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THE EFFECT OF THE CONTACT ANGLE ON THE MACROSCOPIC TRANSPORT PROPERTIES

A PORE-SCALE MODELING APPROACH

by

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Abstract

Low-salinity water flooding is a promising technique for the improvement of oil recovery. Despite intensive research, there are controversies about the pore-scale mechanisms behind the low-salinity effect (LSE). One of the proposed LSE mechanisms is wettability alteration, which is reflected in a decrease in contact angle. However, it is not known how a variation in contact angle affects the macroscopic transport properties such as capillary pressure and relative permeability.

The effect of contact angle variation on the transport properties is investigated by simulating capillary dominated, two-phase flow with a quasi-static pore-scale modeling method. The simulations are performed with real rock samples and, therefore, the effects of heterogeneities in the rock are incorporated. We distinguish three levels of analysis: single pore throat, bundle of tubes and pore network model. The first two levels of analysis comprise microscopic effects of the contact angle, whereas the pore network also includes macroscopic effects due to the connectivity characteristics of the network. For this reason, percolation theory is used to enhance the understanding of the effect of the connectivity on the flow properties.

The pore-scale fluid configuration is influenced by the wettability of the pore walls. However, previous research has not related the conventional wettability definition with the definition from an engineering perspective, which is based on the capillary pressure curve. Therefore, to include wettability effects on the transport properties, the definition of "pore wettability" has been revised such that the curvature of the fluid-fluid interface is consistent with the capillary pressure. As a result, the pore wettability is not solely dependent on the contact angle, but also on the pore geometry. The geometry now plays a crucial role, which implies that it is of high importance that the extraction algorithm provides accurate pore geometries.

Modeling results reveal that the contact angle has a negative effect on transport properties in perfectly homogeneous media. However, real rock representations always have a certain degree of heterogeneity. Heterogeneity negatively affects the transport properties, because it decreases the connectivity and thus the conductivity of the network. In presence of permeability contrasts, variation in contact angle influences the pore filling sequence, which affects the transport properties. Snap-off displacements suppress the effect of permeability contrasts, which means that regards oil recovery water-wet systems are favoured over oil-wet systems. In contrast, in case of heterogeneity at pore-level, snap-off leads to oil entrapment and has a negative effect on the residual oil saturation. This implies that oil recovery improves at increasing oil-wetness. For this reason, maximum oil recovery is obtained under intermediate-wet conditions. Since heterogeneities play an important role in snap-off, the optimum wetting state is dependent on the network topology.

When aging is taken into account, an opposite flow behaviour is observed. Transport properties are positively - instead of negatively - affected by an increasing contact angle. These conflicting results might be an explanation for the inconsistent experimental results.

Since capillary dominated flow neglects differences in displacement rates, further research is required to investigate the effect of contact angle variation in the presence of dynamic forces. Furthermore, a dynamic model would allow mobilization of the trapped oil phase, which enhances the accuracy of the oil recovery predictions. The size of the oil clusters might provide an indication on the mobilization of the oil entrapment.
When writing this preface, I realize that it is almost one year ago that I started with my final graduation project, though it seems like yesterday. I still remember my first day when Vahid introduced me to my future colleagues. When they asked what I was going to work on, I carefully answered that I was going to write my thesis about “pore-scale modeling of wettability effects”, looking at Vahid hoping for a confirmative nodd. Until then, I did not know anything about pore-scale modeling, let alone that I knew how to model wettability effects. Luckily, Vahid was there to educate me to be a well-rounded pore-scale modeler.

Although I was always excessively enthusiastic about my graduation project, the word ‘modeling’ had some deterrent effect on my colleagues. I honestly had a hard time in convincing them that pore-scale modeling is a useful tool to enhance our understanding of the displacement mechanisms underlying the techniques that we use in enhanced and improve oil recovery methods. My modeling campaign finally paid off after nine months, when some colleagues showed their interest after my team presentation. So for once and for always: dear colleagues, pore-scale modeling is not rocket-science.

I would like to gratefully and sincerely thank Vahid for all the support, knowledge and guidance during my graduation project. When I could not see the forest for the trees anymore, you always sent me in the right direction without giving the answer to my question. You unlocked the inner research in me. Furthermore, I would like to thank Cor for your supervision during my project. Although I had some low points towards the end, I could not have wished for a better graduation project than this. Thank you for your confidence in me to make this project a success.

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"If you do not fear your deadline, you set the bar too low"

P.L. Hogenkamp
Delft, September 2014
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Understanding multi-phase flow through porous media is of importance in many hydrological and environmental applications including soil remediation, contaminant transport, and enhanced oil recovery. In order to explain multi-phase fluid flow at reservoir scale, one needs to understand the pore-scale properties of multi-phase systems [34]. Macroscopic properties as capillary pressure and relative permeability are primarily dependent on the pore-scale fluid configuration [34], which is determined by the individual fluid properties, the geometry of the pore space, and the saturation history [18, 62]. Pore-scale modeling is used to simulate fluid displacements in randomly disordered media, such as reservoir rock. It provides insights in the effect of pore-scale properties on the macroscopic transport properties.

In two-phase flow, individual fluid phases are competing for pore space. The resulting pore occupancy determines which phases can flow and at which rate [28]. The flow rate depends on the total resistance, or conductivity, of the flow path, which consists of an array of pore segments linked in a chaotic series-parallel way [28]. Since the subpopulation of pore segments that form the array results from the competition for pore space occupancy, the total conductivity of the flow path is dependent on flow history.

For Newtonian fluids with a sufficient low flow rate, the volumetric flux is proportional to the potential gradient and inversely proportional to the viscosity. According to Darcy’s law, the coefficient of proportionality is the permeability. This coefficient is the product of the absolute and the relative permeability. The absolute permeability reflects the permeability when the pore space is filled by a single fluid phase, whereas the relative permeability measures the phase conductivity when the fluid phase participates in multi-phase flow. Hence, the relative permeability depends on the historical-dependent occupancy.

To effectively model the macroscopic fluid transport, we first need to know the microscopic configuration.

1.1. Modeling the Void Space of a Rock

Pore scale-modeling requires, in addition to the physics that describes the fluid flow at pore-scale, a description of the void space of a porous medium [3]. Once a 3D representation of the void space is obtained, it can be used to simulate fluid flow through the network. The simplest representation of a porous medium is a regular lattice consisting of pore bodies and pore throats [22, 28, 29, 48, 52]. However, these networks are based on stochastic parameters rather than on physical properties of a porous medium.

Network models based on topologically equivalent structures are leading to more accurate predictions of the flow properties [1, 9, 13, 62, 84]. There are three ways in which a topologically equivalent pore network can be obtained. First, pore networks can be described on the basis of the sedimentary process by which the rock is formed [9, 16, 58]. These methods create a pore network by simulating the deposition of grains with different sizes. Secondly, by reproducing structural patterns observed in a 2D thin section a 3D network can be generated with help of multiple point statistics. Thirdly, a 3D image can be created by using micro-CT scanning [10, 27, 44]. This pore space model can be simplified by replacing the void space by a network of pores and throats with well-defined geometrical shapes [1]. Although this advancing imaging approach provides a direct description of the void space, it is limited by the resolution of the micro-CT scanner.
1.2. **Pore-Scale Modeling of Wettability Effects**

Wettability is determined by a force balance between adhesive and cohesive forces. When the surface has a high affinity with a certain fluid, the fluid spreads over the surface and hence it is fully wet. In contrast, when the surface does not have an affinity with the fluid, the fluid does not spread but forms a spherical cap. The shape of the spherical cap is described by the curvature and the contact angle, which is the angle at which the fluid-fluid interface meets the solid surface. Distinction is made between drainage, which describes the displacement of the wetting phase (e.g., migration of oil from source rock to reservoir rock), and imbibition where the wetting phase displaces the non-wetting phase. Moreover, the literature discriminates between *spontaneous imbibition* and *forced imbibition*. During spontaneous imbibition, the advancing phase is "sucked" into the pores. In contrast, in forced imbibition the advancing phase is forced into the pores. In fact, this is equal to drainage.

Initially, pores are water-saturated and it is assumed that the pore walls are strongly water-wet. Following primary oil flooding (during migration), a thin water film protects the walls from the oil components that can alter the wettability. In some pores the film might collapse and as a result, a fraction of the pore walls become oil-wet [38]. Therefore, wettability may be considered as non-uniform and the system may contain of fractions of oil-wet, water-wet pores and intermediate-wet pores. Distinction is made between fractional wettability and mixed wettability [48]. Fractional wettability is the result of differences in surface chemistry of the minerals in the pore wall. As a result, the asphaltenes in the crude oil may adsorb onto some pore wall while ignoring others, which means that fractionally wet rock may contain oil-wet pores of all sizes. This is in contrast with mixed wettability, which is used to describe networks where the oil-wet pores correspond to the largest pores, with the small pores remaining water-wet.

Network models representing strongly water-wet networks have a good match with experimental data on water-wet rock. However, very few studies have been reported that attempt to simulate flow in networks of heterogeneous wettability. Pore networks representing rock that shows heterogeneous wettability have been developed by Mohanty and Salter [52], Heiba et al. [28, 29], McDougall and Sorbie,[48], and Dixit et al.[22]. Pore elements are randomly assigned different wettability. However, none of these network models have been based on a physical scenario for variations in wettability at pore-scale. The pore elements in these regular networks are assumed to be circular capillaries, which does not allow for heterogeneous wettability within a single pore.

Blunt [11] has developed a network model that captures wettability discontinuities at sub-pore level, based on Radke et al.'s pore scale description of wettability alteration. In his work, the pore throats are modeled as square-shaped tubes, which allows the existence of corner films. Subsequent primary oil flooding, the water phase remains in the corner films. The oil that entered the pore space occupies in the center of the cross section. Assuming that initially the rock is water-wet, the pore walls that are in direct contact with the oil will have an altered wettability. Blunt [11] included contact angle hysteresis in his model by assigning each intrinsic contact angle a receding and advancing value.

Valvatne and Blunt [84] and Piri and Blunt [62, 63, 66] improved the pore-scale model predictions by using a topologically equivalent pore network, based on a geologically realistic pore size distribution. Variation in wettability is represented by uniformly distributed contact angles. The distribution parameters are modified to match measured wettability indices from experimental data. Valvatne and Blunt's [84] results reveals that predictive relative permeability was in better agreement with experimental data when oil-wet pores are spatially correlated than when correlation is based on pore size only. Furthermore, the results demonstrate the effect of the initial water saturation on the capillary pressure, the relative permeability and the oil recovery efficiency.

1.3. **Applications of Pore-Scale Modeling**

Pore-scale modeling enables us to valuate the effect of pore-scale properties on the macroscopic transport properties. This research focuses on the contact angle as pore-scale property. In the next sections, some practical applications of the valuation of the contact angle are discussed.

1.3.1. **Low-Salinity Water Flooding**

To improve oil production, several new recovery techniques have been suggested. One of the emerging enhanced oil recovery (EOR) techniques is Low-Salinity (LS) water flooding. Experimental data shows that oil recovery is higher at decreased brine salinity. Tang and Morrow [83] first reported the Low-Salinity Effect (LSE) after they saw an increase in crude oil recovery in their LS core floodings. However, despite extensive
research on the LSE, controversies still exist about the pore-scale mechanisms that induce the improvement in oil recovery. LSE mechanisms that are proposed are wettability alteration [69, 91, 92], interfacial tension reduction, in-situ emulsification [49, 86] and fines migration [25, 54, 65, 91].

This research focuses on wettability alteration, reflected by a decrease in contact angle. Several hypotheses for the mechanisms underlying the wettability alteration have been proposed by prior research. The most prominent hypotheses are Multicomponent Ion Exchange (MIE) [39] and Double Layer Expansion (DLE) [43]. Both mechanisms reinforce the repulsive forces between the rock and the crude oil.

Under typical reservoir conditions, sandstone surfaces are normally negatively charged [5]. Since crude oil also exhibits negatively charges [17], repulsive forces between the sandstone surface and the crude oil prevent the oil from coating the pore wall. As a result, the rock is coated by a thin layer of water. Multivalent cations, such as Ca\(^{2+}\) and Mg\(^{2+}\), are believed to act as a bridge between the solid surface and the crude oil. When the concentration of multivalent cations is high enough, their positive charge can surpass the repulsive forces and altering the wettability to oil-wetness [5, 39, 43]. However, at reduced brine salinities, the shielding potential of the cations is suppressed and the repulsive force becomes dominant, which results in water-wetness.

In contrast with sandstone, carbonate is positively charged. Since there is an attractive force between the carbonate and negatively charged oil, carbonate rock is coated with oil without the need of a cation bridge. Hence, carbonate is either intermediate or oil-wet. However, in the presence of anions, in combination with excess calcium, anion exchange can occur. As a result, the anion adsorbs onto the pore wall and the previously adsorbed oil is released from the rock [7, 43]. This changes the wettability of the carbonate rock from oil-wet towards water-wet. However, RezaeiDoust et al. [68] proposes that the solubility of organic material increases at low brine salinities. When negatively charged organic material is detached from the rock surface, the surface becomes more water-wet. For this reason, it is not clear which pore-scale mechanism is responsible for the increase in oil recovery.

At pore level, wettability alteration manifests in a decrease in contact angle towards a water-wet state [45]. This implies that LS water flooding lowers the contact angle of the sandstone surface. For oil recovery, water-wet pores are preferred over oil-wet or mixed-wet pores, because then oil can be recovered with spontaneous imbibition rather than forced imbibition [4].

1.3.2. LOW-SALINITY POLYMER FLOODING
Polymer flooding is a well-known, mature EOR technique, which is applicable to both sandstone and carbonate reservoirs [85]. Polymers are macro-molecules, composed of many repeated subunits. The injection of polymers increases the water viscosity, which enhances the oil-water mobility ratio. As a consequence, water channeling is minimized and the areal sweep efficiency is improved. However, polymer molecules can potentially block pore throats in the reservoir rock, which tends to amplify permeability contrasts [72]. This is counterproductive for the oil production. Pore-scale modeling is a useful tool to predict the potential pore blockages and the corresponding effect on the relative permeability and fractional flow.

Combining polymer flooding with low-salinity flooding, amplifies the mutual benefits of the individual EOR techniques [85]. Adding polymer to low-salinity flooding improves the displacement efficiency, due to the enhanced mobility ratio and to the mobilization of oil that would have been trapped without polymer [74]. The polymer molecules block the fraction of smallest pores, which are mostly occupied by the connate water saturation. Making these pore throats inaccessible prevents the LS-polymer solution from displacing the connate water ([74]).

In addition, by decreasing the salinity of the polymer solution, the polymer molecules become more elastic. The elasticity enhancement of the polymers induces a decrease in pore blockages, which has a positive effect on the permeability. As a result, the residual oil saturation may reduce [85]. However, no research has been done to the effect on the flow path of the polymer solution. The change of contact angle may lead to a different flow path for the polymer solution, which potentially has significant effect on the oil recovery.

1.4. OBJECTIVES OF INNOVATION
Since wettability is one of the constituents of capillary pressure, which governs flow and fluid distributions in a porous medium, one can expect that wettability plays an important role in the macroscopic flow properties [89]. Prior research has made an effort to include wettability heterogeneity in pore-scale modeling. However, the majority of the pore-scale models has not included the contact angle as the initiating cause of wettability. For this reason, these networks do not succeed in approximating fluid flow through mixed-wet porous
Including the contact angle in the pore-scale models enables us to make better predictions of the macroscopic properties for mixed-wet media.

Previous research has explored the effect of the contact angle during secondary water flooding [11, 84], when the oil phase is receding. No research has been yet on the effect of the contact angle on pore entry. Hence, the pore-scale entry mechanism is not validated for the complete range of contact angles. When dealing with a heterogeneous wettability, the expression for pore entry must be valid for each value of contact angle.

Furthermore, the definition of pore wettability that is used in previous pore-scale modeling literature is inconsistent with the wettability-capillary pressure relationship. This discrepancy implies that water-wet pores are allowed to have a negative capillary pressure, which corresponds to an oil-wet pore element. Hence, the definition of pore wettability must be revised.

Another field of interest is the low-salinity effect. There are controversies whether and how much the wettability alteration improves oil recovery. To evaluate the role of the contact angle in the low-salinity effect, it is of great importance to improve the understanding of the effect of the contact angle on the flow and fluid distribution. An accurate model provides not only key insights in the cumulative oil production, but also the spatial location of the residual oil in the reservoir. These insights can be used to assess the applicability of low-salinity flooding for different types of reservoir rock.

To summarize, a good understanding of the relationship between the pore-scale properties and macroscopic transport properties greatly enhances the accuracy of the predictions for fluid flow behavior through systems with a heterogeneous wettability. Hence, the aim of this research is to investigate the effect of the contact angle on macroscopic properties as the capillary pressure, the relative permeability and the oil recovery.

1.5. Structure of Report

This research is subdivided into four levels of analysis. The first level, the single pore throat, is discussed in Chapter 2. This chapter explains the mutual relationships between pore-scale, or microscopic, transport properties. In Chapter 3 is the single pore throat upscaled to a bundle of tubes model. The macroscopic transport properties are dependent on the characteristics of the individual pore elements. Before we upscale the bundle of tubes to a pore network we have a look at the percolation model, in which the reservoir rock is simplified to a regular lattice. Chapter 4 presents the percolation theory and provides insights in the role of the connectivity and the heterogeneity of the network. The highest level of analysis, the pore network, is discussed in Chapter 5. The network model includes the geometry as well as connectivity of the extracted pore network, which provides the most accurate predictions of the flow properties.

The four levels of analysis are followed by the results (Chapter 7) and a detailed discussion of the modeling methodology (Chapter 8). To conclude, in Chapter 9 we present the conclusions and the recommendations that are derived from the pore-scale modeling results.
TWO-PHASE FLOW MODELLING AT A SINGLE PORE THROAT

The following sections provide an overview of the displacement mechanisms and resulting fluid configurations in a single throat.

2.1. PORE GEOMETRY

The network model consists of pore elements with angular cross-sections. The pore elements are characterized by their cross-sectional shape and can be categorized in three categories: squares, regular triangles and irregular triangles. The shape is determined by the cross-sectional shape factor, which is defined as [46]

\[ G = \frac{A}{P^2} \]  

where \( A \) is the cross-sectional area and \( P \) the perimeter. Square cross-sections have a shape factor that is larger than \( \frac{1}{36} \sqrt{3} \). Their corner half angles \( \beta \) is 45\(^\circ\). When the shape factor is equal to \( \frac{1}{36} \sqrt{3} \), the pore element has a regular triangular cross-section with corner half angles of 30\(^\circ\). When the shape factor is lower than \( \frac{1}{36} \sqrt{3} \), the pore element is considered to be a irregular triangle, with three different corners defined as

\[ 0 \leq \beta_1 \leq \beta_2 \leq \beta_3 \leq \frac{\pi}{2} \]  

The angular cross-sections are shown in Figure 2.1.

(a) Square  
(b) Equilateral triangle  
(c) Scalene triangle

Figure 2.1: Different pore geometries.
2.2. **BASIC DEFINITIONS**

In the following sections, the basic definitions of (quasi-static) pore-scale modeling are explained.

2.2.1. **CONTACT ANGLE**

The contact angle is the angle at which the fluid-fluid interface meets the solid surface. Generally, the contact angle is measured through the wetting phase. For consistency, in this research, the contact angle is measured through the water phase.

The contact angle during imbibition is different from the contact angle during drainage. The contact angle during drainage is called the ‘receding’ contact angle ($\theta_R$), for the reason that the wetting phase recedes. Similarly, during imbibition, when the wetting phase advances, the contact angle is called the ‘advancing’ contact angle ($\theta_A$).

2.2.2. **PORE WETTABILITY**

The wettability of a flat surface is determined by the contact angle, which has a range from $0^\circ$ to $180^\circ$. When the contact angle is $0^\circ$, the surface is *fully water-wet*. Similarly, when the contact angle is $180^\circ$, the surface is *fully oil-wet*. All the values between $0^\circ$ and $180^\circ$ are named *intermediate wet*. In the literature, contact angles between $0^\circ$ and $90^\circ$ are considered to be water-wet, and contact angles between $90^\circ$ and $180^\circ$ are considered to be oil-wet.

Pore wettability is not only dependent on the contact angle, but also on the pore geometry (Figure 2.4). Depending on the corner half angle, the contact angle defines the sign of the curvature of the fluid-fluid interface (Figure 2.2). Contact angles smaller than $(90^\circ - \beta)$ correspond to a positive curvature, and contact angles larger than $(90^\circ + \beta)$ correspond to a negative curvature. Subsequently, the curvature of the fluid-fluid interface dictates the wettability of a pore element. Based on the sign of the curvature, water-wet elements are characterized by a contact angle smaller than $(90^\circ - \beta)$. Similarly, oil-wet elements are characterized by a contact angle larger than $(90^\circ + \beta)$, which is mirrored with respect to the water-wet criterion.

![Figure 2.2: Relationship between contact angle and wettability of pore.](image)

Although pore elements with a contact angle between $(90^\circ - \beta)$ and $(90^\circ + \beta)$ have a negative interface curvature, they are denoted as *neutral pores* instead of oil-wet pores. For this range of contact angles, the curvature is always negative, independently from what phase occupies the corner. The neutral contact angles correspond with the intermediate wet contact angles measured at a flat surface ($\beta = 90^\circ$).
When the pore geometry is irregular, the corner half angles are not equal. As a consequence, a single contact angle can lead to different wettabilities in one pore element, with some corners fully wet and others neutral. However, since the corner half angles are assumed to be smaller than 90°, there are no pore elements with a combination of fully water-wet and fully oil-wet corners.

### 2.2.3. Capillary Pressure

In two-phase flow, the capillary pressure is the pressure in the non-wetting phase minus the pressure in the wetting phase (eq. 2.3). For consistency in analysis of oil-wet, water-wet or mixed-wet systems, we assume

\[ P_c = P_o - P_w \]  

(2.3)

where \( P_o \) is the oil-phase pressure and \( P_w \) is the water-phase pressure. The relationship between the capillary pressure and the mean curvature of the fluid-fluid interface (\( \kappa_m \)) is given eq. 2.4 [24].

\[ P_c = 2\sigma_{nw}\kappa_m = \sigma_{nw}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \]  

(2.4)

where \( \sigma \) is the fluid-fluid interfacial tension and \( r_1 \) and \( r_2 \) are the principal radii of curvature. When the curvature into the direction of the pore throat is zero, eq. 2.4 simplifies into

\[ P_c = \sigma_{nw}\frac{1}{r_c} \]  

(2.5)

where \( r_c \) is the radius of curvature in the cross-sectional direction. This expression is known as the Young-Laplace equation.

The capillary pressure is influenced by the wettability (Figure 2.4) since water-wet pores have a positive capillary pressure and oil-wet pores have a negative capillary pressure.

### Entry Capillary Pressure

Initially, at a zero capillary pressure, a pore element is completely filled with the wetting phase. When the non-wetting phase is advancing, it attempts to enter the pore and to displace the wetting phase. The pressure at which the non-wetting phase can enter a pore throat is the entry capillary pressure. The entry pressure can be determined by using the Mayer, Stowe and Princen (MS-P) theory [47]. This theory is based on the minimization of the free energy [47]. When the contact angle is smaller than 90°, the surface tension between the wetting and non-wetting phase parallel to the solid surface is in the same direction as the surface energy between the wetting phase and the solid rock. By balancing the surface energy between the two phases and the rock, Young’s equation can be derived:

\[ \sigma_{ns} - \sigma_{ws} = \sigma_{ow}\cos\theta \]  

(2.6)

For contact angles that are larger than 90°, the horizontal component of the surface tension is in the opposite direction. Since the contact angle is measured through the water phase, the angle between the surface tension and the solid surface becomes \( \pi - \theta \) instead of \( \theta \). However, \( \cos(\pi - \theta) \) is equal to \( -\cos\theta \), so Young’s equation also holds for oil-wet pore elements.
The capillary pressure between the wetting and non-wetting phase must be in balance with the forces due to the surface tension. Combination of the balance of forces and Young’s equation results in [57]:

\[(P_n - P_w)A_{nw,eff} = \sigma_{nw}(L_{nw} + L_{ns}\cos\theta)\]  

(2.7)

where \(A_{nw,eff}\) is the cross-sectional area filled with the non-wetting phase, \(L_{nw}\) is the total length of the fluid-fluid interface between the wetting and non-wetting phase, and \(L_{ns}\) is the total length of the solid-fluid interface between the solid formation and the non-wetting phase.

Substituting the Young-Laplace equation (eq. 2.4), the balance of forces becomes as follows [57]:

\[\frac{L_{nw} + L_{ns}\cos(\theta)}{A_{nw,eff}} = \frac{1}{r_c}\]  

(2.8)

\(A_{nw,eff}, L_{ns}\) and \(L_{ns}\) can be easily determined from elementary geometry [57]. For water-wet pores, the following geometrical relationships hold:

\[A_{nw,eff} = A_{pore} - r_c^2 \sum_{i=1}^{n} \frac{\cos\theta\cos(\theta + \beta)}{\sin\beta} - (\frac{\pi}{2} - \theta - \beta) \approx \frac{R^2}{4G} - r_c^2 S_1\]

\[L_{ns} = P - 2r_c \sum_{i=1}^{n} \frac{\cos(\theta + \beta)}{\sin\beta} = \frac{R}{2G} - 2r_c S_2\]

\[L_{nw} = 2r_c \sum_{i=1}^{n} (\frac{\pi}{2} - \theta - \beta) = r_c S_3\]

where \(n\) is the number of corners, \(R\) is the inscribed radius and \(G\) is the shape factor (eq. 2.1). For oil-wet pores (\(\theta \geq 90^\circ - \theta\)), the radius of curvature \(r_c\) in these equations becomes negative. Filling these geometrical relationships in eq. 2.8 and solving the equation for \(r_c\) results in [57, 61]:

\[r_c = \frac{R\cos\theta(-1 \pm \sqrt{1 + \frac{4GD}{\cos\theta}})}{4GD}\]  

(2.9)

where \(D = S_1 - 2S_2 \cos\theta + S_3\).
Using the relationship between the capillary pressure and the radius of curvature (eq. 2.4), the entry capillary pressure can be calculated. When the non-wetting phase enters the pore, the contact angle is the receding contact angle (wetting phase recedes) and is denoted as \( \theta_R \). For a square-shaped water-wet pore \((n = 4, \beta = 45^\circ)\), the capillary entry pressure is given by the following equation [36]:

\[
P_{c,\text{entry}} = \frac{\sigma_{nw}}{a} \left( \frac{\frac{2}{3} - 2\theta_R - \sqrt{3}\cos\left(\frac{\pi}{4} + \theta_R\right)\cos\theta_R}{\sqrt{\frac{2}{3} - \theta_R + \cos\theta_R \sin\theta_R - \cos\theta_R}} \right)
\]  

(2.10)

where \( a \) is the length of the sides of the (equilateral) square. For a water-wet equilateral triangle \((n = 3, \beta = 30^\circ)\), the entry capillary pressure is given by eq. 2.11.

\[
P_{c,\text{entry}} = \frac{\sigma_{nw}}{a} \left( \frac{\frac{2}{3} - 2\theta_R - 4\cos\left(\frac{\pi}{6} + \theta_R\right)\cos\theta_R}{\sqrt{\cos^2\theta_R + \frac{\sqrt{3}}{2} \left( \frac{2}{3} - \theta_R - 2\cos\left(\frac{\pi}{6} + \theta_R\right)\cos\theta_R\right) - \cos\theta_R}} \right)
\]  

(2.11)

where \( a \) is the length of the sides of the (equilateral) triangle.

The entry pressure is not applicable to entry of the wetting phase. It is proposed that when the wetting phase wants to enter a pore filled by the non-wetting phase, the wetting phase is "sucked" into the corner space of the pore. When the radius of curvature is such that the corner films meet each other at the solid-liquid boundary, the pore fills completely with the advancing wetting phase (Section 2.2.3). Furthermore, neutral pores do not have an entry pressure. They become filled with the advancing phase, on the condition that the pore is accessible by the advancing phase.

Irregular triangles can be partially wet and partially neutral. When a corner appears to be neutral, it completely fills with the advancing phase. In other words, neutral corners cannot have a corner film. The entry pressure of a neutral pore elements is based on the corner films in the fully wet corners.

**SNAP-OFF CAPILLARY PRESSURE**

Subsequent the entry of the non-wetting phase, the wetting phase occurs as corner films. The size of the corner films depends on the radius of curvature or capillary pressure. When two or more corner films meet, the thin wetting film loses contact with the solid-fluid interface and becomes unstable. As a result, the non-wetting phase will be "snapped-off" and the pore throat will be completely filled with the wetting phase. When the corners have different sizes, the minimum radius at which two adjacent corner films meet each other determines the snap-off pressure.

Snap-off only occurs during imbibition, when the corner films filled by the wetting phase are able to expand along the solid-fluid interface. Since the wetting phase advances, the contact angle at snap-off is the advancing contact angle and is denoted as \( \theta_A \). The snap-off capillary pressure is given by eq. 2.12.

\[
P_{s,\text{snap}} = \sigma_{nw} \min_{i:1:n} \left( \cos(\beta_{i,j} + \theta_A) a_i \sin\beta_{i,j} + \cos(\beta_{i,k} + \theta_A) a_i \sin\beta_{i,k} \right)
\]  

(2.12)

**2.2.4. SATURATION**

The fluid configuration in a single pore throat is a function of the contact angle and the capillary pressure (Figure 2.4) and can be quantified in terms of the saturation. The water saturation is defined as the fraction of water in a given pore throat (eq. 2.13).

\[
s_w = \frac{A_w}{A_{\text{pore}}}
\]  

(2.13)

Assuming that the pore space is filled by two phases, the oil saturation is defined as one minus the water saturation (eq. 2.14).

\[
s_o = 1 - s_w
\]  

(2.14)

**2.2.5. CONDUCTANCE**

Fluid flow through a single pore throat is proportional to the pressure gradient and the hydraulic phase conductance and is inversely proportional to the length of the throat and the fluid viscosity [32]. Since we neglect the gravitational forces, the pressure gradient is solely determined by the difference between the phase pressure at the in- and outlet of the pore throat.

\[
q_p = \frac{g_p \delta P}{\mu_p L}
\]  

(2.15)
where $g_p$ is the phase conductance, $\mu_p$ is the viscosity, $L$ is the length of the pore throat and $\delta P$ the pressure difference between the in- and outlet. Due to the stationary condition, the pressure difference is equal for all phases such that the capillary pressure remains constant. Here it is assumed that the fluid viscosity is constant over the throat. It follows that the relative permeability of one phase is only dependent on the phase conductance.

**Conductance of single phase flow**

Poiseuille’s law can be used to approximate the conductance of (laminar) single phase flow through a circular cylinder (eq. 2.16).

$$g_{p,\text{single}} = \frac{\pi R^4}{8}$$  \hspace{1cm} (2.16)

where $R$ is the inscribed radius of the pore. However, the pore throats in this research are angular instead of circular. Based on Poiseuille’s law, Bryant and Blunt [15] approximate the conductance of single phase flow through an triangular throat by eq. 2.17.

$$g_{p,\text{single}} = \frac{\pi \left( \frac{A_{\text{pore}}}{\pi} + R \right)^4}{128}$$  \hspace{1cm} (2.17)

Moreover, Øren and Arntzen [57] and Patzek and Kristensen [59] demonstrate that the dimensionless conductance ($\frac{g_p \mu}{A_p}$) of non-circular tubes is approximately proportional to the shape factor $G$ (eq. 2.18).

$$g_{p,\text{single}} = C A_p^2 G_p$$  \hspace{1cm} (2.18)

where $C$ is a dimensionless factor. Previous research shows that for angular throats $C$ can be approximated with $\frac{3}{5}$ [57, 59].

**Conductance of two-phase flow**

A circular pore throat is filled with a single phase, whereas an angular pore throat can also be filled with multiple phases. In two-phase flow, the wetting phase occupies the corner space and the non-wetting phase fills the pore center. There are no analytical expressions for the phase conductance in two-phase flow, though many work is done on analytical and numerical approximations of the conductances. The conductance of the corner film can be approximated by combining the hydraulic diameter and the thin-film approximations of Ransohoff et al. [32, 67, 93].

$$g_p = c^2 \frac{A_p^2}{3L^2}$$  \hspace{1cm} (2.19)

where $A_p$ is the flow area, $L$ is the length of the wetting boundary that generates flow resistance, and $c$ is a constant defined as [93]

$$c = \frac{(1 - \sin \beta) B}{\sin \beta (1 - B)}$$  \hspace{1cm} (2.20)

where $B = \left( \frac{A_p}{K} - \beta \right) \tan \beta$. As can be seen in eq. 2.19, the conductance is proportional to the cross-sectional area to the third power, which implies that there is a relationship between the saturation and the conductance (Figure 2.4). Furthermore, the contact angle has an influence on the conductance by determining the length of the wetting boundary (Figure 2.4).

When a no-slip condition holds at the fluid-fluid interface and there is friction between the fluid phases, the interface is also part of the wetting boundary $L$. Since the wetting boundary in single phase flow is equal to the perimeter of the pore throat, eq. 2.19 has the same appearance as the expression for single phase flow through an angular tube (eq. 2.18). Because there is no appropriate equation for the conductance of the bulk fluid, it is approximated by using eq. 2.18. The flow area $A_p$ is substituted by the flow area of the corner film $A_C$.

When there is an oil-layer sandwiched between water in the corner film and water in the center of the pore, the conductance of the layer is approximated in a similar way as the conductance of corner films [93]. However, the fluid-fluid interface between the corner film and the layer is assumed to be a rigid surface, which generates resistance. As a result, there is no-slip at this boundary.
2.3. **Pore Filling Scenarios**

In reservoir rock, pores are initially filled with water. The pore walls are fully water-wet. During migration, oil enters the pore space and displaces a fraction of the water. The resulting fluid configuration is a combination of the water phase and the oil phase. There are four scenarios that describe the pore-scale fluid configuration, depending on the wettability alteration. The four scenarios are explained below.

### 2.3.1. FULLY WATER-WET

In a fully water-wet pore ($\theta \leq 90^\circ - \beta$), the water phase occupies the corner space (Figure 2.5) when the capillary pressure allows the non-wetting phase to enter the pore element. The corner films have the smallest cross-sectional area at the maximum applied capillary pressure. When decreasing the capillary pressure, the corner film expands. As a result, the water saturation increases. Given the half-corner angle ($\beta$) and the contact angle ($\theta$), the position of the oil-water interface can be calculated for each radius of curvature (eq. 2.21) [64].

$$b = r_c \frac{\cos(\beta + \theta)}{\sin \beta}$$

(2.21)

With the position of the oil-water interface, the corner area occupied by the water can be calculated with eq. 2.22:

$$A_C = \sin \beta \cos \beta b^2 + r_c^2 \left( \theta + \beta - \frac{\pi}{2} - \frac{1}{2} \sin(2\theta + 2\beta - \pi) \right)$$

(2.22)

Since the fluid-fluid interface is a free flow boundary, only the solid-water interface generates flow resistance:

$$L_C = 2b = \frac{2r_c \cos(\pi - \theta - \beta)}{\sin \beta}$$

(2.23)
Hence, the conductance of the corner film becomes:

\[
g_C = \frac{c^2}{12} \left( \sin \beta \cos \beta + \left( \frac{b}{r_c} \right)^2 \left( \theta + \beta - \frac{\pi}{2} - \frac{1}{2} \sin(2\theta + 2\beta - \pi) \right) \right) \tag{2.24}
\]

When adjacent corner films meet each other at the solid-fluid interface, the corner films collapse (eq. 2.12). As a consequence, the non-wetting phase is “snapped off” and the pore throat will be completely filled with water. Since the snap-off capillary pressure is positive, the capillary pressure does not decrease below zero.

![Figure 2.5: Fluid configuration in fully water-wet pore.](image)

### 2.3.2. FULLY OIL-WET

In a fully oil-wet pore \((\theta \geq 90^\circ - \beta)\), the oil phase occupies the corner space. The fluid configuration is identical to the configuration in the fully water-wet pore, with the oil phase and the water phase reversed. The change in the radius of curvature indicates a wettability alteration. Since the negative radius of curvature corresponds to a negative capillary pressure, the change in the radius of curvature goes along with a decrease in capillary pressure. Water cannot enter the pore until the (negative) entry capillary pressure is reached. When decreasing the capillary pressure further, the oil-filled corner films shrink. Hence, the oil saturation decreases. The corner area and the phase conductance can be calculated in a similar way as the corner film in a water-wet pore is calculated (eq. 2.22 and 2.24).

### 2.3.3. MIXED-WET

In reservoir rock, pores are initially filled with the water phase and assumed to be water-wet. When oil enters the center of the pore space, the wettability of the pore walls in direct contact with the oil alters. Wettability alteration manifests in an increase in contact angle, which causes a change in radius of curvature and a decrease in capillary pressure. Since the corner film must conserve its volume, the changed radius of curvature leads to a decrease in corner size \(b\). The corner pore walls remain strongly water-wet. As a result, the pore is element is mixed-wet, with different wettability in the corner and the pore center.

After the wettability alteration, the “non-wetting” corner film cannot expand anymore, because the pore wall outside of the corner film has a different wettability. The corner film can also not retreat because the rock adjoining the corner has remained fully water-wet and requires a positive radius of curvature. Due to volume conservation, the radius cannot become positive because it leads to a reduced saturation of the non-wetting
2.3. PORE FILLING SCENARIOS

Figure 2.6: Fluid configuration in mixed-wet pore without oil-layer.

phase. In other words, the solid-fluid interface is pinned \( b_{\text{pinned}} \) at the solid rock. The contact angle of the pinned corner film is denoted as \( \theta_C \).

In the mixed-wet pore, the capillary pressure is negative, which leads to a change in radius of curvature (eq. 2.25). The sign of the minimum radius is negative, because the corner bulges out into the oil.

\[
    r_{\text{pinned}} = -\frac{b_{\text{pinned}} \sin \beta}{\cos(\theta_C + \beta)} \tag{2.25}
\]

When lowering the capillary pressure further, the fluid-solid contact remains pinned and the contact angle \( \theta_C \) adapts to the change in radius of curvature.

\[
    \theta_C = \cos^{-1}\left(\frac{b_{\text{pinned}} \sin \beta}{r_c} - \beta\right) \tag{2.26}
\]

The increasing contact angle reaches a critical value when the absolute radius of curvature is equal to the inscribed radius of the corner. From that point, the absolute radius of curvature can only increase (Figure 2.7), which does not suit with the increasing absolute capillary pressure. As a result, the curvature faces a non-monotonic change which is not consistent with the monotonic change in saturation. It is assumed that the curvature of the corner interface freezes when it reaches the minimum value. In short, the corner film bulges out maximally when it has reached its minimum radius of curvature (eq. 2.27).

\[
    r_{c,\text{min}} = -b_{\text{pinned}} \cos \beta \tag{2.27}
\]

The corner area of the bulging corner can be calculated with eq. 2.22 and the conductance of the corner film can be calculated with eq. 2.24.
**Coalescence of Corner Films**

There is no coalescence between separate corner films, because corner films never reach the size required to meet each other. Hence the corner interface remains stable. The non-wetting corner film bulges out maximally when the radius is minimum. At the minimum radius, the minimum corner size required for coalescence is given by eq. 2.28.

\[
b_{\text{coalescence}} = \frac{a}{2(\cos^2 \beta + \sin \beta)}
\]

where \(a\) is the length of the sides in an equilateral pore geometry. With the minimum corner size required for coalescence, the required corner area can be calculated with eq. 2.22. Since the volume must be conserved during aging, this corner area is equal to the corner area before aging. Subsequently, the radius of curvature of the wetting corner film required for coalescence can be calculated. However, this radius of curvature appears to be larger than the maximum radius of curvature, the entry radius. This implies that the non-wetting corner film after aging never reaches the size required for coalescence (Figure 2.8).

**Collapse of Oil-Layer**

When the capillary pressure reaches the entry capillary pressure, water enters the bulk of the mixed-wet pore. An oil-layer is created between the water in the corner and the water in the pore center (Figure 2.9). It is assumed that the non-wetting corner film freezes when the water has entered the pore center. The area of the oil-layer can be determined by subtracting the total corner area with the corner area occupied by the water (eq. 2.29).

\[
A_{\text{layer}} = A_C - A_{C,pinned}
\]

The conductance of the oil-layer is calculated in a similar way to the conductance of the corner film (eq. 2.24). The flow area is substituted by the area of the layer (eq. 2.29). The interface that generates flow resistance is not only the solid-fluid interface between the oil-layer and the rock, but also the fluid-fluid interface between the oil-layer and the water in the corner (eq. 2.30).

\[
L_{\text{layer}} = r_e \left( \frac{2 \cos(\theta_R - \beta)}{\sin \beta} + \beta + \theta_C - \frac{\pi}{2} \right) - 2b_{\text{pinned}}
\]

When both fluid-fluid interfaces meet, the oil-layer collapses. The capillary pressure at which this displacement occurs is called the collapse pressure. As a consequence, the pore completely fills with the non-wetting phase and there are no corner films left.
2.3. PORE FILLING SCENARIOS

Figure 2.8: The minimum corner size required for coalescence and the corner size in the wet-wet situation.

Figure 2.9: Oil-layer between non-wetting corner and bulk phase.
2.4. SUMMARY OF PORE FILLING SCENARIOS

The pore filling of a single pore throat is dependent on the initial pore filling, the wettability and the capillary pressure. First, the initial pore filling describes whether the pore is filled with the receding or advancing phase. When the pore throat is initially filled with the advancing phase, the element remains filled with the advancing/receding phase. Otherwise, the advancing phase possibly changes the initial pore filling by entering the pore throat. Secondly, wettability is a main driver behind the pore filling mechanisms. The contact angle, wetting uniformity and the character of the advancing phase play an important role in the determination of the pore filling. Thirdly, capillary pressure defines the fluid configuration in the pore element.

Figure 2.11 can be used to determine the pore filling in a single throat. The corresponding pore fillings are shown in Figure 2.10. Furthermore, the relationships used to calculate the pore-scale flow properties (capillary pressure, saturation and conductance) are summarized in Table A.1.

![Different fluid configurations of oil and water in a single pore](image-url)
2.5. CONTRIBUTION TO THE FIELD OF PORE-SCALE MODELING

The literature did not succeed in linking the conventional wettability definition, measured at a flat surface, with the definition from an engineering perspective, related to the capillary pressure. Previous work [11, 12, 66, 84] denoted pores with a contact angle smaller than 90° as water-wet pores and similarly, pores with a contact angle larger than 90° as oil-wet pores. This is in line with the conventional definition of wettability measured at a flat surface. However, this implies that there is a range of water-wet contact angles (90° − β ≤ θ < 90°) that has a negative curvature which from an engineering perspective corresponds to an oil-wet pore.

This research comes up with a new definition of pore wettability that is also consistent with the wettability definition from an engineering perspective. Pore wettability is not only dependent on the contact angle but also on the pore geometry, since the combination of these pore-scale properties defines the radius of curvature. As a consequence, the water-wet and oil-wet pores are separated by a range of neutral contact angles.

This research extends Kovscek et al.’s description of wettability alteration [38] since it included the same pore fillings (Figure 2.10). However, the change in the pore wettability definition required an revision of the displacement mechanisms that potentially lead to these pore fillings. One of the displacements mechanisms that had to be validated was the pore-scale entry mechanism. In prior research, the entry mechanism was only applied to drainage of fully water-wet pores. However, it was unknown whether the entry pressure could be applied to the complete range of contact angles. This research revealed that the entry mechanism is only valid for a certain range of (fully wet) contact angles. Furthermore, this research discovered that there is a range of “neutral” contact angles for which there is no threshold pressure. It is assumed that these ‘neutral pores’ are entered or exited immediately when the pore segment is accessible by the advancing phase.

Combination of the geometry-dependent pore wettability with the existence of irregular pores (with various corner half angles), allows a heterogeneous wettability at sub-pore level. Hence, it might appear that not all corners have a corner film. As a result, the expressions that define the pore filling are based on only the corners that have a corner film. Furthermore, the absence of certain corner films implies that they are not all are connected through the whole reservoir.
3

**TWO-PHASE FLOW MODELLING IN A BUNDLE OF TUBES**

The single pore throat from Chapter 2 is upscaled to a bundle of tubes model. The bundle of tubes model is quasi-static, which implies that the capillary pressure is equal through all tubes. Hence the radius of curvature is equal for all fluid-fluid interfaces. On one side the tubes are connected with a wetting reservoir and on the other side they are connected with a non-wetting reservoir.

### 3.1. Parametrization of the bundle of tubes

The bundle of tubes model consists of a set of unconnected tubes representing the pore throats of a network. The geometry of the throats is extracted from micro-CT images as is described in appendix B. Each tube is assigned a pore radius, a pore length and a shape factor.

### 3.2. Scenarios

The effect of the contact angle is assessed by investigating various wettability scenarios.

#### 3.2.1. Fully wet system

In the scenario where uniform wettability holds, all the pore elements have the same wettability. In a water-wet bundle of tubes, the tubes are assigned contact angles between $0^\circ$ and $90^\circ - \beta$, and in a oil-wet bundle the elements have a contact angle between $90^\circ + \beta$ and $180^\circ$.

In a bundle of uniform wet tubes, the contact angle is related to the maximum corner half angle. Since the corner half angle is uniformly distributed, the contact angle is also uniformly distributed. For water-wet pores, the contact angle is uniformly distributed between $0^\circ$ and $90^\circ$, and for oil-wet pores, the contact angle is uniformly distributed between $90^\circ$ and $180^\circ$.

#### 3.2.2. Fractionally or mixed-wet system

Also in the non-uniformly wet system, distinction is made between a single-value contact angle and a multiple value contact angle. The contact angle is assigned similarly to the uniformly wet system. For a non-uniform wettability, the bundle consists of 50% pore volume of water-wet elements and of 50% pore volume of oil-wet elements. Distinction is made between fractionally wet and mixed-wet systems. When the wettability is independent of the throat size, the system is called fractionally wet. The contact angle is assigned randomly to the pore elements, regardless of their size. This implies that the chance that a large pore element is water-wet is equal to the chance that a small pore element is water-wet. As opposed to a fractionally wet system, a system is called mixed-wet when the wettability is dependent on the throat radius. Since small-sized pores have a higher entry pressure, it is assumed that these pores are not reached by the oil phase during primary oil flooding. Therefore, in the mixed-wet scenario, the 50% of pore volume with the smallest pores is assumed to be water-wet and is assigned a contact angle between $0^\circ$ and $90^\circ - \beta$. The other 50% of pore volume with the largest pores is assigned a contact angle between $90^\circ + \beta$ and $180^\circ$.

When besides the wetting contact angles also the neutral values are included, pore elements can have
contact angles ranging from $0^\circ$ to $180^\circ$. Also here distinction is made between fractionally wet and mixed-wet. When the contact angle is unrelated with the pore size, the system is called fractionally wet. In contrast, when the larger pore elements are assigned a large contact angle, the system is called mixed-wet. The contact angles are assigned to the pore throats according to a normal distribution, characterized by the mean $\mu$ and the variance $\sigma$.

3.3. **AVERAGING FROM A PORE TO A BUNDLE OF TUBES**

The microscopic properties at the level of the single pore throat are averaged over the bundle of tubes. To indicate the higher level of analysis, the variables that describe the bundle of tubes model are denoted by capital letters.

3.3.1. **CAPILLARY PRESSURE**

The capillary pressure in the bundle of tubes is similarly defined as for the single pore (eq. 2.3). The individual phase pressures are measured at the boundary conditions at the in- and outlet of the bundle of tubes. Since the tubes are not connected, the capillary pressure is the same for each tube.

3.3.2. **SATURATION**

In a bundle of tubes, not only the cross-sectional area but also the pore length plays a role in the calculation of the saturation. The water saturation is calculated by dividing the total volume (cross-sectional area $\times$ pore length) of the water phase by the total volume of the bundle of tubes.

$$ S_w = \frac{\sum_{i=1}^{n} [A_{w,n} \cdot L_{w,n}]}{\sum_{i=1}^{n} [A_{pore,n} \cdot L_{w,n}]} $$

Again, the oil saturation is defined as one minus the water saturation:

$$ S_o = 1 - S_w $$

3.3.3. **RELATIVE PERMEABILITY**

The relative permeability is calculated by dividing the flow rate of a fluid phase in two-phase conditions by the total flow rate when the tubes are solely filled with that fluid phase. Since the tubes face a similar capillary pressure and the fluid viscosity is assumed to be constant through the network (eq. 2.15), the flow rate through each tube can be expressed in terms of the conductance and pore length. Hence, the relative permeability is the ratio of the sum of phase conductances in two-phase conditions divided by the pore length, and the total phase conductance when the bundle of tubes is filled with one single phase divided by the pore length (eq. 3.3).

$$ k_{r,p} = \frac{\sum_{i=1}^{n} \left[ \frac{g_{mp,i}}{L_i} \right]}{\sum_{i=1}^{n} \left[ \frac{g_{sp,i}}{L_i} \right]} $$

3.3.4. **FRACTIONAL FLOW**

Fractional flow quantifies the fraction of phase $p$ flowing with respect to the total flux.

$$ f_p = \frac{q_p}{q} $$

where $q = q_i + q_j$. Since the total flux is a summation of the flow rates of both fluid phases, the fractional flows must add up to unity. The flow rates of the individual phases can be expressed as Darcy’s law.

$$ q_p = -\frac{k k_{r,p} A}{\mu_p} \left( \frac{\partial P}{\partial x} + \rho_p g \sin \alpha \right) $$

Combination of eq. 3.4 and 3.5 gives an expression for fractional flow.

$$ f_i = \frac{1 + \frac{k_{r,i} A}{\mu_i} \left( \frac{\partial P}{\partial x} - \Delta \rho g \sin \alpha \right)}{1 + \frac{k_{r,j} \mu_j}{\mu_i}} $$

where the subscripts refer to either the water or oil phase. When the flow is horizontal and under stationary conditions (time-invariant system), the gravitational and capillary forces can be neglected. Furthermore, it is assumed that the phase viscosities are equal ($\mu_i = \mu_j$). The fractional flow expression reduces to

\[
 f_i = \frac{1}{1 + \frac{k_{r,j}}{k_{r,i}}}
\]  

(3.7)
Percolation theory attempts to predict fluid flow through randomly disordered medium with use of a simplified topological structure. A disordered topology, such as reservoir rock, can be described in terms of 'bonds' and 'nodes', which represent respectively the throats and bodies of a pore network. The pore segments is occupied by fluid, either the wetting or non-wetting phase.

There are two types of percolation models: bond percolation and site percolation. In bond percolation models, the properties of the pore network are assigned to the bonds, whereas the nodes are zero-dimensional features that interconnect the bonds. A bond is occupied with probability $p$, and is empty with probability $1-p$. In site percolation, the bonds are zero-dimensional features represented by the edges of the sites. The sites are occupied with probability $p$ or empty with probability $1-p$.

The bond-percolation model allows a variability in the coordination number, which is defined as the average number of bonds bound to a node, whereas the site-percolation model has a constant number of neighbours. The coordination number describes the connectivity of a medium. In order to match the connectivity of a given rock sample, the coordination number can be adjusted by removing pore throats at random from a regular lattice [22].

4.1. PARAMETRIZATION OF THE PORE NETWORK

In this research, there will be made use of a bond-percolation model based on a Bethe lattice, or Caley network. A Bethe lattice, or Caley network, is an infinite network where each node is connected to a constant number of bonds, indicated by the coordination number, $Z$. The network analysis in Appendix B reveals that both the Isba and Omar core samples have an average coordination number of 4. Hence, percolation theory approximates these networks with a Bethe lattice with $Z = 4$.

4.1.1. PORE GEOMETRY

Percolation theory assigns the pore radii randomly to the pore elements according to a probability distribution. In this work, pore throats are assigned a radius according to the discrete probability distributions extracted from the core samples as described in Appendix B. The radius represents the inscribed radius of the angular-shaped pore throat. The actual shape of the throat is determined by the shape factor. It is assumed that the complete Lattice consists of triangular pore throats with a constant shape factor of 0.0313, which is the average shape factor extracted from the Isba and Omar core samples.

Although originally the pore bodies in bond-percolation are zero-dimensional, previous research reveals that pore bodies play an important role in imbibition. The non-wetting phase in the pore bodies can be snapped off by the wetting phase in the smaller pore throats. Therefore, in this research also the pore bodies are assigned a pore geometry.

Besides a radius and shape factor, each pore element (throats and bodies) is assumed to have a volume. In an angular pore segment, the wetting phase fills the corner space and the non-wetting phase occupies the bulk of the pore. The volume of the corner space is neglected and the volume is a function of the inscribed radius.

\[ v(R) = R^3 \] (4.1)
4.1.2. **Conductance**

As regards the hydraulic conductivity, only the pore throats are assigned a conductance. Assuming that the throats are filled with only one phase, each pore throat is assigned a constant value for the conductance, related to the throat radius.

\[ g(R) = R^\mu \]  

(4.2)

where \( 3 \leq \mu \leq 4 \). The pore bodies are not assigned a value for the conductance. However, they contribute to the hydraulic conductivity by their connectivity \( (Z = 4) \).

4.2. **Basic Definitions**

In the next sections, the basic definitions of percolation theory are explained.

4.2.1. **Enterability**

Initially, pores are filled with the wetting phase. During drainage, the non-wetting phase is the advancing phase and is forced into the pore space. Similarly, in imbibition the wetting phase is the advancing phase and displaces the non-wetting phase. Whether the advancing phase can enter a pore throat, depends on the so-called entry radius of curvature. The entry radius is dependent on the shape factor, the inscribed radius and the contact angle (eq. 2.9).

Pore segments that have a greater entry radius than the effective radius of curvature are enterable for the non-wetting phase. Similarly, pore segments are enterable for the wetting phase when their entry radius is smaller than the effective radius of curvature [28–30].

\[ X_w = \int_0^{r_e} \alpha(r) \, dr \]  

(4.3)

\[ X_{nw} = \int_{r_e}^{\infty} \alpha(r) \, dr \]  

(4.4)

where \( X_p \) is the fraction of pore segments that is enterable by phase \( p \), \( \alpha \) is the bond radius distribution and \( r_e \) is the effective radius of curvature.

4.2.2. **Allowability and Accessibility**

Percolation theory makes a distinction between pores that are allowable and accessible [28–30]. The allowed set of pore segments consists of the bonds that are initially occupied and the bonds that are enterable for the advancing phase. However, allowability ignores the possibility that a bond is surrounded by segments that are not enterable. Hence, an allowable bond is not necessary accessible. The accessible set of pore segments is a subset of the allowed set of pore segments. Accessible bonds are not only allowable but also the surrounding bonds are allowable and accessible. Otherwise, the advancing phase cannot reach the allowable pore and hence the pore element is not accessible. The fraction of accessible pore segments with respect to the allowable fraction is expressed as \( X_p^A \). The accessible fraction in a regular Bethe tree can be calculated with eq. 4.5 [28].

\[ X_p^A = Q_A \left( 1 - \frac{Q_*^{Z-2}}{Q_A} \right) \]  

(4.5)

where \( Q_A \) is the fraction of pore segments allowed to phase \( p \) and \( Q_* \) is the root of

\[ Q_* (1 - Q_*)^{Z-2} - Q_A (1 - Q_A)^{Z-2} = 0 \]  

(4.6)

The accessible pore distribution is denoted as \( \alpha_p^A \).

4.2.3. **Percolation Threshold**

The percolation threshold is the largest fraction of allowed bonds below which the fraction of accessible bonds is zero [14], which implies that the conductivity is zero. When the allowed fraction is below the percolation threshold, the allowed bonds are isolated and form a finite cluster [28]. A cluster is defined as a set of occupied bonds that are interconnected. However, when the allowed fraction exceeds the percolation threshold, some of the allowed bonds are accessible. Hence, a flow path through the pore network is formed. In case of a capillary bundle model, the percolation threshold is zero, which implies that all the allowable bonds are accessible.
4.2. BASIC DEFINITIONS

In a Bethe lattice, each bond gives rise to $Z - 1$ bonds. Since each bond is occupied with a probability $p$ and $Z$ is the number of bonds that originate in a node, each bond has on average $(Z - 1)p$ occupied neighbours. If $(Z - 1)p < 1$, the probability that there exists a continuous flow path though the network drops to zero [14].

$$\lim_{n\to\infty} ((Z - 1)p)^n \to 0$$  \hspace{1cm} (4.7)

Hence, the percolation threshold occurs when $(Z - 1)p = 1$, or the percolation threshold for a Bethe lattice is:

$$X_C = \frac{1}{Z - 1}$$  \hspace{1cm} (4.8)

The relationship between the coordination number and the percolation threshold is displayed in Figure 4.1.

4.2.4. SATURATION

After the displacement process, the occupied pore segments comprise the pore segments that were occupied by phase $p$ before the displacement process plus the accessible segments at the present pressure difference between the advancing and the receding phases. The occupied pore fraction is given by $X_{Op}$ and the occupied pore-size distribution is given by $\alpha_{Op}$. The occupancy is then used to calculate the saturation and the phase conductance. The saturation is defined as the volume fraction occupied by phase $p$ divided by the volume fraction of the total pore network.

$$S_p = X_{Op} \int_0^{\infty} \alpha_{Op}(r)V(r)dr \int_0^{\infty} \alpha(r)V(r)dr$$  \hspace{1cm} (4.9)

During drainage $X_{Op}$ is equal to $X_{Ap}$, because there is initially no trapped cluster of the advancing non-wetting phase.

4.2.5. RELATIVE PERMEABILITY

The relative permeability is the ratio of the phase conductance to the conductivity of the total pore network (eq. 4.10). The phase conductance can be derived by numerically solving Stinchcombe’s equation [79], which only includes the throat occupation. Similarly, the conductivity of the network can be evaluated with Stinchcombe’s equation, assuming that the network is filled by a single phase and that all bonds are allowed and accessible ($X_{Ap} = 1$).

$$k_{rp} = \frac{C_p}{C_{single}}$$  \hspace{1cm} (4.10)

where $C_{single}$ is obtained by allowing all bonds to one phase ($Q_p = 1, a_{Ap} = a_p$).
4.3. Contribution to the field of percolation theory

Percolation theory does not distinguish between drainage and imbibition in terms of pore-scale displacement mechanisms. However, it is known that drainage and imbibition are controlled respectively by the entry and snap-off capillary pressure (Chapter 2). These threshold values can be related to the inscribed radius of the single pore segment. Therefore, difference between drainage and imbibition is reflected in the capillary pressure curves.

Furthermore, during drainage and imbibition, fluid displacements are controlled by different pore segments (throats versus bodies). To capture the effect of the body-throat aspect ratio, the pore body distribution is included in the percolation model. In drainage, large pore segments are invaded by the advancing non-wetting phase before the small pore elements are entered. The average pore throat is smaller than the average pore body, which implies that in drainage the throat defines the accessibility of the subsequent pore body ($X_p^A = X_p^{A, throat}$).

As opposed to drainage, in imbibition is the accessibility not only dependent on the pore throats, but also on the pore body distribution. It is assumed that the throat accessibility is equal to the allowability ($X_p^{A, throat} = Q_{p, throat}$), due to the presence of connected thin films that enable snap-off displacements in all pore segments. In contrast, the pore body accessibility is dependent on the occupancy of the pore throats. The accessibility is defined as the body allowability minus the fraction of pore bodies that is obstructed by its adjacent pore throats. Since the coordination number $Z$ indicates the pore body's connectivity, the chance that a body is obstructed by the advancing phase is equal to $(1 - X_{p, throat}^O)^Z$. However, the increasing throat occupation does not affect the connectivity of the pore bodies that are already invaded. The resulting body accessibility is as follows

$$X_{p, body}^A = Q_{p, body} - \int_{r_{end}}^{r_c} \left[ \alpha_{body}(r) \cdot \left(1 - X_{p, throat}^O(r)\right)^Z \right]$$

(4.11)

The resulting saturation is a weighted combination of the saturation resulting from the pore throat distribution and the saturation resulting from the pore body distribution (eq. 4.12).

$$S_p = \frac{V_{throat}}{V_{total}} \cdot S_{p, throat} + \frac{V_{body}}{V_{total}} \cdot S_{p, body}$$

(4.12)

where $V_{total}$ is the total pore volume, $V_{throat}$ is the volume within pore throats and $V_{body}$ is the volume in pore bodies.
5.1. Parametrization of the Pore Network

The pore network can be parametrized with the network properties that are extracted from the micro-CT images as described in Appendix B. As opposed to the bundle of tubes model, the pore elements are not only assigned a pore geometry, but also a spatial location in the network. This enables us to model the effect of the network topology on the fluid configuration and the corresponding flow properties.

5.1.1. Pore Geometry

In the pore network, the pore throat distribution is the same as used in the bundle of tubes model. However, in contrast with the bundle of tubes, the network also contains pore bodies which are connecting the pore throats. As a result, the network captures also connectivity, which indicates to what extent the fluid is permitted to move from one pore element to another. The geometry of the pore bodies is extracted from the micro-CT images as described in appendix B. Since the average pore body has a larger radius than the average pore throat, the pore bodies contain relatively large volumes of the fluid phases.

During drainage, the entry capillary pressure determines which pore elements are enterable by the advancing phase. Since pore throats are smaller than the pore bodies, the entry pressure for a pore throat is much higher than the entry pressure for a pore body. As a result, when the capillary pressure reaches the entry pressure of a pore throat, the advancing phase does not only fill the throat but it also fills the neighbouring pore body (Figure 5.1a). Hence, drainage is governed by the pore throats.

In contrast, imbibition is controlled by the pore bodies. The imbibition process is not determined by the capillary entry, but by the snap-off mechanism. Snap-off occurs first in the smallest pore elements, which are logically the pore throats. Subsequently, when a pore body is enclosed by snapped-off pore throats, the non-wetting phase in the pore body is so-called trapped (Figure 5.1b). As a result, a fraction of the non-wetting phase cannot be produced and remains in the pore space.

5.1.2. Coordination Number

The coordination number is used as a quantification of the connectivity. In the percolation model the pore bodies were assigned a constant coordination number, whereas in the pore network the coordination number is different for each pore body. The coordination number distributions for the Isba and Omar sandstones are shown in Figure B.7. Again, the zero values are erased from the data set, because pore bodies with a zero coordination number are by definition isolated and do not contribute to the relative permeability. Also the pore bodies with a coordination number of one are erased, because those pore bodies are ‘dead ends’ and do not influence the relative permeability.
5.2. MACROSCOPIC RELATIONSHIPS FOR A NETWORK MODEL

The microscopic variables from Chapter 2 are upscaled to macroscopic variables characterizing flow properties through a pore network model.

5.2.1. CAPILLARY PRESSURE

The network model is a quasi static model, which implies that the capillary pressure is equal for each pore element in the network and that fluid-fluid interfaces are kept static. The capillary pressure determines the radius of curvature of the interfaces and the fluid configuration in the pore throat. As a result, the capillary pressure determines the saturation.

5.2.2. SATURATION

In the network model, the water saturation is calculated in a similar way as in the bundle of tubes model (eq. 5.1). However, in the network model not only the pore throats (‘tubes’) can contain fluid, but also the pore bodies contain fluid phase.

\[
S_w = \frac{\sum_{i=1}^{n} [A_{w,n} \cdot L_{w,n}]}{\sum_{i=1}^{n} [A_{pore,n} \cdot L_{w,n}]} \tag{5.1}
\]

The oil saturation is defined as one minus the water saturation:

\[
S_o = 1 - S_w \tag{5.2}
\]

The saturation is dependent on the saturation path or saturation history [78]. This ‘path-dependency’ refers to hysteresis. From the point of pore-scale processes, there are two sources of hysteresis: contact angle hysteresis, and hysteresis caused by entrapment of the non-wetting phase [78]. Contact angle hysteresis is independent of connectivity and is the only source of the hysteresis in the unconnected pore models. However, in a network model, there is also hysteresis due to trapping of the non-wetting phase. When a fraction of the non-wetting phase becomes trapped, the fluid loses its connection with the bulk portion of that fluid and hence it becomes surrounded by the wetting phase [35]. As a result, the non-wetting fluid becomes isolated. The trapping of non-wetting fluid results in a certain residual saturation of the non-wetting phase. The larger the isolated regions, the higher the trapped/residual saturation of the non-wetting phase.
5.2.3. Relative Permeability
The relative permeability is calculated by dividing the phase flux at the network outflow in two-phase conditions by the total flux at the outflow when the network is solely filled with that single fluid phase. The conductance of each pore throat is dependent on the pore-scale properties. Pore bodies are not assigned a conductance, but have effect on the relative permeability by having different coordination numbers. Since the capillary pressure is constant through the network and the viscosity is assumed to be constant for each fluid phase, the relative permeability can be calculated with the conductance and length of each pore throat (eq. 5.3).

\[ k_{r,p} = \frac{\sum_{i=1}^{n} \left( \frac{g_{mp,i}}{L_i} \right)}{\sum_{i=1}^{n} \left( \frac{g_{sp,i}}{L_i} \right)} \]  

Analogous to saturation, relative permeability is also dependent on the saturation history. When a region is isolated from the bulk fluid, this fraction still contributes to the saturation of the trapped phase but it does not have an effect on the relative permeability. Hence, when fluid is trapped, a higher saturation is required to reach a similar relative permeability.

5.2.4. Fractional Flow
Also the fractional flow is calculated based on the flux at the network outflow. Hence, \( k_{r,i} \) and \( k_{r,j} \) in eq. 5.4 is substituted by the calculated relative permeabilities at the network outflow (eq. 5.3).

\[ f_i = \frac{1}{1 + \frac{k_{r,i}}{k_{r,j}}} \]  

Since the relative permeability is path-dependent, also the fractional flow is dependent on the saturation history.

**Determination of Shock Saturation**
Fractional flow curves are used to determine the saturation of the shock-front. The shock front is defined as a saturation discontinuity that results from a self-sharpening wave. Such a wave occurs when slower waves from saturations close to the initial conditions originate ahead of faster waves, a shock will form as the faster waves overtake the slower waves. For continuous saturation changes the differential mass balance is as follows:

\[ \frac{\partial S}{\partial t} + \frac{df}{dS} \frac{\partial S}{\partial x} = 0 \]  

The accumulation of saturation must be equal to the net influx of fluid (eq. 5.6).

\[ dS = \frac{\partial S}{\partial t} dt + \frac{\partial S}{\partial x} dx = 0 \]  

Combining eq. 5.5 and 5.6, the following expression is obtained.

\[ \left( \frac{dx}{dt} \right)_{dS=0} = \frac{df(S)}{dS} \]  

This expression reveals that the saturation velocity is equal to the slope of the fractional flow curve. The shock saturation can be defined by deriving the integral mass balance (eq. 5.8).

\[ \left( \frac{dx_D}{dt_D} \right)_{\Delta S} = \frac{\Delta f(S)}{\Delta S} \]  

Since the shock front velocity is not allowed to have a higher saturation velocity than the initial saturation, the shock saturation is found by setting the saturation velocity and change in fractional flow with respect to change in saturation are equal. Therefore, the shock saturation can be found to setting the shock velocity equal to the change in fractional flow divided by the

\[ \left( \frac{dx}{dt} \right)_{dS=0} = \frac{\Delta f(S)}{\Delta S} = \frac{f_{shock} - f_{initial}}{S_{shock} - S_{initial}} \]  

In other words, the shock saturation can be determined by drawing a tangent that starts at the initial saturation and touches the fractional flow curve at the shock saturation (Figure 5.2). Steep fractional flow curves have low shock saturations and thus low oil recovery. Hence, we have a preference for gentle fractional flow curves.
5.3. **SEQUENCE OF DISPLACEMENTS**

There are two displacement mechanisms that play a role in capillary dominated fluid flow: entry and snap-off. For capillary entry it is necessary that the pore element is connected with the advancing non-wetting phase. When the pore filling is determined by the snap-off mechanism, the pore element does not have to be connected with the advancing phase. Once the receding non-wetting phase is snapped off, the pore element cannot conduct that phase anymore. These snap-off events reduce the connectivity through a network, which results in lower phase conductivity. Trapped elements form a cluster, in which the capillary pressure is frozen.

All the possible displacement events are listed and subsequently sorted. If the capillary pressure is increased, the possible displacement with the lowest capillary pressure is executed first. In contrast, if the capillary pressure is decreased, the possible displacement with the highest capillary pressure is executed first.

5.4. **SCENARIOS**

The effect of the contact angle is analogous to the bundle of tubes model assessed by investigating various wettability scenarios.

5.4.1. **FULLY WET SYSTEM**

In the fully water-wet system, all the pore elements are assigned a contact angle that is lower than $90^\circ - \beta_{\text{max}}$. Similarly, in the oil-wet system, all the pore elements are assigned a contact angle that is higher than $90^\circ + \beta_{\text{max}}$.

5.4.2. **MIXED-WET SYSTEM**

In the mixed-wet system, the pore elements are assigned a contact angle in the range from $0^\circ$ to $180^\circ$. Similar to the contact angle in the bundle of tubes model, the distribution is characterized by a mean $\mu$ and a standard deviation $\sigma$.

Oil-wet pores are generally associated with a high clay content because as opposed to sandstone, clay has a positively charged surface. Since shale distributions are spatially correlated, it is likely that there is a mutual influence between the wettability of two adjacent pore elements. Valvatne and Blunt [84] suggest that good relative permeability predictions require the contact angle to be spatially correlated rather than correlating it with the pore size. Therefore, the pore elements in the network are assigned a contact angle with an exponential covariance function (Appendix C). It is assumed that the network is isotropic, which means that the covariance is equal in all directions.
Experimental Studies on Wettability Effects

Experimental results can be used to validate the outcomes of the pore-scale modeling work. In this chapter, prior imbibition experiments on low-salinity flooding and corresponding wettability effects are discussed.

From experimental studies, it is known that oil recovery, as function of injected pore volume, is higher for water-wet cores than for oil-wet cores. However, a few authors have indicated that recovery from water-wet and oil-wet cores is lower than recovery from intermediate wet cores [71]. Core flood experiments have shown that in mixed-wet porous media oil is drained down to a relatively low residual oil saturation [70]. Maximum recovery is observed at close to neutral wettability.

Salathiel [71] explains the high recovery from mixed-wet media with his observation of film drainage. This can only occur when the oil phase is connected through the reservoir. However, film drainage is not observed in all restored/preserved core experiments, which indicates that there must be another reason for the higher oil recovery in mixed-wet media.

In addition, Morrow et al. [53] observed higher displacement efficiencies when the cores were cleaned after the aging process. This suggests that the experimental results of waterflood experiments may seem to be contradictory. Therefore, the question remains how wettability affects the pore-scale fluid configuration and the corresponding flow properties.

6.1. Experimental Studies on Low-Salinity Water Flooding

In an number of laboratory and field studies, it is shown that low-salinity water flooding potentially leads to an improved oil recovery [73, 87, 88]. However, in some cases there is no incremental oil recovery observed [77, 92]. Since there is no consensus about the pore-scale mechanisms behind the low-salinity effect (Chapter 1), it cannot be determined in advance how the fluid flow through a certain rock responds to the low-salinity flooding. To predict the outcome of applying LSF in a given field, a deeper understanding of the underlying pore-scale mechanisms is required [81]. This reduces the wasteful application of LSF to fields with low pay-off [81].

Suijkerbuijk et al. [80] presented experimental results with core plugs from two Middle Eastern Fields. The core plugs are aged in the presence of the same brine. However, the core plugs show different imbibition behaviour 6.1. Upon immersion in synthetic formation brine, reservoir core 1 has an oil production of approximately 31% of Original Oil In Place (OIIP). Changing the brine from high-salinity to low-salinity leads to an additional oil production of approximately 10% of OIIP. As opposed to core 1, reservoir cores 2A/2B do not show any oil production during exposure to high salinity brine. However, subsequent immersion leads to an oil recovery of approximately 35 − 43% of OIIP.

The absence of oil production during the high-salinity flood indicates strong oil-wetness of core 2, whereas core 1 is rather mixed-wet. However, when Berea is immersed in the same crude as are found in the native systems of core 1 and 2A/2B, the spontaneous imbibition test shows (relatively) water-wet behaviour. Furthermore, the improved oil recovery is larger for the native systems than for Berea systems.
There is no consensus about the pore-scale mechanism that leads to the differences in imbibition behaviour. One of the prominent hypotheses is that the oil-wet characteristics are caused by oil components that adhere to the reservoir rock, which are not removed during cleaning. Though they are taken out by the low salinity brine during LSF. The native systems of the Berea cores presumably do not have these oil components. Hence, these core plugs remain relatively water-wet.

6.2. EXPERIMENTAL STUDIES ON LOW-SALINITY POLYMER FLOODING

Experimental studies show that the addition of low-salinity brine to polymer flooding has benefits over traditional polymer flooding. The experiments of Vermolen et al. [85] show that low-salinity polymer flooding leads to an increase in oil production. Also water-wet reservoir rocks experience a positive effect of combined low-salinity polymer flooding, because the required polymer concentration decreases with a factor two to four [85]. This is explained by the low-salinity effect on the elasticity of the polymers, which decreases the inaccessible pore volume and thus improves the sweep efficiency.

In addition, the experimental study of Shaker and Shiran [74] revealed that the oil recovery was improved significantly in the case where low-salinity was injected at initial water saturation rather than residual oil saturation. This indicates that the sequence of displacements plays a role in the displacement efficiency.
The pore-scale modeling results are presented in the sections below. Since we allow heterogeneous wettability, distinction is made between primary oil flooding and secondary water flooding rather than drainage and imbibition.

7.1. SINGLE PORE THROAT
For single pore throats, the capillary pressure curve is plotted for three different geometries: square ($\beta = 45^\circ$), regular triangle ($\beta = 30^\circ$) and irregular triangle ($\beta_1 = 15^\circ; \beta_2 = 30^\circ; \beta_3 = 45^\circ$). Distinction is made between the water-wet ($\theta \leq \frac{\pi}{2} - \beta$) and oil-wet scenarios ($\theta \leq \frac{\pi}{2} + \beta$).

It is assumed that the pore throats initially are filled with water. In a single pore throat, fluid cannot be trapped. Hence, when the capillary end pressure is sufficiently high, the residual water saturation is negligible.

7.1.1. PRIMARY OIL FLOODING
The capillary pressure curves for the water-wet pore throats (Figure 7.1a, 7.2a and 7.3a) show that the entry capillary pressure is decreasing for increasing contact angle. This is in line with the expectations, because an increasing contact angle indicates that the pore throat becomes more oil-wet. As a result, for the oil it is easier to enter the pore throat which is reflected in a lower entry pressure.

For the oil-wet pores, the advancing oil is sucked into the pores at negative capillary pressure. When the snap-off pressure is reached, the corner films filled with oil meet each other and the pore fills completely with oil. The graphs in figure (Figure 7.1b, 7.2b and 7.3b) shows that the snap-off pressure decreases for increasing contact angle. The more oil-wet the pore throat, the larger the corner size. As a consequence, the corners meet each other at a lower pressure.

![Figure 7.1: Capillary pressure curve for oil flooding through a square-shaped pore throat.](image)
7.1.2. SECONDARY WATER FLOODING

The capillary pressure curves for secondary water flooding are similar to the curves for primary oil flooding. However, in contrast with oil flooding, during water flooding is snap-off the mechanism that determines the pore filling in water-wet pores, and the fluid configuration in oil-wet pores is determined by the entry capillary pressure.

Furthermore, the system might contain non-uniformly wet pore elements. In the non-uniformly wet pores, the displacements are determined by the entry pressure and subsequently by the pressure at which the oil-layer collapses. The pressure at which the oil-layer collapses is dependent on the contact angle. Figure 7.4 shows that the receding contact angle \( \theta_A \) affects the entry pressure, but do not influences the collapse pressure. The collapse pressure is affected by the contact angle of the non-wetting corner film \( \theta_C \). The larger the contact angle, the higher the (absolute) collapse pressure. This means that the collapse pressure approximates the entry pressure for low contact angles (\( \theta_C > 90° - \beta \)). This would lead to less oil entrapment in a network, since the collapse occurs at the displacement front.
7.2. BUNDLE OF TUBES

A bundle of tubes consists of a set of pore throats, which can be assigned different wettability. For this reason, distinction is made between fully wet systems, in which the elements have the same wettability, and mixed-wet systems, in which the elements are allowed to have different wettability.

It is assumed that the tubes are initially filled with water. Similar to the single pore throat, the residual water saturation is negligible when the end pressure is sufficiently high.

7.2.1. PRIMARY OIL FLOODING

FULLY WET

A fully wet bundle of tubes has a similar capillary pressure curve as the single pore throat. Similar to the single pore throat, the entry pressure and snap-off pressure decrease with increasing contact angle. This is logical because the bundle of tubes is a linear combination of individual throats.

Besides the capillary pressure curve, also the relative permeability and fractional flow curves are plotted. Figures 7.6a/7.6b and 7.9a/7.9b show that an oil-wet contact angle leads to a higher water relative permeability at all saturations, while it leads to a lower oil relative permeability. Logically, it leads to a lower fractional flow for the water phase (Figures 7.7a/7.7b and 7.10a/7.10b).
7. Results

(a) Water-wet

(b) Oil-wet

Figure 7.5: Capillary pressure for oil flooding through fully water- and oil-wet bundle of tubes extracted from Isba.

(a) Water-wet

(b) Oil-wet

Figure 7.6: Relative permeability for oil flooding through fully water- and oil-wet bundle of tubes extracted from Isba.

(a) Water-wet

(b) Oil-wet

Figure 7.7: Fractional flow for oil flooding through fully water- and oil-wet bundle of tubes extracted from Isba.
7.2. **Bundle of Tubes**

(a) Water-wet

(b) Oil-wet

Figure 7.8: Capillary pressure for oil flooding through fully water- and oil-wet bundle of tubes extracted from Omar.

(a) Water-wet

(b) Oil-wet

Figure 7.9: Relative permeability for oil flooding through fully water- and oil-wet bundle of tubes extracted from Omar.

(a) Water-wet

(b) Oil-wet

Figure 7.10: Fractional flow for oil flooding through fully water- and oil-wet bundle of tubes extracted from Omar.
**Mixed-wet**
When the bundle of tubes is mixed-wet, individual pore throats are assigned contact angles corresponding to a different wettability. In the first scenario are the pore elements either fully water-wet ($\theta = 0^\circ$) or fully oil-wet ($\theta = 0^\circ$). It is assumed that 50% of the pore volume is water-wet and 50% of the pore volume oil-wet. Figures 7.11a and 7.12a show that the capillary pressure curve is similar for either a fractionally wet system or a mixed-wet system. However, for both core samples is the fractionally wet curve lower than the mixed-wet curve. The entry pressure in the fractionally wet system is lower than the entry pressure in the mixed-wet system, because not only small pore elements but also large elements can be assigned a water-wet contact angle. Assuming that the contact angle and the corner half angles are equal, large pore throats have a lower entry pressure than small pore throats. Similarly, in the fractionally wet system snap-off occurs earlier than in the mixed-wet system, because the oil-wet pores also comprise small throats.

When looking at the flow properties there are significant differences between fractionally wet and mixed-wet systems (Figures 7.11b and 7.12b). The fractional flow curve of a mixed-wet system is decreased with respect to the curve of a fractionally wet system. This can be explained by the fact that the 50% volume of largest pores contribute more to the conductivity than the 50% volume of smallest pores. The sorting effect has a larger effect in the Isba core sample than the Omar core sample. The gentle slope at low values of the water saturation (Figure 7.11b) indicates that the 50% volume of smallest pores has only a minor contribution to the transport properties.

When neutral contact angles are included in the model, the pore throats can be assigned any contact angle in the range from 0° to 180°. These contact angles are generated by a normal distribution with a mean $\mu$ and a standard deviation $\sigma$. Figure 7.13 show the effect of the mean of the normal distribution, while the standard deviation remains constant $\sigma = 15^\circ$. The capillary pressure curve shifts down with increasing mean. Furthermore, the intersection of the water relative permeability and the oil relative permeability moves to a
lower water saturation. As a consequence, the fractional flow of the water phase increases for a raising contact angle.

Besides varying the mean of the normal distribution, also the variance can be adjusted (Figure 7.13). An increase in the variance results in a smaller range of neutral contact angles, which is reflected in the horizontal line segment at the height of the x-axis. The relative permeability does not show much difference for a varying standard deviation. The intersection between the water and oil relative permeability remains at approximately 0.5 water saturation and \( k_{r,w} = k_{r,o} = 0.5 \). Another interesting observation is that the fractional flow curve becomes steeper with increasing variance. Nevertheless, in general the effects of the variance are significantly less than the effects observed after changing the mean.

Figure 7.13: Transport properties for oil flooding through bundle of tubes extracted from Omar with normal contact angle distribution.
7.2.2. **SECONDARY WATER FLOODING**
Also in the bundle of tubes model, the secondary water flooding curve includes the mixed-wet pore elements. The non-uniformly wet pores have non-wetting corner films. The entry pressure is lower for large pore elements, which implies that the non-wetting phase first fills the large pores and subsequently the small pores. However, since the tubes are unconnected in the bundle of tubes model, the oil phase in the small pores cannot be trapped.

When the system moves towards an oil-wet condition, the entry pressure and the collapse pressure are higher than for an intermediate system. As a result, the capillary pressure curve moves downwards at increasing contact angles (Figure 7.14). This is similar to the capillary pressure behaviour that is earlier observed for fully oil-wet systems (Figure 7.1/7.2/7.3).

![Capillary pressure curves for water-flooding through mixed-wet bundle of tubes extracted from Omar with varying contact angles.](image)

The effect of the contact is also visible in the relative permeability curves. The intersection between the water and oil relative permeability curve moves right-downwards at increasing oil-wetness (Figure 7.15a). This is reflected in a lower fractional flow curve of the water phase (Figure 7.15b), which is contradicting with the findings from primary oil flooding (Figure 7.13c). This might be an explanation for the contradicting results from the experiments on wettability effects.

![Macroscopic transport properties for water-flooding through mixed-wet bundle of tubes extracted from Omar with varying contact angles.](image)

In water-wet pore systems, the fractional flow grows with increasing contact angle. However, in the non-uniformly pores, the flow properties of the water phase deteriorate with increasing contact angle. Although there is no shock wave in a bundle of unconnected tubes, we use the fractional flow curves to assess the residual saturations. A low fractional flow curve is favourable for the oil recovery, because it leads to a high shock saturation. Hence, the higher the contact angle in the non-uniformly wet pores, the lower the shock saturation. In contrast, in water-wet pores, a low contact angle is preferred.
Although the water-wet bundle of tubes has a favourable fractional flow curve, the water-wet network does not have a high oil recovery due to trapping. In a pore network, the oil phase can be snapped off in water-wet elements which results in a higher residual oil saturation.

7.3. PERCOLATION MODEL

The results of the percolation model are presented in the sections below. The capillary pressure curves are plotted for different values for the contact angle.

7.3.1. CAPILLARY PRESSURE

The capillary pressure curves resulting from the percolation model (Figures 7.17 and 7.16) show that an increase in contact angle leads to a decrease in capillary pressure. This is consistent with the water-wet results from the pore-scale models at single pore and bundle of tubes level. The lower capillary pressure curve can be explained by the decrease in entry and exit pressure at increasing contact angles.

The drainage and imbibition curves for Omar are higher than the capillary pressure curves for Isba. This is explained by the smaller average pore size in the Omar network. For this reason, there is a higher capillary pressure curve required to enter the invade the same amount of pore elements.

(a) Drainage  
(b) Imbibition

Figure 7.16: Capillary pressure curves for Bethe lattice ($Z = 4$) extracted from Isba.

(a) Drainage  
(b) Imbibition

Figure 7.17: Capillary pressure curves for Bethe lattice ($Z = 10$) extracted from Omar.

7.3.2. RELATIVE PERMEABILITY

As opposed to the capillary pressure curve, the relative permeability curve is not influenced by the contact angle. Flow properties are dependent on the shape of the throat distribution, which is unrelated to the contact angle. Figure 7.18 and 7.19 shows that the addition of pore bodies leads to a lower residual saturation, which is logical since the larger bodies are potentially snapped off by invaded pore throats.
When the body/throat aspect ratio is higher, there is a larger fraction that is snapped off. Hence, a larger body/throat aspect ratio has a negative effect on the residual non-wetting phase saturation. Since the body/throat aspect ratio is higher for Omar than for Isba, the addition of pore bodies has a larger effect on the residual saturation in Omar than in Isba (Figure 7.18 and 7.19).

Furthermore, when assigning dimensions to the pore body, the relative permeability curve has a different shape from the percolation model with zero-dimensional nodes. The intersection between the wetting phase and non-wetting phase curve moves to a higher wetting phase saturation. In addition, the improved percolation model indicates that the smallest pore elements (invaded at low wetting phase saturation) contributes less to the flow properties than the large pore elements. This is consistent with the results presented in Section 7.2.

![Figure 7.18: Relative permeability for Bethe lattice \( (Z = 4) \) with geometry extracted from Isba.](image)

![Figure 7.19: Relative permeability for Bethe lattice \( (Z = 4) \) with geometry extracted from Omar.](image)

### 7.4. PORE NETWORK

At the highest level of analysis, primary oil flooding is simulated for a topologically realistic pore network. In this chapter, the results of this network model will be discussed.

#### 7.4.1. WATER-WET SYSTEM

In the water-wet system, all the pore elements are assigned a contact angle of \( \theta = 0^\circ \). As can be seen, all pore elements are filled at a positive capillary pressure. There is significant difference between the capillary pressure curve of the Isba network and the curve of the Omar network. Omar requires a much higher capillary (entry) pressure to reach the same saturation as the Isba system. The abrupt change in saturation and relative permeability in the Isba curve indicates a breakthrough of the oil phase. Apparently, this network has a chain of relatively large pores that connect the network input with the output.
Furthermore, there is a large difference in end-point relative permeability of the oil phase. Due to the heterogeneity of the Isba core sample, a lot of small pore elements are “snapped off”. As is discussed in Appendix B, the smallest 10 – 20% pores in the Isba network contribute insignificantly to the voxel volume. Hence the snapped-off pore elements do not influence the saturation, but they reduce the number of flow paths. This results in a low relative permeability.

![Macroscopic flow properties of water-wet pore network (θ = 0°) extracted from Isba.](image1)

![Macroscopic flow properties of water-wet pore network (θ = 0°) extracted from Omar.](image2)

### 7.4.2. Oil-Wet System

In the oil-wet system (θ = 0°), we observe a similar behaviour as in the water-wet system. As opposed to the water-wet system, the pores are filled at a negative pressure, which means that the oil is sucked into the network. Snap-off occurs first in the small pores, whereafter the oil fills the large pores that contribute the most to the saturation and relative permeability. For this reason, the macroscopic properties in the oil-wet Isba network change less abrupt than in the water-wet system. Trapping due to snap-off is not included in this model, which leads to an overestimation of the oil phase properties.

Since Omar is relatively homogeneous, there is no significant difference between the displacement patterns through water-wet and oil-wet system. Though, the transport properties deteriorate with increasing oil-wetness, as is shown by the bundle of tubes model.
7.4.3. MIXED-WET SYSTEM
We observe a similar behaviour in the mixed-wet system. At increasing oil-wetness, the capillary pressure curves shifts downwards, which implies that at the same capillary pressure water saturation is higher under water-wet conditions than under oil-wet conditions. Figure 7.25 shows that an increase in contact angle has a negative effect on the fractional flow and thus shock saturation.

As opposed to Omar, the Isba curve (Figure 7.24) shows a positive effect on the fractional flow of primary oil flooding. This is caused by the change from piston-like displacement towards snap-off displacements, which suppress permeability contrasts. However, in water flooding snap-off displacement occur in water-wet media instead of oil-wet media, which implies that the contact angle has the opposite effect on the flow properties as is observed for oil flooding.
The correlation length of the spatially correlated contact angle has influence on the network transport properties. The larger the correlation length, the higher the likelihood that the network contains a set of connected equally-wet elements. This negatively affects the shock saturation, as can be seen in Figure 7.26.
In performing this research, we encountered several limitations on this research during the quasi-static modeling of the contact angle. These limitations are discussed in the sections below. Furthermore, we present our substantive findings.

8.1. ROLE OF NETWORK TOPOLOGY
At the single pore throat level, it was explained that pore wettability is dependent on the contact angle, and on the geometry. When we upscale the single pore throat to a pore network, not only the geometry of the individual pore elements plays a role but also the topology of the network. As is revealed by the percolation model, connectivity is of high importance for the transport properties. The higher the coordination number, the lower the percolation threshold. This implies that a high connectivity improves the transport properties. However, a high coordination number increases the probability that pore elements become trapped, which negatively affects oil recovery.

Also the pore network results show that the network topology plays an important role in the transport properties. In this research, distinction is made between two levels of heterogeneity: heterogeneity at pore level and heterogeneity at network level. At network level, snap-off displacements suppress permeability contrasts. Hence, during water flooding, increasing oil-wetness has a negative effect on transport properties. In contrast, variations in pore radii cause trapping due to snap-off of relatively large pore elements. However, trapping due to heterogeneities at pore-level is not included in the pore network model. This means that the flow properties of the oil phase are overestimated and inclusion of snap-off leads to a lower oil recovery.

The opposite effect of heterogeneities at pore-level and network-level emphasizes the importance of the representative elementary volume (REV). What seems to be heterogeneous at a small scale might be homogeneous at a large scale. For this reason, the choice of REV might influence the assessment of the transport properties.

8.2. QUASI-STATIC VERSUS DYNAMIC MODELING
In this research, the macroscopic properties are predicted with a quasi-static time-independent model which neglects the dynamic forces. After each change in capillary pressure (which is constant throughout the network) the final static position of the fluid-fluid phases is calculated. This is only valid when the displacement rates are low and when the viscous pressure drops are insignificant, which is represented by a low capillary number (eq. 8.1). The capillary number is a dimensionless measurement of the balance between the capillary and viscous forces [31].

\[ N_{\text{cap}} = \frac{\mu \nu}{\sigma} \]  

(8.1)

where \( \mu \) is the viscosity, \( \sigma \) is the interfacial tension and \( \nu \) is the fluid velocity.

According to [12], the quasi-static conditions are reasonable when the capillary number is lower than \( 10^{-4} \). However, at higher capillary numbers, quasi-static modeling neglects differences in displacement rates. The assumption that flow properties are independent of the displacement rate is valid for drainage [56]. However, previous network modeling literature shows that this assumption is not necessarily true for imbibition displacements [11, 21, 33, 50]. In imbibition, snap-off of non-wetting fluid ahead of the displacement front is
an important displacement mechanism [19, 20, 37, 42, 51]. The order in which frontal and snap-off displacements occur determines the shape of the relative permeability curves and the residual oil saturations [56]. If imbibition is dominated by snap-off, the relative permeability is low and the residual oil saturation is high. The other way around, when imbibition displacements are dominated by frontal displacement, the relative permeability is high and the residual oil saturation is low.

In quasi-static models, the competition between frontal and snap-off displacements is entirely determined by the contact angle [55]. However, when dynamic forces are included, fluid flow through wetting films introduces significant pressure gradients in the films (pressure gradient in bulk is neglected [24] ahead of the displacement front [12, 21, 33, 50]. Consequently, this increases the capillary pressure between the wetting and non-wetting phase, which leads to a contraction of the snap-off events towards the displacement front [55]. In other words, the high displacement rates the snap-off events are suppressed by frontal displacements. Hence, the order of the displacement events is altered and less fluid will be trapped. Since the competition between snap-off and frontal displacements controls the imbibition displacements [55], the effect of the dynamic forces will be mainly seen in imbibition.

8.2.1. **Time-dependent effects of wettability alteration**

The definition of pore wettability requires a change in capillary pressure when the wettability is altered. Since the quasi-static condition demands a constant capillary pressure throughout the network, the curvature of the fluid-fluid interface must be changed equally for all pore elements. However, this requirement does not allow the existence of mixed-wet systems where the pore elements have different capillary pressures. In contrast, a dynamic model includes viscous and inertial forces and as a result, allows pore elements to have different capillary pressure. For this reason, the dynamic model is able to describe the internal fluid redistribution as a consequence of wettability alteration.

During spontaneous imbibition, there will be snap-off in the water-wet pore elements and the oil phase will be trapped. Decreasing the capillary pressure further, in the mixed-wet pores water will invade the center of the pore and an oil-layer will be created. When the fluid-fluid interfaces meet, the oil-layer collapses. However, since the collapse of the oil-layer occurs at the frontal displacement front of the invading water, the oil will not be “snapped off”. As a result, the mixed-wet pore filling will lead to a higher ultimate oil recovery than the water-wet scenario. Moreover, the recovery time will be smaller than in a fully oil-wet system, since oil-wet pores store the oil in thin films where flow rates are low.

8.2.2. **Mobilization of oil entrapments**

In quasi-static models, trapped non-wetting phase cannot be mobilized once disconnected, since the model does not include displacement mechanisms driven by viscous forces. However, it is known that when the capillary forces are higher than the viscous forces, the unconnected cluster of non-wetting phase can be mobilized and transported to the outlet of the reservoir [8]. This can be realized by either an increase in the viscous forces or reduction in capillary forces [19, 64, 82, 90]. At pore-scale level, the balance between the viscous and capillary forces can be expressed in terms of the capillary number 8.1. According to [24], the residual trapped saturation can be mobilized at capillary numbers between $10^{-5}$ and $10^{-7}$. However, there is no straightforward approach to predict the non-wetting phase mobilization in complex network topologies [6].

The definition of the capillary number assume that the viscous and capillary forces act over the same length scale. Nevertheless, the capillary forces act over the length scale of a pore throat (on the order of a few micrometers), whereas the viscous shear forces act over the whole cluster interface, which can extend over many pores ranging up to several millimeters [26]. To predict the non-wetting phase mobilization the fluid topology cannot be omitted from the expressions that compare capillary and viscous forces. Therefore, the length distribution of the trapped clusters is a key factor in determining the recovery efficiency [40, 41, 51, 82]. The final fluid configuration in the quasi-static model provides information on the cluster sizes that are trapped by the advancing wetting phase.

8.3. **Validation of displacement mechanisms**

The displacements in quasi-static modeling are capillary dominated displacements. This implies that the fluid configuration is established by the interaction between the contact angle and the interface curvature, which is dependent on the capillary pressure. Assuming that the pore walls are covered by a water-wet thin film, the curvature is besides capillary pressure also influenced by disjoining pressure. This is defined as
8.3. Validation of Displacement Mechanisms

the attractive interaction between two parallel surfaces (e.g. solid-water/water-oil interface). However, the disjoining pressure is considered to have an insignificant effect on the pore filling because it influences the curvature only at nanoscale, which is three orders smaller than the pore-scale level that is analyzed in this work. Furthermore we do not include surface roughness in this model for the same reason as the disjoining pressure was excluded. Although the disjoining pressure and the surface roughness have an impact on the actual contact angle, in this work is the effect of the apparent contact angle assessed.

8.3.1. Displacements controlled by entry capillary pressure

The entry pressure based on the MS-P principle is calculated for the full range of contact angles \(0^\circ \leq \theta \leq 180^\circ\). Figure 8.1 shows that the MS-P method appears to be inappropriate to calculate the entry capillary pressure for the neutral pores \(90^\circ - \beta \leq \theta \leq 90^\circ + \beta\). They give no exclusion which phase is the wetting phase, because the radius of curvature is for each fluid configuration negative. Hence these pores are assumed to have no ‘preference’ for one phase over the other.

![Figure 8.1: Entry capillary pressure for different contact angles calculated with the MS-P method.](image)

For a contact angle of \(90^\circ \pm \beta\), the capillary pressure and corresponding curvature are equal to zero. The corner size \(b\) at the entry pressure can be calculated for \(P_c = 0\) and \(\theta = 90^\circ\). This results in a negative corner size (Figure 8.2), which is physically impossible. Therefore, it is proposed that neutral corners have no entry capillary pressure. Pore entry occurs immediately when the pore element is accessible and no contact angle can be observed.

Although no contact angles can be observed in a pore with neutral characteristics, neutral or intermediate-wet contact angles \(0^\circ \leq \theta \leq 180^\circ\) can be observed on a flat surface \(\beta = 90^\circ\). The assumption for the pore entry implies that a droplet of water on an intermediate surface can be displaced by any force. This must be verified with experimental evidence.
In Figure 8.1 it can be seen that the entry pressure is negative for contact angles larger than \(90^\circ + \beta\), which is logical since these contact angles are considered to be oil-wet. The negative sign implies that the advancing phase is "sucked" into the pore element and the resulting corner films have a convex shape. However when the curvature is convex, the size of the "non-wetting" corner films increase with increasing radius of curvature. This is inconsistent with the monotonic decrease in capillary pressure. Therefore, it is proposed that the MS-P principle is only valid for drainage, where the contact angle is smaller than \(90^\circ - \beta\).

For contact angles higher than \(90^\circ + \beta\), the advancing phase is assumed to be sucked into the corner space rather than into the pore center. The negative radius of curvature leads to concave corner films. When the curvature is decreased, the individual corners films meet at the solid-liquid boundary and the corner phase snaps off the bulk phase. Consequently, the pore fills completely with the wetting phase.

As Figure 8.1 shows, there entry pressure for an equilateral triangle does not reach zero for \(\theta < 90^\circ + \beta\). As a consequence, the capillary pressure curves has a jump from zero to the minimum entry pressure. However, we discovered that the entry pressure approximate zero for infinitely small corners, in combination with a contact angle of \(90^\circ\). Since it is known that the shape factor is overestimated due to assumptions in the maximum ball extraction algorithm (Appendix B), it is likely that a pore network with smaller corner angles representing cracks and vugs improves the flow predictions.

When giving the pore elements a very low shape factor (\(G \leq 10^{-6}\)), the triangular pores have one small wetting corner and two large "neutral" corners. Figure 8.3 shows the macroscopic properties of a network characterized by the geometry extracted from the Omar core sample (Appendix B) and a shape factor of \(G = 10^{-9}\). The contact angle is represented by a normal distribution with a mean \(\mu = 90^\circ\) and a standard deviation \(\sigma = 30^\circ\).
8.4. CONTRIBUTION OF VISCOUS FORCES

In Chapter 2, we noted that there was no convenient analytical expression for the phase conductance. We used empirical relationships to approximate the conductance. However, these empirical expressions do not have a term accounting for viscosity differences. This implies that friction forces due to differences in viscosity are neglected in the model.

When the viscosities are assumed to be equal, and in absence of dead ends, the conductance of both phases should add up to the same level as the single phase conductance. However, the expressions for the conductance of the corner film and the bulk phase are unrelated. As a result, the sum of both conductances is less than the single phase conductance. Accordingly, the empirical expressions provided by [93] generate a small error in the pore-scale flow properties. This error grows with decreasing curvature (Figure 8.4). At the minimum curvature (at the entry pressure), the loss in conductance is approximately 27%. From this it can be derived that in a bundle of tubes, the loss in conductance is the highest in the smallest pores, because in the small pores is the dimensionless radius of curvature large. However, it is known that the small pores contribute less to the macroscopic flow than the large pore elements (Appendix B), the conductance loss has no significant effect on the transport properties.

Another limitation of these empirical relationships arise when the pore has only one corner film. Snap-off occurs when the corner film reaches one of the opposite corners and the interface becomes unstable. However, before the corner film collapses, the conductance surpasses the conductance of single phase flow. To correct for these unrealistic values, they are reduced such that the conductances of the two phases add up to the conductance of single phase flow.

![Figure 8.4: Loss in conductance due to increasing corner film.](image)

8.4.1. NUMERICAL APPROXIMATIONS

Besides the empirical expression of Zhou et al. [93], there are many numerical-empirical approaches to approximate the flow properties of two-phase flow. [60] used the Finite Element Method to solve the Navier-Stokes equations for the flow through a corner film. The numerical approximation is dependent on the boundary conditions on the solid-fluid interface ($\Gamma_{sj}$) and on the fluid-fluid interface ($\Gamma_{nw}$). At the solid-fluid boundary, a no-slip boundary condition is imposed. This means that there is infinite surface shear stress at the solid-fluid boundary and thus the fluid velocity along the pore walls is zero (eq. 8.2).

$$\tilde{v}_j = 0, \quad j = w, n, \quad \text{on} \quad \Gamma_{sj}$$

where $\tilde{v}_j$ is defined as the dimensionless velocity, which is given by

$$\tilde{v}_j = \frac{v_j}{b\Xi_j}, \quad j = w, n$$

where $b$ is the meniscus-apex distance and $\Xi_j$ is minus the average gradient of the total driving force per unit area. When the viscous forces are neglected, the driving force per unit area is the capillary pressure.

When the corner interface is approached as a surfactant-laden rigid wall, the no-slip condition also holds.
for the fluid-fluid interface. Hence, there is no flow along this boundary [60]. In contrast, when the perfect slip condition holds, there is no shear stress on the fluid-fluid interface and hence the fluid phases have a non-zero velocity along the boundary. However, either for perfect slip and no-slip, there is no momentum transfer across the fluid-fluid interface and therefore no velocity continuity (eq. 8.4) [60].

\[ \nabla \tilde{v}_j \cdot \tilde{n}_j = 0, \quad j = w, n, \quad \forall (\tilde{x}, \tilde{y}) \in \Gamma_{nw} \]  

(8.4)

Patzek and Kristensen [60] formulate a single quadratic function that fits the numerical approximations of the corner film conductance for both the no-slip and perfect slip conditions. However, as opposed to the no-slip and perfect-slip cases, there is no velocity continuity across the liquid-liquid boundary. Furthermore, they do not provide convenient numerical-empirical relationships for the conductance of the bulk fluid, which plays an important role when there is velocity continuity across the boundary.

When two immiscible liquids are separated by a clean interface, there is momentum transfer at the fluid-fluid interface which means that there is velocity continuity and shear stress. Assuming that the fluid viscosity is constant, the boundary condition becomes [60]:

\[ \nabla \tilde{v}_w \cdot \tilde{n}_w = \frac{\mu_n}{\mu_w} \tilde{v}_n \cdot \tilde{n}_n = 0, \quad j = w, n, \quad \forall (\tilde{x}, \tilde{y}) \in \Gamma_{nw} \]  

(8.5)

Eq. 8.5 shows that the viscosity ratio plays a role in the approximation of the velocity profile and corresponding conductances. The velocity profile in the corner phase is not only dependent on the corner size, but also on the fluid flow through the bulk phase. By solving the Navier-Stokes equations for this boundary condition, the conductance of the corners films and the bulk phase are more accurate.

The conductance of an oil-layer between a corner film and the bulk phase can be numerically approximated in a similar way. Al-Futaisi and Patzek [2] provided numerical-empirical relationships for the conductance of intermediate layers (in case of three-phase flow). However, similar to the corner film conductance, there is no convenient relationship for the conductance when velocity is continuous across the liquid-liquid border.

Although the numerical-empirical expressions are considered to be more reliable than the empirical expressions provided by Zhou et al. [93], they do not differ significantly for the perfect slip and no-slip condition. For this reason, it is acceptable to approximate the corner film conductance with the empirical expressions, assuming that there is no velocity continuity across the liquid-liquid boundary.
CONCLUSIONS AND RECOMMENDATIONS

Our conclusions and recommendations based on the pore-scale modeling results are presented in the sections below.

9.1. CONCLUSIONS

Increasing oil-wetness lowers the capillary pressure, because the contact angle reduces the entry pressure and suppresses snap-off displacement. This effect is observed at all levels of analysis. As a result, oil-wet systems have a lower oil recovery from spontaneous imbibition than water-wet systems, which is observed in imbibition experiments.

In a perfectly homogeneous medium, the contact angle has a negative effect on the transport properties as it decreases the shock saturation. Oil-wet systems have a much lower shock saturation than water-wet systems. The remaining oil phase behind the shock front has a low velocity, which might be observed as film drainage. However, realistic representations of reservoir rock are not perfectly homogeneous.

Heterogeneity negatively affects the transport properties, because it decreases the connectivity and thus the conductivity of the network. Distinction is made between two levels of heterogeneity: permeability contrasts and pore radii variations. Permeability contrasts are heterogeneities at network-level and lead to unstable displacements. However, this heterogeneity effect is less strong in spontaneous imbibition than in forced imbibition (or drainage), because small pores are snapped off before large pores are filled. Hence, regards permeability contrasts, water-wet systems are favoured over oil-wet systems.

In contrast, in case of heterogeneity at pore-level, snap-off has a negative effect on the residual oil saturation and thus oil recovery. For this reason, maximum oil recovery is obtained at intermediate-wet conditions, depending on the network topology. This is consistent with experimental studies on wettability effects in which maximum oil recovery was obtained from intermediate-wet systems. Though in low-salinity experiments improved oil recovery is observed at increasing water-wetness. Since wettability is altered at the displacement front, there is no oil entrapment in front of the low-salinity front. In other words, the negative consequence of pore-level heterogeneities does not contribute to the low-salinity effect.

When pore wettability is altered towards an oil-wet state, flow properties improve with increasing oil-wetness. An increase in contact angle leads to a higher rather than lower shock saturation. Moreover, since oil-layer collapse occurs close to the displacement front, there is less trapping at pore-level. This is contradicting with the conclusion that is drawn above which says that the contact angle negatively affects the transport properties. Hence, these results might be an explanation for the contradicting experimental results previously reported in the literature.

9.2. RECOMMENDATIONS

First of all, we recommend to include snap-off entrapments in the pore network model. This effect is not validated in the model that is used in this research since pores cannot get disconnected by snap-off displacements in adjacent pore elements. As a consequence, the macroscopic transport properties are overestimated for imbibition displacements. Furthermore, it would imply that intermediate wet conditions are favoured over water-wet conditions.
Secondly, we would like to recommend to improve the algorithm that is used for the pore network extraction. The maximum ball algorithm overestimates, resulting in higher corner angles than is observed in the voxel image. As a result, the pore network is an oversimplified image of the voxel image. However, since the pore geometry - in combination with the contact angle - defines the wettability and thus the macroscopic properties, it is essential that the pore network is a realistic representation of the rock.

Thirdly, we recommend to develop better expressions for the quasi-static phase conductance. In the current empirical relationships, it is assumed that there is no velocity continuity at the fluid-fluid interface. Moreover, the difference in viscosity the resulting friction are not taken into account. Therefore, it is recommended to develop convenient expressions that include these aspects and provide accurate microscopic flow properties.

In the fourth place, there should be a further investigation into the size of the oil clusters resulting from secondary water flooding. The size gives an indication of the trapped oil saturation that can be mobilized. Large oil clusters require a high capillary pressure to overcome the frictional forces between the oil phase and the rock.

Lastly, in future the quasi-static model must be translated into a dynamic model by including viscous and inertial forces. Dynamic models take into account fluid entrapment due to differences in displacement rate. Hence, these models are more accurate than the quasi-static model used in this research.
### Summary Table of Pore-Scale Relationships

<table>
<thead>
<tr>
<th>Relationship</th>
<th>Uniformly wet</th>
<th>Non-uniformly wet</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Entry capillary pressure</strong></td>
<td>$P_{\text{entry}} = \sigma_{\text{nw}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$D = \sum_{i=1}^{N} \left( \frac{\sqrt{\sum_{j=1}^{N} \frac{A_{ij}}{L_{ij}}} \beta_{ij}}{2} \right)$</td>
<td></td>
</tr>
<tr>
<td><strong>Snap-off capillary pressure</strong></td>
<td>$P_{\text{snap}} = \sigma_{\text{min}} \min \left( \cos \theta_{i} \cos \beta_{ij} \right)$</td>
<td></td>
</tr>
<tr>
<td><strong>Saturation wetting phase</strong></td>
<td>$S_{w} = \begin{cases} 1 &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} &gt; P_{\text{entry}} \ 0 &amp; P_{i} \geq P_{\text{entry}} \end{cases}$</td>
<td>$S_{w} = \begin{cases} 1 &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \ 0 &amp; P_{i} \geq P_{\text{entry}} \text{ or } P_{i} &lt; P_{\text{entry}} \end{cases}$</td>
</tr>
<tr>
<td><strong>Saturation non-wetting phase</strong></td>
<td>$S_{g} = \begin{cases} 0 &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} &gt; P_{\text{entry}} \ 1 \sum_{i=1}^{N} \frac{A_{ij}}{L_{ij}} &amp; P_{i} \geq P_{\text{entry}} \end{cases}$</td>
<td>$S_{g} = \begin{cases} 0 &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \ 1 \sum_{i=1}^{N} \frac{A_{ij}}{L_{ij}} &amp; P_{i} \geq P_{\text{entry}} \text{ or } P_{i} &lt; P_{\text{entry}} \end{cases}$</td>
</tr>
<tr>
<td><strong>Conductance wetting phase</strong></td>
<td>$G_{w} = \begin{cases} \left( \sqrt{\frac{\sum_{i=1}^{N} A_{ij}}{2}} + R \right)^{4} &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \ 0 &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \end{cases}$</td>
<td>$G_{w} = \begin{cases} \left( \sqrt{\frac{\sum_{i=1}^{N} A_{ij}}{2}} + R \right)^{4} &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \ 0 &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \end{cases}$</td>
</tr>
<tr>
<td><strong>Conductance non-wetting phase</strong></td>
<td>$G_{n} = \begin{cases} \left( \sqrt{\frac{\sum_{i=1}^{N} A_{ij}}{2}} + R \right)^{4} &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \ 0 &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \end{cases}$</td>
<td>$G_{n} = \begin{cases} \left( \sqrt{\frac{\sum_{i=1}^{N} A_{ij}}{2}} + R \right)^{4} &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \ 0 &amp; P_{i} &lt; P_{\text{entry}} \text{ or } P_{i} \geq P_{\text{entry}} \end{cases}$</td>
</tr>
</tbody>
</table>

Table A.1: Table of microscopic relationships within a single pore.
In this research, two core rocks are used to validate the results from the modeling work. One core sample that is used is from the El Isba field and the other core sample is from the Omar field, both consisting predominantly of sandstone. Micro-CT images are made to extract the properties of the voxel space in the rock.

Hu Dong [23] has developed an algorithm that is capable of extracting pore geometry from voxel images, which is called the ‘maximum ball algorithm’ [75, 76]. This maximum ball method measures the radius of the maximum inscribed sphere that touches the pore walls. These maximum balls are the building blocks for pores and throats. Since it is likely that the pore elements are angular rather than circular, the approximated radius represents the inscribed radius of the pore elements.

The maximum balls extracted from the cores are grouped into pore bodies and pore throats, according to a clustering algorithm with a grading system. The clustering algorithm allows the maximum ball to absorb direct neighboring balls with their center located in a certain range around the principal maximum ball (Figure B.1). In this research, the range around the principal maximum ball is defined as $2R$. This is called a single cluster. When we extend the single cluster to a multi cluster, the subordinates can also absorb smaller neighboring balls.

The common ancestor of each multi cluster defines a pore, and the throats are defined by the subordinates that are connected to different common ancestors. Between the pore and throat, there is a chain of maximum balls, which capture the topology of the pore space.

Figure B.1: Single cluster of principal maximum ball and neighboring subordinates (Hu Dong, 2007).
The voxels in the pore-throat chain are labeled as either pores or throats, according to an arbitrary border. [23] presents evidence that this border has significant impact on the flow properties. Eventually every pore element in the voxel image is assigned a pore or throat label. Maximum balls that do not contribute to the pore-throat chain are not needed to define the topology, but they are used to describe the size and shape of the pores and throats [23].

Figure B.2 displays a zoomed-in picture of the voxel space extracted from the Isba and Omar core. It can be easily seen that the Isba core sample is much more heterogeneous than the Omar core sample. In the next sections, the properties of these extractions are discussed.

![Isba](image1.png) ![Omar](image2.png)

Figure B.2: Extracted network structure of core samples.

## B.1. PORE GEOMETRY

### B.1.1. PORE RADIUS

The pore radius is defined as the radius of the principal maximum ball. The radius of a pore throat is defined as the inscribed radius of the biggest maximum ball that connects two (or more) pore bodies. Plotting the pore size versus the frequency gives us the radius distribution, which provides insight in the heterogeneity of the sample.

The pore size distribution of the Omar core sample is hardly skewed, which implies that the core rock is homogeneous. In contrast, the pore size distribution of the Isba core sample is highly right-skewed, so the core rock has a heterogeneous character. The pore elements at the tail of the distribution \( R > 30 \mu m \) have very low frequencies. To reduce the sample to a set of pore elements with a significant frequency, the distribution is cut-off at 30 \( \mu m \). As a result, 1.7% of the pore throats and 6.2% of the pore bodies are excluded from the Isba sample, as opposed to the Omar sample, from which 7.0% of the pore bodies are removed. All the throats in the Omar sample are smaller than the cutoff value.

Figure B.3 shows that the body/throat aspect ratio of both core samples is not high, though the aspect ratio is slightly higher for the Omar sample than for the Isba sample. It indicates that the pore bodies are hardly larger than the pore throats. In the Omar core sample, there is even a fraction of pore throats that is larger than the average pore body. It can be discussed whether the pore elements below 2\( \mu m \) are valid, because the resolution of the micro-CT scanner is 2\( \mu m \) per pixel.
B.1. PORE GEOMETRY

B.1.2. SHAPE FACTOR

Hu Dong (2007) simplifies the pore elements as cylindrical capillaries. Although the shape factor of a circular cross-section is equal to $\frac{1}{4} \pi$, each capillary is assigned a dimensionless shape factor. The shape factor $G$ can be derived from the geometrical properties of the maximum ball (eq. B.1).

$$G = \frac{V L}{A_s^2}$$  (B.1)

where $V$ is the volume, $L$ is the length and $A_s$ is the surface area, which is defined as the area between the rock and the void. This expression is an equivalent to the shape factor equation as defined in chapter 2. Since the maximum balls are made up of cubes, depending on the resolution of the micro-CT image, Hu Dong defines the volume as the number of void blocks associated to a pore element multiplied by the single block volume. Similarly, the pore length is defined as the number of void blocks multiplied by the block length. The surface area is calculated by counting the block surfaces between the void and the rock. The higher the resolution of the micro-CT image, the more accurate the approximations of the pore volume, pore length and surface area. One of the disadvantages of the maximum ball algorithm is that is assumes that the capillaries are circular (like a ball). Real pores and throats have complex and high irregular geometrical profiles. Therefore, the surface area between the rock and the void is in reality larger than is assumed in the maximum ball algorithm. As a consequence, the shape factor of the pore elements is overestimated.

In both core samples, more than 99% of the pore throats appear to have a shape factor smaller than $\frac{\sqrt{3}}{36}$. Figure B.4 shows that the average shape factor is 0.0313. This means that the core samples used here mainly consist of triangular-shaped pore throats.

Pore elements that have a shape factor larger than $\frac{\sqrt{3}}{36}$ are assumed to be square-shaped ($\beta = \frac{\pi}{4}$). The square is characterized by the inscribed radius, which defines the cross-sectional area ($A = 4R^2$) and the perimeter ($P = 8R$). When the pore elements are triangular, the corner half angles can be determined by the expressions given by [59]. The corner half angles are defined in ascending order: $0 \leq \beta_1 \leq \beta_2 \leq \beta_3 \leq \frac{\pi}{2}$. The middle corner half angle, $\beta_2$, is bounded by the values of the other two half angles and can be assigned a minimum and maximum value [59].

$$\beta_{2,min} = \arctan\left(\frac{2}{\sqrt{3}} \cos\left(\frac{\arccos(-12\sqrt{3}G)}{3} + \frac{4\pi}{3}\right)\right)$$

$$\beta_{2,max} = \arctan\left(\frac{2}{\sqrt{3}} \cos\left(\frac{\arccos(-12\sqrt{3}G)}{3}\right)\right)$$

When we assume that the three corner half angles add up to $\frac{\pi}{2}$, $\beta_1$ can be expressed in terms of $\beta_2$ [59].
Figure B.4: Statistical distribution of pore throat shape factors.

$$\beta_1 = -\frac{1}{2} \beta_2 + \frac{1}{2} \arcsin \left( \frac{\tan \beta_2 + 4G \sin \beta_2}{\tan \beta_2 - 4G} \right) \quad (B.2)$$

Then $\beta_3$ can be found by adding the corner half angles up to $\frac{\pi}{2}$.

### B.1.3. Pore Length

Since both the pores and throats are measured in a 2D-dimension and represented by a circular ball, the throat length is underestimated. This underestimation leads to an overestimation of the flow properties, because the conductivity is inversely proportional to the throat lengths [23]. Therefore, the throat length is defined by subtracting the two neighboring pore lengths from the distance between the pore centers, measured in the same 2D-plane as the voxel image. The pore length was defined by an arbitrary border in the pore-throat chain, often related to the pore radius. Figure B.5 shows the throat lengths distribution extracted from the Isba and Omar core samples.

Figure B.5: Statistical distribution of pore throat length.

Not only the conductivity is influenced by the throat lengths, they also contribute to the saturation. The greater the pore length, the more fluid the pore can store and the lower the conductivity. However, the correlation coefficient between the throat length and the throat radius is low ($r = 0.3574$) for Isba. In the Omar sample, the throat length and the throat radius are even negatively correlated ($r = -0.0186$). Hence, large pores do not necessary have a high conductivity.
B.1.4. PORE VOLUME
Combination of the corner half angles and the inscribed radius makes it possible to calculate the cross-sectional area $A$. Then the volume of the pore element can be calculated by multiplying the cross-sectional area with the pore length. Figure B.6 shows that the largest pore elements contribute the most to the voxel volume. Due to the heterogeneous character of the Isba core sample this effect is even larger than in the homogeneous Omar rock. In the Isba core sample, 90% of the pore elements comprise only 20% of the total voxel volume. In contrast, in the Omar core sample 90% of the pore elements are approximately 40% of the pore volume. This implies that for both cores only a limited set of (relatively large) pore elements has influence on the voxel volume. Hence, the pore elements smaller than the micro-CT scan resolution ($< 2\mu m$) do not have a significant effect on the saturation.

![Figure B.6: Contribution of pore volume to (macroscopic) saturation](image)

B.2. COORDINATION NUMBER
The coordination number quantifies the connectivity of the network. Pore bodies that have a coordination number below zero are removed from the data set, because they are isolated elements and cannot contribute to the fluid flow. Furthermore, pore bodies with a coordination number of 1 are also deleted, because they are so-called ‘dead ends’. As can be seen in Figure B.7, the frequency of the coordination number in both cores decreases. However, in the Isba core is the fraction of low coordination numbers slightly lower than in the Omar core. In contrast, Isba contains a larger fraction of high coordination numbers than Omar. For both core samples, the average coordination number is 4.
The average coordination number appears to be very high for sandstones, especially for the Omar core sample. The coordination number is correlated with the pore radius. For the Omar core sample the correlation number is of $r = 0.4957$. With a sample size of 12709 pores, this correlation number is above the significance level of $\alpha = 0.01$. In the Isba core, the pore radius and the coordination number are less correlated ($r = 0.3638$). The Isba core sample has a lower correlation number between the pore size and the coordination number. However, with a set of 17618 pores, this is still above the significance level.
The spatial properties of the pore network are generated by a random field simulation, in which the field is characterized by a 3D regular block grid. Each node in this grid is assigned a contact angle, which is a weighted linear combination of the contact angle values at the $n$ surrounding nodes.

$$\hat{\theta}_0 = \sum_{j=1}^{n} w_j \cdot \theta_j$$  \hspace{1cm} (C.1)

where $w_j$ is the weight of the contact angle at point $x_j$. The set of weights is allowed to change as we estimate unknown contact angle values at different locations.

Contact angle values in the individual pore elements are generated with the ordinary kriging method, which is unbiased and minimizes the variance of the errors $\sigma_R^2$. The average error of an estimation is defined as

$$r_i = \hat{\theta}_i - \theta_i$$  \hspace{1cm} (C.2)

where $\theta_i$ is the real value and $\hat{\theta}_i$ is the estimated value of the contact angle. The unbiasedness condition requires the average estimation error $m_R$ to be zero.

$$m_R = \frac{1}{k} \sum_{i=1}^{k} r_i = \frac{1}{k} \sum_{i=1}^{k} (\hat{\theta}_i - \theta_i)$$  \hspace{1cm} (C.3)

Assuming that the average estimation error is equal to zero, the error variance can be written as

$$\sigma_R^2 = \frac{1}{k} \sum_{i=1}^{k} (\hat{\theta}_i - \theta_i)^2$$  \hspace{1cm} (C.4)

However, since there is no available data of the true contact angle values, the errors of the estimations are unknown. For this reason, ordinary kriging uses a probability model to express the mean error and its variance. These model parameters are denoted as respectively $\hat{m}_R$ and $\hat{\sigma}_R^2$.

**C.1. Ordinary Kriging Method**

Since the true values at the grid nodes are unknown, the contact angles are given by random variables $\Theta_i$. Every pair of random variables has a joint distribution that depends on the distance between the two points. This joint distribution is described by the covariance. The covariance between pairs of random variables is $\hat{C}_\Theta(h)$, where $h$ is the distance between the two random variables.

$$\hat{C}_\Theta(h) = \text{Cov}(\Theta(x) \cdot \Theta(x + h))$$  \hspace{1cm} (C.5)
The covariance function can be calculated from the following equation:

\[ C(h) = \frac{1}{N(h)} \sum_{(x,x+h)} \Theta(x) \cdot \Theta(x+h) - m_x \cdot m_{x+h} \]  

(C.6)

where \( m_x \) is the mean of all the random variables at location \( x \) and \( m_{x+h} \) is the mean of all the random variables whose locations are \( h \) away from location \( x \).

\[ m_i = \frac{1}{N(i)} \sum_{i|h_{ij}=h} \Theta(i) \]  

(C.7)

When \( h \) is larger than the correlation length, the contact angles at location \( x \) and \( x+h \) are uncorrelated. In this research, there is made use of a stationary exponential covariance function. This means that the covariance decreases exponentially with the spatial distance between two nodes and it is independent of time. It is assumed that the covariance function is isotropic, which implies that the covariance is equal for all directions.

The correlation length describes the decay of mutual influence of two different random field locations (Schenk and Schueller, 2005) and is defined as the spatial distance where the covariance is equal to \( \sigma^2 e^{-h} \). Here, \( \sigma^2 \) is the variance of the random field. When the correlation length goes to infinity, the covariance describes a fully correlated random field. In contrast, when the correlation length goes to zero, the generated values are completely uncorrelated. Figure C.1 shows the exponential covariance function for two different correlation lengths. The correlation length in the right graph (Figure C.1a) is twice as large as the correlation length in the left graph (Figure C.1b). Furthermore, as can be seen in both graphs, the covariance at \( h = 0 \) is equal to the variance of the random field.

![Figure C.1: Exponential covariance functions with \( \sigma^2 = 1 \).](image)

**C.1.1. AVERAGE ESTIMATION ERROR**

The expected value of random variable \( \Theta \) is expressed as \( E(\Theta) \). The estimation error can be expressed in terms of the random variables at the \( n+1 \) nodes.

\[ R_0 = \Theta_0 - \Theta_0 = \sum_{j=1}^{n} w_j \cdot \Theta_j - \Theta_0 \]  

(C.8)

The expected value of the estimation error is often referred to as the bias.

\[ E(R_0) = E \left( \sum_{j=1}^{n} w_j \cdot \Theta_j \right) - E(\Theta_0) = E(\Theta) \sum_{j=1}^{n} w_j - E(\Theta) = 0 \]  

(C.9)

To ensure unbiasedness results, the expected value of the estimation error is set to zero. This implies that the sum of the weights must be equal to one.

\[ \sum_{j=1}^{n} w_j = 1 \]  

(C.10)
C.1.2. ESTIMATION ERROR VARIANCE

The variance of the estimation error can be described as

$$Var(\hat{R}_0) = Cov(\hat{\Theta}_0 \hat{\Theta}_0) - 2Cov(\hat{\Theta}_0 \Theta_0) + Cov(\Theta_0 \Theta_0)$$  \hspace{1cm} (C.11)

The first term is the covariance of $\hat{\Theta}_0$ with itself, which is equal to the variance of $\hat{\Theta}_0$. This variance of $\hat{\Theta}_0$ is a linear combination of the random variables at the surrounding nodes.

$$Var(\hat{\Theta}_0 \hat{\Theta}_0) = \sum_{i=1}^{n} \sum_{j=1}^{n} w_i w_j \tilde{C}_{ij}$$  \hspace{1cm} (C.12)

Similarly, the third term is the covariance of the random variable $\Theta_0$ with itself, which is equal to the variance of the random variable. When it is assumed that the $n + 1$ random variables have the same variance, $\tilde{\sigma}^2$, the variance of the random variable $\Theta_0$ can be expressed as

$$Var(\Theta_0 \Theta_0) = \tilde{\sigma}^2$$  \hspace{1cm} (C.13)

The second term can be written as

$$2Cov(\hat{\Theta}_0 \Theta_0) = 2 \sum_{j=1}^{n} w_j \hat{C}_{j0}$$  \hspace{1cm} (C.14)

Combining these three terms provides us with an expression for the error variance that is described by random variables.

$$\tilde{\sigma}^2_R = \tilde{\sigma}^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} w_i w_j \tilde{C}_{ij} - 2 \sum_{j=1}^{n} w_j \hat{C}_{j0} + 2\mu(\sum_{j=1}^{n} w_j - 1)$$  \hspace{1cm} (C.15)

The variance can be minimized by setting the partial derivatives to zero. This provides us with a set of $n$ equations and $n$ unknowns. However, since the unbiasedness condition adds another equation (eq. C.7), the system of $n + 1$ equations and $n$ unknowns cannot be solved. Therefore, a new variable is introduced in eq. C.16: the Lagrange parameter, $\mu$.

$$\tilde{\sigma}^2_R = \tilde{\sigma}^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} w_i w_j \tilde{C}_{ij} - 2 \sum_{j=1}^{n} w_j \hat{C}_{j0} + 2\mu(\sum_{j=1}^{n} w_j - 1) = \tilde{C}_{i0}$$  \hspace{1cm} (C.16)

The addition of this new term does not affect the equality, because this fourth term in the variance expression is always zero due to the unbiasedness condition (eq. C.7). The differentiation with respect to $w_j$ results in the equation

$$\sum_{j=1}^{n} w_j \tilde{C}_{ij} + \mu = \tilde{C}_{i0} \quad \forall i = 1, ..., n$$  \hspace{1cm} (C.17)

This system of $n + 1$ equations can be written in matrix notation.

$$\begin{bmatrix} \tilde{C}_{11} & \cdots & \tilde{C}_{1n} & 1 \\ \vdots & \ddots & \vdots & \vdots \\ \tilde{C}_{n1} & \cdots & \tilde{C}_{nn} & 1 \\ 1 & \cdots & 1 & 0 \end{bmatrix} \begin{bmatrix} w_1 \\ \vdots \\ w_n \end{bmatrix} = \begin{bmatrix} \tilde{C}_{10} \\ \vdots \\ \tilde{C}_{n0} \end{bmatrix}$$  \hspace{1cm} (C.18)

Or, in simplified notation:

$$C \cdot w = D$$  \hspace{1cm} (C.19)

Since the grid is regular, the covariance function can be easily calculated for each pair of nodes. Hence, for each node the $n$ weights can be calculated and we end up with $n + 1$ linear equations. Solving this system provides us with $n + 1$ spatially correlated contact angles.
# Nomenclature

## Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A$</td>
<td>area</td>
</tr>
<tr>
<td>$a_i$</td>
<td>length of side $i$</td>
</tr>
<tr>
<td>$b_i$</td>
<td>position of fluid-fluid interface in corner $i$</td>
</tr>
<tr>
<td>$C$</td>
<td>conductivity</td>
</tr>
<tr>
<td>$f_p$</td>
<td>fractional flow of phase $p$</td>
</tr>
<tr>
<td>$G$</td>
<td>shape factor</td>
</tr>
<tr>
<td>$g_p$</td>
<td>hydraulic conductance of phase $p$</td>
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<tr>
<td>$k_{r,p}$</td>
<td>relative permeability of phase $p$</td>
</tr>
<tr>
<td>$L$</td>
<td>length</td>
</tr>
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<td>$P$</td>
<td>perimeter</td>
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<td>capillary pressure</td>
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<td>pressure in phase $p$</td>
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<td>$Q$</td>
<td>allowability</td>
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<td>$q_p$</td>
<td>flux of phase $p$</td>
</tr>
<tr>
<td>$R$</td>
<td>inscribed radius</td>
</tr>
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<td>$r_c$</td>
<td>radius of curvature</td>
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<td>$s_p$</td>
<td>microscopic saturation of phase $p$</td>
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<tr>
<td>$S_p$</td>
<td>macroscopic saturation of phase $p$</td>
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<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$V$</td>
<td>pore volume</td>
</tr>
<tr>
<td>$X_C$</td>
<td>percolation threshold</td>
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<tr>
<td>$X$</td>
<td>enterability</td>
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<tr>
<td>$X^A$</td>
<td>accessibility</td>
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<tr>
<td>$Z$</td>
<td>coordination number</td>
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<tr>
<td>$\alpha$</td>
<td>pore distribution</td>
</tr>
<tr>
<td>$\beta$</td>
<td>corner half angle</td>
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<tr>
<td>$\kappa$</td>
<td>curvature</td>
</tr>
<tr>
<td>$\theta$</td>
<td>contact angle</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>fluid viscosity of phase $p$</td>
</tr>
<tr>
<td>$\sigma_{ij}$</td>
<td>interfacial tension between phase $i$ and $j$</td>
</tr>
</tbody>
</table>

## Subscript/Superscript

- **$C$** = corner
- **$A$** = advancing
- **$R$** = receding

## Phases

- **$n$** = non-wetting
- **$w$** = wetting
- **$s$** = solid
## List of Figures

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