“Non-linearities and upscaling in porous media“

Master Thesis (Diplomarbeit)

Two-phase flow modeling in porous media with kinetic
interphase mass transfer processes in fractures

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<tr>
<td>$A$</td>
<td>area</td>
<td>$[m^2]$</td>
</tr>
<tr>
<td>$a_{\alpha\beta}$</td>
<td>volume specific interfacial area between phase $\alpha$ and $\beta$</td>
<td>$[m^2/m^3]$</td>
</tr>
<tr>
<td>$D^\kappa$</td>
<td>molecular diffusion coefficient of component $\kappa$ in phase $\alpha$</td>
<td>$[m^2/s]$</td>
</tr>
<tr>
<td>$D^\kappa_s$</td>
<td>macroscale diffusion coefficient</td>
<td>$[m^2/s]$</td>
</tr>
<tr>
<td>$c^\kappa_\alpha$</td>
<td>concentration of component $\kappa$ in phase $\alpha$</td>
<td>$[kg/m^3]$</td>
</tr>
<tr>
<td>$E_{\alpha\beta}$</td>
<td>production rate of interfacial area</td>
<td>$[1/m \cdot s]$</td>
</tr>
<tr>
<td>$e_{\alpha\beta}$</td>
<td>static production rate of interfacial area</td>
<td>$[1/m]$</td>
</tr>
<tr>
<td>$F$</td>
<td>vector of force</td>
<td>$[N]$</td>
</tr>
<tr>
<td>$g$</td>
<td>magnitude of gravitational constant</td>
<td>$[m/s^2]$</td>
</tr>
<tr>
<td>$g$</td>
<td>gravity vector $(0, 0, -g)^T$</td>
<td>$[m/s^2]$</td>
</tr>
<tr>
<td>$G$</td>
<td>solution domain</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$H$</td>
<td>Henry constant</td>
<td>$[Pa^{-1}]$</td>
</tr>
<tr>
<td>$k_{r\alpha}$</td>
<td>relative permeability of phase $\alpha$</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$K_f$</td>
<td>hydraulic conductivity</td>
<td>$[m/s]$</td>
</tr>
<tr>
<td>$K$</td>
<td>intrinsic permeability tensor</td>
<td>$[m^2]$</td>
</tr>
<tr>
<td>$K$</td>
<td>permeability tensor</td>
<td>$[m^2]$</td>
</tr>
<tr>
<td>$m$</td>
<td>Van Genuchten (VG) parameter</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$M^\kappa$</td>
<td>Molar weight of component $\kappa$</td>
<td>$[g/mol]$</td>
</tr>
<tr>
<td>$N$</td>
<td>basis function, ansatz function</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$n$</td>
<td>Van Genuchten (VG) parameter</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$p^\kappa_\alpha$</td>
<td>partial pressure of component $\kappa$ in phase $\alpha$</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$p_c$</td>
<td>capillary pressure</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$p_d$</td>
<td>Brooks–Corey (BC) parameter, denoted as the entry pressure</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$p_{\alpha,\text{sat}}$</td>
<td>saturation vapor pressure</td>
<td>$[Pa]$</td>
</tr>
<tr>
<td>$q$</td>
<td>secondary volume flux (sources and sinks)</td>
<td>$[m^3/(m^3s)]$</td>
</tr>
<tr>
<td>$q_{N,\alpha}$</td>
<td>neumann boundary flux of phase $\alpha$</td>
<td>$[m^3/(m^2s)]$</td>
</tr>
<tr>
<td>$S_\alpha$</td>
<td>saturation of phase $\alpha$</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$S_e$</td>
<td>effective saturation of water</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$S_{r,\alpha}$</td>
<td>residual saturation of phase $\alpha$</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>$[s]$</td>
</tr>
<tr>
<td>$u$</td>
<td>solution variable</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$v_\alpha$</td>
<td>velocity of phase $\alpha$ w.r.t. the solid phase</td>
<td>$[m/s]$</td>
</tr>
<tr>
<td>$v_{\alpha\beta}$</td>
<td>velocity of the interface $\alpha\beta$ w.r.t. the solid phase</td>
<td>$[m/s]$</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
<td>$[m^3]$</td>
</tr>
</tbody>
</table>
\( x_\kappa^\alpha \) mole fraction of component \( \kappa \) in phase \( \alpha \) [-]

\( X_\kappa^\alpha \) mass fraction of component \( \kappa \) in phase \( \alpha \) [-]

\( X_{\kappa,s}^\alpha \) equilibrium mass fraction of component \( \kappa \) in phase \( \alpha \) [m]

\( x, y, z \) coordinates [m]

\( \alpha \) Van Genuchten (VG) parameter \([Pa^{-1}]\)

\( \Gamma \) Boundary of a volume of interest [-]

\( \Gamma_{\alpha\beta} \) Areal mass density of the \( \alpha\beta \)-interface \([kg/m^2]\)

\( \Delta \) increment [-]

\( \varepsilon \) residual [-]

\( \lambda \) Brooks–Corey (BC) parameter [-]

\( \sigma \) surface tension \([N/m^2]\)

\( \tau \) Tortuosity [-]

\( j_\kappa^\alpha \) diffusive flux of component \( \kappa \) \([kg\cdot m^4/s]\)

\( j_{\kappa,\beta}^\alpha \) diffusive flux over the interphase \( \alpha\beta \) \([kg\cdot m^4/s]\)

\( \mu \) dynamic viscosity \([kg/(ms)]\)

\( \nu \) kinematic viscosity, \( \nu = \mu/\rho \) \([m^2/s]\)

\( \rho \) density \([kg/m^3]\)

\( \phi \) porosity [-]

### Exponents:

\( \kappa \) general component

\( A, W \) specific components air, water

\( m \) timestep

\( \bar{\cdot} \) volume averaged quantity

\( \tilde{\cdot} \) approximated nodal value

\( \hat{\cdot} \) discrete nodal value

\( \hat{\cdot} \) discretized terms separated from nodal values \( \hat{u} \)

\( upw \) upwind

\( x, y, z \) coordinate directions

### Indices:

\( \alpha, \beta \) general phase

\( i \) node \( i \)

\( j \) neighboring nodes \( j \) to node \( i \)

\( k \) sum of neighboring nodes \( j \) to node \( i \) and node \( i \)

\( n \) non-wetting phase

\( s \) solid phase

\( w \) wetting phase
Chapter 1
Motivation

1.1 Introduction

Flow and transport processes in porous media gain increasing attention in many natural, industrial, and even biological systems. In most cases, there is more than one fluid involved, which may lead to *multiphase* conditions. Then, phenomena such as mass transfer between the phases or capillary forces are obtainable. Multiphase flow problems in porous media are manifold, and range from natural to technical problems.

Taken the porous medium of the subsurface as a classical natural example, a wide range of possible substances may come into focus. Besides the exploitation of resources such as oil and gas, sustainable management of the groundwater requires profound knowledge of the underlying flow processes. Being an important resource of drinking water, the protection of groundwater from harmful pollution remains an ongoing task for applied science and research. The plentiful sources and types of contaminants range from infiltration through rainfall that is loaded with nutrients to oil spills from leaking tanks, thus remediation techniques have to be chosen in accordance to the problem, whereas they are at all possible. Consequently, multiphase modeling becomes essential to assess the longterm risks, especially in the fields of anthropogenic activities such as nuclear storage, or \( \text{CO}_2 \) injection into deep geological formations.

Technical porous media problems cover large-scale transport processes such as dissolved salt intrusion through concrete which corrodes the iron reinforcement, down to small-scale gas flow composed of oil droplets and solid particles through catalytic converters, or the diffusive flow in the layers of fuel cells. All those presented problems have in common that they require an interdisciplinary approach comprising, amongst others, fluid mechanics, geology, thermodynamics, mathematics, and physics.

1.2 Fractured Media

Under natural conditions, all rock mass on earth is fractured to some extend, which makes fractures an important and fascinating task of research for aquifer systems. It is assumed that fractured or even karstic fractured aquifers contribute to about 75 % or the earth’s surface (Dietrich et al., 2005). Fractures are mechanical breaks in rocks, acting as local...
separations or discontinuity faces in a geological formation. They originate from stress exceeding the rock strength around flaws, heterogeneities, and physical discontinuities. The strains arise from lithostatic, tectonic, and thermal stresses which induces fractures ranging from microscopic to continental scales, and directing in all dimensions. An exemplary picture of a fractured sandstone is given in Figure 1.1. The understanding of fracture properties is very important in the fields of engineering, geotechnology, and hydrogeology, as they strongly influence water or contaminant flow. The abundance of fractured material widens the area of application from industrial applications to petroleum, geothermal and water supply reservoirs, as well as safety assessments for nuclear storage sites or recharge processes in the unsaturated zone, to name only few.

The hydraulic properties of hard rock are predominantly determined by the fractures, both by their properties and by their spatial geometry. Based on their genesis, the different kinds of fractures can be classified into geologically based groups, amongst all of them two are addressed here: joints and faults. Joints are dilating fractures where the rough surfaces moved away from each other in a perpendicular direction. However, the image of a large displacement process may lead to a misapprehension of huge void channels. Instead, larger parts of the fracture area are in contact with the opposite complementary fracture face which thus limits the ideal of two parallel, fully displaced plates. Faults, in contrast, are shear displacement fractures with predominantly lateral movement of the adjoined rocks. Due to the parallel displacement, fault surfaces are polished and marked by linear features in contrast to the ornamented surfaces of joints, and may thus produce potential pathways for fluid flow \cite{Long1996}. Since faults or joints do not usually consist of one single defined fracture, fracture sets or fracture zones are of high interest in regards to fluid flow. The underlying geological processes and scales of interest \cite{2.1.1.1} are thus crucial for the determination of fluid flow in such structures.

Further problems arise if the fractures are modeled as a continuum which is an averaged description of complex discontinuities by a set of continuous state variables, amongst them \cite{Long1996, Dietrich2005}:

- As we have seen, the exact spatial configuration and geometry of possible pathways as streamtubes to flow are incredibly difficult to define on smaller scales, resulting in high uncertainties.

- Dispersion, a process caused by the variation of the different pathways leading to different flow velocities and pathlengths, inhabits highly anisotropic behaviour along the fractures. It is thus questionable to tackle this phenomenon alike procedures in porous media, whilst experimental data for fractured porous media are not yet sufficient.

- As fractures occur on every scale, it is challenging to transform effective parameters from the testing laboratory to the scale of interest of the model domain.

- Flow through fractures may be accommodated using the fracture aperture, the distance between two neighboring fracture walls, as a model parameter. However,
1.3. FRACTURE-MATRIX SYSTEM

As discussed above, fractures occur on a variety of lengthscales, ranging from tiny fissures to faults and joints with considerable aperture sizes. In order to reduce the complexity of the system, it is desirable to disregard structural information when their influence can be detected with the help of effective parameters, while being still able to capture large heterogeneities. The fractured rock mass is thus assumed to be binary divided into fractures or fractured zones on the one side, and average-fractured rock, denoted as the matrix, on the other side (see the concept of an REV in Chapter 2.1.1.1 as well as Chapter 2.1.3). This assumption seems reasonable, because small, unconnected fissures within the rock matrix are not regarded as preferential pathways for contaminant solutes, thus do not increase flow velocity as severe as large-scale and connected fractures do. Following their parallel genesis due to common stress tensors (Figure 1.2), it seems furthermore reasonable to group single fractures together to fracture zones with a defined direction to apply an continuum modeling approach. However, the simplification to a matrix which is pervaded by fractures, gives rise to even more questions (Long et al., 1996), for example:

- What is the right choice of the scale of interest, which processes are negligible, which ones of high interest?
- The contrasts of the fracture and the matrix properties are huge, conductivity differs

since fracture aperture is not constant in nature, its distribution has to be addressed in a statistical manner which should at best be measured in situ, in the place.

Figure 1.1: Exposed wall of fractured sandstone with horizontal fractures caused by sediment layering and vertical fractures due to mechanical stress (Dietrich et al., 2005).
Figure 1.2: Exposed fracture zone of a weathered granite with predominant fracture directions, Norway.
1.4. EXEMPLAR APPLICATION: NUCLEAR STORAGE SITE

by several orders of magnitude. Are the processes in both parts comparable, do assumptions which are valid for porous media (i.e. slow, laminar flow; thermodynamic equilibrium) also hold for flow in fractures? Are mathematical descriptions valid for both parts?

- Since fractures and the matrix interact, how could both parts be connected in a model? Fractures tend to desaturate before the pores of the matrix because of capillary effects, thus dry fractures act as barriers to fluid flow. However, fracture surfaces may be sealed with minerals, thus capillary forces may be too weak to draw water from the high-permeable fractures. This means that water as well as gas migrate through the fracture, which now acts as pathways to fluid flow.

- Which conceptual model is appropriate for a simulatory link between the fracture and the matrix? Which numerical schemes have to be used to successfully connect them?

After all, fracture-matrix systems represent an exciting and challenging task, both for basic research as well as applied science. There is further need to investigate flow processes both numerically and with experiments, to broaden the knowledge and to improve systematic understanding of the underlying processes. In conclusion, fracture-matrix systems are important for a large range of problems - one of them will be exemplarily addressed in the following section in little more detail.

1.4 Exemplary Application: Nuclear Storage Site

Any usage of nuclear energy requires a solution for the nuclear waste. Current political discussions about an extended production of nuclear energy to fight climate change (whether that is appropriate or not will not be addressed in this work) even sharpens the urgent need for convenient disposal sites for spent fuel. Besides the storage in salt cavities, the focus was directed towards rock dumping sites which seems advantageous because they are considered virtually impermeable. As discussed in the chapters afore, the impermeable rock mass, also denoted as “natural barrier”, is usually interlaced with fractures, and if properly connected, significant flow processes may be indeed possible. With regards to the incredible timespans where safety has to be ensured, any migration of pollutants must be taken serious and under careful consideration. Risk assessment over tens of thousands of years demands huge efforts for simulation technology, so basic knowledge of the underlying processes is acutely significant.

While the Yucca Mountain site, a nuclear storage facility in the US, already lies above groundwater level and thus in the unsaturated zone, most projected storage sites will be located around 500m under the groundwater level, thus fully saturated conditions can be expected. Observations from recent experiments from the Åspö Hard Rock Laboratory in Sweden (Figure 1.3(a)), however, report that multiphase conditions even occur under such physical conditions, leading to a drastic reduction of the effective permeability in addition to other effects. The evolution of a second gaseous phase originates on the one side from the effect of degassing, where a pressure drop in the vicinity of the disposal
caverns causes a desolution of the oversaturated water. The pressure may drop, for example, if the usually sealed cavern is reopened for maintenance works, thus lowering the pressure to atmospheric pressure. Degassing is also caused by the enormous heat influx from stored radioactive waste, which lowers the solubility limit of the water. However, since the process of degassing is not treated in particular in this work, it is referred to the work of Jakobs (2004), for instance. On the other hand, a direct infiltration of a gaseous phase results in multiphase conditions (Figure 1.3(b)). The scope of this work is to address infiltration processes into fractured porous media, so this process will be further examined.

\subsection*{1.4.1 Gas Infiltration from Cavern}

If significant rates of gas are produced in the excavations and the gases migrate into the surroundings, two-phase conditions might evolve where potentially radioactive gases propagate through the host rock. Thus their release from the repository, the effect on groundwater movement as well as the transport of dissolved radionuclide have to be addressed appropriately. In the following, the origin of the necessary quantities of gases will be explained.

\textit{a) Corrosion of Metals}

After the storage site is encapsulated, present oxygen is continually consumed by aerobic corrosion of steel canisters or oxidation of pyrite contained in the host rock. It is estimated that such processes lead to anaerobic conditions within decades (Johnson 2002). Yang et al. (2007) carried out models at the Åspö underground laboratory in Sweden simulating geochemical and microbial consumption of dissolved oxygen after backfilling a high level radioactive waste repository. Numerical results show an abbreviation of the time needed to consume Oxygen from 27 years without organic matter in the bentonite to 4 years.
1.5. STRUCTURE OF THE THESIS

Under such anaerobic conditions, the oxidation of iron or steel can be formulated as

\[ 3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2. \] (1.1)

To guaranty the safety requirements for the installed canisters, numerous studies have been undertaken to estimate the corrosion rate of the applied container materials. Since the chemical reaction depends on the partial pressure of the present hydrogen, the temperature, the pH-conditions in the surroundings and the presence of water or humidity, a constant gas production rate over the vast timescale of such a storage site can not be expected. However, results from studies with buried archaeological artifacts indicate that comparable rates are likely to be sustained over thousands of years, so it is reasonable to assume an average gas production rate over a time frame of the order of the canister lifetime (Johnson et al., 2004). Nonetheless, any quantities should be treated with care since the different investigations were undertaken under diverse environments (different rock types, timescales etc.).

The range of the total gas volume that is produced per year varies between $100 - 150\text{m}^3/\text{yr.}$ (Smart, 2008) up to $240\text{m}^3/\text{yr.}$ (Johnson et al., 2004), and are thus high enough to have an impact on flow behaviour and phase composition in the saturated zone. Note that the corrosion of other alloys such as Zircalloy are not taken into account in the context of already high uncertainties of the steel corrosion rate, and because the total mass of the alloy is magnitudes smaller than that of steel in the emplacement tunnels.

b) Radiolysis of Water

Radiolysis denotes the cleavage of a chemical bond, similar to the process of photolysis, but influenced by ionizing radiation. The products of radiolysis are molecules, ions or radicals. In the presence of water, $\alpha-,\beta-$ and $\gamma-$radiation can produce hydrogen and oxygen, hydrogen peroxide and further short-lived radical species (Römpf et al., 1999). Since the canisters effectively shield radiation over their projected lifetime of 10 000 years, significant gas production will commence after canister breaching. However, a rough bounding estimate presuming that a thin water layer covers the complete fuel surfaces yields a production rate of only 5l per year, so radiolysis can be neglected in respect to the production rates due to corrosion (Johnson et al., 2004).

1.5 Structure of the Thesis

Adjacent to the introduction, Chapter 2 provides a general definition of the most important terms and the underlying principal physical concepts. Subsequently, an overview of the conceptual standard models in regards to multiphase flow is given, and the limitations of the approach is presented. The conceptual model of the new approach is introduced in the last section, and the conceptual benefits are discussed. Chapter 3 gives a basic derivation of the mathematical descriptions with respect to each of the conceptual models. Thus, the final governing equations as well as supplementing correlations are presented, and the numerical implementation bridges the gap to the simulatory part of this work. Here, microscale properties have to be implemented in the coarser framework, and test cases for the simulations are assembled in Chapter 4 followed by a discussion of the results. Chapter 5 gives a summary of this work and ventures a brief perspective.
Figure 1.3: Implementation of microscale data to gain macroscale simulative results, with figures taken from Joekar-Niasar et al. (2007); Nuske (2009).
Chapter 2

Model Concepts

2.1 Basic Concepts

As discussed in the previous chapter, the structure of porous media and fracture-matrix systems is particularly complex, and a detailed description of the geometry of the pore structure or fracture-matrix interfaces is not infeasible. In order to model such diverse structures, a continuum approach defined on a larger scale with averaged microscale properties is necessary. The averaging process generates new macroscale properties such as volume-based saturation or fluid-dependent relative permeability are generated, and microscale discontinuities can no longer be identified.

2.1.1 Definitions

2.1.1.1 Scales

Theoretically, most physical processes or properties are based on attributes or interactions of single molecules on a very small scale, denoted in this work as the molecular scale. To examine interactions caused by the dipolar moments of molecules, for example, incredibly large numbers of molecules would have to be considered, since 1g of pure water contains over $10^{22}$ molecules! Thus, it is more common to use a statistical approach,

![Figure 2.1: Fractures on different lengthscales (from Silberhorn-Hemminger (2002)).](image-url)
where molecular attributes are upscaled to fluid properties such as density, viscosity, or interfacial tensions. Since in such a microscale scope the explicit description of molecules vanishes, physical processes which result from molecular interaction have to be described with new properties such as diffusion or heat transfer coefficients. The microscale is the largest scale where a clear spatial separation of fluid phases can be detected, and where clear interfaces between the fluids are present. Flow in porous media can be described on this scale by the NAVIER-STOKES equations for which the exact structure of the solid surfaces needs to be described. For large systems, a larger or coarser scale is needed for the description flow in porous media, what requires another continuum step towards a macroscale.

An averaging procedure over a representative elementary volume (REV) (Bear, 1972) introduces macroscale parameters (see the following sections), as well as constitutive relationships (Chapter 2.1.2) or even new mathematical equations (Chapter 2.1.3). Originating from the inability to solve the real underlying phenomena, Bear referred to them as “parameters of ignorance”, and some of the associated problems are addressed in Chapter 2.2.3.

On the one hand, the size of the REV must be large enough to avoid undesired fluctuations of, for example, grain size distribution which varies the porosity, but on the other hand, its resolution should still be small enough to unravel dependencies of the entire flow domain, for example fractures. While these limits can be defined for homogeneous media using the procedures presented in Bear (1972), it is much more complex with regards to fracture-matrix systems because of the diverse length scales of the heterogeneities (see Nuske (2009); Jakobs (2004), Figure 2.1).

2.1.1.2 Phases $\alpha$ – Wetting and Non-Wetting Fluids

A phase denotes matter with a homogeneous chemical composition and uniform physical properties. Under multiphase conditions, the phases are separated by an interface across
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Non-wetting phase

\[
\theta > 90^\circ
\]

Wetting phase

\[
\theta < 90^\circ
\]

Figure 2.3: Contact angle of different phases (Wolff, 2008).

which discontinuities in the material properties exist. Phases may be differentiated according to their state of matter (solid, fluid, or gaseous), yet phase changes occur due to changes of the conditions, e.g. a pressure drop. Based on their chemical polarity, two fluids may be immiscible on the microscale, thus creating a clear interface between the single phases leading to a pressure difference (see 2.1.2.1). Since there is no interface between different gases, they are completely mixed within one phase.

With respect to the solid matrix, the phases (\( \alpha \)) may be classified as wetting (\( w \)) or non-wetting (\( n \)) phases. Under natural subsurface conditions, the solid matrix is usually polar (which may not hold for technical applications such as the hydrophobic diffusion-layer in fuel cells), and thus the fluid with the higher polarity is more strongly attracted. This behaviour is represented by the contact angle \( \theta \) between the fluid-fluid interface and the solid surface, where the fluid with an acute boundary angle (\( \theta < 90^\circ \)) is referred to as the wetting fluid.

Throughout this thesis, the term “phases” is only used for the fluids, air and water in specific, while the solid phase is denoted as the “solid matrix”. “Two-phase conditions” in this thesis therefore prevail if two fluid phases exist in a porous medium, the underlying third phase.

2.1.1.3 Components \( \kappa \)

In real systems, phases are neither perfectly separated nor absolutely insoluble. Therefore, every phase consists of different chemical constituents which are present in the system, for example dissolved ions in saline water. Considering complex systems, we rather use the concept of components which are chemically independent constituents (Atkins and De Paula, 2006). The number of components \( \kappa \) in a system represents the minimum number of independent constituents for the description of the phase composition. It depends on the conceptional model which chemical species or mixtures are grouped together as one component: Air, for example, can on the one hand be treated as one component if solubility effects of air in water is the point of interest. On the other hand, air is a mixture of several components (nitrogen, oxygen, argon etc) whose composition defines, for example, the partial pressure. The composition of the phases is quantifiable by using the expression of mass fractions \( X^\alpha_\kappa \), which is defined as the mass of a component over the total mass of the phase. Obviously, the sum over all components
in a phase must equal one:
\[
\sum_{\kappa} x_{\kappa} = 1 \quad \text{for all components } \kappa = \kappa 1, \kappa 2, \ldots \tag{2.1}
\]

However, if we are interested in the actual number of molecules with disregard to their masses, we can make a transition to mole fractions, describing the number of moles of the component \( \kappa \) in phase \( \alpha \):
\[
x_{\kappa} = \frac{X_{\kappa}}{M_{\kappa}} \tag{2.2}
\]

\( M_{\kappa} \) denotes the mass of one mole of a component and corresponds to the molecular mass of the substance. Like mass fractions, the mole fractions sum up to one,
\[
\sum_{\kappa} x_{\kappa} = 1 \quad \text{for all components } \kappa = \kappa 1, \kappa 2, \ldots \tag{2.3}
\]

Throughout this work, equations are intended to be as general as possible, thus components are generally denoted as \( \kappa \). However, to improve readability, whenever the components have to be distinguished, the superscripts \( A \) and \( W \) for the components \( \text{air} \) and \( \text{water} \) are used rather then \( \kappa 1, \kappa 2, \ldots \), because a two-phase system of water and air is regarded.

### 2.1.1.4 Porosity \( \phi \)

The concept of an REV requires, among other parameters, a minimum Volume \( V_0 \) to obtain a unique, non-oscillating value for the ratio \( \phi \) of pore volume \( V_{\text{pore}} \) to total volume \( V_{\text{total}} \). This gives the a definition of porosity:
\[
\phi = \frac{\text{Volume of pore space within the REV}}{\text{Total Volume}} = \frac{V_{\text{pore}}}{V_{\text{total}}} \tag{2.4}
\]

In most cases, parts of the pore space is not available for fluid flow since, since not all pores are connected. Therefore, a decreased value \( \phi_{\text{eff}} \) may be used for the description of fluid flow. In addition, the solid phase may change with temperature or pressure variations. Clay, for example, is capable of swelling or shrinking depending on water yield, hence porosity changes with soil saturation. However, the solid phase, and thus porosity, is assumed to remain constant in this work.

In fracture voids, porosity is expectably equal to one. As discussed in Chapter 1, spatial variations of fracture aperture are significant, but ought to be averaged out on the REV-scale. For the numerical model, a single fracture needs to be incorporated in the model framework of larger grid elements, so an upscaling approach gets necessary. In addition, as discussed in Chapter 1, fractures exist on a variety of lengthscales. From the modeling perspective, complex networks of discrete fractures were transferred to a concept of fractured zones or water-conducting features (Figure 2.4). Those areas represent active flow subsystems with considerably higher porosity than the surrounding rock matrix. Thus, if the term “fracture” is used in the following, it may also refer to a fracture zone. The real fracture aperture of several connected single fractures is, therefore, represented by an adjusted artificial porosity of a fracture zone.
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Figure 2.4: Hydrogeological and numerical conceptual models for fractures (Coborn et al., 1994).

2.1.1.5 Saturation

Within the REV, it is not feasible to preassume the exact spatial distribution of fluid phases or the pore matrix, but the ratio of their volumes is taken into account instead. Therefore, new system parameters such as effective saturation are introduced which do not exist below the REV-scale. Under multiphase conditions, each phase can occupy a certain ratio of pore space, which can be written as:

\[ S_\alpha = \frac{\text{volume of phase } \alpha \text{ in REV}}{\text{volume of pore space in REV}} = \frac{V_\alpha}{V_{\text{pore}}} \]  \hspace{1cm} (2.5)

The averaging process to the REV-scale as shown in Figure 2.5 assumes that the pore space in the REV is completely filled by all phases \( \alpha \) combined, which determines the following supplementary constraint:

\[ \sum_\alpha S_\alpha = 1 \]  \hspace{1cm} (2.6)
Displacement processes between phases are referred to as between drainage or imbibition. If a non-wetting fluid moves into a porous medium which was initially saturated with the wetting phase, the saturation $S_w$ of the wetting fluid will gradually decrease. This drainage process may last until no further wetting fluid can be displaced, and a residual wetting saturation $S_{r,w}$ remains. If this displacement process is inverted (i.e., imbibition), the non-wetting saturation converges towards the residual non-wetting saturation $S_{r,n}$. Values of residual saturations depend on the pore geometry, the heterogeneity and the displacement process, but also on the number of drainage and imbibition cycles. In addition, the imbibition curve does not follow the same pathway as the drainage curve, therefore these processes are strongly hysteretic. Detailed discussions on the phenomenon of hysteresis and the underlying causes can be found in \textcite{Sheta1999, Helmig1997}.

Most material laws that are based on the saturation (see Chapter 2.1.2.1, 2.1.2.2) use the effective saturation $S_e$, where the saturation is adjusted by the residual values (see \textcite{Helmig1997}):

$$S_e(p_c) = \frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}}$$  \hspace{1cm} (2.7)

### 2.1.1.6 Permeability, Conductivity

Flow in porous media is slowed down by the solid matrix. To account for this friction, another macroscale parameter which is termed hydraulic conductivity $K_f$ was introduced by \textcite{HenryDarcy}. The ease with which water can propagate through the pore space or fractures is dependent on viscous forces of the fluid, as well as friction with the soil grains.

$$K_f = K \cdot \frac{\eta \alpha g}{\mu \alpha} . \hspace{1cm} (2.8)$$

Note that effects of the fluid and the solid matrix are disconnected, isolating the material parameter $K$ as solely a property of the porous medium, thus denoted as the intrinsic permeability. In general, the permeability is written in tensorial form because the porous medium is usually not homogeneous:

$$K = \begin{pmatrix} k_{xx} & k_{xy} & k_{xz} \\ k_{yx} & k_{yy} & k_{yz} \\ k_{zx} & k_{zy} & k_{zz} \end{pmatrix} . \hspace{1cm} (2.9)$$

The grains are naturally neither well-sorted nor of uniform shape, but rather in a layered configuration, thus the resistance to fluid flow varies with the spatial direction. This non-uniform permeability holds even stronger for fractures, caused by their genesis from well-defined stress tensors, as discussed in Chapter 1.2. However, the three dimensional orientation of soil grains as well as of fractures are not taken into account for the fundamental setups discussed in this thesis, thus from Chapter 4 on, the tensoral property of the permeability is neglected, using a uniform scalar permeability:

$$K = \begin{pmatrix} k_{xx} & 0 & 0 \\ 0 & k_{yy} & 0 \\ 0 & 0 & k_{zz} \end{pmatrix} \equiv K \ \text{ with } k_{xx} = k_{yy} = k_{zz} . \hspace{1cm} (2.10)$$
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Figure 2.6: Intermolecular forces of a fluid molecule within the fluid (a) and at the interface (b) [Römpp et al. 1999].

The predominance of certain flow directions within the fracture are nevertheless accounted for because a harmonic averaging technique is applied for the permeability

\[ K_{\text{average}} = \frac{n}{\sum_{i=0}^{n} \frac{1}{K_i}}. \] (2.11)

Hence, flow from the fracture over the fracture-matrix interface encounters higher resistance since it is increased by neighboring nodes of the matrix.

2.1.2 Constitutive Relationships

If two or more fluids are involved, further functional dependencies arise when describing fluid movement, fluid-solid interaction or interactions at fluid interfaces. To get these accessible on a REV-scale, constitutive relationships determine macroscale capillary pressure and relative permeability. Additional relationships are necessary for the new approach in Chapter 2.3.

2.1.2.1 Capillarity

Whilst molecules within a fluid are equally attracted by intermolecular forces (Figure 2.6 (a)), those forces are not balanced at an interface between the phases (Figure 2.6 (b)). Molecules near the interface are pulled back into the fluid, therefore fluids tend to minimize their surface under multiphase conditions.

If the phases are also in contact with a solid matrix, adhesion forces further influence the shape of the interface since molecules of the wetting phase are supplementarily attracted to the solid (see Fig 2.7). The change of the fluid interface towards a thermodynamic equilibrium (a minimum of the total energy of the system) results in a pressure difference at the interface, referred to as the capillary pressure:

\[ p_c = p_n - p_w, \] (2.12)

where \( p_n \) is the pressure of the non-wetting phase, and \( p_w \) denotes the pressure of the wetting phase. The Young-Laplace-equation relates the capillary pressure to the shape of
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\[ p_c = \frac{4\sigma \cos \theta}{d}, \quad (2.13) \]

where \( \sigma \) represents the interfacial tension, \( \theta \) the contact angle, and \( d \) the pore diameter. Equation (2.13) shows that any decrease of the diameter results in an increase of the capillary pressure. Such a decrease in occupied diameter occurs, for example, when a water-saturated soil is drained and the wetting phase retreats to smaller pores or fractures. The phenomenon of capillarity on the macroscale is therefore upscaled in standard approaches as a function of the saturation,

\[ p_c = p_c(S_w). \quad (2.14) \]

Of the numerous capillary pressure–saturation relationships which were developed in the last decades, those of Brooks and Corey (1964) and of Van Genuchten (1980) are most widely used. Both the Brooks-Corey and Van Genuchten formulation are related to the effective saturation \( S_e \) (equation (2.7)):

**Brooks-Corey:** \[ p_c(S_w) = p_d S_e^{1 \frac{n}{m}}; \quad \text{for} \ p_c \geq p_d \quad (2.15) \]

**Van Genuchten:** \[ p_c(S_w) = \frac{1}{\alpha} \left(S_e^{\frac{1}{m}} - 1\right)^\frac{1}{\gamma}; \quad \text{for} \ p_c \geq 0 \quad (2.16) \]

The parameters \( p_d \) and \( \lambda \) as well as \( n, m \) and \( \alpha \) are determined by fitting curves to experimental data. Examples are shown in Figure 2.8. The right axis intercept of the Brooks-Corey curve represents the parameter \( p_d \), denoted as entry pressure. This is the minimum pressure required to start a drainage process and can be seen as a useful material parameter to easily distinguish different materials. However, especially in fractures, the entry pressure is not observable that clearly.
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2.1.2.2 Relative Permeability

Under multiphase conditions (see Figure 2.9), a migrating phase might be hindered by the other phase, a process which changes the resistance to flow and thus the hydraulic conductivity. According to the separation principle described in Chapter 2.1.1.6, this hindering process is decoupled from general fluid properties as well as the resistance of grains. A relative permeability is therefore introduced to account for fluid-fluid interactions which are mainly a function of the saturation:

\[
K_f = K \cdot \frac{\alpha \cdot \mu_w}{\mu_a} \\
K_f = K \cdot k_{ra} \cdot \frac{\alpha \cdot \mu_w}{\mu_a}
\]

Figure 2.9: Fluid movement in porous matrix under singlephase (left) and under multiphase (right) condition.
\[ K_f = K \cdot k_{ra} \cdot \frac{\rho \alpha g}{\mu \alpha} \]  
\[ 0 \leq \sum_{\alpha=1}^{\text{\#phases}} k_{ra} (S_\alpha) \leq 1 \]

The extension of the relative permeability can be determined either mathematically (equation (2.19)) or experimentally, for example, by a pore network model that combines macroscale capillarity and empirical approaches. Both tortuosity, the elongation of pathways or change in flow velocities due to differing streamlines, may be regarded as well as the flow reduction caused by a reduced cross-section, which is in turn proportional to saturation. Generally, in case of an applied \textit{Van Genuchten} model, the theorem of \textit{Mualem} is used:

\[ k_{rw} = S_e \left[ 1 - \left( 1 - S_e^{\frac{1}{m}} \right)^m \right]^2 \]  
\[ k_{rn} = (1 - S_e)^{\frac{1}{2}} \left[ 1 - S_e^{\frac{1}{m}} \right]^{2m} \]

\subsection*{2.1.3 Flow in Porous Media: Darcy’s Law}

The first examinations of advective flow through porous media was done by French engineer \textit{Henry Darcy} in 1856. He found that the advective flow rate through a sand column is, in good approximation, linearly proportional to the gradient of the so-called hydraulic head \( \nabla h \):

\[ v = -K \frac{\partial \cdot g}{\mu \alpha} (\nabla h). \]  

The Darcy velocity \( v \) is a macroscopic quantity, which does not exist below the macroscale. The velocity within the pore channels is indeed higher (\( v/\phi \)). For modeling purposes, we use the formulation

\[ v = -K \frac{1}{\mu \alpha} (\nabla p - \rho g) \]  
\[ v_\alpha = -K \frac{k_{ra}}{\mu \alpha} (\nabla p_\alpha - \rho_\alpha g) \]

While the original \textit{Darcy} law was obtained for slow, laminar, linear flow of one phase, it is now regarded by consensus as a macroscale momentum equation (the derivation can be found in \textit{Hassanizadeh and Gray} (1980)). Using the relative permeability \( k_{ra} \) as a scaling factor, it is applied for multiphase flow (\textit{Helmig}, 1997) with the following assumptions:

- The momentum transfer between the phases caused by mass transfer is neglected.
- The momentum transfer by viscous shear within a phase is neglected. Newton’s law for an incompressible fluid is assumed for the viscous stress.
- The solid phase is rigid, and the no-slip condition prevails at the fluid-rock interphase.
- Due to the slow fluid velocities, inertial or cross coupling terms are ignored.
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Equivalents to Darcy’s law in fractures are discussed, for example, in Dietrich et al. (2005); Jakobs (2004). In this thesis, we use a Darcy-like approach for the fractures, where the parameters corresponding to the hydraulic conductivity are deduced using normalisation schemes for a statistical distribution of fracture aperture (Nuske, 2009). Compared to flow in porous media, fractures as active flow subsystems possess considerably higher conductivity and are thus subject to higher flow velocities.

2.1.4 Compositional Model

The terms phases and components are introduced at the beginning of this chapter, and mixing procedures or solubility effects of the components have already been mentioned. A spatial or temporal variance in the composition of the phases may cause mass transfer between the phases or diffusive flow evening out the concentration differences. However, the underlying physical and chemical processes for phase transitions or phase changes are manifold (e.g. chemical reactions and chemical equilibria, evaporation and condensation, changes of boundary conditions altering solubility etc.). Thus, it is only focused on diffusive mass transport and the thermodynamic states of equilibrium. Note that no mass transfer between the fluids and the solid matrix is taken into account in this work, so processes of sorption or matrix dissolution are disregarded.

2.1.4.1 Diffusion

As explained above, mixing procedures of the components affect the phase composition and may thus lead to concentration differences: Let us consider a large water bottle, for example, where the base is covered by coloured material such as copper sulfate. As parts of the solid phase go into solution, the colour front slowly propagates upwards through the water. This is a diffusive process which is caused on the molecular scale by random movement of the solute particles or molecules. As always, we are seeking a macroscale approach where complex particle movement is averaged and transferred to a larger scale in an Eulerian approach. The first major step was done by Adolf Fick, who treated diffusion similar to Fourier’s law for heat and Ohm’s law for electrical conduction (Cussler, 1997). Fick’s first law suggested a proportionality factor $D^\kappa$, called diffusion coefficient, to relate the diffusive flux $j^\kappa$ to the concentration gradient $\nabla c$:

$$j^\kappa = -D^\kappa \nabla c^\kappa$$

$$= -\varrho^\alpha D^\kappa \nabla X^\kappa$$

If we examine the diffusive process at an interface between two phases, mass conservation demands that the diffusive flux from one of the phases results in a diffusive flux of equal magnitude in the other phase, i.e. $j^A = -j^A$. However, if diffusive processes are overlain by chemical reactions or cumulative surfactants at the interface or other phenomena modulating the mass balance at the interface, this suggestion does not hold.

2.1.4.2 Equilibrium Laws for Fluids

Whenever change is induced on a real system, it undergoes kinetic processes until it achieves a state of equilibrium. As an example for such a process, we can consider a
bottle of carbonized water that is filled with additional pressure to increase the solubility of carbon dioxide in order to evoke an even fresher drinking experience. If we now open the bottle, the pressure drops to atmospheric level, and we can hear the fizzling noise of escaping gas: The pressure drop lowers the solubility of the gas in the water phase, leading to an evolution of a separated gaseous phase forming bubbles. Those kinetic processes as well as the correct thermodynamic description of the underlying change in the phase composition are hard to tackle. It thus became a common assumption to describe multiphase flow processes in a porous medium as a series of equilibrium states which can be addressed by simplified formulations following the laws of HENRY, RAOULT or DALTON. With regards to the bottle, we can regard the process as a series of partial pressure drops, each reaching an equilibrium state of composition, i.e. gas volume and thus water saturation while disregarding the actual kinetic process. The equilibrium assumption seems reasonable as long as the kinetic process is much faster than the flow velocities or temporal changes of the system - which may hold for porous medium, but certainly not for the water bottle.

Let us reconsider the closed water bottle at given temperature in equilibrium, the number of molecules that leave the water phase also enter it, therefore, the composition remains constant. The pressure above the liquid phase has converged to the so-called saturation vapor pressure which is a function of the substance and the temperature

\[ p_{\alpha,\text{sat}} = p_{\alpha,\text{sat}}(T). \]  

(2.24)

For pure substances as well as for most mixtures, such functions are well-defined and can be found in the literature. As an example for pure substances below boiling point, the ANTOINE equation may be chosen with the form

\[ \ln p = A - \frac{B}{C + T}, \]  

(2.25)

where \( A, B \) and \( C \) being material constants (Römpp et al., 1999).

a) **Dalton’s law**

In most natural cases, the substances of interest are not pure but mixtures of several components. If the components do not react with each other, DALTON’s law holds. This states that the sum of the pressures of all components equals to the total pressure of the gaseous mixture,

\[ p_\alpha = \sum_\kappa p^\kappa_\alpha. \]  

(2.26)

Here, \( p^\kappa_\alpha \) is the pressure of a component \( \kappa \) if it would fill the whole volume of the mixture by itself, denoted as the partial pressure. Thus, with the definition of equation (2.3), we get

\[ p^\kappa_\alpha = x_\alpha^\kappa p^\kappa_\alpha. \]  

(2.27)

b) **Raoult’s law**

The relationship between the vapour pressures of mixtures and their concentration was first examined by French chemist FRANÇOIS MARIE RAOULT in 1882. He describes the
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decrease in vapour pressure of a pure substance in a mixture by relating it to the mole fraction,

\[ p^\kappa_\alpha = x^\alpha p^\kappa_{\alpha,\text{sat}}. \] (2.28)

As discussed above, \( p^\kappa_{\alpha,\text{sat}} \) is the partial pressure of the pure substance which can be deduced for example from the ANTOINE-equation. However, RAOULT’s law is only valid for ideal solutions, which are highly diluted such that the dissolved substances have no significant effect on the vapour pressure and do not attract each other. For the scope of this thesis, this is applied to the amount of water dissolved in the non-wetting phase because it is expected to be considerably low.

c) Henry’s law

We have discussed the composition of the gaseous phase. The corresponding fractions within the liquid phase, however, cannot be addressed by a combination of RAOULT’s and ANTOINE’s law. Thus, we make use of the work of WILLIAM HENRY which dates back to 1803 and states that the solubility of gases in liquids is proportional to the partial pressure of the gas. As discussed in the example with the bottle of carbonized water, more gas goes into solution if the pressure rises. For ideal gases and ideally diluted solutions, meaning again low ranges of solute concentration and low pressure, a linear relationship is obtained,

\[ x^\kappa_\alpha = H^\kappa_\alpha p^\kappa_\alpha. \] (2.29)

The parameter \( H^\kappa_\alpha \) denotes the Henry coefficient which is strongly dependent on temperature. The ranges of validity of both HENRY’s law and RAOULT’s law are illustrated by Figure 2.10 where both approaches are compared with the real behaviour of a mixture. Note that both laws are also only valid if a state of equilibrium is already reached which may not valid for fast kinetic processes or states where one phase has completely disappeared (see section 2.3).

![Figure 2.10: Comparison of real mixture behaviour with RAOULT’s law and HENRY’s law.](image.png)
2.2 Conceptual Models for Multiphase Flow

Scientific models create an abstract of the usually very complex reality. Their main goal to describe all relevant processes and entities of a system has to be balanced with the necessity to reduce and simplify the considered system. In regards to hydrosystems, the degree of abstraction varies with scales, conditions and compositions, and need careful consideration. Yet computational performance has multiplied during the last decades, so more and more detailed and complex descriptions became both possible and handable. Anyway, the knowledge of the assumptions behind the conceptual models are crucial to bridge the gap between model and nature.

2.2.1 Two-Phase Model

To evolve the conceptual model for multiphase flow, we start with two phases within a porous media (Figure 2.11). It is first assumed that the phases are fully immiscible, and effects such as dissolution or sorption are neglected. However, since the displacement properties of both phases are coupled, dependencies and relationships have to be used to examine two-phase flow. The mathematical and numerical framework must be able to describe the phase properties, and the actual phase state: A subvolume can either be completely filled by one of the phases, or partially by both of them.

2.2.2 Two-Phase Two-Component Model

In contrast to the two-phase model described above, mass can be exchanged between the phases. Thus every phase is subdivided into several components (Figure 2.12), in our
case each phase consists of two components. Multicomponent models have to reproduce thermodynamic mixing processes and thus the composition of the phases, as well as their general spatial distribution and changes with time. However, proper kinetics of the mass exchange between the phases are most often ignored by assuming a reversible process that run through a series of equilibrium states. The actual non-static process is approximated by a series of quasi-static states. This so-called local thermodynamic equilibrium assumption may hold for slow processes which seem usual in porous media, but comes with the price of indispensable side-effects to account for non-static behaviour of real natural systems.

2.2.3 Shortcomings of the Discussed Approaches

As we have seen, the complex flow regime of multiphase flow and multicomponent transport is depicted by an extension of Darcy’s Law (see Chapter 2.1.3) with the help of phase- or component-dependent constitutive relationships. This abstraction gives rise to the following concerns:

a) Application of Darcy’s Law

While the original empirical relationship was found examining singlephase flow through homogeneous porous medium, it is now used in its extended version for complex regimes such as heterogeneous multiphase flow. The only conceptual change to the Darcy model is an extension by the relative permeability and the adaption of the parameters to the varying phase composition:

\[ \mathbf{v}_\alpha = -K \frac{k_{r\alpha}}{\mu_{\alpha}} (\nabla p_\alpha - \rho_{\alpha}g) \]

Thus the only driving forces for advective flows which are explicitly included are pressure differences and gravity. The relative permeability function has to account for all other driving forces, for example cross coupling of fluids (which means \( \mathbf{v}_n = \mathbf{v}_n(\mathbf{v}_w) \)) as well as interfacial forces. As Hassanizadeh and Gray (1993) put it, the extension of Darcy’s law to complex systems seems analogous to applying the ideal gas law to real gases by an increasingly complex ideal gas constant \( R \), for example. They rather suggest to find a general formulation for real gases, that can in turn be simplified to the ideal gas law,

\[ PV = nRT. \quad (2.30) \]

Such an approach, the derivation of governing equations for multiphase flow which can then be simplified to the extended Darcy method, will be presented in Chapter 2.3

b) Macroscale Capillarity

As described in Chapter 2.1.2.1 capillarity on the microscale can be mathematically described using interface and fluid properties. On the REV-scale, however, standard approaches use dependencies on volume-averaged properties such as saturation in place of interface-related parameters. This approach is not able to depict hysteresis: Capillarity on the macroscale is not only dependent on the state, but also on the process (whether the soil is drained or imbibed) and the history of the soil (whether the soil is primarily drained
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or drainage-imbibition cycles are regarded). Thus, capillary pressure varies between a certain range for a given saturation, as is shown in Figure 2.13. Additionally, several other inconsistencies are discussed in Hassanizadeh and Gray (1993).

As an example, capillary pressure is used to conjoin the averaged pressure of the phases, by using the supplementary constraint in equation (2.12). Whilst state equations for the phases predict a dependence on the density of the phases (i.e. $p_\alpha = p_\alpha(\varrho, T)$), usual capillary pressure functions solely regard the phase saturation as a parameter. Furthermore, let us consider a porous media in equilibrium, where both phases are subject to static pressures. Thus equation (2.12) reduces to the form

$$p_c = \varrho_n g - \varrho_w g,$$

which means that the capillary pressure at equilibrium is independent from saturation, soil type or other properties. Thus the question arises whether a macroscale capillary pressure that is only dependent on saturation is a too simplified approach.

c) Relative Permeability

As already discussed, the relative permeability $k_{ra}(S_w)$ is used to alter the single-phase permeability in the presence of another phase. Although this parameter is not derived from a physical upscaling process, this empirical scaling factor has to account for a combination of all coupling effects under multiphase conditions. In addition, the relative permeability function is also hysteretic, and investigations indicate dependencies on a list of other parameters (Niessen and Hassanizadeh, 2009). Avraam and Payatakes (1995) summarize that relative permeability is also dependent on the capillary number, the viscosity ratio, wettability characteristics expressed by the equilibrium contact angle $\theta$, a coalescence factor, and discovered a strong correlation with the corresponding flow mechanisms:

$$k_{ra} = k_{ra}(S_\alpha; Ca, \tau, \cos \theta, Co, \text{saturation history}, ...).$$

(2.32)
d) Mass Transfer
Mass transfer between the phases can only take place across the fluid-fluid interface. However, since the interfacial area is not known as a parameter, current model concepts make strong assumptions regarding kinetic mass transfer. The approach discussed in Chapter 2.2.2 uses the assumption of a local thermodynamic equilibrium, other methods are reviewed in Niessner and Hassanizadeh (2008b). However, although the interfacial area is obviously important to examine fluxes over the interface, none of those approaches uses interfacial area as a parameter. Thus, no physically motivated description of kinetic mass exchange is possible.

2.3 The new Concept including Interfacial Area

Figure 2.14: Conceptual model of miscible two-phase flow with proper kinetic mass transfer.

To overcome the shortcomings of the standard models, Hassanizadeh and Gray (1980, 1990, 1993) proposed a fundamental approach based on physical principles instead of extensions to an empirical correlation. The concept provides equations that account for traditionally inaccessible phenomena, but can still be reduced to Darcy’s Law and standard approaches which prove to be particularly stable for slow processes, for example. The changes of the conceptual model with regards to the standard models are as follows:

- The parameter held responsible for hysteretic behaviour of multiphase flow, the capillary pressure, is not solely calculated from static experimental curves. Instead, a general constitutive correlation including all the relevant macroscale material properties is employed. An additional balance of specific interfacial area yields for the phenomena of capillarity as an macroscale primary variable.

- The interfaces between the phases are also taken into account. This includes balancing at the interface, as well as considering the total area of the interface as a variable determining the processes. Note that the interface between the solid matrix and the fluids is not included in this work, so sorptive effects are neglected.
• A thermodynamic equilibrium is not presumed, so the new approach is not limited to problems where this assumption holds. Moreover, it is expected that simulations better approximate the natural behaviour of non-equilibrium if thermodynamic considerations are fully included.

The changes to the standard approach can be best described following the mathematical development of the governing equations, which is done in Chapter 3.3.

### 2.3.1 Constitutive Relationships

By extending general balances, new relationships arise for the new concept. Following the principal idea behind the work of Hassanizadeh and Grey, the new correlations are physically motivated and solely based on primary variables. They are meant to represent the complex behaviour of two-phase flow, without the need for artificial fitting or correlation parameters.

#### 2.3.1.1 Relative Permeability $k_{r\alpha}$

Through exploitation of thermodynamic principles, Hassanizadeh and Gray (1993) derived equations of motion, which directly lead to expressions for the phase velocities. In comparison with the multiphase formulation of Darcy’s law, additional dependencies besides the pressure gradient and gravity are observable, while the artificial parameter of the relative permeability reduces to the saturation squared. The coefficients defining these additional terms, however, are only dependent on the saturation and specific interfacial area (besides density and temperature, in the general case). This leads to the conjecture that a comprehension of interfacial area redundantizes complex functions of the relative permeability (Equations (2.19)). Instead, the factor $S_\alpha^2 = k_{r\alpha}$ is used, which is displayed in comparison with the traditional function in Figure 2.15.

#### 2.3.1.2 Specific Interfacial Area $\alpha_{wn}$

Usually, the macroscale capillary pressure is derived from external curves originating from equilibrium experiments, which face problems under dynamic conditions. Substantial derivation of thermodynamics (Hassanizadeh and Gray, 1993) as well as pore network models (Joekar-Niasar et al., 2007) show that macroscale capillarity depends on the saturation and on the specific interfacial area $\alpha_{wn}$, i.e. the interfacial area per representatory elementary volume. Being of biquadratic nature, this new functional relationship $p_c(S_w, \alpha_{wn})$ does not have to be unique for all given saturations and interfacial area (Fig 2.16(a)). The inverse relationship, in contrast, is able to assign capillary pressure and saturation to a specific interfacial area function, $\alpha_{wn}(S_w, p_c)$ which is single valued. Joekar-Niasar et al. (2007) generated the data points for porous media computationally using pore-network models, and obtained workable correlations by fitting bi-quadratic functions to the reading points with the coefficients

$$\alpha_{wn}(S_w, p_c) = a_{00} + a_{10} \cdot S_w + a_{01} \cdot p_c + a_{11} \cdot p_c \cdot S_w + a_{20} \cdot S_w^2 + a_{21} \cdot p_c^2.$$  \hspace{1cm} (2.33)
Concerning the fracture-matrix systems of in this work, a dataset by Joekar-Niasar represents the properties of the matrix.

Alternative data is necessary with regards to the fracture. These correlations are developed by Nuske (2009), who investigates fractures with statistically developed aperture sizes. In his work, different aperture fields with same statistic properties were numerically studied: The microscale fracture is periodically drained and imbibed by altering the boundary pressures. For each pressure configuration, saturation and interfacial area is determined. Main drainage as well as main imbibition bounding curves are extracted from the data points, as well as a biquadratic function defining the specific interfacial area, as shown in Figure 2.16(b).

If typical plots of the interfacial area surface (see Figure 2.17) are projected on a $p_c - S_w$ plane, the usual hysteresis loop is regained. Here, all possible states are restricted by two border functions, a primary drainage $p_c^{\text{drain}}$ and a primary imbibition $p_c^{\text{imb}}$ curve, representing the static behaviour of an initially fully saturated or unsaturated medium.

2.3.1.3 Production/ Destruction Rate of Specific Interfacial Area $E_{wn}$

If we balance interfaces within our modeling volume, interfacial area may propagate in and out of the subdomain, may be created because of temporal change of the variables determining interfacial area or can be produced or destroyed by mass exchange between the phases. Imagine, for example, a pot filled with water. Now thermal energy causes a phase shift of the water within the control volume towards the gas phase (i.e. boiling), see Figure 2.18. Gas bubbles almost spontaneously evolve, creating interfaces between the liquid and the gaseous water phase.
(a) Interfacial area surface for the soil matrix (Joekar-Niasar et al., 2007).

(b) Interfacial area surface for the fracture (Nuske, 2009).

Figure 2.16: Interfacial area surfaces.
2.3. THE NEW CONCEPT INCLUDING INTERFACIAL AREA

Figure 2.17: Specific interfacial area of the fracture and corresponding bounding curves \cite{Nuske2009}.

Obviously, these production or destruction rates, denoted as $E_{wn}$ in the following, are crucial to any balance of interfaces. At this point, there are no experimental data available concerning this rate, thus Niessner and Hassanizadeh \cite{Niessner2008a} proposed the following: A porous medium which is fully saturated with one phase does not possess any fluid interfaces, thus $a_{wn} = 0$. As soon as the other phase infiltrates, interfaces are created. This production is increased the faster the phase gets removed (i.e. the faster the change in the phase saturation), hence $E_{wn} \propto \left( \frac{\partial S_w}{\partial t} \right)$. At some point during the invasion process, production of interfacial area must cease, and is to be reverted because at the end of the displacement process, one-phase conditions recur, i.e. $a_{wn} = 0$. So throughout a complete displacement process, the rate of change of interfacial area $E_{wn} > 0$ ($a_{wn} = 0$) starts with a positive value, reaches a ridge value of $a_{wn}$ (with $E_{wn} = 0$) and settles down towards $a_{wn} = 0$ with a negative value $E_{wn} < 0$. Following this characteristic, a further parameter characterizing the magnitude of change as well as differentiating between production and destruction rate becomes necessary. Being separated from changes in the saturation, it is called the static part of the production rate, $e_{wn}$ which is derived in the following.

2.3.1.4 Static Production Rate of Specific Interfacial Area $e_{wn}$

In the absence of experimental data, a formulation of $e_{wn}$ is gained mathematically by analyzing equation \eqref{eq:3.33c}. We assume that advective fluxes of interfaces play a minor part for the distinction between production and destruction. Reformulation of the simplified
balance equation thus yields:

\[ e_{wn}(S_w, p_c) \cdot \frac{\partial S_w}{\partial t} = \frac{\partial a_{wn}}{\partial t} \]  
\[ e_{wn}(S_w, p_c) = \frac{\partial a_{wn}}{\partial p_c} \cdot \left( \frac{dp_c}{dS_w} \right)_{\text{process}} + \frac{\partial a_{wn}}{\partial S_w}, \]

where \( \left( \frac{dp_c}{dS_w} \right)_{\text{process}} \) stands for the derivative of the actual path along the drainage or imbibition cycle, whereas all other derivatives can be calculated analytically using the general interfacial area function \( a_{wn}(S_w, p_c) \) (Chapter 2.3.1.2). As long as \( \left( \frac{dp_c}{dS_w} \right)_{\text{process}} \) cannot be deduced otherwise, Niessner and Hassanizadeh (2008a) propose to interpolate the production rate of the process path of interest between the two bounding solutions of the primary drainage and primary imbibition process (see Figure 2.19(a)). Within the wide range of possible saturations modeled in this work, numerical problems arise in areas with
steep derivatives of the Van Genuchten-bounding curves. These occur in areas near the residual saturations $S_{w, res}$ and $S_{n, res}$. An interpolation via saturation implies that all values $S_w, S_{w, drain}, S_{w, imb}$ may lie near residual, each producing steep slopes, and leads thus to a predominance of the term $\left( \frac{dp_c}{dS_w} \right)_{process}$. It is hence supposed to interpolate known $\varepsilon_{wn}$-values over capillary pressure, as shown in Figure 2.19(b), because then only the real saturation $S_w$ may lie within the range of the residual saturations. The correct static production or destruction rate is thus interpolated between $\varepsilon_{wn, drain}$ and $\varepsilon_{wn, imb}$ according to

\[
\varepsilon_{wn} = \frac{1}{(p_{c, drain} - p_{c, imb})} \left( \varepsilon_{wn, drain} \cdot (p_{c} - p_{c, imb}) + \varepsilon_{wn, imb} \cdot (p_{c, drain} - p_{c}) \right) \quad (2.36)
\]
Chapter 3
Mathematical and Numerical Model

3.1 Balance Equations for Two-Phase-Flow - $2p$

In general, multiphase flow can be described by balance equations for mass, momentum and energy ([Helmig, 1997]). Figure 3.1 shows a control volume with a solid phase and two fluid phases. To briefly derive a mass balance, we first consider a change of mass within the system over time, which yields a storage term denoted by $M$. Mass may furthermore be transported over the boundary, referred to as the flux term $A$. Sources or sinks within the control volume are denoted by $Q$. Because we disregard mass exchange between the phases and the solid matrix, mass exchange $I$ can only occur over the interface between the phases. In the need of mass conservation, the mass balance can be formulated for all phases $\alpha$:

$$M_\alpha + A_\alpha = I_\alpha + Q_\alpha \quad (3.1)$$

Fluid phases within the control volume $\Omega$ comprise the mass $\int_\Omega S_\alpha \phi_\alpha d\Omega$. However, the phases occupy only the available pore space $\phi$, so the storage term $M_\alpha$ can be formulated
as follows:

\[ M_\alpha := \frac{\partial}{\partial t} \int_\Omega \phi S_\alpha \varrho_\alpha d\Omega \]  

(3.2)

We get the flux term \( A_\alpha \) over \( \Omega \) by applying the Gauss integral theorem yielding the flows over the boundary \( \Gamma \):

\[ A_\alpha := \int_\Omega \nabla \cdot (\phi \varrho_\alpha \mathbf{v}_\alpha) d\Omega \]  

(3.3)

In multiphase models without components, exchange between the phases is neglected, because the phases are expected to be immiscible:

\[ I_\alpha := \int_\Omega i_\alpha d\Omega = 0 \]  

(3.4)

Production or withdrawal due to external sources or sinks is given as follows:

\[ Q_\alpha := \int_\Omega q_\alpha d\Omega \]  

(3.5)

Inserting the terms (3.2), (3.3), (3.4) and (3.5) into equation (3.1) gives:

\[ \frac{\partial}{\partial t} \int_\Omega \phi S_\alpha \varrho_\alpha d\Omega + \int_\Omega \nabla \cdot (\phi \varrho_\alpha \mathbf{v}_\alpha) d\Omega = \int_\Omega q_\alpha d\Omega \]  

(3.6)

Equation (3.6) can also be written in differential form as

\[ \frac{\partial (\phi S_\alpha \varrho_\alpha)}{\partial t} + \nabla \cdot (\phi \varrho_\alpha \mathbf{v}_\alpha) = q_\alpha . \]  

(3.7)

Generally, the term \( \mathbf{v}_\alpha \) has to be expressed by a solution of the NAVIER-STOKES equation, which describes the flow on the pore scale. However, within the concept of an REV, Darcy’s law may be used as a macroscale momentum equation. Replacing \( \mathbf{v}_\alpha \) with equation (2.21b), equation (3.7) results in:

\[ \frac{\partial (\phi S_\alpha \varrho_\alpha)}{\partial t} - \nabla \left( \frac{\varrho_\alpha}{\mu_\alpha} k_{\alpha} \frac{k_{w}}{\mu_w} K (\nabla p_\alpha - \varrho_\alpha g) \right) = q_\alpha \]  

(3.8)

With the additional constraints \( p_n = p_w + p_c \) and \( S_n + S_w = 1 \), the unknowns for which the equation system has to be resolved are reduced to one saturation and one pressure, therefore two mass balance equations are sufficient to close the system. As was discussed in Chapter 2.1.1.4, porosity is kept constant, and may be thus excluded from the partial expression of the storage term. We thus conclude for both phases

\[ \phi \frac{\partial (\varrho_w S_w)}{\partial t} - \nabla \cdot \left( \frac{\varrho_w k_{rw}}{\mu_w} K \nabla p_w - \varrho_w g \right) = q_w , \]  

(3.9a)

\[ \phi \frac{\partial (\varrho_n S_n)}{\partial t} - \nabla \cdot \left( \frac{\varrho_n k_{rn}}{\mu_n} K \nabla p_n - \varrho_n g \right) = q_n , \]  

(3.9b)
3.2 Balance Equations for Components - 2p2c

A résumé of the dominant underlying assumptions of equations \((3.9)\) includes

- No mixture or solution of the two fluid phases.
- Mass transfer between fluids and solid disregarded.
- Porosity is kept constant.
- Velocity of the phases is resolved by Darcy’s law.
- Dispersion is not taken into account.

### 3.2 Balance Equations for Components - 2p2c

If the solubility among the phases cannot be neglected, an expression for the components \(\kappa\) has to be implemented into the pure twophase balance equation \((3.1)\):

\[
M^\kappa_\alpha + A^\kappa_\alpha = I^\kappa_\alpha + Q^\kappa_\alpha
\]  

The single terms are set up as for the 2p-model, but extended by mass fractions \(X^\kappa_\alpha\). Hence the number of unknowns in a twophase two-component system is enhanced by additional mass fractions. However, the corresponding mass fractions can be calculated with the additional supplementary constraint \(\sum \kappa X^\kappa_\alpha = 1\). In order to set up the mass balance, we have to balance all components in the respective phases. For a twophase system consisting of two components, this yields four balance equations. If there are solubility effects, for example, mass is transferred over the interface, and the mass exchange \(I^\kappa_\alpha\) cannot be neglected. Several means to determine mass exchange are discussed in Helmig (1997); Niessner and Hassanizadeh (2008b).

Most standard models assume that the time scale of mass transfer is large compared to the time scale of flow, which means that the composition of the phases is at a local thermodynamic equilibrium. Mass fractions are therefore directly calculated with thermodynamic laws for equilibrium states, which is discussed in Chapter 2.1.4.2 justified by considerably low solubility limits. This equilibrium assumption reduces the unknown state variables to two, thus a reduction to two equations is possible. The total mass of a component is balanced by a summation over equal components, which eliminates the mass exchange terms \(I^\kappa_\alpha\). To enhance readability, components \(A, W\) and phases \(w, n\) are used instead of general expressions:

\[
W : \quad \phi \frac{\partial}{\partial t} \left( \tilde{\varrho}_w S_w X^W_w + \tilde{\varrho}_n S_n X^W_n \right) - \nabla \cdot \left( \tilde{\varrho}_w X^W_w \vec{v}_w + \tilde{\varrho}_n X^W_n \vec{v}_n \right) - \nabla \cdot \left( j^W_w + j^W_n \right) = q_w
\]  

\[
A : \quad \phi \frac{\partial}{\partial t} \left( \tilde{\varrho}_w S_w X^A_w + \tilde{\varrho}_n S_n X^A_n \right) - \nabla \cdot \left( \tilde{\varrho}_w X^A_w \vec{v}_w + \tilde{\varrho}_n X^A_n \vec{v}_n \right) - \nabla \cdot \left( j^A_w + j^A_n \right) = q_n
\]
with

\[ \bar{v}_w = -K \frac{k_{rw}}{\mu_w} (\nabla p_w - \bar{g}_w g) \] (3.12)

\[ \bar{v}_n = -K \frac{k_{rn}}{\mu_n} (\nabla p_n - \bar{g}_n g) \] (3.13)

\[ p_c = p_n - p_w \] (3.14)

\[ S_w + S_n = 1 \] (3.15)

\[ X^W_w + X^A_w = 1 \] (3.16)

\[ X^W_n + X^A_n = 1 . \] (3.17)

Note that the mass balance contains macroscale diffusion \( j_\alpha^e \) within the flux term \( A_\alpha^e \), which can be calculated by a Fick’ian diffusion expression:

\[ j_\alpha^e = -\bar{D}_\alpha^e \bar{\rho}_\alpha \nabla \bar{X}_\alpha^e , \] (3.19)

where \( \bar{D}_\alpha^e \) are macro-scale diffusion coefficients. On the macroscale, structural properties of porous media are described by the tortuosity, which accounts for the elongation of the path lengths due to convolutions, and porosity. Microscale diffusion coefficients \( D_\alpha^e \), which can be found in the literature, are thus upscaled with dependencies on saturation, porosity and tortuosity (Helmig, 1997):

\[ \bar{D}_\alpha^e = \phi \tau S_n D_\alpha^e . \] (3.20)

Here, \( D_\alpha^e \) is the real, microscale diffusion coefficient (see Atkins and De Paula (2006); Cussler (1997)) and the tortuosity \( \tau \) can be gained, for example, through the model of Millington and Quirk (1961):

\[ \tau = \phi \frac{1}{3} S_n^{2/3}. \] (3.21)

To conclude the most important assumptions of equations (3.11):

- Solution and phase mixtures are treated by equilibrium laws (see Chapter 2.1.4.2).
- Mass transfer between fluids and solid disregarded.
- Porosity is kept constant.
- Velocity of the phases is resolved by Darcy’s law.
- Dispersion is not taken into account.
- Diffusion is resolved by an Fick-ian expression.
3.3 Balance Equations including Interfacial Area - \textit{2p2cia}

3.3.1 Mass and Momentum Equations

To introduce the new approach including interfacial area, the derivation of the basic balance equations is discussed in more detail than the standard approaches in the previous chapters. In a two-phase system, both phases and the fluid-fluid interface can be balanced with six mass and three momentum balance equations.

1a) Mass balances for phase components (here for $\kappa \cdot \alpha = 4$ equations):

$$\frac{\partial (\phi S_w \bar{\rho}_w X^\kappa_w)}{\partial t} + \nabla \cdot (\phi S_w \bar{\rho}_w \bar{X}^\kappa_w \bar{v}_w) - \nabla \cdot (\phi S_w \bar{j}^\kappa_w) = \bar{\rho}_w \bar{Q}_w + \frac{1}{V} \int_{A_{wn}} [\bar{\rho}_w X^\kappa_w (\bar{v}_{wn} - \bar{v}_w) + \bar{j}^\kappa_w] \cdot \bar{n}_{wn} \, dA \quad (3.22)$$

$$\frac{\partial (\phi S_n \bar{\rho}_n \bar{X}^\kappa_n)}{\partial t} + \nabla \cdot (\phi S_n \bar{\rho}_n \bar{X}^\kappa_n \bar{v}_n) - \nabla \cdot (\phi S_n \bar{j}^\kappa_n) = \bar{\rho}_n \bar{Q}_n + \frac{1}{V} \int_{A_{wn}} [\bar{\rho}_n X^\kappa_n (\bar{v}_{wn} - \bar{v}_n) + \bar{j}^\kappa_n] \cdot \bar{n}_{wn} \, dA \quad (3.23)$$

1b) Momentum balance for phases (2):

$$\frac{\partial (\phi S_w \bar{\rho}_w \bar{v}_w)}{\partial t} + \nabla \cdot (\phi S_w \bar{\rho}_w \bar{v}_w \bar{v}_w) - \nabla \cdot (\phi S_w \bar{T}^\kappa_w) = \frac{1}{V} \int_{A_{wn}} [\bar{\rho}_w \bar{v}_w (\bar{v}_{wn} - \bar{v}_w) + \bar{t}^\kappa_w] \cdot \bar{n}_{wn} \, dA \quad (3.24)$$

$$\frac{\partial (\phi S_n \bar{\rho}_n \bar{v}_n)}{\partial t} + \nabla \cdot (\phi S_n \bar{\rho}_n \bar{v}_n \bar{v}_n) - \nabla \cdot (\phi S_n \bar{T}^\kappa_n) = \frac{1}{V} \int_{A_{wn}} [\bar{\rho}_n \bar{v}_n (\bar{v}_{wn} - \bar{v}_n) + \bar{t}^\kappa_n] \cdot \bar{n}_{wn} \, dA \quad (3.25)$$

2a) Mass balances for \textit{wn}-interface components (2):

$$\frac{\partial (\bar{\Gamma}_{wn} \bar{X}^\kappa_{wn} a_{wn})}{\partial t} + \nabla \cdot (\bar{\Gamma}_{wn} \bar{X}^\kappa_{wn} a_{wn} \bar{v}_{wn}) - \nabla \cdot (\bar{j}^\kappa_{wn} a_{wn}) = \frac{1}{V} \int_{A_{wn}} [\bar{\rho}_w X^\kappa_w (\bar{v}_w - \bar{v}_{wn}) + \bar{j}^\kappa_w + \bar{\rho}_n X^\kappa_n (\bar{v}_n - \bar{v}_{wn}) + \bar{j}^\kappa_n] \cdot \bar{n}_{wn} \, dA \quad (3.26)$$

2b) Momentum balance for \textit{wn}-interface (1):

$$\frac{\partial (\bar{\Gamma}_{wn} \bar{v}_{wn} a_{wn})}{\partial t} + \nabla \cdot (\bar{\Gamma}_{wn} \bar{v}_{wn} a_{wn} \bar{v}_{wn}) - \nabla \cdot (\bar{T}^\kappa_{wn} a_{wn}) = \frac{1}{V} \int_{A_{wn}} [\bar{\rho}_w \bar{v}_w (\bar{v}_w - \bar{v}_{wn}) + \bar{t}^\kappa_w + \bar{\rho}_n \bar{v}_n (\bar{v}_n - \bar{v}_{wn}) + \bar{t}_n] \cdot \bar{n}_{wn} \, dA, \quad (3.27)$$
where the overbars denote volume-averaged (macro-scale quantities). Besides, $A_{wn}$ is the interface separating the $w$-phase and the $n$-phase in an averaging volume, $\Gamma_{wn}$ is the areal mass density of the $wn$-interface, and $j_{\kappa}^{wn}$ is the diffusive flux of component $\kappa$ in the $wn$-interface. A solution of a system of 9 coupled differential equations requires decent amount of computational power, plus constitutive relationships that are currently not available. Therefore Niessner and Hassanizadeh (2008b) proposed a simplified version, which can be seen as an extension of the equation system presented in Chapter 3.2 to a system of five partial differential equations, which include specific interfacial area as a parameter.

### 3.3.1.1 Balances for Bulk Phases

In analogy to the typical models of multiphase flow, the momentum balances for the bulk phases are simplified to Darcy-equations, which can then substituted the expressions for the velocities $v_\alpha$ on the left hand side in equations (3.22) and (3.23). We then analyze the right hand side representing mass exchange between the phases and interfaces by separating the advective ($I_{adv,\alpha}^\kappa$) and the diffusive ($I_{diff,\alpha}^\kappa$) mass transfer:

$$\frac{\partial (\phi_S \bar{\rho}_\alpha \bar{X}_\alpha^\kappa)}{\partial t} + \nabla \cdot \left[ \phi_S \bar{\rho}_\alpha \bar{X}_\alpha^\kappa ( -K \cdot \lambda_w (\nabla p_\alpha - \bar{\rho}_\alpha g)) \right] - \nabla \cdot \left( \phi_S \bar{\rho}_\alpha j_\alpha^\kappa \right)$$

$$= \bar{\rho}_\alpha Q_\alpha^\kappa + \frac{1}{V} \int_{A_{wn}} [\bar{\rho}_\alpha X_\alpha^{\kappa_s} (v_{wn} - v_\alpha) + j_\alpha^\kappa] \cdot n_{wn} \, dA$$

$$= \bar{\rho}_\alpha Q_\alpha^\kappa + I_{adv,\alpha}^\kappa + I_{diff,\alpha}^\kappa \quad (3.28)$$

Niessner and Hassanizadeh (2008b) argue that the advective transfer of mass over the interface does barely influence the total mass of the bulk phase, so the term $I_{adv,\alpha}^\kappa$ for the bulk phases is negligible. For the interfaces in contrast, advective transfer results in a production (or respectively destruction) term denoted as $E_{wn}$. The diffusive mass transfer term $I_{diff,\alpha}^\kappa$ represents a microscale behaviour, and Niessner and Hassanizadeh (2008b) obtained a first-order Fick’ian expression:

$$I_{diff,\alpha}^\kappa = j_\alpha^\kappa \cdot n_{wn} = \pm \frac{D_\kappa}{d^\kappa} \bar{\rho}_\alpha a_{wn} (X_{\alpha,s}^\kappa - X_\alpha^\kappa)$$

with $D_\kappa$ as the micro-scale Fick’ian diffusion coefficient for component $\kappa$, $d^\kappa$ as the diffusion length of component $\kappa$. $X_{\alpha,s}$ is the mass fraction corresponding to the solubility limit of component $\kappa$, and $X_\alpha$ is the real mass fraction at a distance of $d^\kappa$ from the interface.

Note that in contrast to the diffusive fluxes discussed around equation (3.19), this diffusive process is described by microscale quantities. Thus, it is hard to quantify a correct diffusion length $d^\kappa$ corresponding to the modeled problem.

### 3.3.1.2 Balances for the Interfaces

In their work, Hassanizadeh and Gray (1993) summarized their combination of the mass and momentum balances, plus energy and entropy balances using the second law of thermodynamics. Analogous to their derivation from momentum balances of phases to the
Darcy equation, they reduced the general momentum balance of the interface. On the macroscopic scale, inertial and viscous effects are neglected in the momentum balance of the interfaces, as it is done with the fluids. An exploitation of the entropy balance in combination with the second law of thermodynamics yields a simplified and linearized form of the momentum balance of the interface (Hassanizadeh and Gray, 1990). According to the procedure of phases, cross-coupling effects of viscous drag forces are neglected, which leads to the following equation of motion:

\[ \mathbf{R}_{wn} \cdot \mathbf{v}_{wn} = \nabla (a_{wn} \gamma_{wn}) - a_{wn} \Gamma_{wn} \mathbf{g} - a_{wn} \Gamma_{wn} \Lambda_{wn} \nabla S_{w}, \]  

(3.30)

with the material properties \( \mathbf{R}_{wn} \) and \( \Lambda_{wn} \), velocity of the \( wn \)-interface (i.e. the interface between the fluid phases) \( \mathbf{v}_{wn} \), the macro-scale surface tension \( \gamma_{wn} \), and the interfacial mass density \( \Gamma_{wn} \). If we now state that the effect of gravity on the interfacial movement is negligible, which is reasonable since we disregard any surfactants that possibly increase the mass of the interface significantly, the term \( a_{wn} \Gamma_{wn} \mathbf{g} \) gets zero. Until further investigations are undertaken about the influence of the last term in equation (3.30), we assume that the only driving force for interfacial movement is a gradient of specific interfacial area \( \nabla a_{wn} \). With these assumptions, equation (3.30) can be simplified for two phases to

\[ \dot{a}_{wn} = -K_{wn} \nabla a_{wn}, \]  

(3.31)

where \( K_{wn} \) is a new material property which combines the resistance \( \mathbf{R}_{wn}^{-1} \) to interfacial movement originating from drag forces and the influence of surface tension \( \gamma_{wn} \). We thus end up with a Darcy-like expression for interfacial area movement, analogous to the bulk phases.

Focusing on the mass conservation, we assume that no surfactants are involved, so fluxes through the interface do not affect the composition of the interface. This yields that all the mass propagating from one phase into the interface has to end up in the other phase, or leads to an increase or decrease of interfacial area. The mass balance in equation (3.26) can therefore be summed up to one total mass balance of all components in the interface with \( \sum_{\kappa} X_{wn}^{\kappa} = 1 \), eliminating mass fractions:

\[
\frac{\partial (a_{wn})}{\partial t} + \nabla \cdot (a_{wn} \mathbf{v}_{wn}) = \frac{1}{V \cdot \Gamma_{wn}} \int_{A_{wn}} \left[ \varrho_{w} (\mathbf{v}_{w} - \mathbf{v}_{wn}) + (\mathbf{j}_{w}^{A} + \mathbf{j}_{w}^{W}) + \varrho_{n} (\mathbf{v}_{n} - \mathbf{v}_{wn}) + (\mathbf{j}_{n}^{A} + \mathbf{j}_{n}^{W}) \right] \cdot \mathbf{n}_{wn} dA \\
= \frac{1}{V \cdot \Gamma_{wn}} \int_{A_{wn}} \left[ \varrho_{w} (\mathbf{v}_{w} - \mathbf{v}_{wn}) + \varrho_{n} (\mathbf{v}_{n} - \mathbf{v}_{wn}) \right] \cdot \mathbf{n}_{wn} dA
\]  

(3.32)

Note that all diffusive terms \( \mathbf{j}_{n}^{\kappa} \) on the left hand side vanish after the summation because any loss of matter in one phase has to be fully replaced by the other component, i.e. \( \mathbf{j}_{w}^{W} = -\mathbf{j}_{w}^{A} \). The appropriate consideration also holds for the microscale diffusive fluxes on the right hand side, but since it represents inter-phase transfer, mass is replaced from the respective phase, i.e \( \mathbf{j}_{w}^{W} = -\mathbf{j}_{w}^{A} \). It is not reasonable to neglect the advective mass transfer for interfaces as it was done for the bulk phases (3.3.1.1), therefore
Niessner and Hassanizadeh (2008b) propose the definition of a general production rate of interfacial area as

$$\frac{1}{V \cdot \Gamma_{wn}} \int_{A_{wn}} \left[ \varrho_w (v_w - v_{wn}) + \varrho_n (v_n - v_{wn}) \right] \cdot n_{wn} \, dA =: E_{wn} \, .$$  \hspace{1cm} (3.33)

A mathematical deduction of the term $E_{wn}$ is discussed in Chapter 2.3.1.3.

### 3.3.2 Simplified Differential Equation System

For typical two-phase problems, a system of five differential equations can be derived employing the assumptions made in the chapters above, which can be summarized as follows:

- Mass transfer between the phases is resolved by a Fick’s law.
- Mass transfer between fluids and solid disregarded.
- Porosity, as well as the density of the solid does not change with time.
- The flow of phases is solely driven by the hydraulic head gradient, and for interfaces the driving force is a gradient of specific interfacial area. Plus, cross-coupling terms in flow velocity, both for phases and interfaces, are neglected. Thus, Darcy-equations are used.
- Dispersion is not taken into account.
- Diffusion is resolved by a Fick-ian expression.
- Interfacial mass density $\Gamma_{wn}$ is constant, because surfactants are disregarded.
This leads to the final set of equations for the new approach:

\[ \phi \left( \frac{\partial}{\partial t} (S_w \tilde{\varphi}_w X^W_w) + \nabla \cdot (\tilde{\varphi}_w X^W_w \vec{v}_w) - \nabla \cdot (\tilde{j}^W_w) = \tilde{\varphi}_w Q^W_w - \frac{D^W}{d^W} \tilde{\varphi}_n a_{wn} (X^W - X^W_n) \right) \]  \hspace{1cm} (3.34a)

\[ \phi \left( \frac{\partial}{\partial t} (S_n \tilde{\varphi}_n X^A_n) + \nabla \cdot (\tilde{\varphi}_n X^A_n \vec{v}_n) - \nabla \cdot (\tilde{j}^A_n) = \tilde{\varphi}_n Q^A_n + \frac{D^A}{d^A} \tilde{\varphi}_w a_{wn} (X^A - X^A_w) \right) \]  \hspace{1cm} (3.34b)

\[ \phi \left( \frac{\partial}{\partial t} (S_n \tilde{\varphi}_n X^W_n) + \nabla \cdot (\tilde{\varphi}_n X^W_n \vec{v}_n) - \nabla \cdot (\tilde{j}^W_n) = \tilde{\varphi}_n Q^W_n + \frac{D^W}{d^W} \tilde{\varphi}_w a_{wn} (X^W - X^W_n) \right) \]  \hspace{1cm} (3.34c)

\[ \frac{\partial a_{wn}}{\partial t} + \nabla \cdot (a_{wn} \vec{v}_{wn}) = e_{wn}(S_w, p_c) \cdot \frac{\partial S_w}{\partial t} = E_{wn} \]  \hspace{1cm} (3.34d)

\[ \tilde{v}_w = -K \cdot \frac{S_w^2}{\mu_w} (\nabla p_w - \tilde{\varphi}_w g) \]  \hspace{1cm} (3.34e)

\[ \tilde{v}_n = -K \cdot \frac{S_n^2}{\mu_n} (\nabla p_n - \tilde{\varphi}_n g) \]  \hspace{1cm} (3.34f)

\[ \tilde{v}_{wn} = -K_{wn} \vec{v}_{wn} \]  \hspace{1cm} (3.34g)

\[ p_c = p_n - p_w \]  \hspace{1cm} (3.34h)

\[ S_w + S_n = 1 \]  \hspace{1cm} (3.34i)

\[ X^W + X^A = 1 \]  \hspace{1cm} (3.34j)

\[ X^W + X^A = 1 \]  \hspace{1cm} (3.34k)

\[ a_{wn} = a_{wn}(S_w, p_c) \]  \hspace{1cm} (3.34l)

The macro-scale diffusive fluxes \( \tilde{j}_w \) are calculated according to the standard model by Fick’s law, using equation (3.19) in combination with (3.20).

In order to fully describe present and future states of a given system, a minimal number of independent variables are needed, which are denoted as primary variables. All other state variables can then be obtained by constitutive relationships, as discussed in Chapter 2.1.2. While the traditional approach uses constitutive relationships for mass fractions and capillary pressure, the five balance equations in the new approach permit a solution of five primary values:

- In analogy to the equation system described in Chapter 3.1 we also have a twophase system, so one saturation and one pressure are primary unknown variables (the corresponding pressure and saturation are coupled by \( p_n = p_w + p_c \) and \( S_n + S_w = 1 \)). For further information, it is referred to the GIBBS phase rule in any thermodynamic text book.

- In contrast to the two-component model of Chapter 3.2 we do not postulate equilibrium mass fractions, so two of the real mass fractions are also primary unknown variables (closed by the supplementary constraint \( \sum_n X^\alpha_n = 1 \) for all phases \( \alpha \)).
A thermodynamically derived balance of interfacial area is able to deduce the capillary pressure as the fifth unknown variable from a dependency of $p_c$ on $a_{wn}$ and $S_w$ (i.e. $p_c = p_c(a_{wn}, S_w)$).

To find a unique solution for the partial differential equations, the set of primary variables have to be initially defined to declare the starting state of the system, which are thus called *initial values*. Boundary conditions interrelate the equation system with its spatial surroundings. The spatial boundary conditions mostly used are **Dirichlet** boundary conditions $u^D$ along boundary $\Gamma_D$, as well as **Neumann** boundary conditions $u^N$ along boundary $\Gamma_N$:

\[
\begin{align*}
    u &= u^D \\
    \frac{\partial u}{\partial n} &= u^N
\end{align*}
\]

**Dirichlet** boundary condition \hspace{1cm} (3.35a)  
**Neumann** boundary condition \hspace{1cm} (3.35b)

With respect to the general form of the balance equation, the **Neumann** boundary condition represents a flux across the boundary $\Gamma_N$ (see Chapter 3.4.2) with respect to the exterior unit normal vector $n$, denoted in this work with $q_{N,\alpha}$. 


3.4 Numerical Discretization

All mathematical models described afore are based on a system of balance equations which are both highly coupled and non-linear, where an analytical solution does not exist. To solve the differential equations numerically, a certain discretization scheme is needed to approximate the functions \( f(\hat{u}) \) by discrete values \( \hat{u} \) at certain spatial and temporal nodes corresponding to an underlying grid (see Figure 3.2). The finer the grid is chosen, the closer the numerical approximation gets towards an accurate solution of the mathematical problem, yet a fine grid obviously comes with the price of high computational costs.

As has been discussed in the mathematical models in this chapter, all governing equations are based on time-dependent storage term \( M \), a flux term \( A \) and sources or sinks \( I + Q \) (equations (3.1) and (3.10)). This allows to discretize all three approaches likewise. However, in order to get towards a consistent discretization of the unknowns \( \hat{u} \), they are separated from the terms of equation (3.10) to get a matrix form of the equation system as in Helmig (1997)

\[
\hat{M} \cdot \left[ \frac{d\hat{u}}{dt} \right] + \hat{A} \cdot [\hat{u}] = R, \tag{3.36}
\]

where \( R \) comprises the matrix of the Neumann boundary fluxes, as well as sources and sinks and mass transfer terms. This equation system in matrix form can then be solved using, for example, an iterative Newton method. The discretization of \( M := \hat{M}(\hat{u}) \cdot \left[ \frac{d\hat{u}}{dt} \right] \) in time will be done in Chapter 3.4.1 whereas the spatial discretization will be presented in Chapter 3.4.2.

### 3.4.1 Time Discretization

In this diploma thesis, time dependent problems for the different model concepts are solved by an implicit Euler-method (Helmig, 1997), by what timestep sizes are not generally restricted by stability. While the spatial discretization is conducted with an finite element discretization, a finite difference scheme is applied to discretize in time. Thus the differential operator \( \frac{d}{dt} \) is approximated by a difference quotient over the timestep \( \Delta t \).

Reformulating (3.36) to separate the differential operator yields

\[
\left[ \frac{d\hat{u}}{dt} \right] = \hat{M}^{-1} \cdot \left( -\hat{A} \cdot [\hat{u}] + R \right), \tag{3.37}
\]

which corresponds to an an differential equation of the form

\[
\frac{d\hat{u}}{dt} = f(\hat{u}). \tag{3.38}
\]
The application of an implicit Euler integration will yield for timestep $m$ and its successive timestep $m+1$:

\[
\frac{\hat{u}^{m+1} - \hat{u}^m}{\Delta t} = f(\hat{u}^{m+1}) \quad (3.39a)
\]

\[
\hat{u}^{m+1} = \hat{u}^m + \Delta t \cdot f(\hat{u}^{m+1}). \quad (3.39b)
\]

Thus, transferred back to equation (3.36), the discretization in time yields:

\[
[\hat{u}^{m+1}] = [\hat{u}^m] + \Delta t \cdot \hat{M}^{-1} \cdot (\hat{A} \cdot [\hat{u}] + \hat{R}) \quad (3.40)
\]

It was tested if the static production term in equation (3.34e) has to be also discretized for both timesteps within the implicit Euler-step as

\[
E_{\text{wn}}^{m+1} = \frac{e_{\text{wn}}^{m+1} \hat{S}_{\text{wn}}^{m+1} - e_{\text{wn}}^m \hat{S}_{\text{wn}}^m}{\Delta t},
\]

or directly calculated from the new timestep:

\[
E_{\text{wn}}^{m+1} = \frac{e_{\text{wn}}^{m+1} \hat{S}_{\text{wn}}^{m+1} - \hat{S}_{\text{wn}}^m}{\Delta t}.
\]

Because the latter reduces computational effort to only one static production rate $e_{\text{wn}}^{m+1}$ per timestep, significant performance benefits can be gained without any noticeable effects on the solution. Besides, this solution technique corresponds more to the physical meaning of a static production rate as a source or sink to the interfacial area balance.

### 3.4.2 Space Discretization

The spatial discretization scheme used in this thesis is a fully upwinding finite-element finite-volume method, or box-method (Helmig, 1997; Helmig and Huber, 1998). The whole model domain $G$ is first covered by a finite-element mesh with the nodes at the corners of the elements $\epsilon$. The correct analytical solutions $f(u) = (f(S_w), f(p_c), f(a_{\text{wn}}), \cdots)$ are thus approximated according to a finite-element approach by:

\[
u \approx \hat{u} = \sum_i \hat{u}_i N_i,
\]

where $N_i$ prescribes an interpolation function (also called shape function, ansatz function etc.) at the node $i$, connecting the node $i$ with all neighboring nodes $j$. The order of the shape functions determines the order of approximation, i.e. how close the discretization comes near the original solution $f(u)$. Usually, as was done in this work, linear shape functions were used (see Figure 3.3, part I), with the restriction

\[
N_i(x_l) = \delta_{il} = \begin{cases} 
1 & \text{if } l = i, \text{ which means that } x_l \in B_i \\
0 & \text{otherwise, i.e. } l = j \text{ or } x_l \notin B_i.
\end{cases}
\]

However, this discretization ($u \rightarrow \hat{u}$) leads to a global residual or global defect $\varepsilon$, which
3.4. NUMERICAL DISCRETIZATION

![Image of numerical discretization](image)

Figure 3.3: Box-method.

Figure 3.4: Box construction in two dimensions, after (Class, 2001).

we want to be as small as possible (see Figure 3.3 part II). In case of an exact solution of the primary variables, $\varepsilon$ has to become zero. Therefore a weighting function $W_i$ is introduced which minimizes the error within the domain $G$:

$$\int_G W_i \varepsilon = 0 \quad \text{for all } i \ .$$

(3.43)

A second mesh is layered around each node $i$ of the finite element mesh, with its corners at the edge midpoints or the centres of gravity of adjoined elements, respectively (Figure 3.4). Hence every node is contained within a bounding box $B_i$, building a secondary finite volume mesh (see Figure 3.3 Part III). The whole model domain $G$ is subdivided into smaller subdomains, represented by the boxes $B_i$. Following the purpose of the weighting functions, they must satisfy the condition $\sum_i W_i = 1$ for all boxes $\sum_i B_i$ over the model domain $G$. Thus, the defect can be regarded within each subdomain of the model domain, so from the physical perspective a local mass conservation is enforced for each subdomain:

$$\int_{B_i} W_i \varepsilon \overset{!}{=} 0 \ .$$

(3.44)

This local mass conservation is one of the major advantages of the box method, while it still features the flexibility of Finite Element methods.
CHAPTER 3. MATHEMATICAL AND NUMERICAL MODEL

To visualize the discretization with one example of the governing equations, the representative but clear balance equation (3.34e) is chosen (the discretization of the other balances can be found in, for example, Class (2001)): Inserting equation (3.41) in combination with equation (3.42) into equation (3.34e), with upwinding of specific interfacial area in the flux term, yields

$$\sum_i \frac{\partial (\hat{a}_{wn,i}N_i)}{\partial t} + \nabla \cdot \left( \sum_i \hat{a}_{wn,i} K_{wn} \nabla (\hat{a}_{wn,i}N_i) \right) - \sum_i E_{wn,i} = \varepsilon . \quad (3.45)$$

Upwinding techniques were developed, for example, by S. K. Godunov in 1959, examining shock fronts of advective problems. Over the decades upwinding schemes proved to be very robust by reducing numerical oscillation and producing considerably steep shock profiles (B.van Leer and P. Roe in Hassaini et al. (1997)). Generally, the schemes use the direction of propagation in a flow field, i.e. the characteristic speed, for the computation of advective fluxes. A simple first-order upwinding scheme is used here, defined by

$$\hat{a}_{wn,ij}^{upw} = \begin{cases} \hat{a}_{wn,i} & \text{for } \hat{a}_{wn,i} \geq \hat{a}_{wn,j} \\ \hat{a}_{wn,j} & \text{otherwise, for } \hat{a}_{wn,i} < \hat{a}_{wn,j} \end{cases} \quad (3.46)$$

We use a box-method weighting (equation (3.44)) to diminish the residual within one box $B_i$:

$$\sum_k \int_{B_i} W_i \frac{\partial (\hat{a}_{wn,k})}{\partial t} + \int_{B_i} W_i \nabla \cdot \left( \sum_k \hat{a}_{wn,ik} K_{wn} \nabla (\hat{a}_{wn,k}N_k) \right) - \int_{B_i} W_i E_{wn,i} = 0 \quad (3.47)$$

$k$ comprises the specific node $i$ of box $B_i$ and all neighboring nodes $j$. The integral term in the middle, which was referred to as the flux term $A$ at the beginning of this chapter, is transferred using the Green-Gauss theorem:

$$A := \oint_{\Gamma_{B_i}} W_i \sum_k \hat{a}_{wn,ik} K_{wn} \nabla (\hat{a}_{wn,k}N_k) n_{\Gamma_{B_i}} d\Gamma_{B_i} - \int_{B_i} \nabla W_i \sum_k \hat{a}_{wn,ik} K_{wn} \nabla (\hat{a}_{wn,k}N_k) dB_i \quad (3.48)$$

For the box scheme, the weighting function is piecewise constant within the box

$$W_i = \begin{cases} 1 & \text{if within } B_i \\ 0 & \text{otherwise} \end{cases} \quad (3.49)$$

which means that $\nabla W_i = 0$. Thus, the right integral of equation (3.48) vanishes. For discretized values $\tilde{u}$, it holds that

$$\nabla \tilde{u} = \nabla \left( \sum_k \tilde{u}_k \cdot N_k \right) = \sum_{k \neq i} (\tilde{u}_k - \tilde{u}_i) \nabla N_k = \sum_j (\tilde{u}_j - \tilde{u}_i) \nabla N_j . \quad (3.50)$$

For any given box we also post that $\int_{B_i} N_i dB_i = V_i$, which is the volume of the box $B_i$. All this combined, the equation (3.47) is discretized for each node $i$ as

$$\frac{\partial (\hat{a}_{wn,i})}{\partial t} V_i + 1 \cdot \sum_j (\hat{a}_{wn,j} - \hat{a}_{wn,i}) \hat{a}_{wn,ji}^{upw} \oint_{\Gamma_{B_i} \notin \Gamma_N} K_{wn} \nabla N_j \cdot n_{\Gamma_{B_i}} d\Gamma_{B_i} - V_i \cdot E_{wn,i} = q_{N,\alpha} . \quad (3.51)$$
where $\Gamma_N$ denotes a Neumann boundary, and $q_{N,\alpha}$ denotes Neumann boundary fluxes of phase $\alpha$.

Combining the spatial with the temporal discretization (equations (3.51) and (3.39a)) yields

$$\frac{\hat{a}_{un,i}^{m+1} - \hat{a}_{un,i}^m}{\Delta t} V_i + \sum_j (\hat{a}_{un,j}^{m+1} - \hat{a}_{un,j}^{m+1}) \hat{a}_{un,ji}^{upw,m+1} \oint_{\Gamma_B \notin \Gamma_N} B_i K_{un} \nabla N_j \cdot n_{\Gamma_B} d\Gamma_B = V_i E_{un,i}^{m+1} - q_{N,\alpha}^{m+1}.$$  

(3.52)

The flux integral over the boundaries is time independent as long as the shape functions, the permeability as well as the finite element mesh remain constant with time. Since no adaptive methods are used in this work, this restriction holds.

### 3.4.3 Implementation in DUMUX

All numerical simulations of this thesis are carried out using the programming framework DUNE, the Distributed and Unified Numerics Environment. Using C++ techniques, DUNE is a modular toolbox for the solution of partial differential equations for grid-based problems. The framework consists of modules such as solvers, grids or discretization algorithms etc., forming a ready-to-use toolbox for more specialized applications.

The additional module DuMu$^+$ (Dune for Multi-phase, -physics, -component, -scale Flow in Porous Media) has been developed by Flemisch et al. (2007) to provide a framework for efficient implementation of models for porous media flow problems. Thus the model for fully coupled two-phase flow can be used and adapted for the standard approach models of Chapter 2.2.2, while a new module had to be developed and implemented for the new approach. As DuMu$^+$ is still in the stage of development, one of the major tasks during the thesis was to maintain the interfacial-area module during the process of ongoing structural improvements.
A numerical test scenario for two-phase flow is assembled to investigate the differences between the model approaches on a fundamental basis, and to test the performance of the new approach. Since principle investigations are intended, simple model configurations in two dimensions are chosen to avoid disruptive effects. All study setups are based on the test setup presented in the work of Jakobs (2004). In contrast to his studies, an interface condition at the boundary between the fracture and the matrix is not yet implemented to this stage: A relationship of $p_c(S_w, a_{wm})$ is much more complicated than the standard case of $p_c(S_w)$. However, this will be an important field of further development, as will be presented later.

Despite of the underlying motivation discussed in Chapter 1.4, the purpose of the numerical test cases was to show the functionality of the model concepts in the scope of strong parameter heterogeneities between the fracture and the matrix, as well as to indicate the differences, strengths, or disadvantages of the mathematical models, instead of simulating a proper nuclear storage site. Up to this work, only homogeneous macroscale domains were modeled with the new concept.

### 4.1 Model Setups

The sketches of the case setups are displayed in Figure 4.1. Fully saturated gas is infiltrated into a water-filled domain of 8m times 10m. Impermeable boundary conditions are defined on both sides and at the bottom, aside from the infiltration interval ranging from 3m to 5m. At the top of the model domain, a DIRICHLET-boundary is chosen, see Chapter 4.1.2.4. Three different principal setups may be distinguished:

1. **Homogeneous setup**: The model domain only consists of matrix material, no fractures are implemented. It is thus possible to examine a homogenous flow regime, without disturbance from discontinuities caused by the fracture-matrix interaction (left part of Figure 4.1).

2. **A setup with one fracture**: Located in the middle of the simulation domain, it stretches from 1m above the infiltration zone straight upwards to an height of 8m, comprising a width of 10cm (see the right part of Figure 4.1). Although it is referred
to as “one fracture”, the area is intended to represent an active flow system of connected fractures, see Figure 2.3

3. Several fractures: a further fracture is added to examine the spread of the non-wetting phase under different gravitational influence. In addition, validity and applicability of the new concept are surveyed. Both multifracture model setups are based on Figure 4.1 b), and the actual conformation is explained at the beginning of the respective chapters.

![Figure 4.1](image-url)  
**Figure 4.1**: Sketches of the applied model setups.

### 4.1.1 Grid Generation

The choice of the numerical grid was found to be an important task to gain stability of the simulation runs and to produce valid results. Around the infiltration zone, a finer resolution leads to an increase in the pressure gradients. Thus a lower infiltration rate or smaller timesteps are needed to attain numerical convergence, which obviously results
in longer simulation runtimes until the gaseous front reaches the fracture. Furthermore, especially around the top and bottom node of the fracture, discretization resolution influences the numerical stability.

First attempts were made with a homogeneous quadratic grid, but the stability of the simulation runs appeared enhanceable by using the mesh generator ICEM CFD. That is, the mesh is refined in the areas of interest around the fractures. It became even more important when constructing a more complex geometry (see Chapter 4.2.3). For the setup of 1 fracture, the applied mesh is exemplarily displayed in Figure 4.2.

### 4.1.2 Model Parameters

Besides spatial information about the model domain, physical properties have to be provided. Since the investigations are of principal nature, there was neither experimental data for the specific setup nor an existing natural template for the examined case, thus soil parameters could be chosen freely.

#### 4.1.2.1 Fluid Parameters

In the simulation runs, water represents the wetting phase. Although the motivation would indicate to simulate a gaseous phase composed of mainly hydrogen, gas with the standard composition of air was selected as the non-wetting phase, because the higher molar mass of air caused less numerical fragility. The fluid parameters were displayed in Table 4.1.
Table 4.1: Fluid properties of the wetting and non-wetting phase.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Substance</th>
<th>Density $[kg/m^3]$</th>
<th>Diffusion coefficient $[m^2/s]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetting phase</td>
<td>Water</td>
<td>1000</td>
<td>$2.2 \cdot 10^{-9}$</td>
</tr>
<tr>
<td>Non-wetting phase</td>
<td>Air</td>
<td>Ideal gas</td>
<td>$2.25 \cdot 10^{-5}$</td>
</tr>
</tbody>
</table>

4.1.2.2 Soil and Fracture Parameters

As already mentioned, we were free to use any soil parameters. However, natural conditions call for harsh differences between fractures and matrix, thus high differences in permeability of 4 orders of magnitude are chosen. In order to compare all model concepts, a soil matrix with known interfacial-area surfaces, as well as bounding curves for primary drainage and imbibition are necessary, and appropriate data is found in the work of Joekar-Niasar et al. (2007). Both for primary drainage and primary imbibition, a VAN GENUCHTEN formulation was used, see Table 4.4. However, to visualize the differences between fracture and matrix, Table 4.2 also shows the corresponding entry pressures of a BROOKS-COREY description: The open voids of the fracture are much larger than the biggest pores of the matrix, the non-wetting phase can thus enter the domain of the fracture with ease. Hence, infiltration processes into the fracture proceed at much lower pressures than re-exfiltration into the matrix.

Interfacial area parameters (see Table 4.3) are bound to the biquadratic fitting functions of equation (2.33). The VAN GENUCHTEN model parameters from Table 4.4 correspond to equation (2.16).

Table 4.2: Comparison of soil properties between fracture and matrix.

<table>
<thead>
<tr>
<th></th>
<th>Porosity $\Phi$</th>
<th>Conductivity $K [m^2]$</th>
<th>Initial Saturation</th>
<th>Entry pressure $p_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>0.1</td>
<td>$10^{-12}$</td>
<td>0.95</td>
<td>6009.50 Pa</td>
</tr>
<tr>
<td>Fracture</td>
<td>0.3</td>
<td>$10^{-8}$</td>
<td>0.95</td>
<td>1067.05 Pa</td>
</tr>
</tbody>
</table>

Table 4.3: Interfacial Area Surface Coefficients.

<table>
<thead>
<tr>
<th></th>
<th>$a_{00} \left[1/m\right]$</th>
<th>$a_{01} \left[1/m\right]$</th>
<th>$a_{10} \left[1/mPa\right]$</th>
<th>$a_{11} \left[1/mPa\right]$</th>
<th>$a_{20} \left[1/m\right]$</th>
<th>$a_{21} \left[1/mPa^2\right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>688.886</td>
<td>4167.65</td>
<td>-0.185</td>
<td>-0.039</td>
<td>-4058.7</td>
<td>1.058 $\cdot 10^{-5}$</td>
</tr>
<tr>
<td>Fracture</td>
<td>-73.35</td>
<td>391.95</td>
<td>0.0058</td>
<td>-0.0232</td>
<td>-301.3818</td>
<td>$-2.569 \cdot 10^{-8}$</td>
</tr>
</tbody>
</table>
4.1. MODEL SETUPS

Table 4.4: Boundary Curves.

<table>
<thead>
<tr>
<th></th>
<th>Primary Drainage</th>
<th>Primary Imbibition</th>
<th>Residual Saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha$ $m$ $n$</td>
<td>$\alpha$ $m$ $n$</td>
<td>$S_{w,\text{res}}$</td>
</tr>
<tr>
<td>Matrix</td>
<td>0.00014 0.853 8.818</td>
<td>0.00024 0.928 14.0</td>
<td>0.069</td>
</tr>
<tr>
<td>Fracture</td>
<td>0.000446 0.694 3.268</td>
<td>0.000615 0.885 8.696</td>
<td>0.212</td>
</tr>
</tbody>
</table>

Programming measures are undertaken that the residual saturation of the wetting phase is set to zero if the primary drainage curve is regarded. As the standard approach is bound on drainage-only, the imbibition curve could not be implemented in this model.

4.1.2.3 Model Concepts

Three different model approaches form the basis of the simulations:

1. A standard two-phase two-component model, abbreviated as $2p2c$ (Chapter 3.2). This model is bound to states of equilibrium and macroscale capillarity is calculated by a Van Genuchten description for primary drainage.

2. The extended two-phase two-component model which includes non-equilibrium kinetic mass transfer over the interfaces, denoted as $2p2cia4$. This is a simplified version of the new interfacial-area based approach presented in Chapter 3.3.2 where we disregard hysteretic behaviour of the capillary pressure, thus capillarity is bound on the primary drainage curve. The governing equations of this approach are the four equations (3.34a) to (3.34d).

3. A full interfacial area approach as discussed in Chapter 3.3.2 including the full equation system (3.34). Because of the five equations that are used, this model is abbreviated in the following as $2p2cia5$. The full approach is not restricted to states of equilibrium, and macroscale capillary pressure is obtained from the model.

The motivation for the application of all three models was to use the standard approach $2p2c$ and extend it step by step ($2p2cia4$, $2p2cia5$). It is thus possible to examine stability as well as performance, and compare the simulation results to discuss whether the differences are significant or not.

The more complex the equation system gets, the more independent primary variables may be resolved, see Table 4.5. Note that the standard approach switches the second primary variable ($S_n$) to a mass fraction if one phase disappears.

4.1.2.4 Initial and Boundary Conditions

The set of initial values (Table 4.5) has to be chosen according to the set of primary variables, or the quantity of differential equations, respectively.
Table 4.5: Set of primary variables.

<table>
<thead>
<tr>
<th></th>
<th>Primary Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Approach ((2p2c))</td>
<td>(p_w, S_n)</td>
</tr>
<tr>
<td>Simplified Interfacial Area Approach ((2p2cia4))</td>
<td>(p_w, S_n, X_A^w, X_W^w)</td>
</tr>
<tr>
<td>Interfacial Area Approach ((2p2cia5))</td>
<td>(p_w, S_n, X_A^w, X_W^w, p_c)</td>
</tr>
</tbody>
</table>

Boundary Conditions (Chapter [3.3.2]) are denoted in Figure [4.1] where \textsc{dirichlet} is chosen along the top side, and all other boundaries are of type \textsc{neumann} with

\[
q_{N,n}(x, y) = \begin{cases} 
-0.005 \frac{m^3}{m s} & \text{if } 3m \leq x \leq 5m \\
0 & \text{otherwise, which means a no-flow boundary.} 
\end{cases} \tag{4.1}
\]

Simulation results prove that the solution is independent from the \textsc{dirichlet} boundary at the top, because its distance from the area of interest, mainly the area around the top corner of the fracture, is large enough to negate the influence of the boundary condition.

Table 4.6: Initial Boundary Conditions, identical to applied \textsc{dirichlet} Boundary Conditions.

<table>
<thead>
<tr>
<th></th>
<th>Initial and \textsc{dirichlet} values</th>
<th>Model Concept</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (p_w) [Pa]</td>
<td>(10200 + (10 - y) \cdot 9810)</td>
<td>(2p2c, 2p2cia4, 2p2cia5)</td>
</tr>
<tr>
<td>Saturation (S_n) [-]</td>
<td>0.05</td>
<td>(2p2c, 2p2cia4, 2p2cia5)</td>
</tr>
<tr>
<td>Mass Fraction (X_A^w) [-]</td>
<td>(\frac{p_w}{p_{w,sat}})</td>
<td>(2p2c, 2p2cia4, 2p2cia5)</td>
</tr>
<tr>
<td>Mass Fraction (X_W^w) [-]</td>
<td>(p_{w,sat})</td>
<td>(2p2cia4, 2p2cia5)</td>
</tr>
<tr>
<td>Capillary Pressure (p_c) [Pa]</td>
<td>(p_c(S_w)) (Equation (2.16))</td>
<td>(2p2cia5)</td>
</tr>
</tbody>
</table>

### 4.2 Verification Study for the Conceptual Models

#### 4.2.1 Homogeneous Setup - No Fracture

The homogeneous setup allows general validation and verification of the different model concepts, plus an estimation of the significance of the underlying physical processes. In order to investigate general conformity of the results, the propagation of the gaseous phase is compared after a 100 second simulation run, as shown in Figure [4.3]. The encountered differences are predominantly caused by the different relative permeability descriptions of the respective models, see Chapter [2.1.2.2] versus Chapter [2.3.1.1]. However, if capillarity and mass transfer due to non-equilibrium effects are to be compared, a similar front propagation is favorable. For further comparative studies, the simple relative permeability
4.2. VERIFICATION STUDY FOR THE CONCEPTUAL MODELS

 formulation \( k_{r,\alpha} = S_2^2 \) is thus also applied to the \( 2p2c \)-model, which then yields good congruence (Picture 4.3(d)). The results for all model concepts using the relative permeability function of Chapter 2.1.2.2 are also in full agreement.

 If variables besides the saturation are compared, let them be capillary pressure or mass fractions, the conformity is also approved. Figure 4.3 illustrates the \( 2p2c \)-model drawn by a solid black line, the \( 2p2cia4 \)-model by a grey but dashed line, and the \( 2p2cia5 \)-model by a dotted black line. All characteristics match very well over time, the new approaches are able to resolve comparable results when the same relative permeability function is used for all models. Capillary pressure, however, shows small variances: Figure 4.4(a) indicates a short imbibition process at the beginning of the simulation, thus the whole process is not purely drainage. The model domain is, for numerical reasons to get the \( 2p2c \)-method to convergence, not fully saturated with water at the beginning, therefore an increase in water saturation remains possible. When entering the domain, the propagating gas front pushes forward an evolving water front, creating a small imbibition zone ahead of the strong drainage area at the gaseous front. For the homogeneous setup, however, this imbibition process is too weak to significantly reduce capillary pressure and thus to substantially influence the overall process.

 Additionally, the assumption of an equilibrium process and thus negligible mass transfer seems appropriate for the slow homogeneous case. The real mass fractions gained by the

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**Figure 4.3:** Comparison of the different model concepts for the homogeneous case.
CHAPTER 4. CASE STUDIES

(a) Capillary pressure $p_c$.

(b) Mass fraction of air in water-phase $X^A_n$.

Figure 4.4: Temporal characteristics at an exemplary node.

extended models ($2p2cia4$, $2p2cia5$) are very close to the equilibrium mass fractions of the standard approach (Figure 4.4(b)). Although mass transfer due to non-equilibrium is recognizable in Figure 4.5(a), the variation from equilibrium mass fraction is marginal: the mass transfer term in Equation (3.29) includes a diffusion coefficient which is 5 magnitudes larger than the one for the component air. Recognizable effects of non-equilibrium are solely detectable for the component air (Figure 4.5(b)). Areas below equilibrium, indicated by a positive sign of the mass transfer, are only observable in the vicinity of the infiltration zone.

Figure 4.6 shows the saturation of the non-wetting phase (grey) as well as the non-

Figure 4.5: Mass transfer after 50 seconds.

equilibrium mass transfer of air into water $I^A_w$ (black) along the first meter of infiltration, marked by the white line on the right picture. An infiltration rate of $q_N = -0.005 \frac{kg}{s m^2}$ is represented by a solid line, while the dotted line marks $q_N = -0.007 \frac{kg}{s m^2}$ and the dashed line $q_N = -0.01 \frac{kg}{s m^2}$. With increasing infiltration rates, the phase velocity is also meant to increase to sustain the gas flow. In consequence, more mass gets transferred due to
Table 4.7: Computational expenses for a 100 second simulation run.

<table>
<thead>
<tr>
<th>model concept</th>
<th>timesteps</th>
<th>computational time</th>
</tr>
</thead>
<tbody>
<tr>
<td>2p2c</td>
<td>14</td>
<td>80 s</td>
</tr>
<tr>
<td>2p2cia4</td>
<td>14</td>
<td>158 s</td>
</tr>
<tr>
<td>2p2cia5</td>
<td>15</td>
<td>228 s</td>
</tr>
</tbody>
</table>

non-equilibrium near the infiltration area, hence the distance of obtained mass fractions from equilibrium mass fractions also increases. For problems with high infiltration rates which may be observed near the wells of sites for subsurface storage of carbon dioxide, non-equilibrium effects may thus play a significant role.

As expected, the solution of more nonlinear equations enhances the computational demand. Table 4.7 lists the time to complete the simulation of 100 seconds as well as the necessary timesteps. Both new concept require much more NEWTON-iteration steps to reach convergence, which explains increased computational demand without an increase in timesteps.

Figure 4.6: Mass transfer with respect to infiltration rates (black, in $\frac{kg}{sm^3}$) and saturation of the gaseous phase (grey, in [-]).
4.2.2 Fracture-Matrix System with One Fracture

The next model setup under investigation is a fracture-matrix system with one single vertical fracture, see Figure 4.1 (b). As discussed in the previous chapter, the standard approach is used with the simplified relative permeability function to gain comparable results. The pictures in Figure 4.7 show the saturation of the gaseous phase at the beginning of the simulation (after three seconds which equals three timesteps). Gravity causes the initial gas volume inside the fracture to propagate upwards and accumulate at the top node of the fracture. That is the saturation of gas is lower inside the fracture compared to the matrix which is generally still subject to initial saturations of around $S_n = 0.05$. Thus gas infiltrates from all sides into the fracture, slightly lowering the gaseous content around the fracture. In accordance to the homogeneous simulations, all model descriptions draw a comparative phase propagation. At this early stage of the simulation, mass fractions of the interfacial-area models are lower than equilibrium mass fractions in the lower and upper part of the fracture, because the flow velocity is instantly very high. This effect is caused by an initial gas volume in the fracture that is driven upwards by gravity. Since that flow regime is dependent on the initial conditions and is not subject to the infiltration process, these starting effects are not discussed here.

Throughout the simulation, mass transfer of water is primarily caused by numerical fluctuations rather than real differences in mass fractions, because the diffusion coefficient is five orders of magnitude larger compared to that of the component air. Thus, slightly enhanced flow velocities due to worse grid elements, for example, may already cause considerable mass transfer without any significant change in mass fractions.

In contrast, mass transfer of the component air due to states of non-equilibrium, as defined by equation (3.29), is further examined. Apart from starting effects, mass fractions
4.2. VERIFICATION STUDY FOR THE CONCEPTUAL MODELS

of air below equilibrium (and thus positive mass transfer) are only observable at the infiltration zone, which was already discussed for the homogeneous case, and is therefore not visualized here. Figure 4.8 shows the mass transfer of air with a negative sign, i.e. transfer of the component air into the non-wetting phase, at two representative timesteps. Apart from the infiltration front, negative mass transfer is encountered within the fracture as soon as it is flushed with gas (Figure 4.8(a)). The reason for this effect is ambiguous. One possible explanation may be numerical diffusion, which counteract.

Later, as the upper side fills with gas, negative mass transfer is observable in the areas where significant changes in saturation occur (Figure 4.8(b)). Figure 4.9 compares real mass fraction $X_w^A$ (stroked) and equilibrium mass fraction $X_{w,s}^A$ (dotted) for an exemplary node in the upper area of the fracture with the wetting phase saturation $S_w$ (dashed). As the gaseous plume spreads downwards, it reaches the selected node around 60 seconds, where even more water gets drained. These changes in saturation are too high to actually reach equilibrium. The final mass fraction of air in water can be found in Figure A.1 in the appendix, as well as the final distribution of the non-wetting phase after 100 seconds.

To investigate differences in capillary pressure, both approaches that are bound on primary drainage (i.e. $2p2cia4$ and $2p2cia5$) are compared with the $2p2cia5$-model featuring hysteresis. Figure 4.10 shows the chronological behaviour of the capillary pressure at the bottom node of the fracture, drawn with respect to time (left) and to water saturation (right). The $2p2cia4$-model bound on the primary drainage process is represented by the solid black line. The other lines show instantiations of the $2p2cia5$-model with varying permeability to the interfaces, ranging from $K_{wn} = 10^{-10} \frac{m^3}{s}$ (dotted, black), $K_{wn} = 10^{-11} \frac{m^3}{s}$ (dashed, black) to $K_{wn} = 10^{-12} \frac{m^3}{s}$ (solid, grey). Within the first six seconds, the $2p2cia5$-model is able to simulate the imbibition process of the fracture
Figure 4.9: Mass fractions $X_w^A$ (solid) and $X_{w,s}^A$ (dotted) with saturation $S_w$ (dashed) over the timespan of simulation for an exemplary node.

better than the drainage-bound models. An imbibition cycle which starts on the primary drainage branch decreases stronger with saturation than the pure main drainage curve does, therefore all three $2p2cia5$-models gain much lower capillary pressure (see right picture in Figure 4.10 at $t = 6s$). As soon as the fracture gets refilled with gas, a drainage process prevails, thus capillary pressure rises again parallel to the primary drainage curve. However, some runs encounter a further unphysical decrease in capillary pressure, which

Figure 4.10: Capillary pressure of the different model concepts.

is best observable when the conductivity to interfacial-area movement $K_{wn}$ is high (dotted curve). This is because at this stage, no interface condition between the fracture and the matrix is implemented, thus the continuity of capillary pressure and specific interfacial-area (see Figure 4.11(a)) is not enforced by a discontinuous jump of the saturation. A
limit case of $K_{wn} = 0$ would result in equation (3.34e) being independent of the spatial variation of specific interfacial-area. Thus, from the mathematical perspective, continuity of specific interfacial area does not have to be enforced. Therefore, the missing implementation of an interface condition regarding to specific interfacial area is no more crucial to the solution. In our applied range of $K_{wn}$, interface conductivity with low magnitude permits steep gradients, which produces less problems in regards to a missing interface condition. Higher interface conductivity results in greater fluxes evening out the gradients, therefore equation (3.34e) gets more dominated by diffusive fluxes, which necessitates that the continuity of the state variable has to be preserved.

Compared with the homogeneous case, the heterogeneous setup demands higher computational efforts, thus all three model concepts require more time to finish the simulation, see Table 4.8. Again, the different models concepts require comparable amount of timesteps, thus the computational effort has to be spent to reach convergence within each time step. Note that the performance of the $2p2cia5$-model varies with the parameter of interface permeability, $K_{wn}$.

Table 4.8: Computational expenses for the fractured case.

<table>
<thead>
<tr>
<th>model concept</th>
<th>timesteps</th>
<th>computational time</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2p2c$</td>
<td>21</td>
<td>230 s</td>
</tr>
<tr>
<td>$2p2cia4$</td>
<td>22</td>
<td>503 s</td>
</tr>
<tr>
<td>$2p2cia5$</td>
<td>21</td>
<td>715 s</td>
</tr>
</tbody>
</table>
(a) \( 2p2cia5 \) - Specific interfacial area \( a_{wn} \left[ \frac{1}{m} \right] \).

(b) \( 2p2cia5 \) - Static production or destruction rate of interfacial area \( e_{wn} \left[ \frac{1}{m} \right] \).

Figure 4.11: Interfacial area and static production rate of interfacial area.
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4.2.2.1 Simulatory Challenges for the Heterogeneous Setup

Figure 4.12: Saturation $S_n$ at various nodes over the timespan of simulation.

For various periods, some models fail to converge because of distinct mechanisms, which are addressed chronologically in this subchapter. To gain some orientation, an overview of the temporal changes in saturation is given in Figure 4.12. The first numerical obstacle is formed after around six seconds, when the initial drainage process inside the fracture is reversed by an infiltration of gas from the matrix. Models with high conductivity to interfacial movement fail to reverse the imbibition process (i.e. fail to reelevate saturation and thus capillary pressure) at the bottom corner of the fracture, and the simulation aborts. Such a failing simulation run with $K_{wn} = 10^{-8} \text{[m}^3\text{s}]$ is visualized in Figure 4.13(a) with a dotted black line, in comparison with successful simulations of $K_{wn} = 10^{-12} \text{[m}^3\text{s}]$ (grey solid) and the 2p2cia4-model (black solid).

At the beginning, capillary effects drained the areas around the fracture. Later, when the fracture gets consistently filled with gas, exfiltration into matrix commences around the upper part of the fracture because of gravitational forces. After reinfiltration into the matrix has started, another turning point in the characteristic of the saturation in the upper areas of the fracture indicates a further increase in the gaseous saturation, because there is still a consistent gas flow through the fracture. Around 24 seconds, the front of the gaseous phase reaches the fracture, which thus gets considerably filled with gas (Figure 4.14(a)). While the fracture gets filled up even in the lower parts, the gaseous flow from the matrix into the fracture reverses. These turning points cause the sign of the term $\frac{\partial S_w}{\partial t}$ to alter, which results in convergence problems concerning the fifth balance equation over the Newton-steps: although it is a physically correct behaviour, it is challenging for numerical stability. Some configurations of the 2p2cia5-model with, for example, poor mesh quality or again high permeability values for the interfaces $K_{wn}$, do not succeed in switching the flow process at the adjoined nodes to the fracture, and thus fail to converge.
(a) Capillary pressure over the time at the bottom edge of the fracture.
(b) Production term of interfacial area in an upper node neighboring to the fracture $I_{w}^{A}$.

Figure 4.13: Numerical obstacles at 6 seconds (left) and 30 seconds (right).

around 30 seconds.

To improve convergence, especially for configurations with higher permeability to interfacial area, it was necessary to limit the influence of the term $\frac{\partial a_{\text{w}}}{\partial p} \cdot \left( \frac{dp_{c}}{dS_{\text{w}}} \right)_{\text{process}}$ of equation \(\text{(2.35)}\), because both factors can attain very high values. Models without such a limitation procedure gain such overdominated static production terms that they stop any further charging of the fracture: The fracture then seems sealed after 20 seconds and simulations abort before 40 seconds, without any change in the fracture saturation. Yet it is expected that deeper knowledge about the general production term $E_{\text{un}}$, either by experiments or by microscale simulatory models can redundantize this regulatory artifact. At this stance, proper experimental data is missing both for the permeability to interfacial area as well as for the diffusion length for molecules crossing the interface. The latter is needed for the microscale diffusive flux (Equation \(\text{(3.29)}\)). After all, Somasundaram et al. (1999) suggest that values of below one nanometer are still reasonable. For numerical stability, it is found that significant mass transfer has to be ensured, thus diffusion length is required to be very small. If the prefactor of Equation \(\text{(3.29)}\), $\frac{D_{\text{w}} a}{\kappa}$, gets too small, mass fractions at disproportionate distances from equilibrium are gained. Figure 4.15 plots variables over a line that is limited by the two arrows in the left picture, and compares real (solid black) and equilibrium (dotted, black) mass fractions. A diffusion length of $d = 10^{-7}m$ is shown on top, and $d = 10^{-8}m$ is underneath. Not only the saturation reaches negative values, but the mass fraction of air in water encounter unreasonable fluctuations: The prefactor seems to be too small for the process, hence mass transfer has to be bolstered by a larger interspace from equilibrium.
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(a) $2p2cia5 - S_n$ timestep 11 $\approx 24s$.

(b) $2p2cia5 - S_n$ timestep 12 $\approx 30s$.

Figure 4.14: Saturation $S_n$ at one of the crucial timesteps endangering numerical stability.

Figure 4.15: Comparison of higher (top, $d = 10^{-7}m$) and lower (bottom, $d = 10^{-8}m$) diffusion lengths.
4.2.3 Fracture-Matrix System with Multiple Fractures

The simple model setup with one fracture (Figure 4.1 b)) is extended with an additional second fracture to investigate the kinetic effects of multiple fractures. One instantiation features a second fracture that is implemented rectangular to the first one (Chapter 4.2.3.1), whereas, alternatively, an angular setup was assembled (Chapter 4.2.3.2).

4.2.3.1 Angular Setup

To compare the influence of the gravitational drift upwards on the different processes, an angular setup of two connected fractures was chosen (Figure 4.16), demanding a complex grid. Unfortunately, already at the beginning of the simulation runs, unreasonable peaks in the gaseous saturation are obtained (Figure 4.17). By examining the underlying grid, these peaks solely occur in areas where the triangular elements around the fracture nodes are leaning with respect to the flow direction. The displays in Figure 4.17 originate from the 2p2cia4-model, all other model concepts draw similar results. In contrast to the traditional description of the relative permeability, the problematic elements marked by a black circle combined with the new functional relationship \( k_{\text{r,} \alpha} = S_\alpha^2 \) act as a strong barrier to the gaseous flow, which results in lower gas content at the top of the second fracture, Picture 4.17(b). That is because the relative permeability function of the standard approach applied with the current VAN GENUCHTEN parameters yield higher values than the new description (a comparison is plotted in Figure 2.15). Yet minimal changes to the grid minimize irrational peaks of the saturation as well as the exorbitant hindering of gaseous flow, see bottom row of pictures in Figure 4.17.

In regards to mass transfer, negative mass transfer within the fracture has been discussed in Chapter 4.2.2. Gravitational forces in the additional, angular fracture are expected to be lower in comparison with the vertical fracture, which gains lower flow velocities and less change in saturation. The mass fractions are thus expected to lie closer to equilibrium. Figure 4.18 compares two adjoined nodes with comparable pressure gradients in
4.2. VERIFICATION STUDY FOR THE CONCEPTUAL MODELS

(a) Traditional relative permeability, unfortunate grid.

(b) $k_{r,a} = S_a^2$, unfortunate grid.

(c) Applied grid, enlarged.

(d) Traditional relative permeability, better grid.

(e) $k_{r,a} = S_a^2$, better grid.

(f) Improved grid, enlarged.

Figure 4.17: Dependancy on the applied grid, after 6 seconds.

both parts of the fracture system. Unfortunately, the distance from equilibrium is that small that it can only be visualized by the whole mass transfer term $I_A^a$ of Equation (3.29). Still, non-equilibrium mass transfer is detected to be higher in the vertical fracture than in the angular one, confirming a dependence on process velocity, or on driving forces for advective flow, respectively. Note that the process of mass transfer is subject to the grid, so a comparison of both fracture parts strongly depends on the chosen nodes.

Simulations were carried out until 150 seconds, the final distribution of the gaseous phase is shown in Figure 4.19. Compared to the the angular fracture, gravitational forces pull a higher gas volume into the vertical part. However, the $2p2cia5$-model directs slightly more gas into the angular fracture in comparison with the other drainage-bound models.
Figure 4.18: Mass transfer of air over the timespan of simulation for adjacent nodes in the vertical (dotted) and angular (solid) fracture.

(a) $2p2c$, identical with $2p2cia4$ - saturation $S_n$.

(b) $2p2cia5$ - saturation $S_n$.

Figure 4.19: Final state of the simulation runs which includes a second fracture.
4.2.3.2 Perpendicular Setup

Although the model setup is axially symmetrical, the grid generator is not forced to mesh symmetric, thus differences evolve between the left and the right half of the capping fracture. However, symmetry demands that the underlying physical processes are identical for both branches, so any encountered deviation is of pure numerical origin. Whilst differences are observable for the propagation of the gaseous phase, they are present in all models. The right part of Figure 4.20 shows linear plots between the two arrows marked on the left picture, at a simulation time of 50 seconds. The upper subfigure compares the real mass fraction (solid) with the equilibrium mass fraction (dotted) of the $2p2cia5$-model, compared with the saturation of gas on the right axis. The lower subfigure presents the primary drainage-bound capillary pressure that is gained by the $2p2c$-model (dashed) and the resolved capillary pressure of the unbound $2p2cia5$-model (solid). Compared to the fluctuations of saturation, and thus also capillary pressure, the processes included in the new interfacial-area based models (non-equilibrium mass transfer as well a better determination of capillary pressure) do not enforce larger nonconformity. Nor do they, in regards to meshing, reduce numerical stability.
Figure 4.20: Deviances of $X^A_w$ and $p_c$ gained by the $2p2cia5$-model (black, solid) with $X^A_{w,s}$ (dotted) and the drainage-bound $p_c$ (dashed), in comparison with the saturation (grey).
Chapter 5

Final Remarks

5.1 Summary and Conclusion

An alternative to the standard approach to model multiphase multicomponent transport has been presented which is able to eliminate the hysteretic behaviour of macroscale capillary pressure, and which is not bound on local thermodynamic equilibrium. The new approach was implemented in the modeling framework DuMu$^x$, and several case scenarios were assembled.

Additionally, the distinct properties of fractures and their interconnection with the host matrix were regarded. Measurements determining upscaled effective parameters as well as interfacial area which are gained through the work of Nuske (2009) have been implemented and proved to produce meaningful results on the larger scale. Numerical stability was challenging with regards to the distinct differences between the fracture and the matrix, yet reasonable attempts improving mesh quality significantly enhanced the performance. While the new approach demands longer simulation time compared to the traditional approach, numerical convergence was gained in equal measure. It is expected that further work, an implementation of an interface condition, for example, will further improve performance and stability, and remaining numerical restrictions will dissolve.

The new concept was verified for the test case of an infiltration of a gaseous phase into a saturated, homogeneous domain. An application of conforming concepts for the relative permeability function gained comparable results with regards to the gas distribution. Even when infiltrating into a fractured domain, no significant changes in phase distribution between the different model concepts are observable. However, both additional effects of the new approach, namely mass transfer due to non-equilibrium and process-depending capillary pressure, have been obtained. On the one hand, the new approach exhibits states of non-equilibrium within the fracture due to high process velocities. The states are closer to a state of equilibrium if the flow regime is subject to smaller driving forces. However, the defining parameters (here especially the diffusion length) have to be further examined to improve a correct estimation of the magnitude of such non-equilibrium processes. On the other hand, a determination of capillary pressure that is neither bound on drainage, nor on imbibition cycles, was successfully included in the numerical framework. A dependence besides the saturation on imbibition or drainage processes and process history is once again monitored within the fracture.
5.2 Outlook

To gain better insights into kinetic interphase mass transfer, the experimental knowledge of the underlying processes has to be extended. Parameters which are necessary on the macroscale, such as the interface permeability $K_{wn}$, the production or destruction rate of interfacial area $E_{wn}$, or the diffusion length for microscale mass transfer $d$, have to be further examined on the porescale to revoke current assumptions. If satisfactory information with regards to these underlying processes are gained through experiments, the physically-based models can be verified and adjusted to match the experimental results. Future research has to be done to identify areas with significant local mass transfer according to process characteristics, possibly with a concept of dimensionless numbers (i.e. Damköhler number). A further interesting task would be to examine an example that is capillary dominant with extensive drainage and imbibition cycles, where a physically correct determination of capillary pressure is extremely important (for example the determination of recharge through the unsaturated zone for agricultural needs).

A desirable employment to environmental applications of interest, such as CO$_2$ injection comprising high flow velocities near the injection wells, requires improvements of the numerical framework. Multi-scale and multi-physics techniques save computing time and data demand, thus reduce the comparatively larger simulation time of the new approach. Plus, the additional effective parameters have only to be collected in subdomains where effects of non-equilibrium are expected. Since even large systems in the range of kilometers call for a local determination of fine-scale mass transfer, refinement techniques are necessary.

Furthermore, the set of governing equations has to be extended for non-isothermal processes with energy balances. It is expected that mass transfer through non-equilibrium is significant for non-isothermal applications such as thermally-enhanced soil remediation. As already mentioned, with regards to fracture-matrix systems, an interface condition is to be implemented. This will not only improve system stability and validity, but can further be extended to broaden the range of application to coupling procedures of different flow regimes, i.e. flow through porous media coupled with free-flow. Then, even biologic applications such as the transfer of therapeutic agents into and from the interstitium can be examined.
Appendix A

Heterogeneous Setup with one Fracture

This section presents additional visualizations of the test case of one single fracture, which do not have to be addressed in detail in the recent chapters.
APPENDIX A. HETEROGENEOUS SETUP WITH ONE FRACTURE

Figure A.1: Final state of the simulation runs with one single fracture.
Bibliography


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<th>Authors</th>
<th>Title</th>
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<td>Convergence study and comparison of the multipoint flux approximation L-method</td>
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<td>van Duijn, C.J. / Pop, I.S. / Niessner, J. / Hassanizadeh, S.M.</td>
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