fractures. To incorporate hydraulic fractures in reservoir simulation without time-consuming re-meshing, the so-called embedded discrete fracture method (EDFM) (Lee et al. 2001; Li et al. 2006) is an effective and convenient approach. In the future, MSFLOW-CO2 could be extended to handle EDFM in order to simulate the thermal-hydraulic-mechanical processes during CO\textsubscript{2} flooding in fractured reservoirs.

- In the present work, the fully-connected neural network is used for the proxy flash calculator. In the future, other structures can also be tried and compared, for instance, the convolutional neural network and the recurrent neural network. Moreover, other portions of the simulator may also be accelerated by the deep learning techniques. For example, the wellbore flow part, which is a very time-consuming simulation of multiphase flow, can be replaced by a DL based proxy calculator.
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APPENDIX A

AN EXAMPLE OF THE VISUALIZATION MODULE OF MSFLOW_CO2

The figure below is a comparison between the visualization module of MFLOW and a commercial plotting software.

Figure A-1 Comparison of the visualization module between a commercial plotting software and MSFLOW_CO2.
APPENDIX B

AN EXAMPLE OF THE INPUT FILE OF MSFLOW_CO2

The figure below is an example of the input file of MSFLOW_CO2. The COMPS keyword contains the essential information required by compositional simulation.

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Figure B-1 An example input file of MSFLOW_CO2.
APPENDIX C

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